

Atomically Precise Metal Nanoclusters: Self-Assembly Dynamics, Colloidal Superstructures, and Advanced Device Fabrication

*A Thesis Submitted to the Faculty of Science
University of Calicut in Partial Fulfilment of the
Requirements for the Degree of*

DOCTOR OF PHILOSOPHY IN CHEMISTRY

By

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Under the supervision of

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This is to certify that the thesis entitled “**Atomically Precise Metal Nanoclusters: Self-Assembly Dynamics, Colloidal Superstructures, and Advanced Device Fabrication**” submitted by **Mr. Rival Jose V** to the University of Calicut for the award of the degree of **Doctor of Philosophy in Chemistry**, is a record of precise research carried out at the Department of Nanoscience and Technology, University of Calicut under my guidance and supervision. The contents of the thesis have been checked for plagiarism using the software ‘iThenticate’ and the similarity index falls under the permissible limit. I further certify that the thesis or part has not previously formed the basis for the award of any degree, diploma, or associateship of any other University or Institute. I also certify that the corrections/suggestions recommended by the adjudicators have been incorporated in the thesis and the contents in thesis and the soft copy are one and the same.

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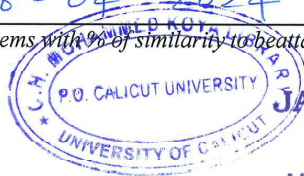
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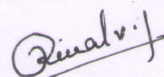
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Rival Jose V

Dedication

This thesis is dedicated to my family, whose love, encouragement, and sacrifices have been my source of strength and inspiration throughout this endeavor.

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LIST OF SYMBOLS AND ABBREVIATIONS

Au	Gold
Ag	Silver
Cu	Copper
Pt	Platinum
Pd	Palladium
Ru	Ruthenium
SR	Thiolate
DCM	Dichloromethane
DT	1-Dodecanethiol
THF	Tetrahydrofuran
DMF	N,N-Dimethylformamide
DMSO	Dimethyl sulfoxide
CH ₃ CN	Acetonitrile
NaOH	Sodium hydroxide
NP	Nanoparticle
NC	Nanocluster
QD	Quantum dots
OD	Optical density
BE	Binding energy
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
PL	Photoluminescence
QY	Quantum yield
SPR	Surface plasmon resonance
EPR	Electron paramagnetic resonance
SWIR	Short-wave infrared
PAGE	Polyacrylamide gel electrophoresis
HPLC	High-performance liquid chromatography

TLC	Thin-layer chromatography
SEC	Size exclusion chromatography
HILIC	Hydrophilic interaction liquid chromatography
LEIST	Ligand-exchange induced structural transformation
SAM	Self-assembled monolayer
BCC	Body-centered cubic
LMCT	Ligand-to-metal charge transfer
LMMCT	Ligand-to-metal-metal charge transfer
LED	Light-emitting diodes
WLED	White light-emitting diodes
AIE	Aggregation induced emission
ECL	Electrochemiluminescence
NIR	Near-infrared
CPL	Circularly polarized luminescence
MOR	Methanol oxidation reaction
EOR	Ethanol oxidation reaction
FAO	Formic acid oxidation
ORR	Oxygen reduction reaction
HER	Hydrogen evolution reaction
OER	Oxygen evolution reaction
CO ₂ RR	Carbon dioxide reduction reaction
DNIC	Double nanocluster ion compound
SNIC	Single nanocluster ion compound
RAFT	Reversible addition-fragmentation chain-transfer
LCST	Lower critical solution temperature
PAMAM	poly(amidoamine) dendrimer
p(MEO ₂ MA-co-AcSEMA)	[(poly-2-(2-methoxyethoxy) ethyl methacrylate and poly-2-(acetylthio)ethyl methacrylate)
SpCas9	<i>Streptococcus pyogenes</i> bacterial protein
GNCF	Gold nanocluster framework

MOF	Metal-organic framework
LOD	Limit of detection
Cys	Cysteine
PTEN	phosphatase and tensin homolog
Tyr	Tyrosine
UV-vis	Ultraviolet-visible absorption spectroscopy
IR	Infrared spectroscopy
NMR	Nuclear magnetic resonance spectroscopy
DLS	Dynamic light-scattering
XPS	X-ray photoelectron spectroscopy
EDS	Energy dispersive X-ray spectroscopy
HR-TEM	High-resolution transmission electron microscopy
ET	Electron tomography
HAADF	High-angle annular dark-field imaging
STEM	Scanning transmission electron microscopy
FE-SEM	Field emission-scanning electron microscopy
AFM	Atomic force microscopy
DFT	Density functional theory
SCXRD	Single crystal X-ray diffraction
MALDI	Matrix-assisted laser desorption/ionization
ESI-MS	Electrospray ionisation mass spectrometry
LDI-MS	Laser desorption/ionization mass spectrometry
FT-EXAFS	Fourier transform extended X-ray absorption fine-structure
TBBT	4- <i>tert</i> -Butylbenzenethiol
BBSH	4- <i>tert</i> -Butylbenzyl mercaptan
PET	2-Phenylethanethiol
HSBu	n-Butanethiol
BDT	1,3-Benzenedithiol
DMBT	Dimethylbenzenethiol

BINAS	1,1'-Binaphthyl-2,2'-dithiol
MHA	Mercaptohexanoic acid
TDT	Tetra(ethylene glycol) dithiol
BSA	Bovine serum albumin
MBA	Mercaptobenzoic acid
GSH	Glutathione
EBT	2-Ethylbenzenethiol
TPP	Triphenylphosphine
MBT	Methylbenzenethiol
BINAP	2,2'-Bis(di- <i>p</i> -tolylphosphino)-1,1'-binaphthyl
DPPM	Bis(diphenylphosphino)methane
HSET	Ethylthiol
PAH	Poly(allylamine hydrochloride)
MNA	2-Mercaptonicotinic acid
PEI	Polyethyleneimine
PNIPAm	Poly(<i>N</i> -isopropylacrylamide)
PEG	Poly (ethylene glycol)
MOPS	3-(<i>N</i> -morpholino)propane sulfonic acid
FGGC	N-terminal Phe-Gly-Gly-Cys peptide
CB[7]/[8]	Cucurbiturils 7/8
ad-ad	Di(adamantan-1-yl)phosphine
SH- β -CD	Mono-(6-mercapto-6-deoxy)- β -cyclodextrin
S ^t BU	<i>tert</i> -Butylthiol
CF ₃ COOH	Trifluoroacetic acid
Bpy	4,4'-bipyridine
NB	Nitrobenzene
MA	Methacrylic anhydride
MPA	3-Mercaptopropionic acid
Trp	Tryptophan
CEES	2-Chloroethyl ethyl sulfide

TPyP	Tetrapyrrolyl porphyrin
HDT	Hexa(ethylene glycol) dithiol
Ac	Acetylacetone
AMT	Azobenzene Monothiol
PU	Polyurethane
OB	Optical Brightener
BBOT	2,5-Bis(5-tert-butyl-2-benzoxazol-2-yl) thiophene
QR code	Quick-response code
EL	Electroluminescent
EQE	External quantum efficiency
TCSPC	Time-correlated single photon counting
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
nm	Nanometer
eV	Electron volt
μm	Micrometer
mA	Milliampere
μA	Microampere
°C	Degree Celsius
K	Kelvin
h	Hour
min	Minute
s	Second

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PREFACE

Nanomaterials are fascinating because of their small size and high surface area-to-volume ratio, which cause them to act completely differently from their bulk counterparts and display unique optical and photophysical properties. To fully comprehend their unique characteristics, in-depth compositional and structural investigations are necessary. However, in the case of metallic nanoparticles (NPs), one problem faced by researchers is the lack of monodispersity. Later, size-focused synthesis of NPs led to the discovery of atomically precise metal nanoclusters (NCs). NCs consist of a metal core protected by organic ligands, with a core size of less than 2 nm. Since the number of metal atoms in the core and ligands is finite, they can be denoted as $[M_xL_y]^z$, where x and y represent the number of metal atoms and ligands (e.g., L= thiolate (SR)), and z denotes the overall charge of the NC. NCs exhibit strong quantum confinement effects owing to their ultrasmall size, resulting in molecule-like properties such as distinct optical absorption features, photoluminescence, and enhanced catalytic activity. This makes them valuable for diverse applications in catalysis, sensing, energy, and biology. Recently, the self-assembly of NCs has become a “hot topic” in both fundamental and applied research. Many nanoscale molecular interactions at the NC surface play crucial roles in self-assembly, which can occasionally result in the crystallization of NCs and provide information about their structural and property relationships. The self-assembly of NCs into hierarchical superstructures led to enhanced photophysical properties due to the coupling effect of neighboring NCs. One could foresee that such enhanced photophysical properties are important for the development of advanced devices in the near future.

This thesis is organized into seven chapters. **Chapter 1** offers an overview of NCs, covering their synthesis, isolation, properties, and applications. The

second half of this chapter will discuss in detail the hierarchical self-assembly of NCs and their properties and applications. **Chapter 2** discusses the materials and experimental methods used for our investigations.

Chapter 3 discusses the synthesis and photon-assisted reversible self-assembly of thiolated azobenzene-stapled Au₂₅ NCs. Photoactivation of functionalized NCs ([Au₂₅C₃AMT)₁₈]⁻) in dichloromethane by irradiating ultraviolet light at 345 nm resulted in a visual change and formation of disc-like colloidal superstructures ($d \sim 100\text{-}1000$ nm). The superstructures are readily disassembled into individual NCs upon irradiating with the visible light at 435 nm. Systematic changes in both the electronic absorption bands and nuclear magnetic resonance spectra of chromophores in solution suggest that the photoisomerization of surface ligands drives the self-assembly. High-resolution transmission electron microscopy, electron tomographic reconstruction, dynamic light scattering, and small-angle X-ray powder diffraction show that the disc-like superstructures contain densely packed NCs. Long-range self-assembly and disassembly under ultraviolet and visible light, respectively, demonstrate reversible photo-switching in NCs.

Chapter 4 discusses the role of chromophore-spacer length in the light-induced self-assembly. Herein, the self-assembly is studied in detail using two photoswitchable NCs (C₃-NC and C₉-NC) fabricated using the thiolated-azobenzene molecule with different spacer lengths (C₃-AMT and C₉-AMT). The core and molecular information of both NCs were meticulously explored using various spectroscopic and microscopic techniques. Photoactivation of both NC solutions at ambient temperature using 345 nm light resulted in the formation of self-assembled superstructures. The C₉-NCs show a fast assembly due to their improved photoswitching efficiency resulting from the negligible steric hindrance experienced at the NC-chromophore interface.

Chapter 5 discusses the room temperature fabrication of a stable, flexible, nontoxic, and low-cost precision NC-based luminescent ink for the stencil printing of an optically unclonable security label. NC-based printing ink showed brilliant photoluminescence owing to its extended C–H $\cdots$ $\pi/\pi\cdots\pi$ interactions. Spectroscopic and microscopic investigations show that intercalated NC in printed security labels are highly stable as their optical features and molecular compositions are unaffected. The exceptional mechanical, thermal, photo, and aqueous stabilities of the printed security labels endorsed to demonstrate the printing and smartphone-based electronic reading of the quick response code on a currency. Finally, confidential information protection and decryption under a precise window of light have been achieved by adopting the optical contrast illusion. The polyurethane elastomeric binder helped to hold the printed QR code on currency even after multiple folding and wetting. The overall cost of the security label is found to be approximately 0.013 USD per stamp.

Chapter 6 discusses a highly stable, solid-state emitting bimetallic copper-gold nanocluster $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$, using adamantane thiol and 1,2-bis(diphenylphosphino)ethane as primary and secondary ligands. During the synthesis, only one phosphine is bound to gold and the second one has oxidized to P = O bond. The strong hydrogen bonding between P = O and the adamantane hydrogen atom facilitated rapid crystallization. The NC film and crystals show better photostability compared to its solution. Due to the exceptional photostability and solid-state photoluminescence, $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NC has been successfully employed to fabricate an electroluminescent light-emitting diode without additional host materials. The fabricated electroluminescent light-emitting diode shows a maximum brightness of 1246 cd/m² and an external quantum efficiency of 12.6 %.

ആമുഖം

നാനോ പദാർത്ഥങ്ങൾ അവയുടെ ചെറിയ വലിപ്പവും ഉയർന്ന ഉപരിതല വിസ്തീർണ്ണ-വ്യാപ്ത അനുപാതവും കാരണം ആകർഷകമാണ്. അതുകൊണ്ട് അവയുടെ വലിയ പദാർത്ഥങ്ങളിൽനിന്ന് തികച്ചും വ്യത്യസ്തമായി പ്രവർത്തിക്കുകയും അതുല്യമായ ഒപ്റ്റിക്കൽ, ഫോട്ടോഫിസിക്ക് ഗുണങ്ങൾ പ്രദർശിപ്പിക്കുകയും ചെയ്യുന്നു. അവയുടെ അതുല്യമായ സവിശേഷതകൾ പൂർണ്ണമായി മനസ്സിലാക്കാൻ, രൂപപരവും ഘടനാപരവുമായ അന്വേഷണങ്ങൾ ആവശ്യമാണ്. എന്നിരുന്നാലും, ലോഹ നാനോകണങ്ങളുടെ കാര്യത്തിൽ, ഗവേഷകർ അഭിമുഖീകരിക്കുന്ന ഒരു പ്രശ്നം ഏകീകൃത വലുപ്പത്തിലുള്ള നാനോകണങ്ങളുടെ അഭാവമാണ്. പിന്നീട്, നാനോകണങ്ങളുടെ വലിപ്പം കേന്ദ്രീകരിച്ചുള്ള നിർമ്മാണപ്രക്രിയ, കൃത്യമായി കണക്കാക്കാവുന്ന ആറ്റങ്ങളാൽ നിർമ്മിതമായ ലോഹ നാനോക്ലസ്റ്ററുകളുടെ കണ്ടെത്തലിലേക്ക് നയിച്ചു. നാനോക്ലസ്റ്ററുകളിൽ ഓർഗാനിക് ലിഗാൻഡുകളാൽ സംരക്ഷിതമായ ഒരു ലോഹകോർ അടങ്ങിയിരിക്കുന്നു. ഈ ലോഹകോറിന്റെ വലുപ്പം 2 nm ൽ താഴെയാണ്. ലിഗാൻഡുകളുടെയും കോറിലെ ലോഹ ആറ്റങ്ങളുടെയും എണ്ണം കൃത്യമായി അറിയാവുന്നതിനാൽ, അവയെ $[M_xL_y]^z$ എന്ന് സൂചിപ്പിക്കാം. ഇവിടെ x ഉം y ഉം ലോഹ ആറ്റങ്ങളുടെയും ലിഗാൻഡുകളുടെയും (ഉദാ: $L =$ തയോലേറ്റ് (SR)) എണ്ണത്തെ പ്രതിനിധീകരിക്കുന്നു. z നാനോക്ലസ്റ്ററുകളുടെ മൊത്തത്തിലുള്ള ചാർജിനെ പ്രതിനിധീകരിക്കുന്നു. നാനോക്ലസ്റ്ററുകൾ അവയുടെ അതിസൂക്ഷ്മമായ വലുപ്പം കാരണം ശക്തമായ ക്വാണ്ടം കൺഫൈൻമെന്റ് ഇഫക്റ്റുകൾ പ്രകടിപ്പിക്കുകയും തന്മാത്രകളുടെ സ്വഭാവഗുണങ്ങളായ വ്യതിരിക്തമായ ഒപ്റ്റിക്കൽ അബ്സോർപ്ഷൻ സവിശേഷതകൾ, ഫോട്ടോലൂമിനസെൻസ്, മെച്ചപ്പെടുത്തിയ കാറ്റലിക് പ്രവർത്തനം എന്നിവ ഉണ്ടാകുകയും ചെയ്യുന്നു. ഇത് കാറ്റലിസിസ്, സെൻസിംഗ്, എനർജി, ബയോളജി എന്നീ വ്യത്യസ്ത മേഖലകളിലെ പ്രയോഗങ്ങൾക്ക് അവയെ വിലപ്പെട്ടതാക്കുന്നു. അടിസ്ഥാനപരവും പ്രായോഗികവുമായ ഗവേഷണങ്ങളിൽ സമീപകാലത്തായി നാനോക്ലസ്റ്ററുകളുടെ സെൽഫ്-അസംബ്ലി ഒരു "പ്രധാന മേഖലയായി" മാറിയിട്ടുണ്ട്.

നാനോക്ലസ്റ്ററിന്റെ ഉപരിതലത്തിലെ പല തന്മാത്രാ ഇടപെടലുകളും സെൽഫ്-അസംബ്ലിയിൽ നിർണായകപങ്ക് വഹിക്കുന്നു. ഇത് ചിലപ്പോൾ നാനോക്ലസ്റ്ററുകളുടെ ക്രിസ്റ്റലൈസേഷനിലേക്ക് നയിക്കുകയും അവയുടെ സ്വഭാവസവിശേഷതകളും ഘടനയും തമ്മിലുള്ള ബന്ധങ്ങളെക്കുറിച്ചുള്ള വിവരങ്ങൾ നൽകുകയും ചെയ്യും. നാനോക്ലസ്റ്ററുകളെ ഹൈറാർക്കിക്കൽ സൂപ്പർ സ്ട്രക്ചറുകളായി സെൽഫ്-അസംബ്ലി ചെയ്യുന്നത് അടുത്തടുത്തുള്ള നാനോക്ലസ്റ്ററുകളുടെ ക്ലിംഗ് ഇഫക്റ്റിലേക്ക് നയിക്കുകയും ഫോട്ടോഫിസിക്ക് ഗുണങ്ങൾ വർദ്ധിപ്പിക്കുന്നതിന് കാരണമാവുകയും ചെയ്യുന്നു. സമീപഭാവവിധിയിൽ വിപുലമായ പല ഉപകരണങ്ങളുടെയും വികസനത്തിന് ഇത്തരം മെച്ചപ്പെടുത്തിയ ഫോട്ടോഫിസിക്ക് ഗുണങ്ങൾ പ്രധാനമാണെന്ന് ഒരാൾക്ക് മുൻകൂട്ടി കാണാൻ കഴിയും.

ഈ പ്രബന്ധം ഏഴ് അധ്യായങ്ങളായി ക്രമീകരിച്ചിരിക്കുന്നു. അദ്ധ്യായം ഒന്നിൽ നാനോക്ലസ്റ്ററുകളുടെ ഒരു അവലോകനമാണ് ഉൾപ്പെടുത്തിയിരിക്കുന്നത്. അവയുടെ നിർമ്മാണം, വേർതിരിക്കൽ, സവിശേഷതകൾ, ഉപയോഗങ്ങൾ എന്നിവ

ഇതിൽ ഉൾക്കൊള്ളുന്നു. ഈ അധ്യായത്തിന്റെ രണ്ടാം പകുതിയിൽ നാനോക്ലസ്റ്ററുകളുടെ ഹൈറാർക്കിക്കൽ സെൽഫ് അസംബ്ലിയെയും അവയുടെ ഗുണങ്ങളെയും ഉപയോഗങ്ങളെയും കുറിച്ച് വിശദമായി ചർച്ച ചെയ്യുന്നു.

രണ്ടാം അധ്യായത്തിൽ, ഗവേഷണത്തിനായി ഉപയോഗിക്കുന്ന മെറ്റീരിയലുകളും പരീക്ഷണരീതികളും ചർച്ച ചെയ്യുന്നു.

മൂന്നാം അധ്യായത്തിൽ, തയോലേറ്റഡ് അസോബെൻസീൻ-സ്റ്റേപ്പിൾഡ് Au_{25} നാനോക്ലസ്റ്ററുകളുടെ പ്രകാശപ്രേരിതമായ റിവേഴ്സിബിൾ സെൽഫ് അസംബ്ലിയെക്കുറിച്ച് ചർച്ച ചെയ്യുന്നു.

നാലാം അധ്യായത്തിൽ പ്രകാശപ്രേരിതമായ സെൽഫ്-അസംബ്ലിയിൽ ക്രോമോഫോർ-സ്പേസർ ദൈർഘ്യത്തിന്റെ പങ്ക് ചർച്ചചെയ്യുന്നു.

അഞ്ചാം അധ്യായത്തിൽ, ഒപ്റ്റിക്കലി അൺക്ലോണബിൾ സെക്യൂരിറ്റി ലേബലിന്റെ സ്റ്റെൻസിൽ പ്രിൻറിംഗിനായി, സ്ഥിരതയുള്ളതും വഴക്കമുള്ളതും വിഷരഹിതവും കുറഞ്ഞ ചെലവിൽ നിർമ്മിക്കാവുന്നതുമായ നാനോക്ലസ്റ്റർ അധിഷ്ഠിത ലൂമിനസെന്റ് മഷിയുടെ റൂം ടെമ്പറേച്ചർ ഫാബ്രിക്കേഷനെക്കുറിച്ച് ചർച്ച ചെയ്യുന്നു.

ആറാം അധ്യായത്തിൽ, ബൈമെറ്റാലിക് കോപ്പർ-ഗോൾഡ് നാനോക്ലസ്റ്ററുകൾ ഉപയോഗിച്ച് അധിക ഹോസ്റ്റ് മെറ്റീരിയലുകളോന്നുമില്ലാതെ ഇലക്ട്രോലൂമിനസെന്റ് ലൈറ്റ്-എമിറ്റിംഗ് ഡയോഡുകളുടെ നിർമ്മാണം ചർച്ച ചെയ്യുന്നു.

CHAPTER 1

INTRODUCTION

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INTRODUCTION

1.1 General Introduction

1.1.1 Overview

The material scientists made breakthroughs in Chemistry by fabricating fascinating nanomaterials such as plasmonic nanoparticles (NPs), up-conversion NPs, semiconductor quantum dots (QDs), perovskites, carbon nanotubes, graphene, etc. Among these, graphene and QDs received the Nobel prizes in 2010 and 2023, respectively. Such smart and functional nanomaterials with diverse surface functionalities have been extensively used for a variety of applications in modern Science and Technology. Later, the size-focused synthetic attempts of metal-based plasmonic NPs resulted in the birth of atomically precise noble metal nanoclusters (NCs) having diverse optical and photophysical properties compared to their ancestors. Though NCs could be synthesized in gaseous, solid, and solution phases, the option for improving the stability in the solution state is more by employing different protecting ligands, such as thiols, alkynyls, phosphines, carbenes, selenol, and many more.^[1,2] NCs are usually prepared using the modified Brust-Schiffrin, size-focusing, ligand exchange, and solid-state methods.^[1-4] These synthetic techniques helped with the controlled and tailored production of NCs with specific core sizes and functionalities. NCs have a finite or precise number of atoms in their metallic core, stabilized by an adequate number of ligands with a core size in the sub-nano regime (< 2 nm).^[5] In terms of size, NCs exist in a regime between metal complexes and plasmonic NPs^[2,6] (**Figure 1.1A**). As a result, NCs could bridge the missing gap between atoms and nanomaterials. The superatom model has been used to explain the electronic stability of NCs,^[7] in which they became more stable

when the number of free electrons falls in the magic number series.^[8] Due to their extremely small size, quantum confinement effect, well-defined energy gaps, and enhanced chemical/photostability, NCs received significant attention in the recent past. They possess diverse surface functionalities and exhibit unique optoelectronic and catalytic properties, which make them suitable for a wide range of applications in the fields of catalysis, sensing of toxic metal ions/molecules, bioimaging, therapeutics, green energy production, device fabrication, and so on.^[1,2]

The NCs have a general formula of $[M_xL_y]^z$, where x , y , and z represent the number of metal atoms (M), ligands (L), and the overall surface charge of NCs, respectively. Constant attempts resulted in the development of innovative and effective methods for the production of monodisperse NCs. Even a minute difference in x , y , or z is found to influence their optoelectronic, photophysical, and catalytic properties. Hence, precise control over these elements is one of the primary research directions in this field. The UV-Vis absorption spectra of these NCs showed molecule-like electronic transitions due to their quantum confinement (**Figure 1.1B**). Such discrete energy levels exhibit varying HOMO-LUMO (Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular Orbital) gaps depending on the number of atoms in the metal core of NCs^[1,2,9,10] (**Figure 1.1C**). The isolation and purification of NCs have been achieved through techniques ranging from simple solvent extraction to sophisticated chromatographic methods, ensuring the highest levels of purity.^[11-14] The molecular composition of NCs has been explored using mass spectrometry and single-crystal X-ray diffraction (SCXRD) studies. Advanced mass spectrometry techniques, including matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization mass spectrometry (ESI-MS), could help to find out the exact mass of NCs and hence confirm their formation and purity.

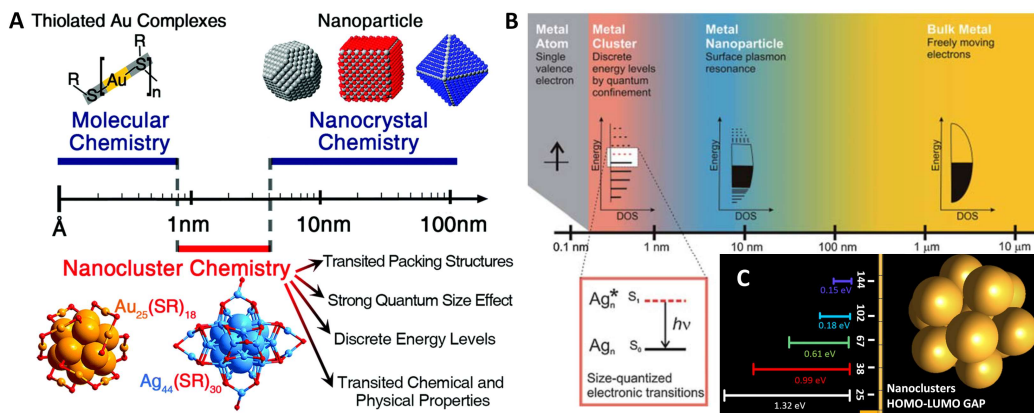


Figure 1.1: (A) Illustration representing the scope of NC Science. Metal NCs bridge the gap between metal complexes and plasmonic NPs (SR = thiolate). (B) Effect of size on the energy levels of a metal. (C) HOMO-LUMO energy gap of different gold NCs. Adapted from Refs.[6,9,10].

Among different combinations, the coinage metal (gold, silver, and copper) based NCs have been explored more due to their stability and the ability to resolve their crystal structure. For example, Jadzinsky *et al.* were able to resolve the crystal structure of $[Au_{102}(SR)_{44}]$ NC.^[15] Subsequently, Jin and Murray's group revealed the icosahedral structure of $[Au_{25}(SR)_{18}]$ NC,^[16,17] which helped to open up new directions for such materials. Later, a variety of NCs including, $[Au_{18}(SR)_{14}]$, $[Au_{22}(SR)_{16}]$, $[Au_{28}(SR)_{20}]$, $[Au_{30}(SR)_{18}]$, $[Au_{36}(SR)_{24}]$, $[Au_{38}(SR)_{24}]$, $[Au_{144}(SR)_{60}]$, $[Ag_{25}(SR)_{18}]$, $[Ag_{29}(S_2R)_{12}]$, $[Ag_{44}(SR)_{30}]$, and many more were successfully synthesized and characterized. The photophysical properties of NCs could be altered or improved depending on factors such as (i) the number of atoms present in the metallic core, (ii) based on the alloying or doping with other metal atoms, (iii) integration of various functional ligands, (iv) incorporation with other functional materials, and (v) aggregation or assembly of NCs. As previously mentioned, a mere alteration of a single metal atom within the metal core of NC could lead to entirely distinct photophysical properties. For example, the comparison between Au_{25} and Au_{24} NCs reveals the distinct differences in

both structure and optical properties, despite a single gold atom difference.^[18] Similarly, the dynamic field of heterometallic NC science explored a broad spectrum of alloy NCs. Notably, the incorporation of Pt, Pd, Ru, and other transition metals also have been used to enhance the photophysical and catalytic activity of NCs.^[19,20] Furthermore, ligand engineering using the organic synthetic toolbox helped to develop a wide range of functional NCs. Such NCs have been successfully used for light-triggered electron or energy transfer,^[21] optical chirality,^[22] targeted bioimaging, and drug/gene delivery.^[23] On the other hand, integrating NCs with other functional materials such as carbon-based nanomaterials (graphene, carbon nanotube, etc.), TiO₂ NPs, and MoS₂ nanosheets resulted in the formation of NC-based composite materials with enhanced electrochemical sensing/catalytic activities.^[24–26] Furthermore, the supramolecular interactions between the neighboring NCs *via* nanoscale surface forces resulted in assembled superstructures having collective and enhanced optical characteristics compared to the individual NCs.

1.1.2 Synthesis of NCs

Self-assembled monolayers (SAMs) of organic moieties grown on two-dimensional (2D) bulk metal surfaces played a crucial role in shaping metal-based nanosystems. Particularly, the evolution of thiol chemisorption has significantly contributed to the growth and diversification of various metal-based nanostructures. The synthesis of thiol-stabilized NPs was initially carried out in the early 1990s by simultaneously anchoring thiols on the growing nuclei.^[4] Such robust interaction between metal and thiol not only aided oxidation prevention but also reduced metal atom agglomeration resulting in the formation of stable NPs. The synthesis of monolayer-thiol-protected gold NCs became easier after the introduction of the two-phase

Brust-Schiffrin method^[4,27] (**Figure 1.2A**). Here, an aqueous solution of Au^{3+} ions ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was initially phase-transferred into an organic layer (toluene) using a phase-transferring agent (tetraoctylammonium bromide, TOAB). The subsequent introduction of long-chain alkyl thiols into the phase-transferred Au^{3+} ions (1:1 molar ratio with gold) results in the partial reduction and formation of Au(I) -thiolates. The final reduction of as-prepared Au(I) -alkyl thiolates using an aqueous solution of sodium borohydride (NaBH_4) resulted in the formation of organic soluble NPs (**Figure 1.2B**).

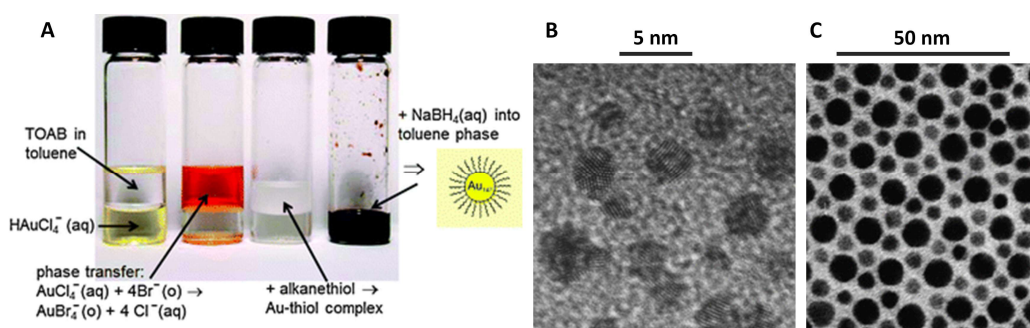


Figure 1.2: (A) Two-phase Brust-Schiffrin method for the synthesis of gold NPs. (B) The TEM (Transmission electron microscopy) micrographs of as-prepared gold NPs. Adapted from the Ref.[27].

Based on this two-step reduction method, the research groups of Whetten and Murray separately developed a size-focused route for the synthesis of water-soluble glutathione (GSH)-protected gold NCs (Au@SG) by increasing the gold-to-thiol molar ratio to 1:3.^[28,29] The chemical reduction followed by precipitation and purification of the blackish-brown solution using the excess antisolvents (ethanol (EtOH) or acetone) resulted in the formation of black crystalline powder. The purified NCs were then characterized using mass spectrometry and various analytical techniques. By taking advantage of Liquid Desorption Ionization Mass Spectrometry (LDI-MS), Whetten *et al.* demonstrated the formation of a range of alkyl thiolate-protected gold NCs

having molecular masses ranging from 27 to 93 kDa.^[28] The overall compositions of these NCs were assigned and reassigned by using the LDI-MS.^[30] For example, 5.6 kDa NC was initially assigned as $[\text{Au}_{28}(\text{SG})_{18}]$.^[31] Later it was reassigned to $[\text{Au}_{25}(\text{SG})_{18}]$, which became one of the most relevant NC in the current research.^[32]

Later, the organic soluble Au_{25} NCs were successfully synthesized using 2-phenylethanethiol (PET) as the protecting ligand. Here, the two-phase Brust-Schiffrin method was initially adopted for the size-selective production of $[\text{Au}_{25}(\text{PET})_{18}]$ NCs in toluene.^[33] In this approach, a better yield of NCs was achieved by controlling the reaction temperature. Specifically, large quantities of NCs were harvested when $\text{Au}(\text{I})$ -thiolates were reduced at 0°C (**Figure 1.3**). To address the challenges associated with the two-phase reduction approach, a modified one-pot procedure based on the Brust-Schiffrin method was proposed, in which toluene was replaced with tetrahydrofuran (THF).^[34] However, when the reduction was carried out in a more polar solvent such as acetonitrile (CH_3CN) or methanol (MeOH), larger NCs such as Au_{144} were formed.^[35,36] This clearly suggested that, by employing the size-focusing methodology, one could control the formation of NCs precisely.

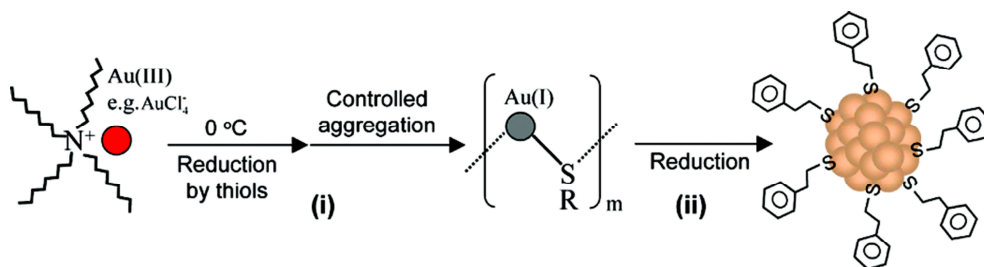


Figure 1.3: Modified Brust-Schiffrin method used for the synthesis of $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs. Adapted from Ref.[34].

The size-focusing strategy involves two steps, in which the first step is kinetically controlled and the second one is thermodynamically favored. In

the first step, the reduction of gold(I) – thiolates results in the formation of a mixture of NCs $[\text{Au}_x(\text{SR})_y]$. However, the subsequent step favors the formation of a thermodynamically stable metal core. As a result, highly monodisperse NCs will be formed from a mixture of NCs through the size-focusing technique.^[37] The manipulation of reactant amount, reducing agents, temperature, and solvent composition plays an important role in shaping the formation of kinetically and thermodynamically controlled NCs. The schematic of the size-focusing procedure is shown in **Figure 1.4A**. A variety of NCs, including $[\text{Au}_{144}(\text{SR})_{60}]$, $[\text{Au}_{64}(\text{SR})_{32}]$, $[\text{Au}_{99}(\text{SR})_{42}]$,^[38] and $[\text{Ag}_{25}(\text{SR})_{18}]$,^[39] have been successfully synthesized using this method. Later, the ligand exchange-induced structural transformation (LEIST) method has been developed to fabricate diverse magic-numbered NCs, which were unable to be synthesized *via* conventional size-focusing methods (**Figure 1.4B**).^[40] This process creates new and stable NCs that are completely distinct from the precursor NC by directly introducing a large amount of an external ligand to a well-shaped NC or a combination of NCs. One notable application of LEIST is demonstrated by Qian *et al.*, who successfully employed a thiol-for-thiol ligand exchange pathway to achieve a high yield $[\text{Au}_{38}(\text{SC}_{12}\text{H}_{25})_{24}]$ NCs.^[41] This process involved exchanging a mixture of aqueous $[\text{Au}_x(\text{SG})_y]$ NCs with excess organic-soluble thiols such as DT (1-dodecanethiol). Such ligand exchange strategy not only facilitates the synthesis of monodisperse NCs but also enhances the versatility of the process. A few examples illustrate the advantage of LEIST method from the literature include the conversion of (i) $[\text{Au}_{25}(\text{PET})_{18}]$ to $[\text{Au}_{28}(\text{TBBT})_{20}]$ (TBBT- 4-tert-Butylbenzyl mercaptan),^[42] (ii) $[\text{Au}_{38}(\text{PET})_{24}]$ to $[\text{Au}_{36}(\text{TBBT})_{24}]$,^[43] and (iii) $[\text{Au}_{144}(\text{PET})_{60}]$ to $[\text{Au}_{133}(\text{TBBT})_{52}]$ ^[44] NCs. The mechanistic investigation focused on the transformation of $[\text{Au}_{38}(\text{PET})_{24}]$ into $[\text{Au}_{36}(\text{TBBT})_{24}]$ NC revealing that the conversion process occurs through

four distinct steps (**Figure 1.4C**).^[43] Here, in the first step, the ligand exchange occurs due to the presence of foreign ligands. The subsequent structural distortion due to excess ligands resulted in the formation of a mixture of Au₄₀ and Au₃₆ NCs by the disproportionation reaction. Finally, the size focusing of these two products results in the formation of [Au₃₆(TBBT)₂₄] NCs.

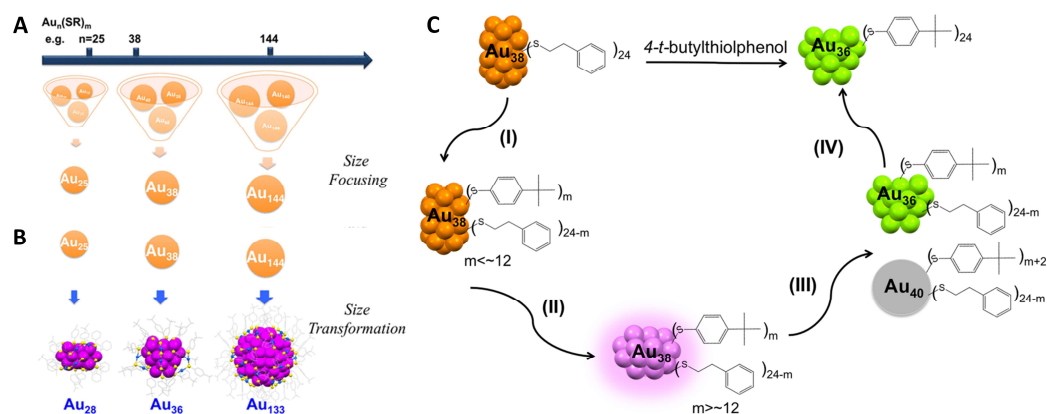


Figure 1.4: (A) Illustrate the size-focused method used for the synthesis of different NCs and (B) Size transformation using the LEIST method. (C) Different stages involved in the synthesis of [Au₃₆(PET)₂₄] NC by LEIST are shown. Adapted from Refs.[40,43].

Later, the Brust-Schiffrin chemical reduction method was further extended to fabricate a variety of other metal NCs (silver and copper) as well. One such example is the fabrication of TBBT-protected Ag NCs using a two-step Brust-Schiffrin protocol.^[45] Following that, many Ag and Cu NCs were synthesized by using the chemical reduction method by introducing new precursors and ligands. Similarly, heterometallic NCs have also been synthesized using the simple chemical co-reduction method.^[46] Here, a mixture of metal precursors was used and proceeded in the same way as the Brust-Schiffrin protocol executed. In addition to this, post-synthetic methods such as galvanic or ant galvanic exchange reactions were also been employed to synthesize different combinations of heterometallic NCs.^[46]

1.1.3 Isolation of NCs

The purity of NCs is very critical for crystallization and structural elucidation. The conventional synthetic methods always produce a mixture of NCs, including unwanted thiolated complexes. Such impurities not only cause NC stability but also interfere with their accurate physical measurements. In the beginning stage, the research groups of R. L. Whetten and C. B. Murray used solvent-selective extraction and fractional precipitation techniques for the isolation and purification of NCs. Later, Tsukuda *et al.* introduced Polyacrylamide Gel Electrophoresis (PAGE) for the separation of hydrophilic NCs.^[32] They could separate and characterize a series of water-soluble Au@SG NCs using ESI-MS (**Figure 1.5**).

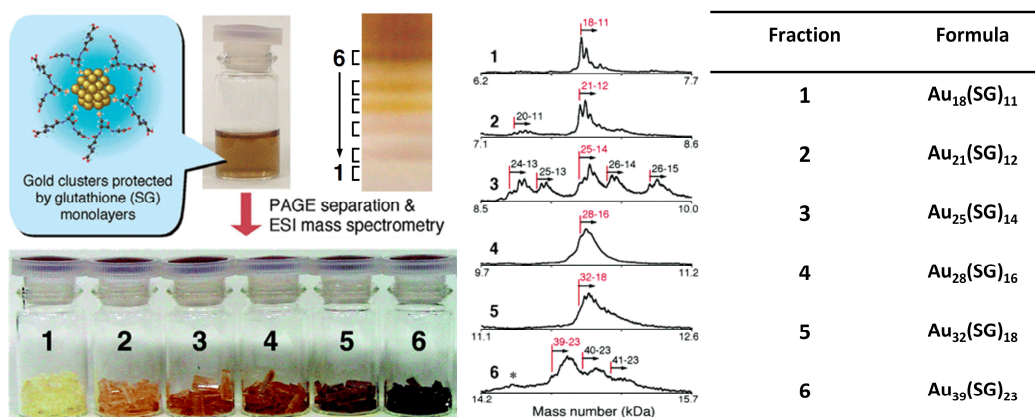


Figure 1.5: Photographs of the PAGE method used for the separation of a mixture of Au@SG NCs into six well-distinguished fractions and their ESI-MS are shown. Adapted from Ref.[8].

Later, R. W. Murray's research group introduced the chromatographic techniques for the isolation and purification of NCs. They used reverse-phase high-performance liquid chromatography (HPLC) for separating alkyl thiol-protected gold NCs and subsequently characterized them using electrochemical and optical techniques. Subsequently, the service of HPLC was extended to isolate a mixture of monometallic and heterometallic NCs.

For example, Niihori *et al.* successfully isolated $[\text{PdAu}_{24}(\text{PET})_{18}]$ from $[\text{Au}_{25}(\text{PET})_{18}]$.^[47] The same method has also been used to separate the mixed-ligand protected NCs such as $[\text{PdAu}_{24}(\text{DT})_{18-n}(\text{SBB})_n]$ (BBSH- 4-tert-Butylbenzyl mercaptan).^[12] Here, the separation was accomplished in two steps. In the first step, NCs were absorbed into the column, followed by gradual elution from the stationary phase. Here, a linear gradient program was used for the transition of the mobile phase from pure MeOH to THF. Notably, the polarity difference between BBSH and DT ligands influenced the elution sequence, resulting in the earlier elution of NCs with a higher count of BBSH ligands. Later, Thin-layer chromatography (TLC) has also been used for the successful separation of NCs. By using this method, one could even crystallize Au_{144} NCs obtained from the fractions isolated from preparative TLC. In another example, Ghosh *et al.* demonstrated the separation of two different Au_{25} NCs ($[\text{Au}_{25}(\text{SBu})_{18}]$ and $[\text{Au}_{25}(\text{PET})_{18}]$; (HSBu= n-butanethiol)) by the TLC method.^[14] Later, size exclusion chromatography (SEC) was also employed to isolate NCs based on their sizes.^[13] SEC exploits the permeation characteristics of molecules through pores, leading to a faster elution time for bigger NCs and a slower elution time for smaller molecules (smaller molecules have to travel through more pores). SEC not only helps to separate NCs holding different core sizes but also will remove the excess ligands accompanied during the synthesis. Other chromatography techniques, including ion-pair chromatography, hydrophilic interaction liquid chromatography (HILIC), and chiral chromatography were also rarely used to separate the NCs successfully.

1.1.4 Characterization of NCs

Optical absorption spectroscopy, mass spectrometry, and single-crystal X-ray diffraction analysis (SCXRD) stand out as the primary tools for

characterizing NCs. In the case of gold NPs, the intensity of the surface plasmon resonance (SPR) diminishes as the size of the NPs decreases. When the size drops below 2 nm, the SPR completely vanishes and starts to show molecular-like electronic transitions (**Figure 1.6A, B**). Such changes are attributed to the quantum confinement effect in NCs. Also, the number of atoms in the metallic core has a significant impact on the absorption characteristics of NCs.^[1,2] For example, Au₂₅ NC exhibits three distinct absorption peaks (unique to Au₂₅ NC irrespective of protecting ligands). Density functional theory (DFT) showed that the optical absorption features in [Au₂₅(SR)₁₈]⁻ arise from transitions between different molecular orbitals as depicted in the Kohn-Sham (KS) orbital energy level diagram (**Figure 1.6 C, D**).

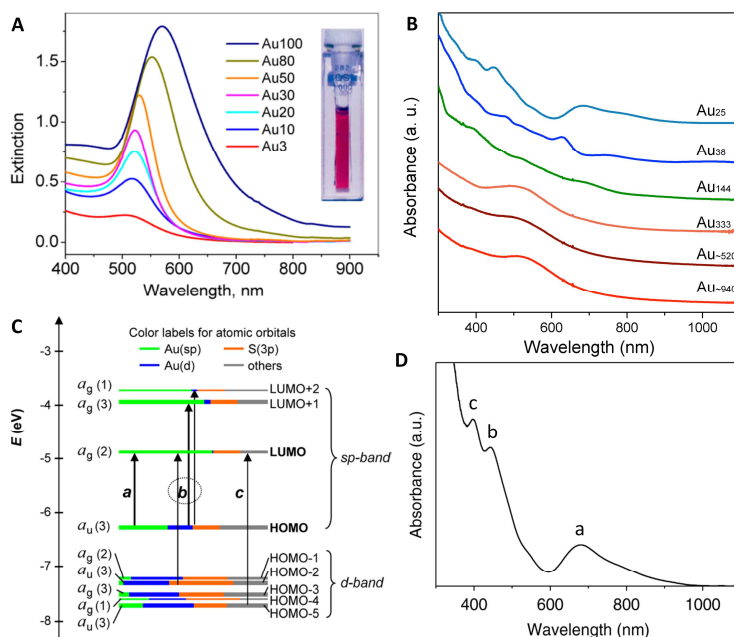


Figure 1.6: (A) Optical absorption spectra recorded from different-sized gold NPs. (B) UV-Vis absorption spectra of a series of Au_n NCs. (C) Kohn-Sham orbital energy level diagram of [Au₂₅(SH)₁₈]⁻ NC (The relative contributions of atomic orbitals of Au (6sp), Au (5d), and S (3p) to each KS orbital are indicated by colored lines). (D) The experimental absorption spectrum of [Au₂₅(SH)₁₈]⁻ NC. Adapted from Refs.[2,16,48].

Though the absorption spectrum of each NC shows unique optical features, finding out the exact number of core atoms and protecting ligands is the next challenge in this area of research. This has been solved by using the advantages of advanced mass spectrometric techniques, including LDI/MALDI and ESI-MS. Even though these mass spectrometric techniques can precisely measure the mass of NCs, the uncontrolled fragmentation of NCs eventually limits the use of this method. Despite this drawback, this technique seems to be more convenient for neutral-charged NCs. The second method, ESI-MS is a soft ionization technique, which requires an intrinsic charge on the NC surface to produce the mass spectrum. Hence, while using neutral NCs, cesium acetate (CsOAc) or similar ionizing agents have also to be co-injected to induce a charge on NC. The ESI-MS could also show isotopic distribution and hence is able to find the charge state from neighboring peaks in the isotope distribution. For example, the single intense peak and zoomed isotopic pattern of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ (BDT= 1,3-benzenedithiol),^[49] $[\text{Ag}_{25}(\text{DMBT})_{18}]^{-}$ (DMBT= 2,4-dimethylbenzenethiol),^[39] and $[\text{Au}_{25}(\text{PET})_{18}]^{-}$ NCs were shown in **Figure 1.7A-C**. $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ NC consists of three -ve charges and shows the 1/3 difference in m/z value between two successive isotopic peaks. The other two NCs consist of one -ve charge and show a difference of 1 in m/z value between two successive isotopic peaks.^[50]

A comprehensive idea of the surface and kernel structure of NCs is necessary for a better understanding of their stability and unique properties. As the NCs behave like larger molecules, one could crystallize if they are extremely pure. However, producing single crystals from metal NCs is still challenging due to multiple reasons such as stability, polydispersity, and sensitivity. To a great extent, these difficulties have been addressed by a variety of recently developed advanced synthesis procedures and purifying methods. The

potential method utilized to produce NC-based single crystals was vapor diffusion. In this process, the NC insoluble solvent gradually diffuses into a solution containing soluble NC, leading to the formation of NC single crystals. Additionally, evaporation and electro-crystallization techniques were also employed to facilitate NC crystal formation.

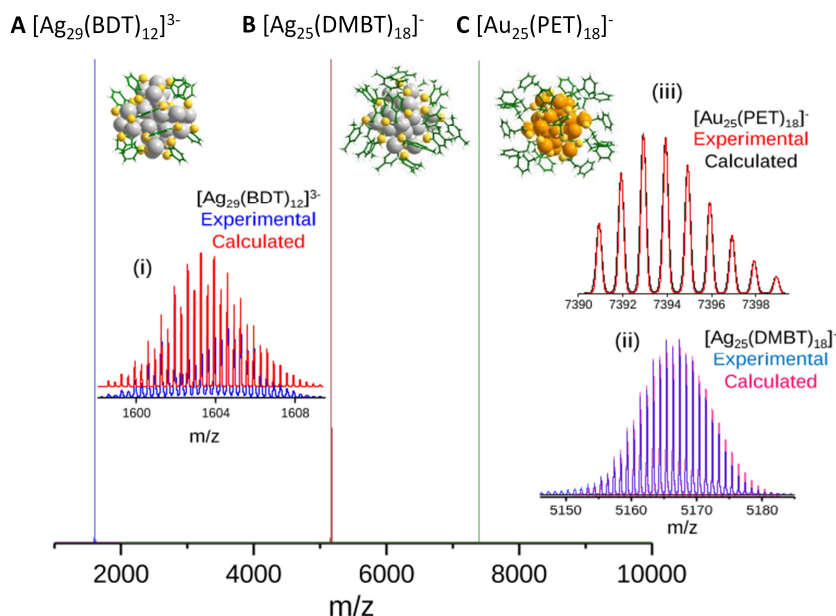


Figure 1.7: ESI-MS of (A) $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$, (B) $[\text{Ag}_{25}(\text{DMBT})_{18}]^{-}$, and (C) $[\text{Au}_{25}(\text{PET})_{18}]^{-}$. (i), (ii), and (iii) show the theoretical and experimental isotopic distribution of respective NCs. Adapted from Ref.[50].

The single crystals obtained from NCs helped to understand the complexities of the ligand surface structure and metal core by using SCXRD analysis. For instance, Jadzinsky and his research team at the very first time achieved a noteworthy breakthrough in this field when they successfully crystallized $[\text{Au}_{102}(\text{SR})_{44}]^{-}$ NC.^[15] Here, NC showed a truncated Au_{49} decahedral kernel, derived from a fivefold symmetric 19-atom core. Further, the Au_{49} kernel is supplemented by two 15-atom caps, positioned at the top and bottom, respectively. The resulting Au_{79} kernel possesses five -SR-Au-SR- monomeric staples at the top, an additional five at the bottom, and nine monomers along

with two dimers ($-\text{SR-Au-SR-Au-SR}-$) at the waist (**Figure 1.8**). On top of this success, researchers could crystallize many NCs, with the notable achievement in the crystallization of $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs. Au_{25} NC comprises an Au_{13} icosahedral core shielded by six $\text{Au}_2(\text{SR})_3$ staples (**Figure 1.9**).^[16,17] Later, a wide variety of monometallic and heterometallic NCs have been successfully crystallized using different techniques described above and solved their total structure.

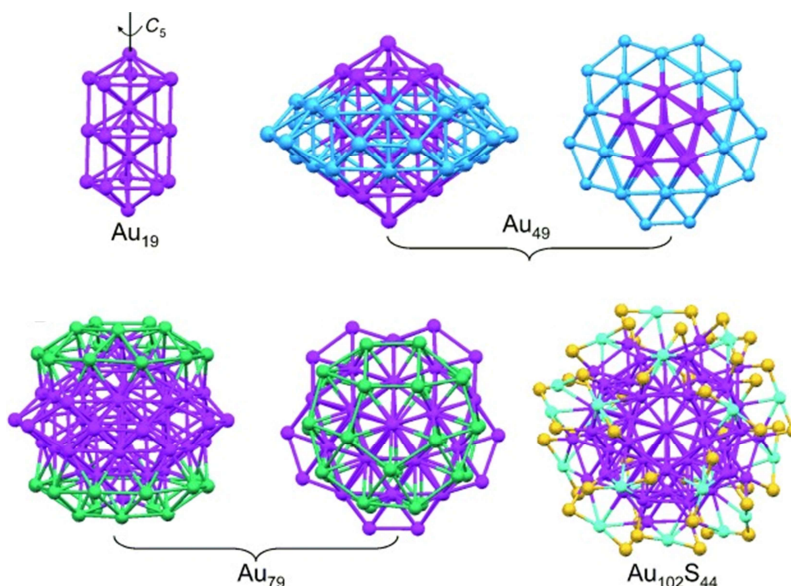


Figure 1.8: Total SCXRD structure of $[\text{Au}_{102}(\text{p-MBA})_{44}]$ NC. Adapted from Ref.[15].

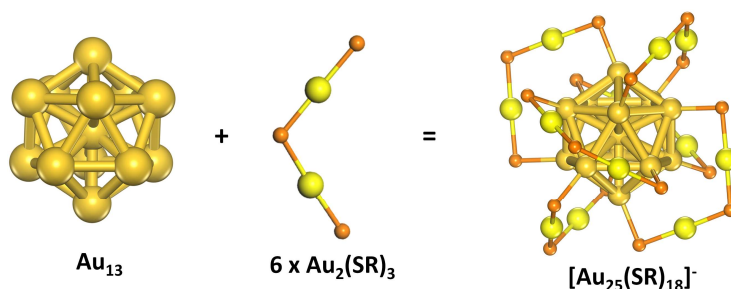


Figure 1.9: Structural anatomy of $[\text{Au}_{25}(\text{SR})_{18}]^-$ NC, which shows an Au_{13} metal core protected by six $\text{Au}_2(\text{SR})_3$ staples; Au (yellow), S (orange). Adapted from Refs.[16,17].

1.1.5 Properties and applications of NCs

NCs received considerable attention in diverse fields owing to their extremely small size, discrete energy levels, magnetism, chirality, and photoluminescence (PL). NCs are known to show reversible charge-dependent magnetism. For example, though $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs do not exhibit any electron paramagnetic resonance (EPR) signal, oxidation to zero charges could show a paramagnetic nature with an intense EPR signal. NCs also exhibit both intrinsic and ligand-induced chirality. For example, many NCs, including $[\text{Au}_{38}(\text{SR})_{24}]$, $[\text{Au}_{102}(\text{SR})_{44}]$, $[\text{Au}_{28}(\text{SR})_{20}]$, and $[\text{Au}_{40}(\text{SR})_{24}]$ have been identified as chiral based on their ligand arrangement. Though NCs such as $[\text{Au}_{38}(\text{2-PET})_{22}(\text{BINAS})_1]$ (BINAS= 1,1'-Binaphthyl-2,2'-dithiol) and $[\text{Au}_{25}(\text{PET})_{18-x}(\text{BINAS})_x]$ showed chirality due to the presence of chiral ligands, $[\text{Au}_{55}(\text{TPP})_{12}\text{Cl}_6]$ (TPP= Triphenylphosphine), $[\text{Au}_{20}(\text{PP}_3)_4\text{Cl}_4]$ (PP_3 = tris(2-(diphenylphosphino)ethyl) phosphine), $[\text{Au}_{49}(\text{SR})_{27}]$, and $[\text{Ag}_{23}(\text{TPP})_8(\text{PET})_{18}]$ NCs exhibit intrinsic chirality due to their chiral core. NCs could emit light in a wide range of wavelengths (from visible to infrared), depending on their atomic composition and ligand types. Unfortunately, their low photoluminescence quantum yield (PLQY) was a major drawback. This issue was addressed by developing diverse heterometallic NCs holding better PLQYs. The luminescent NCs found applications in PL-based sensing, biolabeling, bioimaging, and optoelectronic device fabrication. For example, the PL-based sensing using Au@BSA (BSA= Bovine Serum Albumin) NCs for the selective detection of mercury ion (Hg^{2+})^[51] is shown in **Figure 1.10**. The specific d^{10} - d^{10} interaction between Au(I) and Hg(II) led to the PL quenching of NCs, even in the presence of trace amounts of Hg. Later, NCs were extensively used for selective and sensitive detection of metal ions, biomolecules, DNA (Deoxyribonucleic acid), and so on.

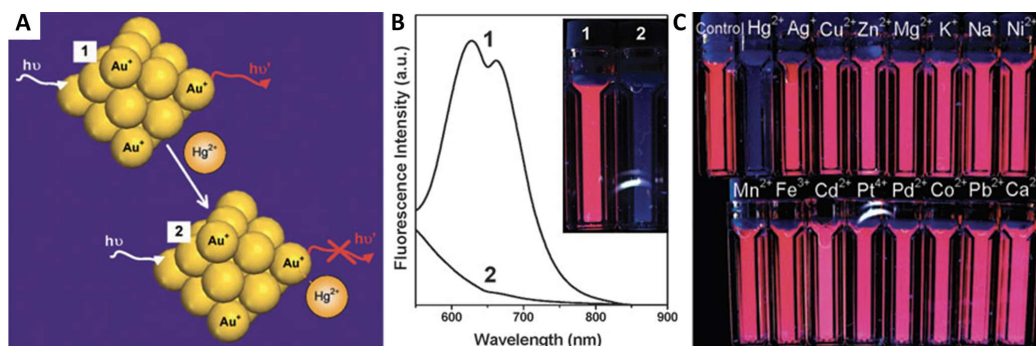


Figure 1.10: (A) Schematic representation of Hg(II) sensing based on the PL quenching of Au@BSA NCs. (B) PL spectra and photographs of Au@BSA NCs under UV light in the (1) absence and (2) presence of Hg(II) ions (50 μM). (C) Photographs of an aqueous solution of NCs (20 mM) under UV light in the presence of 50 μM concentration of various metal ions. Adapted from Ref.[51].

NCs have been used for one-photon, two-photon, and short-wave infrared (SWIR)-based imaging. For instance, Yu *et al.* used mercaptohexanoic acid (MHA) and tetra(ethylene glycol) dithiol (TDT)-co-stabilized luminescent gold NCs for SWIR imaging of a mouse vascular network system with better spatial resolution and contrast.^[52] Such type of imaging techniques highlight the potential of NCs in advanced biomedical imaging applications. NCs also found applications in other biomedical fields including drug delivery, photodynamic therapy, and photothermal therapy. For example, the incorporation of a stable photosensitizer (chlorin e6) into the surface of gold NCs offered a promising platform for targeted photodynamic therapy. This synergistic nanocomposite not only disrupts thioredoxin reductase activity but also amplifies $^1\text{O}_2$ generation, thereby increasing the efficiency of photodynamic treatment^[53] (**Figure 1.11A-B**).

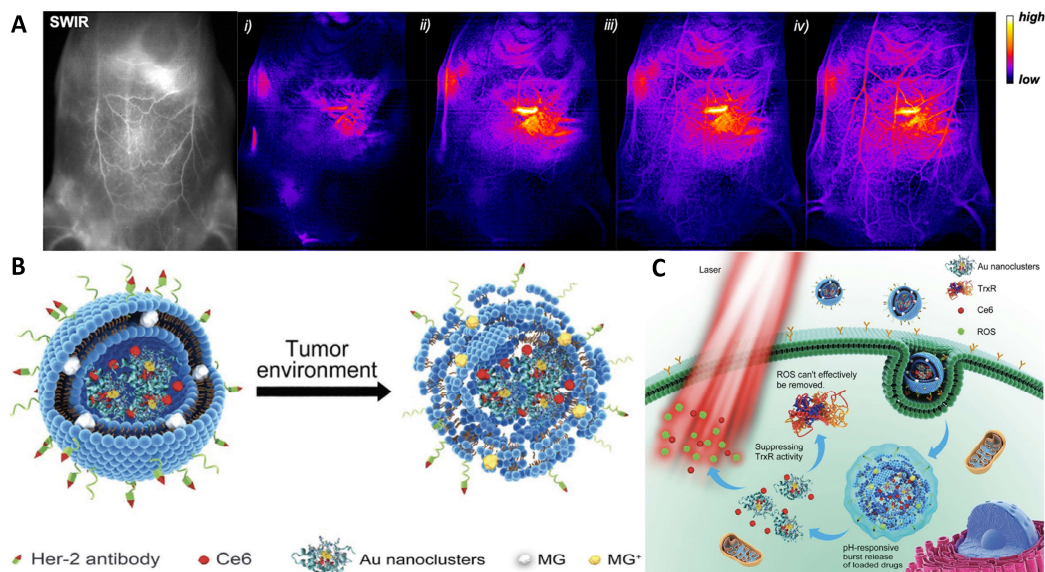


Figure 1.11: (A) SWIR image of blood vasculature in mice after intravenous injection of AuMHA/TDT and MCR+ HP filter treated SWIR images (false colors) (i) 1.5 s, (ii) 5 s, (iii) 25 s, and (iv) 65 s after AuMHA/TDT bolus intravenous injection. (B, C) Schematic illustration of gold NCs and photosensitizer Ce6 dual loaded spatiotemporal controllable liposomal nanocomposites to enhance tumor photodynamic therapy effect by inhibiting thioredoxin reductase. Adapted from Refs.[52,53].

The properties of NCs such as ultra-small size, high surface area, and enhanced electrochemical activity have been successfully used in electrocatalysis, particularly in the fuel cells [methanol or ethanol oxidation reaction (MOR or EOR), formic acid oxidation (FAO), oxygen reduction reaction (ORR)], CO₂ reduction reaction (CO₂RR), and electrocatalytic water splitting [hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)] (**Figure 1.12**).^[54] For example, Zhou *et al.* investigated different sizes of thiolate-stabilized gold NCs (Au₂₅, Au₃₈, Au₁₄₄, Au₃₃₃, Au_{~520}, and Au_{~940}) for EOR.^[48] Interestingly, Au₁₄₄ NC exhibited the highest current density (114.7 mA/mg), showing the size-dependent activity and highlighting the transition from the molecular to the plasmonic state as a crucial factor for optimal EOR performance. In the case of water-splitting reactions,

[Au₂₅(SR)₁₈] and [PtAu₂₄(SR)₁₈] NCs showed better HER activity, especially for the Pt-doped Au₂₅.^[55] Similarly, a few copper-based NCs and gold NCs showed better activity towards electrocatalytic CO₂RR. The unique electrochemiluminescence (ECL) properties of NCs were also have been addressed. NC-based ECL sensing applications provide increased sensitivity and selectivity with a zero-background signal for various analytes. For instance, a recent investigation of the near-infrared (NIR)-ECL activities of [Au₂₅(PET)₁₈], [Au₃₈(PET)₂₄], and [Au₁₄₄(PET)₆₀] NCs will create new opportunities in this field.^[56]

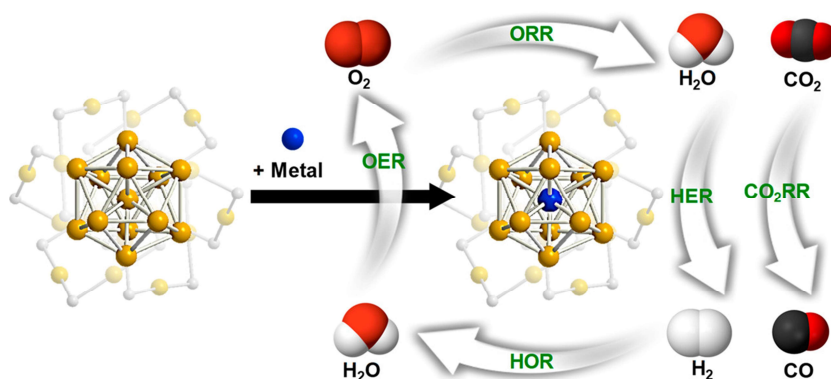


Figure 1.12: Schematic illustrating tailored electrocatalysis by rationally engineered metal NCs. Adapted from Ref.[54].

The wide bandgap and broad absorption NCs are beneficial for photocatalysis. The ability of NCs to transfer electrons to O₂ and generate singlet oxygen (¹O₂) under visible light is crucial for various photocatalytic reactions. For example, when Au₂₅ NCs combined with TiO₂ NPs, they demonstrate (i) selective photooxidation of amines^[57] (**Figure 1.13A**) and (ii) enhanced visible-light-induced photocatalytic degradation of dyes^[58] (**Figure 1.13B**). The photocatalytic water splitting and CO₂RR have also been explored very recently. The capacity of Au₂₅ NCs such as (i) to function as a small-band-gap semiconductor, (ii) facilitate electron-hole separation, and (iii) ability to produce ¹O₂ resulted in their enhanced photocatalytic activity.

These NCs have also been used in photocatalytic water splitting and NC-sensitized solar cells. For example, NCs loaded on BaLa₄Ti₄O₁₅ play a crucial role in harvesting solar energy for photocatalytic water splitting. They showed enhanced hydrogen and oxygen production with a decrease in the size of NCs. Further, the photosensitizing ability of NCs has been utilized for solar energy conversion. The initial photocurrent reported (290 $\mu\text{A cm}^{-2}$) was later boosted to 8.18 mA cm^{-2} (**Figure 1.14**).^[59,60] NCs have also been used as versatile hetero-catalysts in many organic reactions. They exhibit enhanced efficiency in selective oxidation and reduction reactions, as well as coupling reactions.

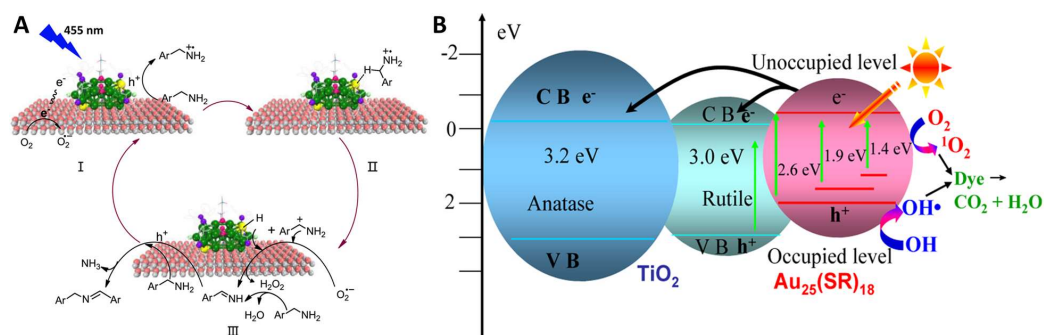


Figure 1.13: Proposed mechanisms under visible light-induced (A) photo-oxidation of benzylamine by [Au₂₅(TPP)₁₀(MPTES)₅]/TiO₂ (MPTES= 3-mercaptopropyltriethoxysilane) (B) photocatalytic degradation of dye by [Au₂₅(PET)₁₈]/TiO₂. Adapted from Refs.[57,58].

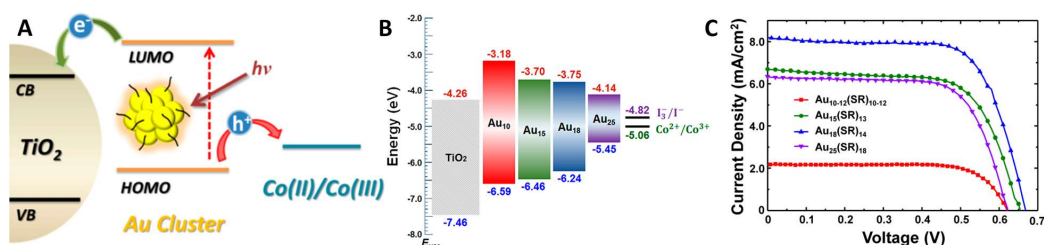
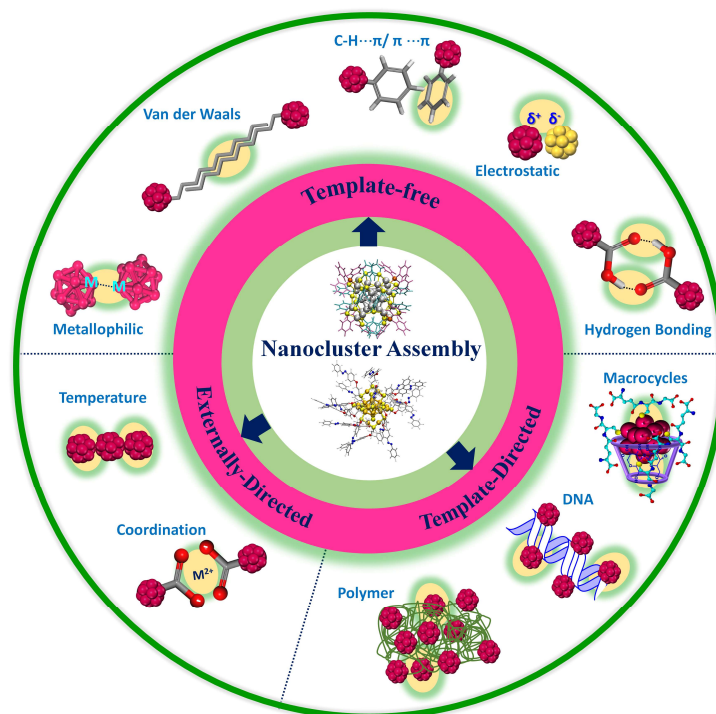


Figure 1.14: (A) Schematic illustration for the working principle of a NC-sensitized solar cell. (B) Energy band diagram and (C) Current density-Voltage (J-V) characteristics of [Au₁₀₋₁₂(SR)₁₀₋₁₂], [Au₁₅(SR)₁₃], [Au₁₈(SR)₁₄], and [Au₂₅(SR)₁₈] NCs-sensitized solar cells. Adapted from Refs.[59,60].

1.2 Self-Assembly of NCs

The spontaneous organization of fundamental building blocks into patterns or superstructures as a result of molecular interactions is known as self-assembly. This self-assembly strategy can be extended to nanoscale materials for creating an ensemble of nanoscale structures. Researchers used a variety of driving forces, including hydrogen bonding, electrostatic interactions, van der Waals interactions, dipolar interactions, C-H $\cdots$ π / π $\cdots$ π interactions, amphiphilicity, metal chelation, metal-metal interactions, light-triggered dipole-induced attractions, and external templates, to self-assemble plasmonic NPs into supercrystals, supraparticles, capsids, and protein-NP superlattices. Hence, these superstructures fabricated from NPs are perfect examples for replicating the nanoscale-driven self-assembly in NCs. NCs offer several advantages compared to plasmonic NPs, (i) NCs are strictly monodisperse, i.e., structures with an exact number of metal atoms and ligand molecules; (ii) the covalently bound ligands with functional groups allow facile chemical transformation without affecting the metal core; (iii) their patchy ligand distribution offer better control over the directional assembly; and (iv) their dispersion behavior is similar to supramolecular complexes allowing self-assembly in solution. Therefore, atomically precise NCs are often considered as colloidal molecules. However, there are also certain challenges to achieving NC self-assembly; for example, due to their small size, the thermal fluctuation energy of the surroundings is close to the inter-NC interactions. Moreover, the traditional Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability,^[61] interactions between colloidal particles and their aggregation behavior are not applicable to NCs.^[62,63] Nevertheless, successful attempts have been made on NC self-assembly in recent years. The self-assembly of NCs *via* such interactions is categorized into three sections, *viz* (i) template-free self-assembly (hydrogen

bonding, electrostatic interactions, van der Waals interactions, $C-H\cdots\pi$, and $\pi\cdots\pi$ interactions, and metallophilic interactions), (ii) template-directed self-assembly (polymers, DNA, and macrocycles) (iii) directed self-assembly using external stimuli (temperature and metal ions). Different interactions used to accomplish the self-assembly of NCs are summarized in **Scheme 1.1**.



Scheme 1.1: Different molecular interactions are used to accomplish the self-assembly of NCs.

1.2.1 Template-free assembly of NCs

1.2.1.1 Hydrogen bonding interactions

Hydrogen bonding-induced crystallization of NCs was first reported by Jadzinsky *et al.* in water-soluble $[Au_{102}(p-MBA)_{44}]$ NCs ($p-MBA$; p -mercaptobenzoic acid).^[15] In another study, Yoon *et al.* investigated the large-scale synthesis and superlattice formation of ultra-stable $[Na_4Ag_{44}(p-MBA)_{30}]$ NCs and their quantum-mechanical simulation studies.^[64] To

demonstrate the hydrogen bonding-mediated self-assembly, $[\text{Na}_4\text{Ag}_{44}(\text{p-MBA})_{30}]$ NCs were initially synthesized in a semi-aqueous solution protected with *p*-MBA ligand shells. Storage of NCs in DMF (N,N-Dimethylformamide) solution produced superlattice crystals. Here, every carboxylic acid group of the ligands was completely protonated to dissolve NCs in DMF. The free carboxylic acid group tends to form dimers or trimers through hydrogen bonding, which results in the formation of rhombus-shaped superlattice crystals. SCXRD revealed that the superlattice crystal possesses a triclinic unit cell containing two NCs in the asymmetric unit of the crystal lattice. Intriguingly, *p*-MBA ligands were aligned parallelly to form two types of molecular bundles. The hydrogen bonding bundles *viz*, double (L2) and triple (L3) bundles facilitate the intralayer and interlayer hydrogen bonding, respectively. The thirty interfacing pairs of ligands from a NC and its nearest neighbors in the superlattice crystal could form sixty hydrogen bonds, including twenty-four intralayer and thirty-six interlayer bonds (**Figure 1.15A-D**). Such sophisticated networks of hydrogen bonds with flexible and structure-directing properties provided chiral rotation to NC and their superstructures. Furthermore, the anisotropic distribution of hydrogen bonding in NCs helps to activate the pressure-softening behavior of superlattice structures under hydrostatic compression. Subsequently, Yao *et al.* demonstrated the formation of superstructures from $[\text{Ag}_{44}(\text{p-MBA})_{30}]^{4-}$ NCs under highly alkaline conditions.^[65] The complete deprotonation of *p*-MBA followed by the addition of counterions in DMSO/water (DMSO=Dimethyl sulfoxide) crystallization system, NCs resulted in the formation of engineered superstructures with controllable shapes. The addition of cesium (Cs^+) counterions perturbed the directional hydrogen bonds, which resulted in the packing of deprotonated $[\text{Ag}_{44}(\text{p-MBA})_{30}]^{4-}$ NCs into polymorphic octahedral single crystals *via* electrostatic interactions. Further, the

supplement of Cs^+ ions created a charge screening environment in $[\text{Ag}_{44}(\text{p-MBA})_{30}]^{4-}$ NCs to induce a concavity in octahedral crystal faces and therefore contributed concave octahedral shaped crystals. Highly monodisperse self-assembly of $[\text{Au}_{102}(\text{p-MBA})_{44}]$ NCs into 2D colloidal crystals and spherical capsids were reported by Nonappa *et al.*^[66] To demonstrate the self-assembly *via* partial hydrogen bonding, $[\text{Au}_{102}(\text{p-MBA})_{44}]$ NCs were synthesized by chemical reduction method in the presence of *p*-MBA. The dispersion of NCs in sodium hydroxide (NaOH) solution resulted in the formation of partially deprotonated NCs. Subsequent solvent exchange from water to MeOH using dialysis triggered the inter-NC hydrogen bonding furnished 2D nanosheets and crystals (**Figure 1.15E and F**). Using a spherical coordinate system, the authors hypothesized that the anisotropic and patchy distribution of the ligands drives the 2D colloidal crystal formation. More interestingly, by changing the crystallization kinetics *via* electrostatic interactions, they were able to tune the shapes of assembled superstructures. For example, instead of dialysis, the direct addition of an aqueous dispersion of NCs into MeOH resulted in the formation of spherical superstructures with monolayer shells. The electron tomographic (ET) three-dimensional (3D) reconstruction studies demonstrated the formation of spherical capsids. Later, Zhang *et al.* established the spherical self-assembly from GS-protected Au_{22} NCs to mimic the capsid protein self-assembly.^[67] $[\text{Au}_{22}(\text{SG})_{18}]$ NCs were synthesized by the pH-mediated reduction of a mixture of gold precursor ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and GSH in the presence of tetrabutylammonium borohydride at low temperatures.^[68] To demonstrate the self-assembly of NCs, the hydrogen bonding network between water molecules and NCs was initially interrupted by introducing DMSO. Subsequently, hydrogen bonding between SG ligands from the adjacent NCs was achieved by displacing the hydrated water molecules

around the NCs *via* evaporation (50 °C) method. The pH-dependent studies showed the formation of larger self-assembled spheres at lower pH. In parallel, dialysis of NCs using water-DMSO or water-DMF binary solvent systems was also implemented to engage hydrogen bonding between SG ligands. The higher dielectric constant of water-DMSO cosolvents resulted in larger assemblies than water-DMF cosolvents due to the efficient screening of the repulsive electrostatic forces between negatively charged NCs. Such self-assembly processes could be useful to understand the protein self-assembly mechanism, as it follows the capsid-like assembly.

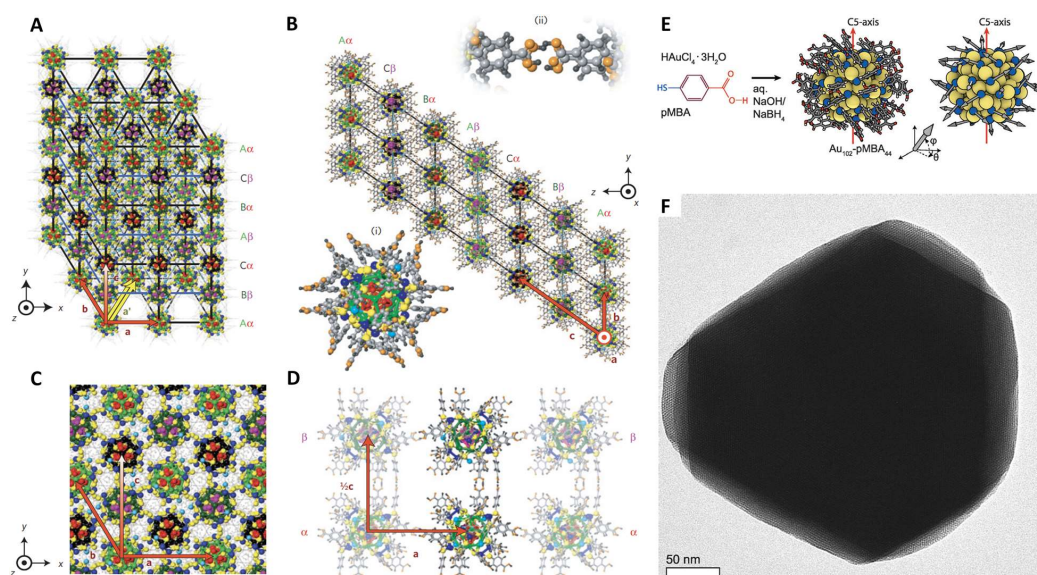


Figure 1.15: (A) 3D and (B) 2D views of [Na₄Ag₄₄(p-MBA)₃₀] NC superlattice structures. A view of a single NC is provided in the inset (i). (C) The stacking of NC layers in the assembly is depicted in the XY three-layer projection. (D) The interlayer hydrogen bonding between neighboring NCs, involving triply bundled ligands are shown. An enlargement of the hydrogen-bonded region is given in inset (ii), showing two hydrogen bonds between each pair of interfacing ligands. (E) Synthetic route for [Au₁₀₂(p-MBA)₄₄] NCs and their internal structure extracted from the solid-state structure. (F) HR-TEM image of 2D colloidal crystal fabricated from [Au₁₀₂(p-MBA)₄₄] NCs with faceted edges showing the stacked NC layers. Adapted from Refs.[64,66].

Xie, Sun *et al.* investigated the significance of the position (*ortho* or *para*) of -COOH group on the bound ligands during the self-assembly of NCs *via* hydrogen bonding.^[69,70] To address this, $(\text{NH}_4)_9[\text{Ag}_9(o\text{-MBA})_9]$ and $(\text{NH}_4)_9[\text{Ag}_9(p\text{-MBA})_9]$ NCs were prepared in water by the pH-mediated reduction of silver nitrate (AgNO_3) in the presence of *o*-MBA or *p*-MBA. The addition of EtOH (antisolvent) into $(\text{NH}_4)_9[\text{Ag}_9(o\text{-MBA})_9]$ NCs resulted in the gelation of NCs by forming self-assembled nanofibers.^[69] Though such gelation was not observed in $(\text{NH}_4)_9[\text{Ag}_9(p\text{-MBA})_9]$ NCs, they could self-assemble into nanorods by carefully adjusting the pH of the solution.^[70] The self-assembled nanofibers fabricated from $(\text{NH}_4)_9[\text{Ag}_9(o\text{-MBA})_9]$ NCs showed fluorescence to phosphorescence switching.

1.2.1.2 Electrostatic interactions

Electrostatic interactions are generally strong attractions or repulsions between two oppositely charged ions, mostly positive and negative charges. To demonstrate the self-assembly of NCs *via* electrostatic interactions, it is necessary to introduce charge separations between the neighboring units either by selecting the oppositely charged NCs or by adding the counterions in monocharged NCs. For example, $[\text{Na}_4\text{Ag}_{44}(p\text{-MBA})_{30}]$ NCs were initially self-assembled using hydrogen bonding as a significant driving force.^[64] However, the adequate supplement of counterions in $[\text{Ag}_{44}(p\text{-MBA})_{30}]^{4-}$,^[65] or $[\text{Au}_{102}(p\text{-MBA})_{44}]$,^[66] NCs allow electrostatic interactions apart from their inherent hydrogen bonding. The balanced control over these two interactions offered customized morphologies during the self-assembly. He *et al.* were able to successfully demonstrate the self-assembly of cationic and anionic Au-Ag bimetallic NCs in a one-pot method.^[71] NCs were synthesized by a two-step method, in which the multi-sized Ag-thiolates were initially prepared by the chemical reduction of AgNO_3 in the presence of thiol (2-

ethylbenzenethiol= 2-EBT) and TPP. Subsequent reaction of Ag-thiolates with a mixture of $[\text{Au}(\text{TPP})\text{Cl}]$ complex and TPP molecule resulted in the formation of $[\text{Ag}_{26}\text{Au}(\text{2-EBT})_{18}(\text{TPP})_6]^+ [\text{Ag}_{24}\text{Au}(\text{2-EBT})_{18}]^-$ NCs with a molar ratio 1:1. This NC is an example of an ionic compound originated from NC ions, which is called as a double NC ion compound (DNIC). The authors exclusively synthesized $[\text{PPh}_4]^+ [\text{Ag}_{24}\text{Au}(\text{2-EBT})_{18}]^-$ NCs ($[\text{PPh}_4]^+=$ tetraphenylphosphonium ion), an example of a single NC ion compound (SNIC). Interestingly, the cationic $[\text{Ag}_{26}\text{Au}(\text{2-EBT})_{18}(\text{TPP})_6]^+$ and anionic $[\text{Ag}_{24}\text{Au}(\text{2-EBT})_{18}]^-$ NCs in DNIC was found to gather and assemble in an unusual alternating array of cationic and anionic stacking structure *via* strong electrostatic interactions and weak $\text{C-H}\cdots\pi/\pi\cdots\pi$ interactions. SNIC displayed a k-vector-differential crystallographic arrangement (**Figure 1.16A-C**).

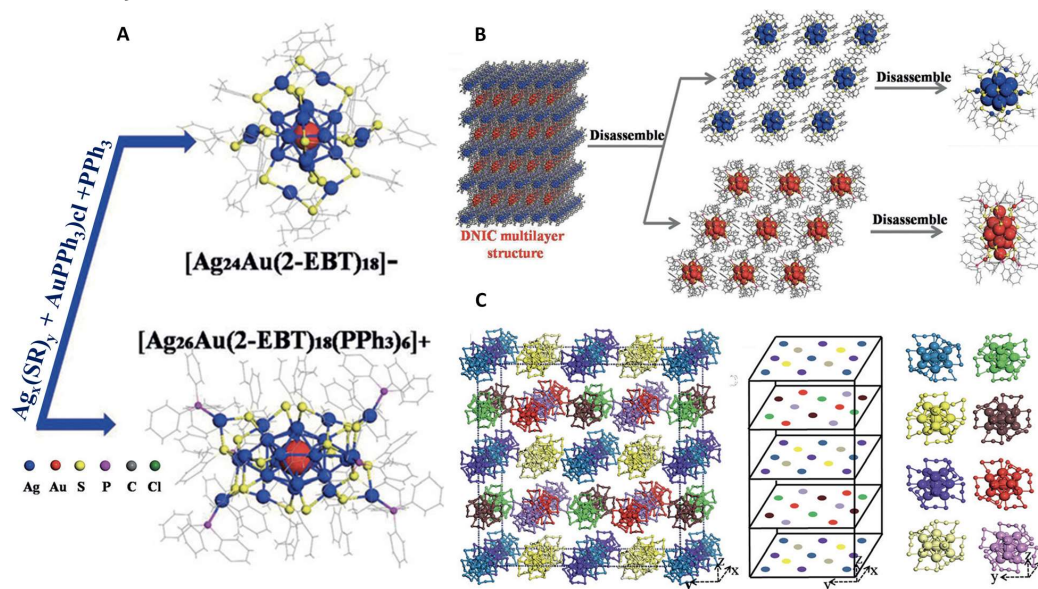


Figure 1.16: (A) Crystal structure of $[\text{Ag}_{26}\text{Au}(\text{2-EBT})_{18}(\text{TPP})_6]^+ [\text{Ag}_{24}\text{Au}(\text{2-EBT})_{18}]^-$ NC-based DNIC. (B) Illustrates the self-assembly of $[\text{Ag}_{26}\text{Au}(\text{2-EBT})_{18}(\text{TPP})_6]^+ [\text{Ag}_{24}\text{Au}(\text{2-EBT})_{18}]^-$ NCs. (C) Crystallographic arrangement of $[\text{PPh}_4]^+ [\text{Ag}_{24}\text{Au}(\text{2-EBT})_{18}]^-$ NCs. Adapted from Ref.[71].

Such a significant difference in the crystallographic arrangement was governed by the exciting influence of ligands and counterions. Wei *et al.* demonstrated the electrostatic self-assembly of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NCs by simply mixing with cesium (Cs^+) ions.^[72] To address such assembly, Ag_{29} NCs were initially prepared by the chemical reduction of Ag-S complexes pre-synthesized by mixing BDT and TPP in AgNO_3 solution.^[49] The replacement of TPP ligands by Cs^+ cations produces $[\text{Cs}_3\text{Ag}_{29}(\text{BDT})_{12}(\text{DMF})_x]^0$ NCs ($x = 5$ or 6), which leads to the formation of the 1D assembly *via* different surface forces including electrostatic attraction, Cs-S bond formation, and Cs- π interactions.

1.2.1.3 Van der Waals interactions

The van der Waals forces are distance-dependent weak electrostatic attraction or repulsion that arise due to the fluctuating electromagnetic polarization of nearby atoms, molecules, or particles. Such van der Waals attractions are expected to initiate the long-range periodic self-assembly in NCs. For example, Wu *et al.* demonstrated the self-assembly of 1-dodecanethiol (DT)-tethered Au NCs at high temperatures.^[73] Initially, Au_{15} NCs were synthesized using room-temperature reduction of HAuCl_4 in the presence of DT. When the temperature of colloidal dispersion (liquid paraffin/dibenzyl ether) was increased above 140°C in vacuum, NCs self-assembled into nanosheets. At high temperatures, NCs were held together by the attractive hydrophobic interactions between the long alkyl chains of ligands. Here, the lamellar interface offered by the solvent microphase separation has acted as a soft template to trigger the assembly. The calculated hydrophobic attractions between the ligands around the neighboring NCs were found to be $7 k_B T$, where k_B is the Boltzmann constant and T is the absolute temperature. The attractive hydrophobic interaction

technique has been further extended to study the self-assembly of Cu NCs.^[74] $[\text{Cu}_{12}(\text{DT})_8\text{Ac}_4]$ NCs synthesized by the reduction of copper (II) acetylacetonate (CuAc_2 ; Ac= acetylacetonate) in the presence of DT was used to demonstrate the assembly. The permanent dipole moment of NC core helped to induce a robust dipolar attraction apart from the expected van der Waals attraction of ligands. Such combined dipolar and van der Waals attractions resulted in the self-assembly of NCs into long nanowires. However, at high temperatures, $[\text{Cu}_{12}(\text{DT})_8\text{Ac}_4]$ NCs could be converted into $[\text{Cu}_8(\text{DT})_8]$ by removing the Ac-ligands, which eventually reduced the overall dipole moment of NC core. Hence, when the temperature increased, nanowires were switched into nanoribbons owing to the prominent van der Waals attractions (**Figure 1.17A-I**). Later, the combined dipolar and van der Waals attractions have been employed to self-assemble $[\text{Au}_{15}(\text{DT})_{15}]$ ^[75] and $[\text{Co}_{14}(\text{DT})_9]$ ^[76] NCs. Zeng *et al.* reported the hierarchical structural complexity of $[\text{Au}_{246}(p\text{-MBT})_{80}]$ NCs ($p\text{-MBT}$ = p -methylbenzenethiol) in its single-crystal X-ray structure and superlattice crystals with translational, rotational, and orientational orders.^[44] Interestingly, $p\text{-MBT}$ ligands were self-organized into α -rotational (pole site) and β -parallel (waist) patterns on the NC surface *via* intermolecular C-H $\cdots\pi$ interaction. The α -rotation pattern forms four pentagonal circles at the pole site by using twenty-five $p\text{-MBT}$ ligands having the same latitude and rotational direction. The top and bottom of NCs were covered by two of such α -rotation patterns. But the waist is wrapped with five β -parallel patterns with each pattern includes three alternating parallel pairs of six $p\text{-MBT}$ ligands. Such symmetry and packing density of $p\text{-MBT}$ surface patterns helped to achieve the directional packing of $[\text{Au}_{246}(p\text{-MBT})_{80}]$ NCs *via* the maximum van der Waals interactions between nearby ligands.

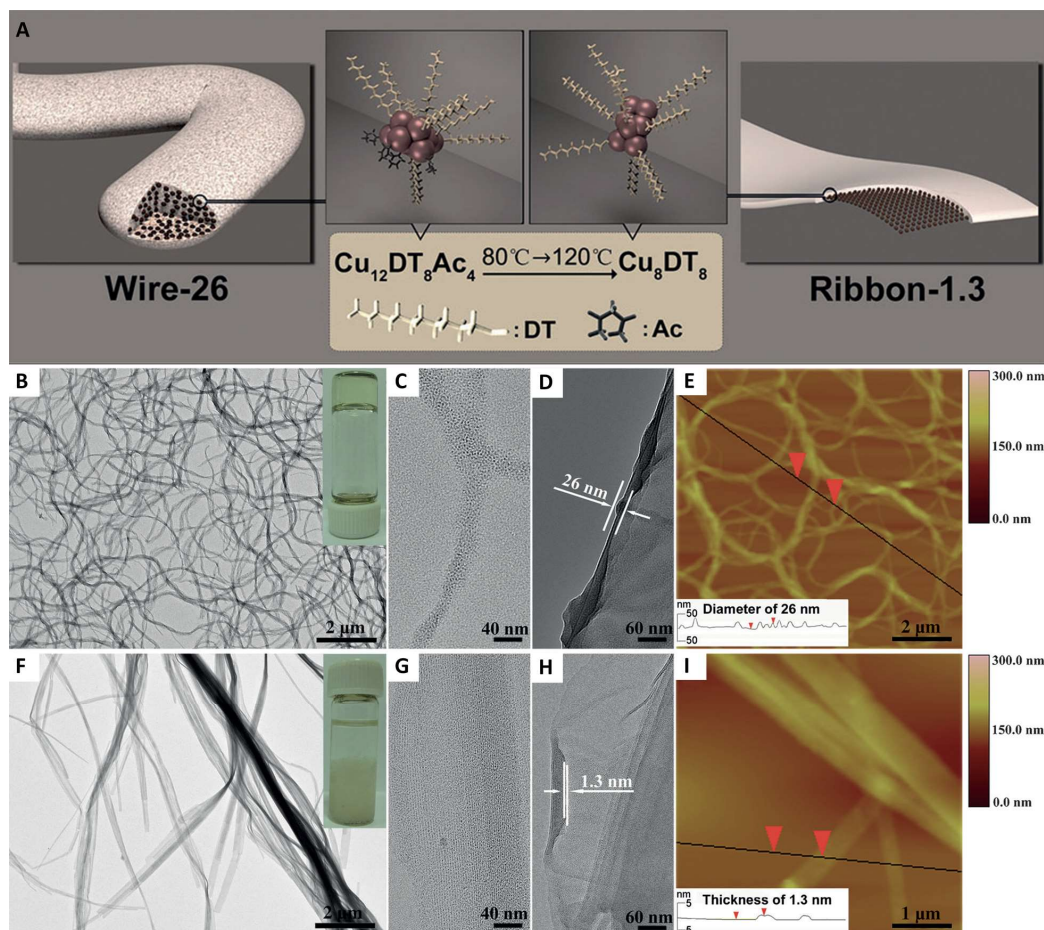


Figure 1.17: (A) Schematic illustration shows the evolution of [Cu₁₂(DT)₈Ac₄] NC self-assembly architectures from nanowire to nanoribbon. (B-D and F-H) TEM and (E and I) tapping-mode AFM images of (B-E) nanowire and (F-I) nanoribbon. TEM images of a small region captured from nanowire and nanoribbon oriented (C and G) parallel to, and (D and H) vertical on the TEM grid are indicated. Photographs of nanowire and nanoribbon dispersions are shown in the inset B and F, respectively. Adapted from Ref.[74].

1.2.1.4 C-H...π/π...π interactions

The weak attraction between the C-H bond and the delocalized π electron system is known as C-H... π interaction.^[77] A similar kind of attraction between the delocalized π electrons are called π ... π interaction. The C-H... π

attraction is often considered the weakest hydrogen bonding interaction occurring between the soft acids and bases. Though the dispersion interaction is the primary source of attraction in C-H $\cdots\pi$ interactions, a small percentage of electrostatic interaction is also accompanied. Remarkably, C-H $\cdots\pi$ interactions play an important role in the nanoscale assemblies and crystal packing of NCs. For example, AbdulHalim *et al.* demonstrated the C-H $\cdots\pi$ interaction-driven crystallization of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NCs using the solvent evaporation technique.^[49] Room temperature evaporation of NC solution (DMF) drop-casted on a glass slide resulted in the formation of self-assembled macroscopic cubic lattice crystals. Later, Nag *et al.* reported polymorphism in the self-assembled $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC crystals owing to the solvent-dependent C-H $\cdots\pi$ interaction of TPP molecules.^[78] Interestingly, they could tune the crystal packing of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NCs into two different polymorphic forms, trigonal (T) and cubic (C) lattices by using different crystallization methods. Though solvent evaporation of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NCs resulted in the formation of C crystals, vapor-diffusion of MeOH into DMF solution of NCs produced T crystals. Here, the intra and intermolecular interactions between BDT and TPP molecules bound on the NC surface drive the self-assembly. In the intra-NC interactions, the C-H bond of TPP molecules interacts with the benzene ring of BDT molecules bound on the same NCs. However, in the inter-NC interactions, the C-H bond of BDT interacts with the phenyl ring of TPP ligands connected in the nearby NCs. The dominating C-H $\cdots\pi$ interaction of TPP molecules during solvent evaporation resulted in the formation of C crystals. The C lattice crystal has shown enhanced PL owing to the restricted molecular rotations and vibrations. The electronic coupling between nearby NCs in the C crystals resulted in a bathochromic shift in their PL spectrum. A similar strategy has been further extended to crystalize $[\text{Ag}_{46}(2,5\text{-DMBT})_{24}(\text{TPP})_8]$, and

cocrystals of $[\text{Ag}_{40/46}(\text{2,4-DMBT})_{24}(\text{TPP})_8]$ (DMBT= dimethylbenzenethiol) NCs.^[79] Another important NC assembly triggered by the C-H $\cdots\pi$ interaction was reported by Shi *et al.* in chiral Au NCs.^[80] The smallest chiral $[\text{Au}_3\{(\text{R})\text{-Tol-BINAP}\}_3\text{Cl}]$ and $[\text{Au}_3\{(\text{S})\text{-Tol-BINAP}\}_3\text{Cl}]$ NCs (BINAP= 2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl) were initially synthesized by the chemical reduction method. The drop-wise addition of n-hexane (antisolvent) into the NC solution prepared in dichloromethane (DCM) helped to induce a strong intermolecular interaction among the ligands. When the concentration of n-hexane reaches 40%, an orange emission was observed from the NC solution, indicating the formation of assembled body-centered cubic (BCC) nanocubes *via* strong C-H $\cdots\pi$ interactions (**Figure 1.18**). The intermolecular interactions helped to improve the circularly polarized luminescence (CPL) and chiral responses from the assembled superstructures owing to the restricted movements of ligands. Recently, Huang *et al.* reported the synthesis and structural characterization of racemic anisotropic $[\text{Ag}_{30}(\text{C}_2\text{B}_{10}\text{H}_9\text{S}_3)_8(\text{DPPM})_6]$ NCs, ($\text{Ag}_{30}\text{-rac}$) protected with a mixture of achiral carboranetrithiolate and phosphine ligands ($\text{C}_2\text{B}_{10}\text{H}_9\text{S}_3$ = 8,9,12-trimercapto-1,2-*closo*-carborane and bis(diphenylphosphino)methane; DPPM) *via* one-pot reduction method using hydrazine.^[81] The spiral arrangement of the ligands directed by unusual B-H $\cdots\pi$ and C-H $\cdots\pi$ bonding interactions between the carborane cages and benzene rings could induce chirality for $\text{Ag}_{30}\text{-rac}$. During the crystallization of $\text{Ag}_{30}\text{-rac}$ in dimethylacetamide, the racemates (*R*- Ag_{30} and *L*- Ag_{30}) were self-resolved into the racemic conglomerates and the enantiomeric NCs self-assembled into helical structures. The noncovalent interactions, including B-H $\cdots\pi$, C-H $\cdots\pi$, $\pi\cdots\pi$, and van der Waals interactions direct such helical superstructures.

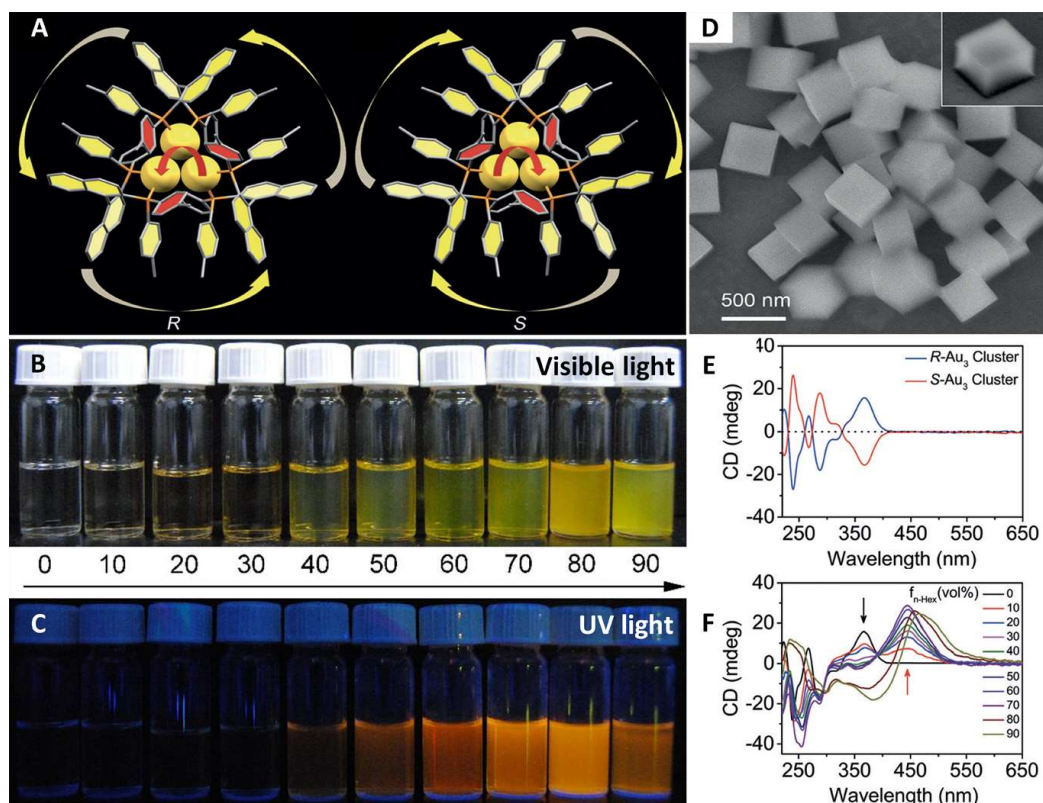


Figure 1.18: (A) Chiral $[\text{Au}_3\{(\text{R})\text{-Tol-BINAP}\}_3\text{Cl}]$ and $[\text{Au}_3\{(\text{S})\text{-Tol-BINAP}\}_3\text{Cl}]$ NCs. (B-C) Photographs of $[\text{Au}_3\{(\text{R})\text{-Tol-BINAP}\}_3\text{Cl}]$ NCs in DCM with a different fraction of n-hexane under (B) visible light and (C) UV light. (D) SEM (Scanning Electron Microscopy) image of $[\text{Au}_3\{(\text{R})\text{-Tol-BINAP}\}_3\text{Cl}]$ NC assembly fabricated in DCM with 70% n-hexane. (E) CD (Circular Dichroism) spectra of $[\text{Au}_3\{(\text{R})\text{-Tol-BINAP}\}_3\text{Cl}]$ and $[\text{Au}_3\{(\text{S})\text{-Tol-BINAP}\}_3\text{Cl}]$ NCs in DCM. (F) CD spectra of $[\text{Au}_3\{(\text{R})\text{-Tol-BINAP}\}_3\text{Cl}]$ NCs in DCM with various n-hexane contents. Arrows show the direction of change with increasing n-hexane content. Adapted from Ref.[80].

1.2.1.5 Metallophilic interactions

The non-covalent attractions between the closed-shells (d^{10} , s^2) or pseudo-closed-shell (d^8) of metal cations can hold NPs together to form self-assembled superstructures. Such interactions are known as metallophilic interactions.^[82] Transition metals such as Pt, Pd, Au, Ag, and Cu have been reported to display metallophilic interactions, especially at nanoscale

assemblies. Though such interactions are weak, they will be very prominent in the presence of particular solvents. Gold-gold (Au-Au) interactions (aurophilic interactions) and their possible structure-directing assemblies are known in the literature.^[83] Au NCs are emerging candidates to examine the chemistry of such self-assemblies. For example, Nardi *et al.* demonstrated the formation of 1D linear crystalline self-assembly from $[\text{Au}_{25}(\text{SBu})_{18}]^0$ NCs (HSBu= n-butanethiol) *via* the aurophilic interaction.^[84] To address such $[\text{Au}_{25}(\text{SBu})_{18}]^0_n$ polymer assembly, initially, the neutral $[\text{Au}_{25}(\text{SBu})_{18}]^0$ NCs were prepared by passing the anionic $[\text{Au}_{25}(\text{SBu})_{18}]^-$ through a silica gel column under aerobic conditions. The slow crystallization (4 °C) of $[\text{Au}_{25}(\text{SBu})_{18}]^0$ NC solution in DCM in the presence of CH_3CN (NC insoluble solvent) resulted in $[\text{Au}_{25}(\text{SBu})_{18}]^0_n$ assembly, in which the $[\text{Au}_{25}(\text{SBu})_{18}]^0$ units were interconnected by Au-Au bonds. A twist-and-lock mechanism between neighboring NCs and bound ligands also played an important role in the formation of polymer assembly. However, such assembly was not observed in the case of $[\text{Au}_{25}(\text{SET})_{18}]^0$ (HSET= ethylthiol) under similar experimental conditions due to less steric hindrance offered by the bound ligands. Later, the aurophilic-induced 1D self-assembly of $[\text{Au}_{25}(\text{S-C}_n\text{H}_{2n+1})_{18}]^0$ NCs ($n = 3, 4, \text{ and } 5$) and $[\text{Au}_{25}(\text{PET})_{18}]^0$ into millimeter-long polymers using the electrocrystallization approach has been introduced.^[85] Various bimetallic NCs including $[\text{Au}_{24}\text{Hg}(\text{SBu})_{18}]^0$, $[\text{Au}_{24}\text{Cd}(\text{SBu})_{18}]^0$, $[\text{Au}_4\text{Pt}_2(\text{SR})_8]^0$, and $[(\text{AuAg})_{34}]$ NCs were successfully self-assembled into 1D polymers *via* the metallophilic interactions.^[86–88] Among these, the single crystal polymer fabricated from $[(\text{AuAg})_{34}]$ NCs showed anisotropic p-type semiconducting properties.^[88]

Recently, Wu *et al.* investigated the aurophilic interaction-induced colloidal (3D) self-assembly in Au NCs.^[89] In their study, $[\text{Au}_{25}(p\text{-MBA})_{18}]^-$ NC has been taken as a model system to understand the structure-directional

assembly and their enhanced PL. To address such nanoscale assembly, $[\text{Au}_{25}(\text{p-MBA})_{18}]^-$ NCs were initially synthesized by the pH-adjusted chemical reduction of Au-thiolates in the presence of NaBH_4 .^[90] The cyclic dialysis process has been used to decrease the pH of NC solution, which eventually transformed the parent $[\text{Au}_{25}(\text{p-MBA})_{18}]^-$ NCs to surface-motif reconstructed NCs having Au^1 centers with d^{10} electronic configuration. These surface-reconstructed NCs consist of long $\text{SR}-[\text{Au}^1\text{-SR}]_x$ motifs ($x > 2$) and a small Au^0 core. The overnight incubation of the above NC solution resulted in the formation of self-assembled nanoribbons. Self-assembly is triggered by surface-motif reconstruction of NCs from the short $\text{SR}-[\text{Au}^1\text{-SR}]_2$ units into long $\text{SR}-[\text{Au}^1\text{-SR}]_x$ ($x > 2$) staples followed by the structural change of intrinsic Au_{13} kernel. The Fourier transform extended X-ray absorption fine-structure (FT-EXAFS) revealed an enhancement in the Au-S and $\text{Au}_{\text{staple}}\text{-Au}_{\text{staple}}$ character, which confirms the formation of long $\text{SR}-[\text{Au}^1\text{-SR}]_x$. The rich Au^1 content and short aurophilic $\text{Au}^1\cdots\text{Au}^1$ interactions in the primary stage of assembly have driven NCs into 1D nanowires. Successive formation of nanoribbons from nanowires has been attributed to the $\pi\cdots\pi$ stacking between *p*-MBA ligands from the adjacent nanowires, which is evident from the reduced inter-nanowire spacing (**Figure 1.19**). Interestingly, nanoribbons displayed two independent emission bands (at 77 K) and temperature-responsive luminescence. In contrast to the lower PLQY of $[\text{Au}_{25}(\text{p-MBA})_{18}]^-$, nanoribbons have shown enhanced PLQY of 6.2% (at 77 K). The authors adopted a similar strategy to fabricate the self-assembled nanoribbons from $[\text{Au}_{38}(\text{p-MBA})_{24}]$ and $[\text{Au}_{44}(\text{p-MBA})_{26}]^{2-}$ NCs too.

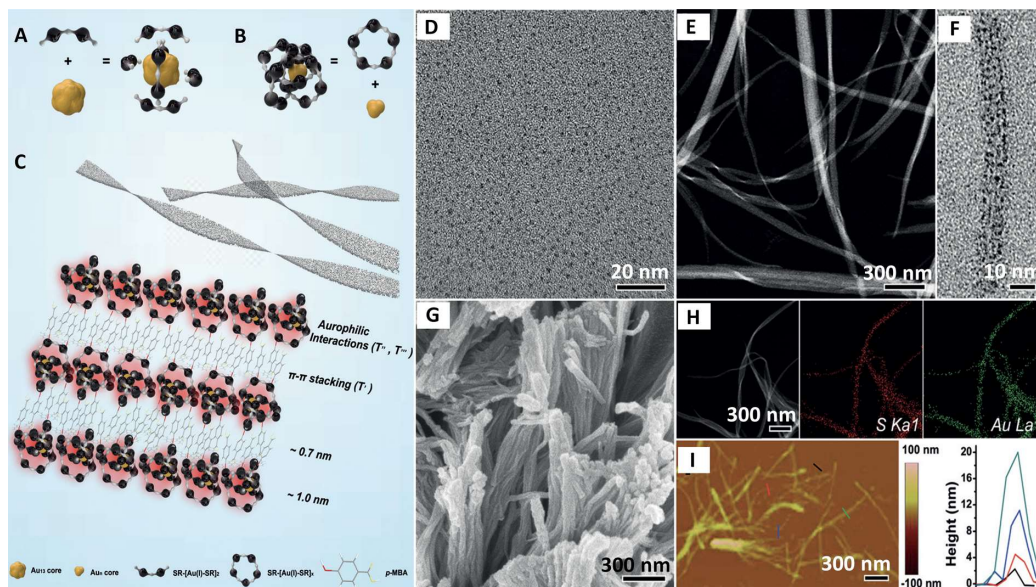


Figure 1.19: Schematic shows the evolution of [Au₂₅(p-MBA)₁₈]⁻ NCs into well-defined self-assembled nanoribbons. The cartoon pictures illustrate the structure of (A) [Au₂₅(p-MBA)₁₈]⁻ NCs (B) the as evoked smaller NCs, and (C) their spatial arrangement within nanoribbons. (D) TEM image of [Au₂₅(p-MBA)₁₈]⁻ NCs, (E) High-angle dark-field scanning (HAADF) TEM, (F) HR-TEM, and (G) SEM images of the nanoribbons. (H) HAADF-TEM (left), corresponding energy-dispersive X-ray (EDX) element maps (middle and right), and (I) AFM image of the representative nanoribbons are shown. Adapted from Ref.[90].

In another study, Wu *et al.* reported the self-assembly of [Cu₁₄(DT)₁₀] NCs *via* cuprophilic interactions.^[91] NCs were synthesized by the chemical reduction of copper chloride (CuCl₂ · 2H₂O) in the presence of DT. The detailed structural investigations revealed that individual NC is composed of Cu⁰₄Cu¹₁₀DT₁₀. The high-temperature (128 °C) annealing of the above NC solution in dibenzyl ether in the presence of excess DT triggered the formation of self-assembled nanoribbons. The PL properties of assembled NCs were found to depend on DT ligands and cuprophilic Cu¹...Cu¹ interactions. Such NC assembly shows reversible thermochromic PL.

Further, Sun *et al.* reported a similar chemistry behind the argentophilic interactions in Ag NCs.^[92] The interaction of water-soluble $[\text{Ag}_9(o\text{-MBA})_9]$ NCs with succinic acid resulted in the conversion of NCs into well-ordered phosphorescent hydrogels. The acid interaction helped to induce a topography reconstruction of NCs into Ag^1 species on the surface. The subsequent argentophilic ($\text{Ag}^1 \cdots \text{Ag}^1$) interactions triggered a long-range self-assembly of NCs into nanofibers. The inter-ligand interactions such as hydrophobic interactions, hydrogen bonding, and $\pi \cdots \pi$ stacking also played an important role in the hydrogel formation. The assembled NCs have shown temperature-sensitive phosphorescence.

1.2.2 Template-directed assembly of NCs

1.2.2.1 Polymer templated assembly

Polymers can act as an active scaffold to induce the anisotropic ordering of NCs. Though the polymers and NCs are entirely different functional moieties, mutually compatible NCs can be well dispersed in a polymer matrix, resulting in homogeneous assemblies. By introducing the interactive functional groups into polymers and NCs, one could control such assemblies. For example, Yahia-Ammar *et al.* demonstrated the pH-dependent and size-controllable self-assembly of $[\text{Au}@\text{SG}]$ NCs in aqueous medium by introducing a cationic polymer.^[93] The electrostatic interaction between the positively charged amine group of poly(allylamine hydrochloride) (PAH) and a negatively charged carboxylic acid moiety of NC ligand resulted in the self-assembled $[\text{Au}@\text{SG-PAH}]$ spheres. Such self-assembled superstructures showed an aggregation-induced emission (AIE). Shen *et al.* extended a similar protocol for the fabrication of self-assembled nanospheres and nanovesicles from $(\text{NH}_4)_6[\text{Ag}_6(\text{MNA})_6]$ NCs (MNA= 2-mercaptonicotinic acid) *via* multiple electrostatic interactions with polyethyleneimine (PEI).^[94]

Later, Yin *et al.* modified the polyamine-based assembly by introducing a salt of polyvalent anions.^[95] Here, the polymer-salt aggregates helped to entrap charged NCs to produce Au NC-containing microcapsules. The multi-layered and semipermeable matrix of microcapsules was further stabilized with SiO₂ NPs. The assembled composite has shown PL enhancement about five times greater than parent NCs. Hembury *et al.* synthesized Au NCs protected with thermosensitive diblock copolymers of poly(*N*-isopropylacrylamide) (PNIPAm) and poly (ethylene glycol) (PEG) to demonstrate micellar assembly of NCs.^[96] The polymers were prepared using a reversible addition-fragmentation chain-transfer (RAFT) polymerization approach, followed by functional group conversion to produce the thiol-terminated PEG-PNIPAm-SH polymers. The *in situ* preparation of thiolated-polymer-capped NCs was carried out using the chemical reduction method. Interestingly, when the temperature was above the lower critical solution temperature (LCST) of the polymers, [Au@S-PNIPAm-PEG] NCs formed the hydrophobic cores of micellar assemblies. Further, Yang *et al.* demonstrated the self-assembly of Au NCs inside the poly(amidoamine) dendrimer (PAMAM) by mixing the pre-synthesized [Au@SG] NCs with aqueous PAMAM.^[97] The electrostatic interaction between negatively charged carboxylic groups in [Au@SG] NCs and positively charged amine groups in PAMAM resulted in self-assembled structures with enhanced PL. More recently, Benavides *et al.* successfully self-assembled Cu NCs inside the multi-thiolated thermo- and pH-responsive copolymer, p(MEO₂MA-co-AcSEMA) [(poly-2-(2-methoxyethoxy) ethyl methacrylate and poly-2-(acetylthio)ethyl methacrylate)].^[98] The one-pot reduction of copper sulfate (CuSO₄·5H₂O) using hydrazine in the presence of p(MEO₂MA-co-AcSEMA) resulted in the formation of greenish-yellow emitting assembled [Cu@S-p(MEO₂MA-co-AcSEMA) NCs inside the polymer matrix with better

photostability and oxidation resistance. The biopolymers (peptides, proteins, lipids, etc.) have been used to demonstrate the self-organization of NCs. For example, Ju *et al.* demonstrated the pH-dependent assembly and disassembly of [Au@SG] NCs *via* electrostatic interactions with *Streptococcus pyogenes* bacterial protein (SpCas9).^[99] The controlled addition of positively charged SpCas9 to the negatively charged [Au@SG] NC in phosphate buffer resulted in a self-assembled NC-protein composite ([Au@SG]-SpCas9).

1.2.2.2 DNA templated assembly

A combination of DNA and metallic NPs were successfully self-assembled to form a wide variety of hybrid materials.^[100] Replacing metallic NPs with precision NCs could bring more exciting monodisperse assemblies. The quantum confinement and PL properties of NCs would be added advantages for such template-based assemblies. Recently, Ouyang *et al.* demonstrated DNA-nanoribbon templated self-assembly of Cu NCs.^[101] The DNA-nanoribbon templates (C-DNR) composed of multiple units of single-strand DNA were prepared by a simple and effective thermal annealing method. Based on the position of DNA sequences, six types of C-DNR assemblies were prepared. Subsequently, NCs were prepared *in situ* on the C-DNRs, by mixing CuSO₄ with C-DNR solution in a mixture of MOPS (3-(N-morpholino)propane sulfonic acid) buffer and NaCl (Sodium Chloride). Chemical reduction of metal ions with sodium ascorbate followed by keeping the solution at room temperature for 30 min resulted in the periodic self-assembly of NCs on C-DNR (**Figure 1.20**). The incubation period of the metal salt and C-DNR is crucial for the formation of NCs. The control experiments with single-stranded DNA could not produce NCs, which confirms that NCs were formed only in the presence of C-DNRs. The self-assembled NCs protected with C-

DNRs have shown better photostability and temperature-dependent PL compared to the luminescent Cu NPs stabilized on the double-stranded DNA reported earlier. Later, Wang *et al.* fabricated the self-assembled Au NCs-DNA (GNC-DNA) complexes *in situ* by introducing the Au precursor and double-stranded DNA solution into the cancer cells.^[102] To confirm the self-assembly inside the cell, GNC-DNA complexes were isolated and analyzed with different microscopic techniques. Assembled NCs were used for cancer diagnosis and theranostics.

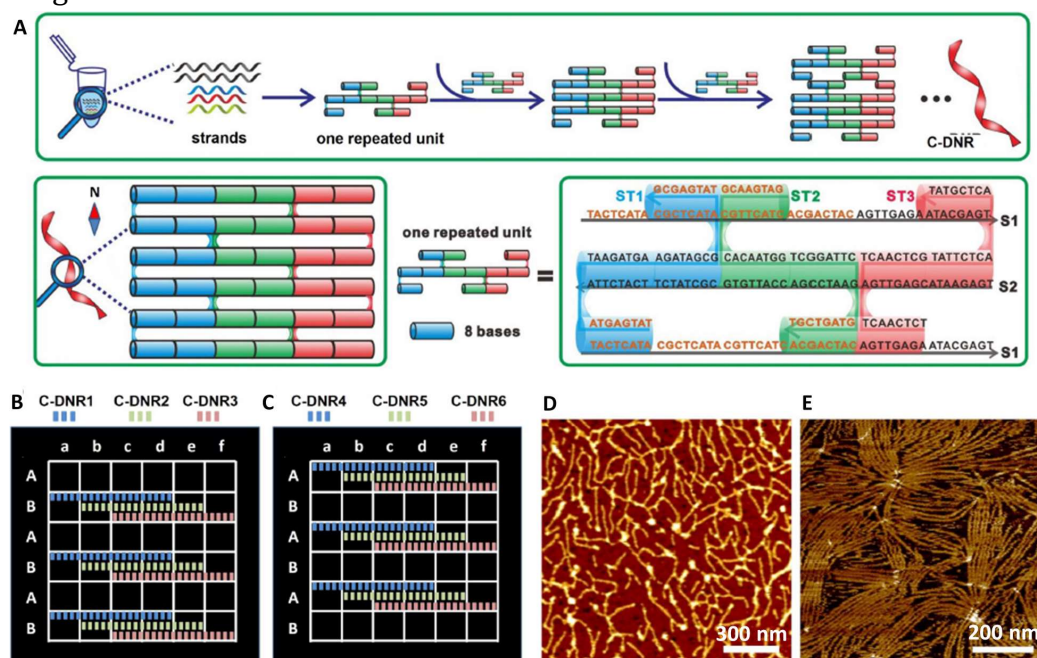


Figure 1.20: (A) Top: Formation scheme of C-DNRs. Bottom: Schematic diagram of C-DNR, the double helix structure is represented by a cylinder, and each small cylinder contains eight complementary base pairs. A repeating unit consists of five short chains of scaffold strand 1 (S1), scaffold strand 2 (S2), staple strand 1 (ST1), staple strand 2 (ST2), and staple strand 3 (ST3). Schematic diagram of (B) C-DNR1, C-DNR2, C-DNR3, and (C) C-DNR4, C-DNR5, C-DNR6 are shown. Sequence A is indicated by a square bar; each square lattice represents eight base pairs, row A represents the DNA helix containing S2 strand, row B represents the DNA helix containing S1 strand. AFM images of C-DNR1 under (D) tapping mode in air and (E) in liquid. Adapted from Ref.[101].

1.2.2.3 Macrocycles templated assembly

The molecular recognition between the host and guest molecules through the non-covalent bonding resulted in the evolution of supramolecular assemblies. A proper combination of host-guest interactions could also produce assembled NCs with improved photophysical properties. For example, the non-covalent interactions between the macrocyclic host and ligand-protected NCs (guest) created a rigid-NC framework with enhanced optical features and stability.^[103] Though, some of those assemblies were restricted to host single NCs. Later, the long-range NC assembly was achieved by the careful selection of the host and guest molecules. For example, Jiang *et al.* demonstrated the self-assembly of Au₂₂ NCs by utilizing the non-covalent ligand interaction of NCs with cucurbituril host cavities.^[104] [Au₂₂(FGGC)₁₈] NCs were initially synthesized by the pH-adjusted reduction of HAuCl₄ in the presence of N-terminal Phe-Gly-Gly-Cys peptide (FGGC). NCs purified by the preparative TLC techniques were allowed to interact with cucurbiturils 7 and 8 (CB[7] and CB[8]), separately. Though CB[7] accommodates only one peptide moiety, the large cavity of CB[8] could accommodate two peptides from two adjacent NCs. Such interactions resulted in the formation of self-assembled spheres with an improved PLQY (CB[8]-39%). Further, Chakraborty *et al.* demonstrated the supramolecular host-guest interaction-based co-assembly of [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NCs with crown ether (dibenzo-18-crown-6; DB18C6).^[105] Vapor-diffusion of MeOH into the DMF solution of NCs and DB18C6 resulted in the formation of DB18C6 co-assembled NC crystals. The electrostatic interaction between the cationic DB18C6Na⁺ units and anionic [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NCs helped to trigger the assembly. The source of Na⁺ in the crystallization medium could be the previously used NaBH₄ during NC synthesis. Further intra and intermolecular C-H... π interactions between the crown ether and TPP/BDT resulted in long-range

assembled NC crystals composed of hexameric DB18C6Na⁺ units (**Figure 1.21**). The assembled [Ag₂₉(BDT)₁₂(TPP)₄][(DB18C6Na)₃] crystals showed enhanced PL (3.5-fold) compared to the parent NCs.

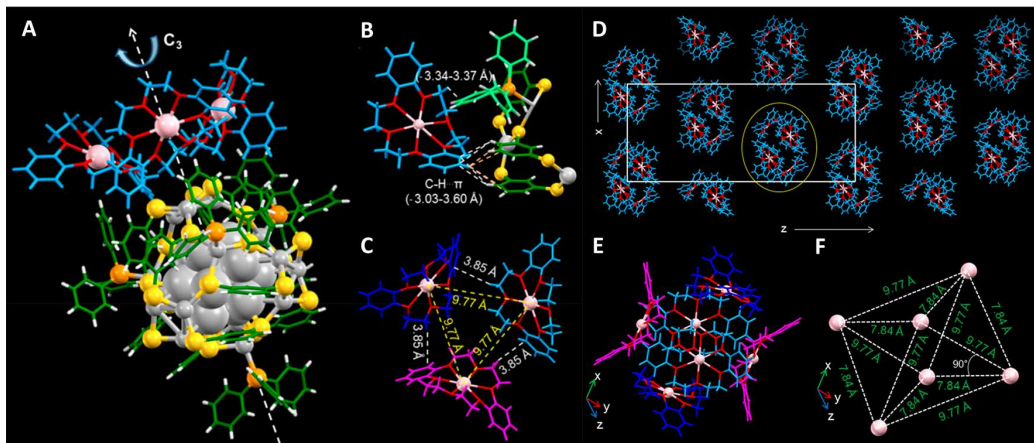


Figure 1.21: (A) Structure of [Ag₂₉(BDT)₁₂(TPP)₄][(DB18C6Na)₃]. (B) expanded view showing the interaction between one of the DB18C6Na⁺ molecules and BDT/TPP ligands of the NC, and (C) expanded view of the three DB18C6Na⁺ molecules attached on the NC surface. (D) Packing of DB18C6Na⁺ molecules into hexameric units throughout the crystal lattice view from the y-axis. (E) Expanded view of one of the hexameric units showing the formation of cage-like structures. Opposite crown ethers, shown in similar colors, are related by a center of inversion. (F) The orientation of Na⁺ of the crown ether hexamer in a rectangular bipyramidal geometry. Adapted from Ref.[105].

Further, Muhammed *et al.* demonstrated the host-guest interaction-based self-assembly in Ag₂₉ NCs stabilized with dithiol lipoic acid terminated copillar[5]arene (LA-P5).^[106] To address such interactions, [Ag₂₉(LA-P5)₁₂(TPP)₂] NCs were initially synthesized by the chemical reduction of AgNO₃ in the presence of TPP and LA-P5. In this particular case, host molecules are chemically bound on the NC surface *via* Au-S bond. The addition of cationic quaternary ammonium salts (guest molecules) into the above NCs resulted in the formation of assembled spheres owing to cation-π

interactions. Such assembled structures showed ~2000-fold enhancement in their PL due to AIE. More interestingly, the injection of MeOH (polar solvents) into the assembled NCs could demolish them into well-separated individual NCs. Recently, Huang *et al.* demonstrated the self-assembly of cyclodextrin functionalized Cu NCs *via* host-guest interactions with di(adamantan-1-yl)phosphine molecule (ad-ad).^[107] To address such assembly, water-soluble NCs were initially synthesized by reducing the copper nitrate in the presence of mono-(6-mercapto-6-deoxy)- β -cyclodextrin (SH- β -CD) as both reducing and stabilizing agents. The addition of ad-ad into the β -CD-tethered NCs showed enhanced PL due to AIE resulting from the supramolecular assembly triggered by host-guest interactions. The membrane-associated glycoprotein (Mucin 1 protein; MuC1) has been successfully imaged using the enhanced PL from ad-aptamer conjugated NC assembly.

1.2.3 Externally directed assembly of NCs

1.2.3.1 Coordination-assisted assembly

Coordination of NCs with suitable metal ions and subsequent formation of metal-organic frameworks (MOFs) is another exciting possibility to self-assemble NCs. For example, the electrostatic interaction between negatively charged NCs and polyvalent cations under ambient conditions could produce NC-based coordination complexes. Yao *et al.* first introduced such a strategy, in which the [Au@SG] NCs were coordinated with Zn^{2+} or Cd^{2+} using the pH-adjusted protocol.^[108] The early screening effect between Zn^{2+} and carboxylate anions reduced the negative charge around the NC surface, triggering the intra-NC assembly. The subsequent bridging effect between nearby NCs resulted in stable inter-NC spherical assemblies *via* NC crosslinking. Such solid-spherical assemblies displayed an enhanced PLQY

compared to pristine NCs due to reduced non-radiative relaxation and improved charge-transfer interaction.^[109] Recently, Chandra *et al.* reported the fabrication of highly luminescent Au NC frameworks (GNCFs) by coordinating divalent cations with carboxylate anions present on the NC surface.^[110] [Au@SG] NCs were prepared by heating the pre-synthesized Au-thiolates at 70 °C for 24 h. Surprisingly, the addition of Sn^{2+} ions into the above-prepared NCs has shown a seven-fold enhancement in their PL due to the coordination-assisted assembly. Interaction of negatively charged carboxylate group of SG with divalent Sn^{2+} cations resulted in the formation of GNCFs *via* inter-NC crosslinking, which was confirmed by observing 3D spherical colloidal structures in Scanning Transmission Electron Microscopy (STEM) and Electron Tomography (ET) (**Figure 1.22**).

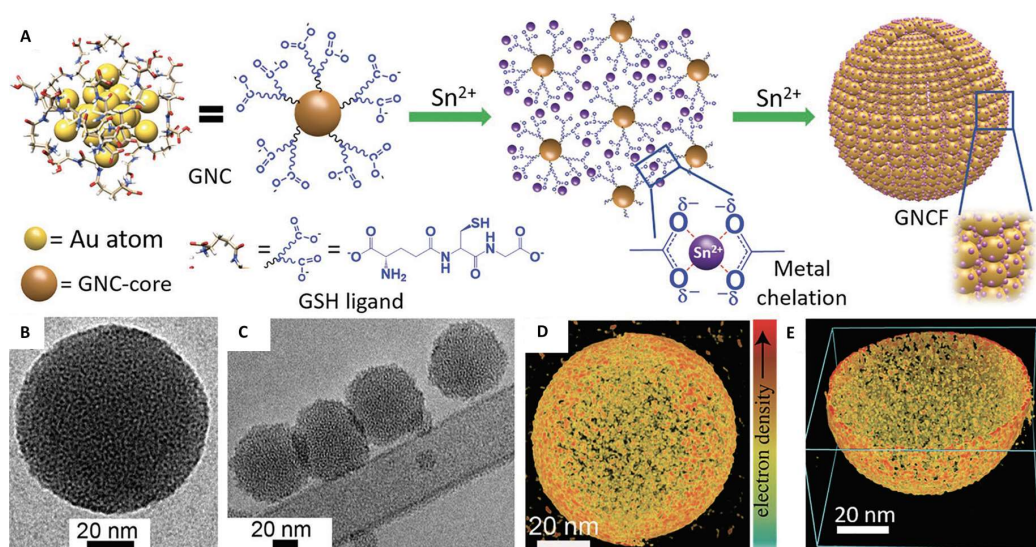


Figure 1.22: (A) Representation of a luminescent [Au@SG] NC, the possible interactions between the metal ions and COO^- groups of the ligand over NCs through chelation, and the schematic illustration for the formation of GNCFs. (B) HR-TEM micrograph of GNCF-100 dispersed in water, (C) cryo-TEM micrograph of GNCF-100, (D) ET reconstruction of a GNCF-100, and (E) its cross-sectional view. Adapted from Ref.[110].

NC-based MOFs were also achieved by using bridging ligands instead of metal coordination. The ability to control the length and the denticity of linkers could help to tune the assemblies. For example, Huang *et al.* demonstrated the formation of 3D Ag(I) chalcogenide NCs-based MOFs using bipyridine bridges.^[111] Ligand exchange reaction of $[\text{Ag}_{12}(\text{S}^t\text{Bu})_6(\text{CF}_3\text{COO})_6(\text{CH}_3\text{CN})_6] \cdot \text{CH}_3\text{CN}$ NCs (S^tBu = *tert*-butylthiol; CF_3COOH = trifluoroacetic acid) using 4,4'-bipyridine (bpy) resulted in the replacement of CH_3CN with linearly coordinated bipyridine (**Figure 1.23**).

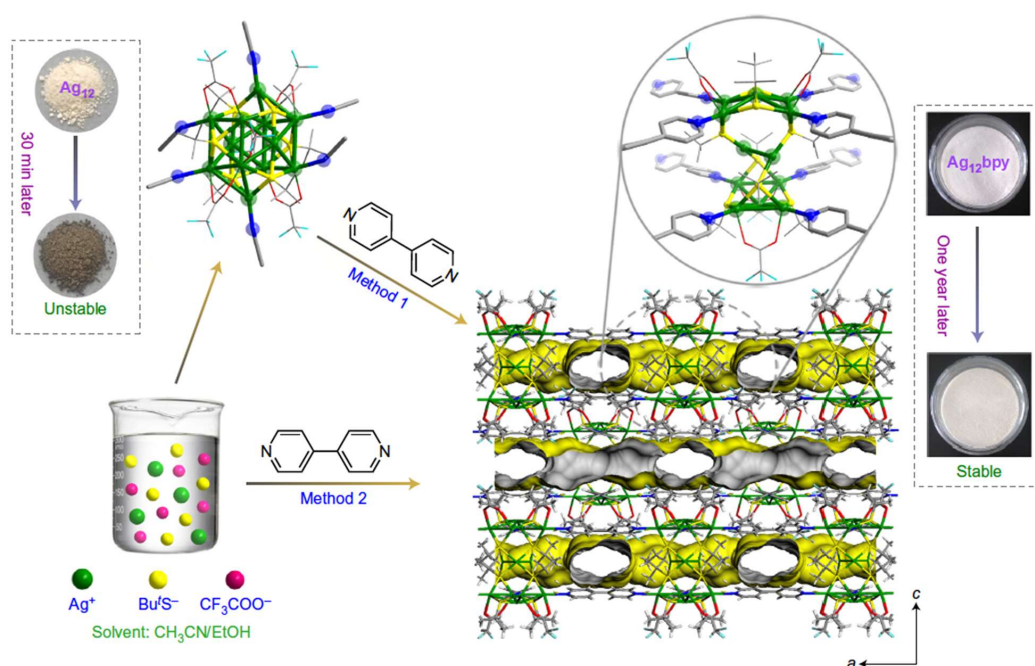


Figure 1.23: Schematic representation of the ligand-exchange strategy used to obtain Ag_{12}bpy crystals (Method 1, giving low yield) and one-pot synthesis (Method 2, for gram quantity production) under identical conditions. Interconnected channels of Ag_{12}bpy are viewed along with the *a* and *b* axes, where the yellow surface represents the pore surface. Insets: photographs showing the changes of Ag_{12} and Ag_{12}bpy crystals under ambient conditions. Adapted from Ref.[112].

Subsequent coordination of bipyridine linker with adjacent Ag_{12} nodes produced light-emitting porous $[\text{Ag}_{12}(\text{S}^t\text{Bu})_8(\text{CF}_3\text{COO})_4(\text{bpy})_4]_n$ (Ag_{12}bpy)-

MOF. Surprisingly, the single-emissive tetragonal (Ag_{12}bpy) NCs were transformed into a dual-emissive trigonal ($\text{Ag}_{12}\text{bpy-2}$) crystals ($[\text{Ag}_{12}(\text{S}^t\text{Bu})_6(\text{CF}_3\text{COO})_6(\text{bpy})_3]_n$) when the crystallization medium changed.^[112] The temperature-dependent dual emission occurred due to the Ag core compression originating from the argentophilic interaction. Bridging chemistry has been further extended to demonstrate self-assembly of Ag_{10} ,^[113,114] Ag_{12} ,^[115,116] $\text{Ag}_{12}\text{Ag}_8$,^[117] Ag_{14}Cl and Ag_{15}Cl ,^[118] and Ag_{14} ,^[119] NCs using diverse organic bridges.

1.2.3.2 Temperature-controlled assembly

The temperature has a vital role in NCs self-assembly, especially those protected with long-alkyl chain ligands. In general, the careful elevation of temperature helps to facilitate or hinder some intermolecular interactions. To establish the self-assembly in long-chain hydrophobic ligands-protected NCs, sufficient thermal energy is required to cross their thermodynamic barrier. The annealing of NCs at high temperatures could help to increase the mobility of the alkyl chains. Subsequent inter-ligand interactions, especially the van der Waals interactions, drive the long-range self-assembly. More details are provided in the van der Waals section.

1.3 Enhanced optical and mechanical properties of assembled NCs

NCs are emerging nanomaterials with exciting photophysical properties. Some of these NCs show excellent PL with relatively better photostability. PLQY of NCs is lower compared to semiconductor QDs or organic dyes. However, one could improve the PL of NCs by ligand engineering,^[120] encapsulation of NCs inside protein pockets,^[121] self-assembly,^[110] doping,^[122] and aggregation-induced emission (AIE).^[123] AIE has been further investigated in the self-assembled superstructures originating from

different NCs, and their potential applications have been reviewed.^[362] For example, Wu *et al.* have shown improved PL from the assembled $[\text{Cu}_{14}(\text{DT})_{10}]$ NCs.^[91] Though the isolated NC was non-emissive, the self-assembled nanoribbons have shown bright emission with an improved PLQY of up to 6.5%. The restricted movements of DT ligands and improved cuprophilic interactions resulted in the formation of a highly ordered assembly with maximum rigidity and compactness. Such compact structures helped to improve the radiative energy transfer channel *via* ligand-to-metal charge transfer (LMCT) and/or ligand-to-metal-metal charge transfer (LMMCT) process. To demonstrate the significance of compact assembly in AIE, NCs were loosely assembled into nanosheets by controlling a lower annealing temperature for a longer time. The PLQY of nanosheets was lowered to 3.6% owing to the increased movement of DT ligands and reduced cuprophilic interactions. More remarkably, the self-assembly strategy allowed to tune the regularity of NCs in the assemblies, which could produce polymorphic assemblies with different emission colors owing to the mechanochromic PL. For example, the mechanical grinding of self-assembled nanoribbons fabricated from $[\text{Cu}_{14}(\text{DT})_{10}]$ NCs has shown a reduced PLQY (3.8%) with a bathochromic shift in their PL.^[91] The color change is attributed to the decreased average $\text{Cu}^1 \cdots \text{Cu}^1$ distance in the nanoribbon caused by the grinding treatment. The creation of metal defects in the assembled nanostructures can also enhance their PL. For example, Wu *et al.* showed that the addition of EtOH into $[\text{Cu}_{14}(\text{DT})_{10}]$ NC solution accelerates the self-assembly by altering the coordination environment of metal with increased Cu^1 defects on the surface.^[124] The assembled ultrathin nanosheet shows bright-yellow PL with an improved PLQY of up to 15.4%. The metal defect-rich nanosheets possess an increased Cu^1 to Cu^0 ratio, which significantly facilitates the radiative relaxation of excitons by influencing the LMMCT

process. More interestingly, the self-assembly could help to delay the PL of NCs. For example, the self-assembled nanofibers fabricated from $(\text{NH}_4)_9[\text{Ag}_9(o\text{-MBA})_9]$ NCs *via* hydrogen bonding method showed an enhanced AIE together with a transition from fluorescence to phosphorescence owing to their structural rearrangement within nanofibers.^[69] AIE has been further extended to different assembled NCs, including $[\text{Au}_{25}(p\text{-MBA})_{18}]^-$,^[89] $[\text{Au@SG-PAH}]$,^[93,109,110] $[\text{Au}_3\{(\text{R or S})\text{-Tol-BINAP}\}_3\text{Cl}]$,^[80] and $(\text{NH}_4)_9[\text{Ag}_9(p\text{-MBA})_9]$,^[70] etc.

The periodic self-organization of NCs allows amplification of their optical and mechanical properties. For example, Musnier *et al.* reported the enhanced optical absorption from $[\text{Au}_{25}(\text{MHA})_{18}]$ NCs while increasing the concentration of externally added HDT (hexa(ethylene glycol) dithiol) molecules during the formation of $[\text{Au@MHA-HDT}]$ network.^[125] The UV-Vis absorption spectrum of $[\text{Au}_{25}(\text{MHA})_{18}]$ shows a major hump *ca.* 670 nm (HOMO-LUMO) with two shoulder peaks *ca.* 440 nm and 770 nm. However, the replacement of MHA with HDT resulted in the disappearance and enhancement of the shoulder peaks *ca.* 440 nm and 770 nm, respectively. The additional bands were formed *ca.* 610 nm and 985 nm along with the red-shifted HOMO-LUMO band (690 nm). The enhanced optical features observed from the assembled NCs are attributed to the surface charge anisotropy created on NC during the ligand replacement. In another example, Shi *et al.* reported an enhanced CPL from the assembled chiral $[\text{Au}_3\{(\text{R})\text{-Tol-BINAP}\}_3\text{Cl}]$ and $[\text{Au}_3\{(\text{S})\text{-Tol-BINAP}\}_3\text{Cl}]$ NCs.^[80] The self-assembled nanocubes showed enhanced circular dichroism with a significant CPL signal compared to pristine NCs. The restricted intramolecular rotation of inward *p*-tolyl rings could populate the excited state radiative decay pathway by quenching their non-radiative relaxation channels. As a result, PL and CPL are generated through the triplet ligand-to-metal charge transfer

(³LMCT) or triplet ligand-to-metal-metal charge transfer (³LMMCT) processes. Recently, Sugi *et al.* studied the enhanced mechanical properties of single-crystal solids self-assembled from dithiol-protected Ag₂₉ polymorphs (Ag₂₉ C and Ag₂₉ T), monothiol-protected Ag₄₆ (Ag₄₆ T), and cocrystals of Ag₄₀/Ag₄₆ (Ag_{40/46} M).^[79] Interestingly, the assembled solid fabricated from dithiol protected Ag₂₉ showed higher Young's modulus (E_r) and hardness (H) compared to single-crystal solids from monothiol-protected Ag₄₆ having the trend Ag₂₉ T > Ag₂₉ C > Ag_{40/46} M > Ag₄₆ T. Higher E_r and H values for Ag₂₉ T crystals is due to the inter-NC interactions, the presence of two pairs of H...H interactions, and a pair of C-H... π interactions between BDT ligands. While comparing Ag₄₆ T and Ag_{40/46} M systems, Ag_{40/46} M holds supramolecular interactions between the primary DMBT ligands, similar to Ag₂₉ T systems, which provide higher E_r and H values. These unusual mechanical properties of assembled solids are comparable to the mechanical properties of zeolitic imidazolate frameworks.

1.4 Applications of assembled NCs

1.4.1 Device fabrication

Self-assembled NCs have been used to construct multi-color light-emitting diodes (LEDs), in which NC assembly acts as a color conversion layer. For example, Wu *et al.* successfully demonstrated the fabrication of LEDs from the assembled [Cu₁₄(DT)₁₀] NCs using a 365 nm GaN LED chip as the light source.^[91] The authors have also fabricated the white light-emitting diodes (WLEDs) by using a combination of [Cu₁₄(DT)₁₀] ribbons, [Cu₁₄(DT)₁₀] sheets, and [Au@NC] sheets (**Figure 1.24**). Later, multi-colored LEDs were fabricated from NC assembly. For this, different approaches were introduced to generate multi-colored PL from the assembled NCs. For example, Ai *et al.* were able to tune the PL from the assembled Cu NCs by modulating the inter-

NC distances in the assembly.^[126] To regulate the inter-NC distances, the experimental variables such as solvents, ligands, duration of assembly, and temperature were adjusted. Aromatic thiols with different electron-donating functionalities were also used to synthesize Cu NCs to address the color-tunable emissive assemblies.^[127] The successive doping of Au¹ into Cu NCs helped to enhance the PLQY up to 23.5%.^[128] By changing the percentage of doping, one could control the PL intensity.

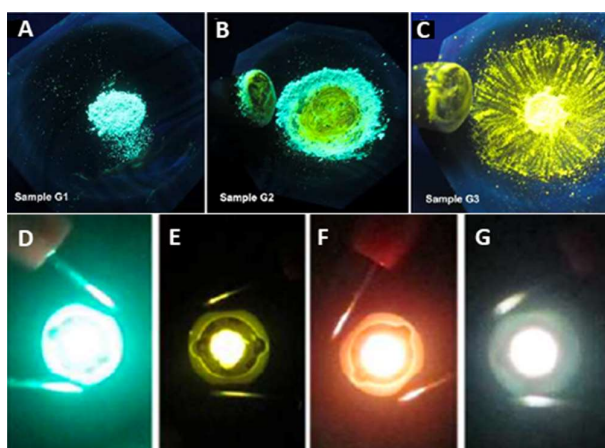


Figure 1.24: (A-C) Photographs show the mechanochromic PL of assembled [Cu₁₄(DT)₁₀] NCs. (D-G) Photographs of LEDs fabricated from different NC-assemblies; (D) [Cu₁₄(DT)₁₀] nanoribbon, (E) [Cu₁₄(DT)₁₀] nanosheet, (F) [Au@NC] sheet, and (G) WLED fabricated by mixing [Cu₁₄(DT)₁₀] ribbon, [Cu₁₄(DT)₁₀] sheet and [Au@NC] sheet. Adapted from Ref.[91].

Later, the electrophoretic deposition of a mixture of assembled nanosheets separately fabricated from Au and Cu NCs has been used to generate the white-light emission.^[129] Huang *et al.* fabricated WLED from solid-state emitting Zn-coordinated NC assemblies ([Zn-Au@SG]).^[109] The careful physical blending of green-emitting carbon nano-dots and yellow-orange emitting NC assembly could generate multicolor nano-phosphors. The combination of the above-prepared nano-phosphors with blue emissive LEDs facilitated the preparation of WLED. Furthermore, the self-assembled

$(\text{NH}_4)_9[\text{Ag}_9(p\text{-MBA})_9]$ or $(\text{NH}_4)_9[\text{Ag}_9(o\text{-MBA})_9]$ NCs were utilized to produce white-light emission by incorporating commercially available phosphors.^[70,92] The above-discussed NC assemblies have been successfully used to fabricate the color conversion layers in LEDs.

1.4.2 Molecular and metal ion sensing

The assembled NCs have been efficiently used to fabricate molecular sensors. For example, Wang *et al.* reported the rapid and cyclic detection of explosives such as nitrobenzene (NB) using a polymer hybrid membrane fabricated from $[\text{Ag}_{12}(\text{S}^t\text{Bu})_6(\text{CF}_3\text{COO})_6(\text{NH}_2\text{-bpz})_3]_n\text{-MOF}$ ($\text{NH}_2\text{-Ag}_{12}\text{bpz}$).^[130] To demonstrate the sensing, $\text{NH}_2\text{-Ag}_{12}\text{bpz}$ was initially synthesized by connecting Ag_{12} NCs with (1,4-bis(pyrid-4-yl)benzenamine ($\text{NH}_2\text{-Ag}_{12}\text{bpz}$) linker. Further modification with methacrylamide functional group was performed by reacting in the presence of methacrylic anhydride (MA). The subsequent crosslinking of $\text{MA-Ag}_{12}\text{bpz}$ with acrylate monomers (butyl methacrylate or triethylene glycol dimethacrylate) through a convenient photo-polymerization resulted in a hybrid Ag_{12}bpz -polymer membrane. Notably, the addition of butyl methacrylate and triethylene glycol dimethacrylate monomer resulted in a rigid and flexible polymer membrane, respectively. The physical and chemical properties of the Ag_{12}bpz polymer membrane were significantly altered compared to the pristine NCs, which is evident from their improved chemical stability and PLQY. The interaction of NB with polymer membrane caused a reasonable quenching in their PL due to the efficient electron transfer. The detection limit of NB using the polymer membrane was calculated to be 3.19 ppb. In another example, Kuppan and Maitra developed an assembled $[\text{Au@MPA}]$ (MPA= 3-mercaptopropionic acid) NC-based fluorescence sensor to detect Zn^{2+} ions in drinking water.^[131] The tunable PL of $[\text{Au@MPA}]$ NCs in the presence of varying concentration of

Zn^{2+} , due to the *in situ* formation of coordination-assisted assembly is the basic concept of such devices. They could detect Zn^{2+} ions with a detection limit of 30 μM and 9 nM by visual and fluorometric methods, respectively. A similar strategy has been further employed to detect Al^{3+} using $(\text{NH}_4)_6[\text{Ag}_6(\text{MNA})_6]$ NCs assembled within PEI template.^[94] The self-assembled luminescent NCs have been further employed for the selective detection of biomolecules. For example, Xue *et al.* used the dual-emissive spherical assemblies made up of $[\text{Au}@\text{SG}]$ NCs and silicon NPs for the ratiometric detection of protamine and trypsin.^[132] Strong adsorption of positively charged protamine on the NC surface could inhibit the electrostatic attractions in the self-assembly as well as the AIE. However, the addition of trypsin helped to dissociate the protamine/ $[\text{Au}@\text{SG}]$ NCs complex by hydrolyzing the protamine, which eventually brings back the self-assembly and AIE. In another example, Benavides *et al.* demonstrated the selective detection of Hg^{2+} using the assembled $[\text{Cu}@\text{S-p}(\text{MEO}_2\text{MA-co-AcSEMA})]$ NCs fabricated inside the multi-thiolated polymer.^[98] The inherent PL from assembled NCs was quenched selectively in the presence of Hg^{2+} . Such chemistry has been further extended for the detection of Hg^{2+} present in human urine. Also, Au_5 NCs prepared inside PAMAM dendrimer (poly- Au_5) were used for the selective detection of intracellular endogenous GSH.^[97] The electrostatic affinity between carboxylic groups of GSH (present in cells) and amine groups in poly- Au_5 resulted in the self-assembly of NCs within the cells. The enhanced PL originated from the self-assembly has been used to probe the intracellular endogenous GSH. Basu *et al.* successfully demonstrated the chiral recognition of D- and L-Trp (Trp= tryptophan) using the assembled enantiomeric $[\text{Au}_{14}(\text{MPA})_6(\text{D/L-Trp})_4]$ NCs fabricated by the Zn^{2+} coordination.^[133] Interestingly, the addition of D/L-Trp into the similar enantiomeric NC assembly could quench PL. On the other hand, the extent of

PL quenching reduced when D/L-Trp was injected into the counter enantiomeric NC assembly. Such assembly has been further used for the discrimination of geometrical isomers.^[134]

1.4.3 Gas sensing and storage

The self-assembled NCs are found to be excellent materials for gas sensing and storage. For example, Huang *et al.* developed Ag NCs-based MOF sensors for the selective detection of a variety of sensitive gas molecules.^[112] The assembled porous (Ag₁₂bpy)-MOF has shown precisely the OFF and ON switchable PL in the presence of molecular oxygen (³O₂) and volatile organic compounds, respectively. More interestingly, the authors were able to harvest multicolor PL from (Ag₁₂bpy)-MOF, depending on the polarity of organic compounds detected. Further, the ligand engineering of same NC using 3-amino-4,4'-bipyridine (bpy-NH₂) resulted in the formation of [Ag₁₂(S^tBu)₈(CF₃COO)₄(bpy-NH₂)₄]_n (Ag₁₂bpy-NH₂)-MOF.^[135] Introduction of amino groups into the bpy-linkers resulted in dual emissive (fluorescent-blue and phosphorescent-yellow) MOF under vacuum. (Ag₁₂bpy-NH₂)-MOF showed a prolonged lifetime owing to the enhanced triplet excitons resulting from strong spin-orbit coupling and increased rate of the intersystem crossing. Later, (Ag₁₂bpy-NH₂)-MOF has been used for the ultrasensitive ratiometric sensing of ³O₂. The interaction of (Ag₁₂bpy-NH₂)-MOF with ³O₂ quenched their yellow emission and left the blue emission of the ligand. On the other hand, such interactions in (Ag₁₂bpy)-MOF completely destroyed their green PL (**Figure 1.25**). By using such MOF, authors could detect ³O₂ with a limit of detection (LOD) of 0.1 ppm, and 0.3 s response time, which is visualized by the naked eye. Furthermore, different substituents such as -CH₃ and mixed -NH₂ and -CH₃ groups were employed for the detection of ³O₂ at different concentration ranges.

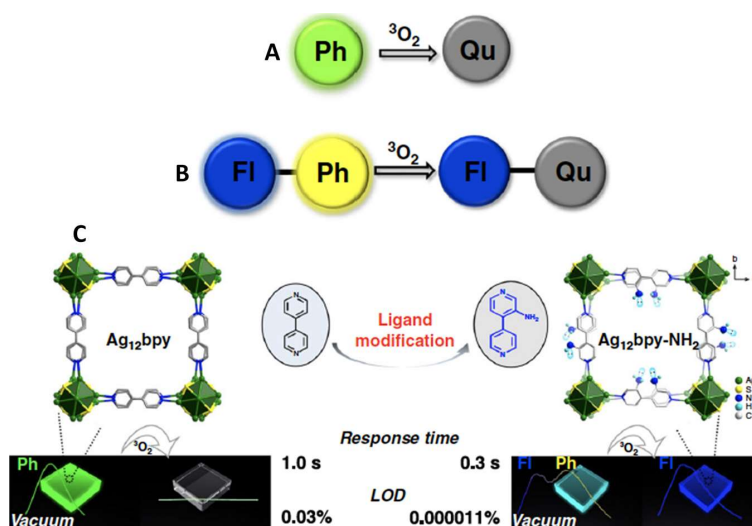


Figure 1.25: Schematic of triplet oxygen ($^3\text{O}_2$) sensing based on (A) a single Ph emission and (B) dual FI-Ph emissions (FI= Fluorescence, Ph= Phosphorescence, Qu= Quenched). Each colored circle represents an emissive center. (C) Schematic of Ag_{12}bpy crystals emitting a single green color under vacuum that is quenched by $^3\text{O}_2$ with a response time of approximately 1.0 s, and a LOD of 0.03%; the isostructural $\text{Ag}_{12}\text{bpy-NH}_2$ crystal modified with $-\text{NH}_2$ groups on the bpy linkers emits nearly a different cyan color that is composed of a blue FI and a yellow Ph component under a certain vacuum, but only emits blue FI under $^3\text{O}_2$. Note: the color emitted by $\text{Ag}_{12}\text{bpy-NH}_2$ is variable under different vacuum conditions. When using $\text{Ag}_{12}\text{bpy-NH}_2$ as a ratiometric oxygen sensor, the response time decreased to 0.3 s, and the LOD dropped to 0.000011%. Adapted from Ref.[135].

Further, Basu *et al.* demonstrated the reversible storage of hydrogen and oxygen gas using the Zn-coordinated self-assembled superstructures fabricated from luminescent Au_{14} NCs protected with MPA and amino acids.^[134] The reversible hydrogen storage was achieved using the 3D assembled crystalline framework designed from $[\text{Au}_{14}(\text{MPA})_7(\text{His})_5]$ NCs. The hydrogen storage capacity has been determined to be 0.244 mM g^{-1} of the assembled framework at 20°C and under 20 bar pressure. The enhanced PL from the assembled framework could indicate the hydrogen adsorption

and desorption process. A similar strategy was further employed for the recyclable storage of oxygen and carbon dioxide gases using 2D nanosheets of $[\text{Au}_{14}(\text{MPA})_{10}(\text{Phe})_4]^{3+}$ NCs^[136] and crystalline 3D assembly of $[\text{Au}_{14}(\text{MPA})_{10}(\text{Cys})_4]$ NCs (Cys= cysteine),^[137] respectively. The storage capacity of oxygen and carbon dioxide gas under ambient conditions is restricted to $\sim 0.266 \text{ mM g}^{-1}$ and 1.79 mM g^{-1} , respectively.

1.4.4 Delivery, bioimaging, and therapeutics

The self-assembled NCs have been further used for delivery, bioimaging, and therapeutic applications. For example, the assembled GNC-DNA complexes fabricated inside the cancer cells have shown an enhanced intracellular PL compared to the normal cells kept in similar experimental conditions. Such assembled materials are excellent biomarkers for targeted nanoscale imaging and cancer therapy. More interestingly, the *in situ* self-assembly of NCs using a tumor-suppressing double-stranded phosphatase and tensin homolog (PTEN) gene (GNC-PTEN) showed an enhanced inhibition of tumor growth in a tumor affected mice (**Figure 1.26**).^[102]

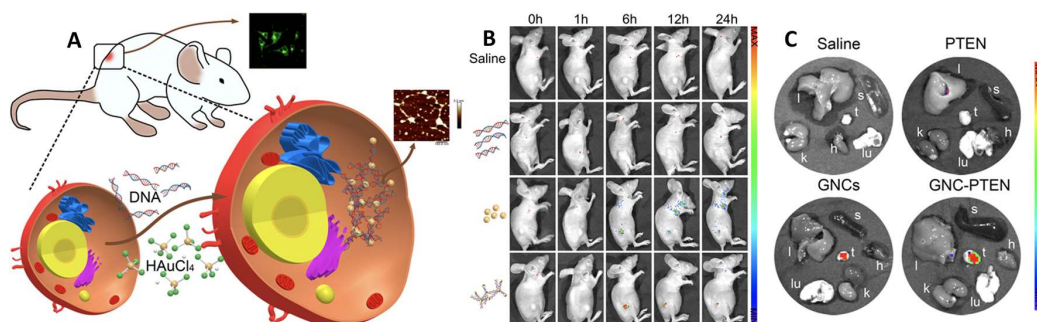


Figure 1.26: (A) Schematic diagram of *in situ* self-assembled GNC-DNA complexes in cancer cells. (B) Dynamic biodistribution of normal saline, PTEN, GNC, and GNC-PTEN complexes in mice using fluorescent imaging. (C) Twenty-four hours after injection, animals were killed, and tumor (t, tumor), major organs (l, liver; k, kidney; s, spleen; lu, lung; and h, heart) were collected for *ex vivo* imaging. Adapted from Ref.[102].

In another study, the temperature-sensitive dual emission originated from the carbon dot-NCs assembly has been used to monitor the intracellular temperature in the range from 20 °C to 80 °C owing to their high reproducibility, stability, and biocompatibility.^[138] Similarly, the *in situ* fabricated gold NC-embedded peptide nanofibers (AuNC-PNF) has been used for cellular imaging and temperature sensing.^[139] The stable PL (QY= 21.3%) and better biocompatibility of AuNC-PNF helped to demonstrate the concept of fluorescent thermometers. Further, the assembled [Au@SG] NCs fabricated using the cationic polymer template were successfully used for cancer cell imaging and drug delivery.^[93] The cellular uptake of self-assembled NCs was found to be higher than that of individual NCs in human monocytic cells. To address the drug delivery, the peptides or antibodies were initially loaded into the NC assembly using a one-pot method. The enhanced PL from peptide/antibody loaded, assembled NCs has been efficiently used to monitor drug delivery. The fluorescence microscopy and flow cytometry data showed better intracellular colocalization of peptides or antibodies compared to free biomolecules. In another study, a tumor-targeted pH-sensitive platinum (Pt) NC assembly was designed by incorporating NCs with a pH-sensitive polypeptide *via* hydrophobic force, followed by surface functionalization with targeting peptide.^[140] The efficient delivery of Pt ions into the subcellular compartments was achieved using such assembled NCs. The intracellular acidic pH helps to disassemble them into individual NCs and release Pt ions for the efficient treatment of chemoresistant hepatocellular carcinoma. Similarly, pH-controlled release of SpCas9 protein and gene therapy using the assembled [Au@SG]-SpCas9 composite was demonstrated.^[99] Very recently, Yang *et al.* reported the targeted delivery, cancer cell imaging, and photothermal/photodynamic therapies using [(Pt)₁(Ag)₂₈] NC-assembly fabricated inside the amphiphilic

chitosan micelles.^[141] Further, the folic acid conjugated-assembled $[\text{Au}_{22}(\text{SG})_{18}]$ NCs have been used to demonstrate the efficient internalization of NCs inside the cancer cells *via* macropinocytosis pathway, which is analogous to the endocytosis mechanism exploited by pathogens during the attack of host cells.^[67] The $[\text{Au}_{22}(\text{FGGC})_{18}]/\text{CB}[7]$ NCs were also used for bioimaging applications.^[104] The red emission of NCs, successfully internalized in human lung adenocarcinoma cells (A549) could help to track the cytoplasm under 515 nm excitation. Several NC-assemblies have been studied for biomedical applications.^[142–144] Among them, Zn^{2+} coordinated $[\text{Au}_{14}(\text{MPA})_6(\text{Tyr})_4]$ (Tyr= Tyrosine) NC-assembly showed mitochondrial enhanced anticancer activities,^[142] Gd^{3+} coordinated $[\text{Au}@\text{SG}]$ NC assembly for its application for multimodal tumor diagnosis,^[143] and Ca^{2+} coordinated $[\text{Au}@\text{SG}]$ NC assembly used for cytosolic protein delivery.^[144]

1.4.5 Catalysis

NCs are excellent candidates for certain catalytic reactions, especially for the reduction of CO_2 , oxidation of CO, and hydrogenation of alkynes. However, the fabrication of assembled NCs without losing the optical integrity of individual NCs and their subsequent performance in catalysis are still in its infancy. Wu *et al.* successfully demonstrated the catalytic efficiency of assembled nanoribbons fabricated from $[\text{Cu}_{12}(\text{DT})_8\text{Ac}_4]$ NCs.^[74] The electrocatalytic oxygen reduction reaction (ORR) efficiencies of assembled nanowires and nanoribbons were compared with the parent NCs as the cathode catalysts. The catalytic activity and durability of assembled NCs are found to be better than individual NCs. In another example, Wu *et al.* demonstrated the electrocatalytic oxygen evolution reaction (OER) efficiency of $[\text{Co}_9\text{S}_8]$ self-assembled nanosheets fabricated by the sulfurization of preassembled $[\text{Co}_{14}(\text{DT})_9]$ NCs in the presence of excess DT

at 400 °C under N₂ atm.^[76] Later, Cao *et al.* demonstrated the photocatalytic degradation (oxidation) of mustard gas simulant (2-chloroethyl ethyl sulfide, CEES) using [Ag₁₂(S^tBu)₆(CF₃COO)₃(TPyP)]_n, (Ag₁₂TPyP)-MOF (TPyP=tetrapyrrolyl porphyrin).^[116] The well-defined porous structure and the strong affinity between NCs and CEES in (Ag₁₂TPyP)-MOF resulted in improved uptake of CEES (74.2 mg g⁻¹). The combined photosensitizing efficiency of both porphyrin and NCs could produce a sufficient amount of ¹O₂, which helped to accelerate the degradation of CEES into a non-toxic oxidation product CEESO (Figure 1.27).

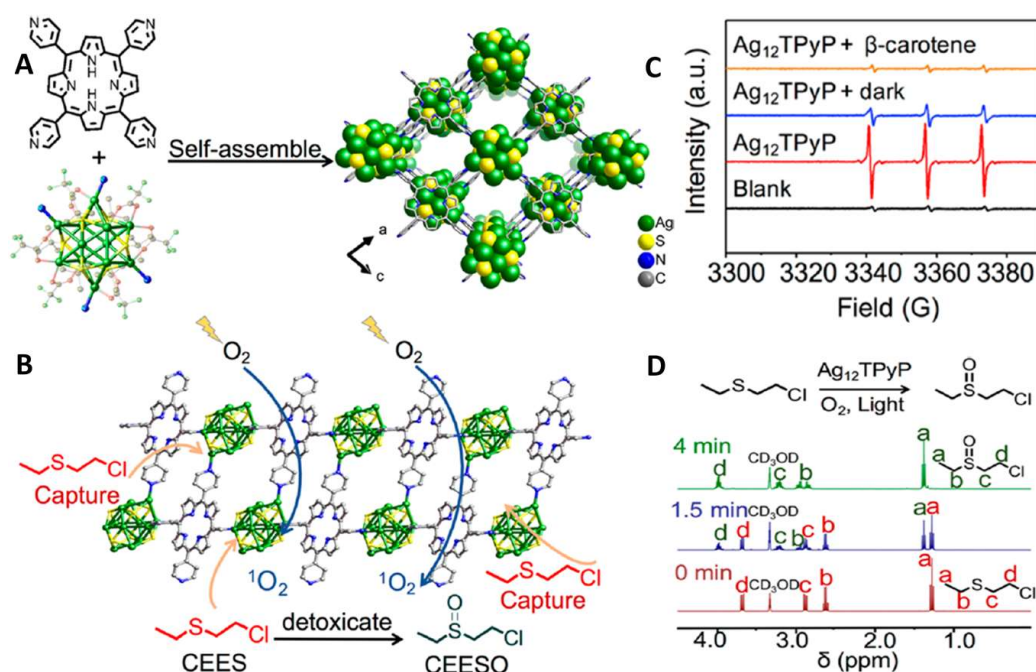


Figure 1.27: (A) Schematic representation for the synthesis of Ag₁₂TPyP. (B) Capture and photo-detoxification of CEES molecule by (Ag₁₂TPyP). (C) EPR spectra of Ag₁₂TPyP under visible-light irradiation or in the dark show the formation of ¹O₂ by the photosensitized mechanism. (D) ¹H NMR (Nuclear Magnetic Resonance) spectra of CEES during the photooxidation reaction by (Ag₁₂TPyP) shows the efficient conversion of CEES to non-toxic CEESO. Adapted from Ref.[116].

Similarly, Zhu *et al.* used the sandwiched [UiO-66@Au₂₅@UiO-66]-MOF as a heterogeneous catalyst for the selective conversion of sulfide to sulfoxide. The ¹O₂ produced by the photosensitization of [UiO-66@Au₂₅@UiO-66]-MOF triggered the photocatalytic transformation.^[145] Very recently, the catalytic activity of {[Ag₂₇S₂(S^tBu)₁₄(CF₃COO)₈(TPyP-H₂)](CF₃COO)}_n, 2D Ag₂₇-MOF has been successfully demonstrated by the chemical fixation of CO₂ *via* the cycloaddition reaction with both terminal and internal propargylamines.^[146]

1.5 Motivation, objective, and scope

Atomically precise NCs act as a link between molecular-level organometallic complexes and colloidal-level plasmonic NPs. Systematic studies on various aspects of NC fabrication, optical properties, enhanced PL, and catalytic activity have been efficiently used to enrich different aspects of materials science. With the introduction of new and improved protocols for synthesis, surface functionalization, and subsequent purification, NCs have been used in various research areas. The applications of NCs in electrocatalysis, solar energy harvesting, photocatalysis, LEDs, molecular recognition, bioimaging, therapeutics, and biosensing have been explored. The well-defined structure, covalently bound functional groups, optoelectronic properties, and inherent structural complexities of NCs make them excellent building blocks for fabricating a wide range of functional 3D periodic superstructures *via* the colloidal self-assembly process. Despite the recent progress in the assembled superstructures, there are several limitations in NC self-assembly. For example, hydrogen bonding assemblies have so far been demonstrated using only a few selected ligands. Such assemblies will face substantial challenges when more than one type of hydrogen bonding motif or competing interactions are available. Electrostatic assemblies often lead to irreversible aggregates. Notably, a wide range of crystal structures was reported only for

organic solvent-soluble NCs. Due to the lack of a well-established crystal structure, the self-assembly of water-soluble NCs faces limitations in understanding the molecular level details and structure-property correlations. However, the assembled superstructures could bring new photophysical properties such as AIE, enhanced CPL, amplified optical absorption, and better mechanical strength. These properties have been effectively utilized to demonstrate molecular and metal ion sensing, gas sensing and storage, bioimaging and therapeutics, catalysis, and device fabrications. So far, the reported structures in the literature are static and equilibrium NC self-assemblies. Hence there is ample scope for dynamic assemblies utilizing NCs. By employing proper ligand engineering methods, reversible dynamic assemblies responsive to external stimuli can be addressed. Chromophores like azobenzene and spiropyran can respond to external light and undergo light-induced photoisomerization. Anchoring such chromophores on the surface of NCs will be fascinating due to their multiple-switchability and molecular interaction of such molecules. Such NC building blocks can be utilized to produce non-invasive reversible self-assembly of NCs. Additionally, enhanced luminescence resulting from the self-assembly process can be used for fabricating anticounterfeiting and electroluminescent devices. This thesis is mainly focusing on the supramolecular assemblies of NCs using different functional ligands and their applications.

1.6 References

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CHAPTER 2

MATERIALS AND METHODS

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials

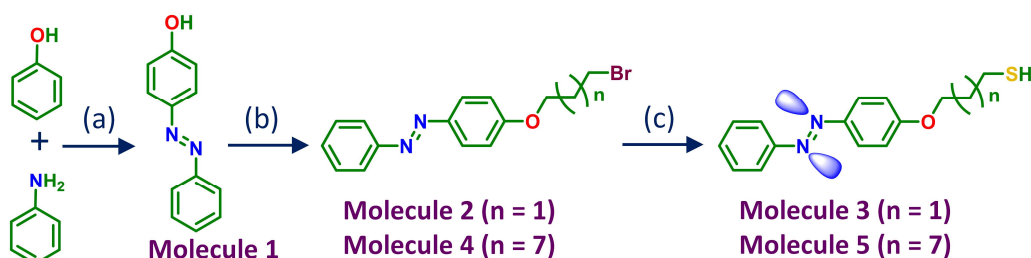
Phenol, aniline, potassium nitrite (KNO_2), 1,3-dibromopropane, 1,9-dibromononane, hexamethyldisilathiane (HMDST), tetrabutylammonium fluoride (TBAF), tetraoctylammonium bromide (TOAB), ammonium chloride (NH_4Cl), ammonia solution (25%), potassium carbonate (K_2CO_3), potassium iodide (KI), 2-phenylethanethiol (PET), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), chloro(dimethyl sulfide)gold(I) ($(\text{CH}_3)_2\text{SAuCl}$), silver nitrate (AgNO_3), copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), 1,3-benzene dithiol (BDT), 1-adamantanethiol (HSadm), sodium borohydride (NaBH_4), potassium hydroxide (KOH), 2,5-Bis-(5-tert-butyl-benzoxaazol-2-yl)thiophene (BBOT), p-mercaptobenzoic acid (p-MBA), toluene, hydrochloric acid (HCl), methanol (MeOH), ethanol (EtOH), acetone, tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile (CH_3CN), and N,N-dimethylformamide (DMF) were purchased from Sigma-Aldrich. Alpha-lipoic acid (LA), triphenylphosphine (TPP), and 1,2-bis(diphenylphosphino)ethane (DPPE) were purchased from Tokyo Chemicals Industry (TCI). sodium hydroxide (NaOH), ammonium acetate (NH_4OAc), chloroform-*d* (CDCl_3), dichloromethane-*d*₂ (CD_2Cl_2), and dimethyl sulfoxide-*d*₆ ($\text{DMSO-}d_6$) were purchased from Sisco Research Laboratories (SRL). Medical grade thermoplastic polyurethane (PU) (TECOFLEX™ EG-93A) was received from Lubrizol Advanced Materials India.

2.2 Methods

2.2.1 Synthesis of C₃-AMT and C₉-AMT ligands

The C₃- and C₉-AMT (AMT= azobenzene monothiol) ligands were synthesized utilizing organic synthesis chemistry in three steps. **Scheme 2.1**

represents the organic synthetic scheme of C₃ and C₉-AMT. Detailed procedure is given below.



Scheme 2.1: Scheme for the synthesis of C₃ and C₉-AMT (**Molecules 1-5**). (a) HONO, 0 °C (b) 1,3-dibromopropane or 1,9-dibromononane, K₂CO₃/KI, acetone, 80 °C (c) HMDST/TBAF, Distilled THF, -10 °C.

Synthesis of molecule 1 (M1): **M1** was synthesized using a reported protocol.^[1] Aniline (4.6 mL; 50 mmol) was dissolved in 15 mL of conc. HCl and cooled to 0 °C. An aqueous solution (15 mL) of KNO₂ (4.4 g; 52 mmol) was added dropwise to the above solution under constant stirring. A clear solution of freshly prepared diazonium salt was added dropwise into phenol (4.7 g; 50 mmol) dissolved in 400 mL NH₃-NH₄Cl buffer solution (pH ~9) at 0 °C. The reaction was carried out at ice-cold temperature for another 3 h followed by adding excess con. HCl. The precipitated product was washed and collected by vacuum filtration. Washing was repeated multiple times to remove excess reagents and starting materials.

Synthesis of molecule 2 (M2): A suspension of **M1** (1.98 g; 10 mmol), 1,3 dibromopropane (~10 mL; 100 mmol), K₂CO₃ (1.66 g; 12 mmol), and catalytic amount of KI were refluxed in acetone (50 mL) for 5 h at 80 °C.^[2] The reaction mixture was cooled and filtered. Excess 1,3-dibromopropane was removed by pumping in a rotary evaporator. The crude product was chromatographed over silica gel and eluted with a 2% ethyl acetate/hexane mixture.

Synthesis of molecule 3 (M3): A stirred solution of **M2** (0.319 g; 1 mmol) in freshly distilled THF (4 mL) was cooled to -10 °C followed by adding a mixture of HMDST (255 μ L; 1.2 mmol) and TBAF (0.35 g; 1.1 mmol) dissolved in THF (1 mL).^[2] The mixture was warmed to room temperature while being stirred. After 1 h, the reaction mixture was diluted with DCM and washed with saturated NH₄Cl solution. The crude product was chromatographed over silica gel and eluted with a 2% ethyl acetate/hexane mixture.

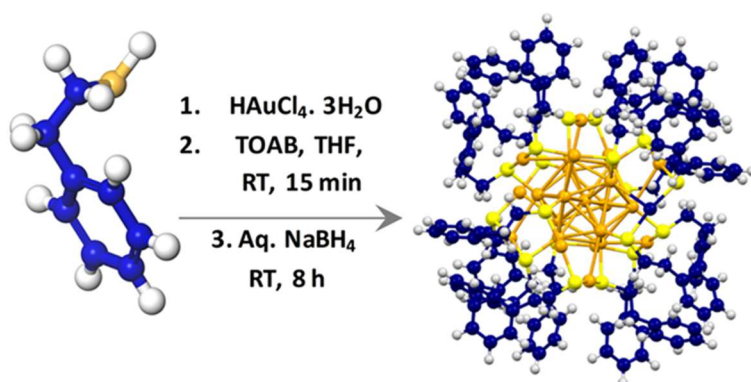
Synthesis of molecule 4 (M4): **M4** was synthesized using a reported protocol with required modifications.^[2] Briefly, a suspension of **M1** (1.98 g; 10 mmol), 1,9-dibromononane (~20 mL; 100 mmol), K₂CO₃ (1.66 g; 12 mmol), and a catalytic amount of KI were refluxed at 80 °C in acetone (50 mL) for 5 h. The reaction mixture was cooled and filtered, followed by removing the solvent in a rotary evaporator. To remove excess 1,9-dibromononane, column chromatography was performed using nonpolar hexane as the eluent. Subsequently, the remaining crude product was chromatographed over silica gel with a 2% ethyl acetate/hexane mixture to yield the product.

Synthesis of molecule 5 (M5): **M5** was synthesized using a reported protocol with required modifications.^[2] Briefly, a solution of **M4** (403 mg; 1 mmol) prepared in freshly distilled THF (4 mL) was initially cooled to -10 °C and stirred at the same temperature. Subsequently, a mixture of HMDST (255 μ L; 1.2 mmol) and TBAF (350 mg; 1.1 mmol) prepared in THF (1 mL) was injected into the above solution. The mixture was warmed to room temperature while being stirred. After completing 1 h stirring, the reaction mixture was diluted with DCM and washed with saturated NH₄Cl solution. The crude product was chromatographed over silica gel and eluted with a 2% ethyl acetate/hexane mixture to yield the final product (**M5**).

M3 is used in Chapter 3. **M3** and **M5** are used in Chapter 4.

2.2.2 Synthesis of $[\text{Au}_{25}(\text{PET})_{18}]^-$

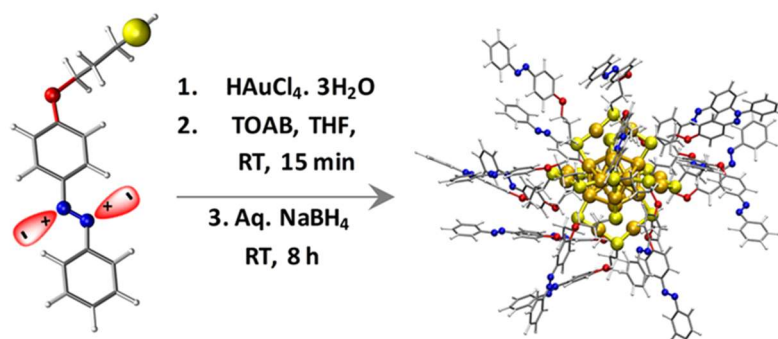
$[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs were synthesized by using a reported protocol.^[3] To a solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (20 mg/2 mL THF), TOAB (33 mg/1.75 mL THF) was added and stirred until color turned to dark red. Following this, PET (34 μL ; 5 mol equivalents w.r.t. gold) was added and stirred at 400 rpm for 1 h. The Au-thiolate solution formed was further reduced by injecting a freshly prepared ice-cold aqueous NaBH_4 solution (19 mg/1.25 mL; 10 mol equivalents w.r.t. gold). The mixture was stirred at room temperature for another 8-9 h to complete the reaction. Using a separating funnel organic and aqueous layers were separated (toluene was added for good separation), and the organic layer was washed several times with Millipore water. Excess thiol and other impurities were removed by precipitating NCs by adding MeOH. This washing step was repeated three times. Insoluble Au-S polymers were removed from the crude by extracting NCs in DCM. Finally, NCs were re-dispersed in acetone to remove byproducts (Au_{144} NCs). Dried $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs were stored at 4 °C for further characterization. $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs were utilized in **Chapter 3**. The **Scheme 2.2** represents $[\text{Au}_{25}(\text{PET})_{18}]^-$ NC synthesis.^[4]



Scheme 2.2: Scheme for the synthesis of $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs.^[4]

2.2.3 Synthesis of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$

Modified Brust-Schiffrin single-phase procedure was used for the synthesis of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$.^[3] To a solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (20 mg/2 mL THF), TOAB (33 mg/1.75 mL THF) was added and stirred until the color turned to dark red. Following this, $\text{C}_3\text{-AMT}$ (69 mg; 5 mol equivalents w.r.t. gold) was added and stirred at 400 rpm for 1 h. The Au-thiolate solution formed was further reduced by injecting a freshly prepared ice-cold aqueous NaBH_4 solution (19 mg/1.25 mL; 10 mol equivalents w.r.t. gold). The mixture was stirred at room temperature for another 8-9 h to complete the reaction. Using a separating funnel organic and aqueous layers were separated (toluene was added for good separation), and the organic layer was washed several times with Millipore water. Excess thiol and other impurities were removed by precipitating NCs by adding MeOH. This washing step was repeated three times. Insoluble Au-S polymers were removed from the crude by extracting NCs in DCM. Finally, NCs were re-dispersed in acetone to remove byproducts (Au_{144} NCs). Dried $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs were stored at 4 °C for further characterization. $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs were used in **Chapter 3**. Schematic representing NC synthesis are given in **Scheme 2.3**.



Scheme 2.3: Scheme for the synthesis of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs.

2.2.4 Synthesis of PET-NC

Synthesis of PET-NCs was performed using a reported method in the literature.^[5,6] Briefly, to a solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (20 mg/2 mL of CH_3CN), TOAB (33 mg/2 mL CH_3CN) was added and stirred until color turned to dark red. The mixture was stirred for 15 min in an ice bath, while it was cooled to 0 °C. Followed by this, PET (36 μL ; 6 mol equivalents w.r.t. gold) dissolved in 6 mL CH_3CN was added and stirred for 15 minutes until an opaque-white mixture was formed. The Au-thiolate was further reduced by injecting a freshly prepared ice-cold aqueous NaBH_4 solution (19 mg/2 mL; 10 mol equivalents w.r.t. gold). The reaction mixture was stirred for another 4 h. The precipitated NCs were collected by centrifugation followed by washing the black precipitate in an excess MeOH/water mixture. This washing step was repeated three times to remove excess thiol. Finally, NCs dispersed in DCM were evaporated, and washed with acetone to remove byproducts. Dried PET-NC powder was stored at 4 °C. PET-NC was used in **Chapter 4**.

2.2.5 Synthesis of C₃-NC

Synthesis of C₃-NCs was performed using a reported method in the literature.^[5,6] Briefly, to a solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (20 mg/2 mL of CH_3CN), TOAB (33 mg/2 mL CH_3CN) was added and stirred until color turned to dark red. The mixture was stirred for 15 min in an ice bath, while it was cooled to 0 °C. Followed by this, C₃-AMT (83 mg; 6 mol equivalents w.r.t. gold) dissolved in 6 mL CH_3CN was added and stirred for 15 minutes until an opaque-yellow mixture was formed. The Au-thiolate was further reduced by injecting a freshly prepared ice-cold aqueous NaBH_4 solution (19 mg/2 mL; 10 mol equivalents w.r.t. gold). The reaction mixture was stirred for another 4 h. The precipitated NCs were collected by centrifugation followed by washing the black precipitate in an excess MeOH/water mixture. This

washing step was repeated three times to remove excess thiol. Finally, NCs dispersed in DCM were evaporated, and washed with acetone to remove byproducts. Dried C₃-NC powder was stored at 4 °C. C₃ NC was used in **Chapter 4**.

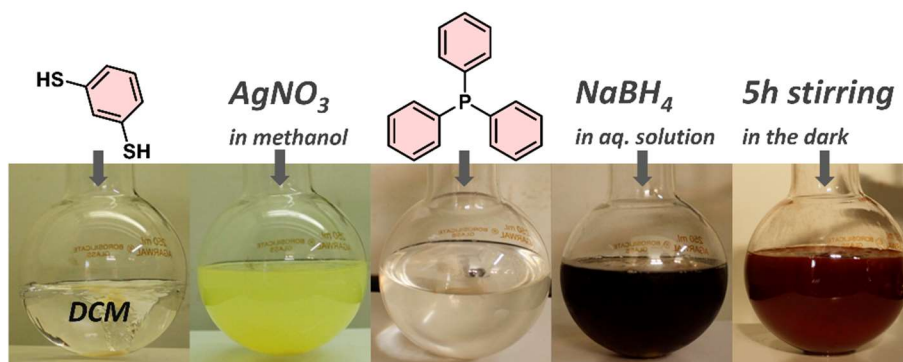
2.2.6 Synthesis of C₉-NC

Synthesis of C₉-NCs was performed using a reported method in the literature.^[5,6] Briefly, to a solution of H₂HAuCl₄·3H₂O (20 mg/2 mL of CH₃CN), TOAB (33 mg/2 mL CH₃CN) was added and stirred until color turned to dark red. The mixture was stirred for 15 min in an ice bath, while it was cooled to 0 °C. Followed by this, C₉-AMT (108 mg; 6 mol equivalents w.r.t. gold) dissolved in 6 mL CH₃CN was added and stirred for 15 minutes until an opaque-yellow mixture was formed. The Au-thiolate solution formed was further reduced by injecting a freshly prepared ice-cold aqueous NaBH₄ solution (19 mg/2 mL; 10 mol equivalents w.r.t. gold). The reaction mixture was stirred for another 4 h. Precipitated NCs were collected by centrifugation followed by washing the black precipitate in excess MeOH/water mixture. The precipitate was further washed three times in acetone to remove excess thiol. Finally, NCs dispersed in DCM were evaporated. This washing step was repeated three times to remove excess thiol. Finally, NCs dispersed in DCM were evaporated, and washed with acetone to remove byproducts. Dried C₉-NC powder was stored at 4 °C. C₉ NC was used in **Chapter 4**.

2.2.7 Synthesis of [Ag₂₉(BDT)₁₂(TPP)₄]³⁻

[Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NCs were synthesized by using a reported protocol.^[7] Briefly, in a glass tube, 13.5 µL of BDT was added to 10 mL of DCM. 20 mg of AgNO₃ was separately dissolved in 5 mL of MeOH by ultra-high sonication. The addition of AgNO₃ solution into the above-prepared reaction mixture

resulted in a turbid yellow solution, indicating the formation of an insoluble silver-thiolate complex. The mixture was cooled to ice-cold temperature. The addition of TPP (200 mg in 1 mL DCM) to the turbid yellow solution resulted in the formation of a colorless solution. The reaction mixture was allowed to stir for another 10 min before adding a freshly prepared aqueous ice-cold NaBH_4 solution (10.5 mg in 500 μL of water). The color of the solution turned dark brown immediately, which gradually changed (over a period of 5 h) to dark orange, indicating the formation of Ag_{29} NCs. NCs were purified by ultra-high centrifugation method (8000 rpm for 2 min). Residual dark orange NCs were washed several times with EtOH to remove all the unreacted materials. Purified NCs were dried under a vacuum and stored at 4 $^{\circ}\text{C}$ for further characterization. Photographs representing the different stages of NC synthesis are given in **Scheme 2.4**. $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC was used in **Chapter 5**.



Scheme 2.4: Scheme for the synthesis of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NCs.

2.2.8 Synthesis of $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$

$[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs were synthesized by using a protocol reported elsewhere.^[8] Briefly, an aqueous solution of KOH (1 M) was added to LA (19 mg, 0.092 mmol) until it dissolves completely. An aqueous solution of NaBH_4 (7 mg/100 μL , 0.185 mmol) was added to the above lipolate solution and

stirred for another 15 min. Followed by this, an aqueous AgNO_3 (2.9 mg/200 μL , 0.017 mmol) solution was injected and stirred for 30 min at room temperature. Addition of ice-cold NaBH_4 (10 mg/100 μL , 0.264 mmol) solution to the above reaction mixture resulted in a color change from black to dark orange (over a period of 4 h), indicates the formation of NCs. NCs were purified by adding an equal volume of acetone followed by ultra-high centrifugation (8000 rpm for 2 min). Further, the residual dark orange supernatant solution was precipitated by adding excess acetone. The precipitate was washed several times with EtOH to remove all the unreacted materials. Purified NCs were dried under vacuum and stored at 4 $^\circ\text{C}$ for further characterization. $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NC was used in **Chapter 5**.

2.2.9 Synthesis of $[\text{Au}_{22}(\text{SG})_{18}]$

$[\text{Au}_{22}(\text{SG})_{18}]$ NCs were synthesized using a reported protocol.^[9] To 23 mL of Millipore water, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (10 mg/1.25 mL H_2O), and GSH (12 mg/0.75 mL H_2O) were added and vigorously stirred until the yellowish solution turned cloudy. Then, the pH of the reaction mixture was adjusted to 12 using aqueous NaOH (1 M), making the color of the solution transparent yellow. The Au-thiolate formed was further reduced by the dropwise addition of dilute aqueous NaBH_4 (3.5 mM, 0.1 mL) solution. During the first 15 min, the solution slowly turned orange. After 30 min, the pH was adjusted to 2.5 using HCl (0.33 M), to quench the BH_4^- activity and stirred slowly (500 rpm) at room temperature for 6 h. The solid crude product was obtained by adding 0.5 equivalent volume of MeOH and subsequent centrifugation at 8000 rpm. Dried $[\text{Au}_{22}(\text{SG})_{18}]$ NCs were stored at 4 $^\circ\text{C}$ for further characterization. $[\text{Au}_{22}(\text{SG})_{18}]$ NC was used in **Chapter 5**.

2.2.10 Synthesis of [Au₁₀₂(*p*-MBA)₄₄]

[Au₁₀₂(*p*-MBA)₄₄] NCs were synthesized using the reported protocol.^[10] To 51.5 mL of Millipore water, MeOH (75 mL), HAuCl₄·3H₂O (209 mg/10 mL MeOH), and *p*-MBA (292 mg/18.43 mL of Millipore water, dissolved by adding 57 μ L of 10 M NaOH) were added respectively. The reaction mixture was stirred at room temperature for 20 h resulting in a white precipitate. The Au-thiolate solution formed was further reduced by adding solid NaBH₄ (20.8 mg; 0.5 mol equivalents w.r.t. gold). The color of the solution immediately turned black and the mixture was stirred at room temperature for another 5 h. The solid crude product was precipitated by adding 800 mL of MeOH and aqueous NH₄OAc (5 M, 40 mL) solution. The precipitate was collected by centrifuging at 3500 rpm for 5 min. The supernatant was decanted, and the precipitate was allowed to dry. To purify further, the precipitate was dissolved in Millipore water (4 mL) and aqueous NH₄OAc (2 M, 10 mL) solution, which was then reprecipitated by adding MeOH (900 mL). The final product was obtained by centrifuging at 3500 rpm for 10 min. Dried [Au₁₀₂(*p*-MBA)₄₄] NCs were stored at 4 °C for further characterization. [Au₁₀₂(*p*-MBA)₄₄] NC was used in **Chapter 5**.

2.2.11 Synthesis of [Au₁₄₄(PET)₆₀]

[Au₁₄₄(PET)₆₀] NCs were synthesized using the reported protocol.^[11] To a solution of HAuCl₄·3H₂O (118 mg/10 mL MeOH), TOAB (190 mg/5 mL MeOH) was added and vigorously stirred for 15 min until the color turned from yellow to dark red. Then, PET (213 μ L; 5.3 mol equivalents w.r.t. gold) was added to the reaction mixture, which rapidly produced white Au-thiolate. After ~15 min, it was further reduced by injecting a freshly prepared ice-cold aqueous NaBH₄ solution (113.5 mg/6 mL, 10 mol equivalents w.r.t. gold) under vigorous stirring. The color of the solution immediately turned

black and stirred for 5 h to produce Au₁₄₄ NCs as a black precipitate. Excess thiol and other impurities were removed by washing with MeOH multiple times. Insoluble Au-S polymers were removed from the crude mixture by extracting NCs in DCM. Finally, dried NCs were washed with acetone to remove byproducts (Au₂₅ NCs). Dried [Au₁₄₄(PET)₆₀] NCs were stored at 4 °C for further characterization. [Au₁₄₄(PET)₆₀] NC was used in **Chapter 5**.

2.2.12 Crystallization of [Ag₂₉(BDT)₁₂(TPP)₄]³⁻

10 mg of thoroughly dried [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NC powder was dispersed in 500 µL of DMF and filtered using a syringe filter with a pore size of 0.22 µm. The filtered solution was then spotted onto glass plates and allowed to slowly evaporate at room temperature under ambient air in darkness. After about 2 days, square-shaped dark orange crystals were collected. Ag₂₉ NC crystals were used in **Chapter 5**.

2.2.13 Fabrication of luminescent NC-based printing ink

PU was used as an elastomeric binder for the development of stretch-enduring luminescent printing ink. A typical synthesis of ink consists of mixing crystallized NCs (7 or 40 mg) in Polyurethane (PU) suspension (24 mL) in a shaker for 30 min, followed by constant stirring for another 5 h. The PU suspension was previously prepared by dispersing PU (2 g) in THF (24 mL) using the ultrasonication (30 min) method, followed by continuous stirring (overnight). Similarly, the OB-PU (OB= Optical Brightener) suspension was prepared by dispersing PU (2 g) and 2,5-Bis-(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT: OB) (1.25 mg) in THF (24 mL). To print QR codes, we have used low-concentration NC-PU (7 mg NC/24 mL PU) dispersion. NC-PU ink was used in **Chapter 5**.

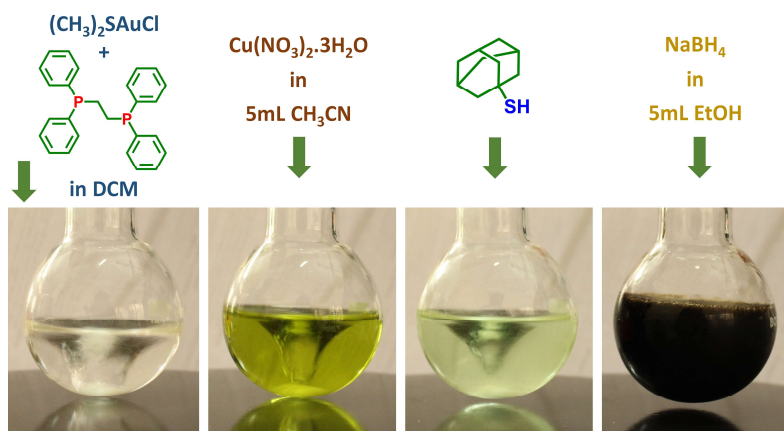
2.2.14 Fabrication of printed QR code

The luminescent ink was manually printed on the desired area of the currency using a stencil-printing technique. Initially, a static QR code image, encrypted with “Reserve Bank of India”, was generated using free available software (<https://www.the-qrcode-generator.com>). The stencil pattern corresponding to the QR code image was designed by Auto-CAD software. The stencil was created on a polyester sheet (100 μm thickness) by engraving the intended sketch using an electronic cutter (Silhouette Cameo, US). An OB-PU interface layer was initially printed (2.5×2.5 cm), to facilitate the luminescent ink adhesion on the currency substrate and cured at 65 °C for 20 min in a convection oven. Subsequently, the QR code was patterned by printing the luminescent ink on the OB-PU layer and cured at 65 °C for 30 min. The movement of luminescent ink over the stencil using a squeegee facilitates printing the QR code pattern on the underlying currency substrate. The freestanding stretchable film was prepared by directly printing the luminescent ink on the temporary transfer paper (tattoo paper). The transfer paper was prepared by coating a water-soluble starch layer on the copier paper (80 gsm).^[12] Typically, 55% starch was dispersed in water by heating at 95 °C for 15 min and cross-linked with D-sorbitol (45%) under stirring for 1 h. The cross-linked starch was printed on the paper substrate and cured at 70 °C for 30 min. The process was repeated twice to get the homogenous water-soluble film on the paper substrate. The printed luminescent film on the tattoo paper can be released by moisturizing it for 1 minute. Printed QR code was discussed in **Chapter 5**.

2.2.15 Synthesis of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$

Briefly, $(\text{CH}_3)_2\text{SAuCl}$ (30 mg; 0.1 mmol) and DPPE (80 mg; 0.2 mmol) were dissolved in 10 mL DCM. In parallel, $\text{Cu(II)NO}_3 \cdot 3\text{H}_2\text{O}$ (50 mg; 0.2 mmol) was

dissolved in 5 mL CH₃CN using ultrasonication. Addition of this copper salt solution into the stirring (~1000 rpm) solution of gold/DPPE mixture prepared in DCM produced a greenish solution within 15 min of reaction. The addition of HSadm (68 mg; 0.4 mmol) into the above-prepared greenish solution turned it back to colorless. To this colorless solution kept at 0 °C, NaBH₄ (40 mg (1 mmol) in 5 mL EtOH) was injected and stirred vigorously for another 20 h till a purple-colored precipitate was formed. The precipitate was washed two-three times with CH₃CN and hexane, extracted in DCM, and final rotary evaporation produced a purple colored NC powder. All the reactions were performed under dark conditions. [Au₂Cu₆(Sadm)₆(DPPEO)₂] was used in **Chapter 6**.



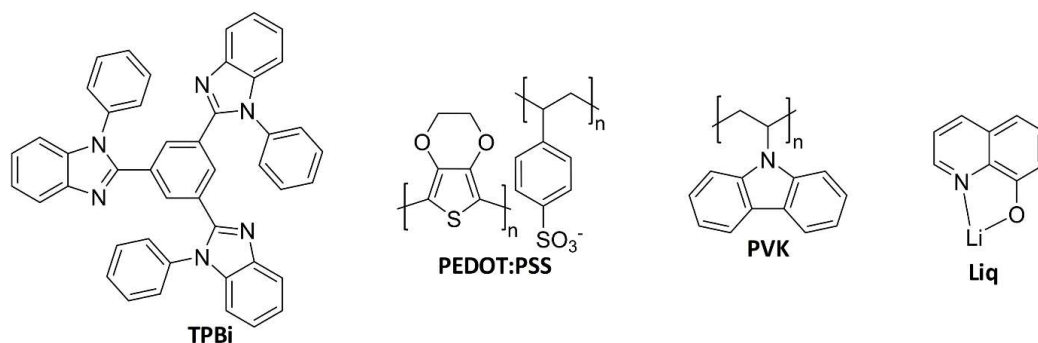
Scheme 2.5: Scheme for the synthesis of [Au₂Cu₆(Sadm)₆(DPPEO)₂] NCs.

2.2.16 Crystallization of [Au₂Cu₆(Sadm)₆(DPPEO)₂]

10 mg of thoroughly dried [Au₂Cu₆(Sadm)₆(DPPEO)₂] NC powder was dissolved in 500 µL of DCM and filtered using a syringe filter with a pore size of 0.22 µm. The filtered solution was slowly evaporated at room temperature under ambient air in darkness. After about a few hours, rod-shaped dark purple crystals were collected. [Au₂Cu₆(Sadm)₆(DPPEO)₂] crystal was used in **Chapter 6**.

2.2.17 Fabrication of LED

First, the indium tin oxide (ITO)-coated glass substrate was cleaned with soap solution, distilled water, acetone, and isopropanol (IPA) and then sonicated for 10 min for each case. The substrate is then dried by N₂ flush and kept for UV-ozone cleaning for 20 minutes. Then, a layer of PEDOT: PSS (poly(3,4-ethylenedioxythiophene): polystyrene sulfonate) was spin-coated onto the ITO-coated glass substrate at 4000 rpm for 60 s and then annealed for 20 min at 150 °C. Above the PEDOT:PSS layer, the layer of PVK (Polyvinylcarbazole; 5 mg/ml in chlorobenzene) was spin-coated at 4000 rpm (2000 acceleration) for 60 s and then annealed at 150 °C for 15 min. Then, above that, an emissive layer of [Au₂Cu₆(Sadm)₆(DPPEO)₂] NC was spin-coated at 4000 rpm (4mg/ml in toluene) for the 60s. Then, a layer of TPBi (2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole); 50 nm), Liq (8-Hydroxyquinoline lithium; 2 nm), and Al (Aluminum; 90 nm) was deposited by thermal evaporation at 5×10⁻⁶ mbar (**Scheme 2.5**). Current density versus voltage characteristics were measured using the Keithley 2400 source meter, multimeter, and photodiode. The electroluminescence (EL) spectra were measured by using a fluorimeter. All the measurements were taken at room temperature. NC-based LED was discussed in detail in Chapter 6.



Scheme 2.6: Chemical structures of different layers used in the device fabrication.

2.3 Techniques

2.3.1 Ultraviolet-visible absorption (UV-Vis) spectroscopy

The optical absorption studies were utilized as a primary characterization tool to identify the formation of NCs. From **Chapters 3 to 5** the absorption measurements were conducted using a VARIAN Cary 500 Scan spectrophotometer, typically in the range of 200-1100 nm. In **Chapter 6**, absorption measurements were recorded using a JASCO-V-750-spectrophotometer. In both cases, samples were placed in a quartz cell of 1 cm path length, and the baseline was corrected using corresponding solvents as reference.

2.3.2 Nuclear magnetic resonance (NMR) spectroscopy

The organic ligands and NCs were characterized using NMR spectroscopy. ^1H , ^{13}C , and ^{31}P NMR measurements were carried out using Bruker AVANCE III HD 400/500 MHz spectrometers. All NMR samples were exclusively characterized in the liquid state by dissolving them in suitable deuterated NMR solvents such as CDCl_3 , $\text{DMSO}-d_6$, CD_2Cl_2 , etc. Data processing was accomplished using MestReNova software, contributing to the comprehensive analysis of the acquired NMR data.

2.3.3 X-ray photoelectron spectroscopy (XPS)

The nature of binding of core and ligand of NC, the composition of NC, the chemical state of the elements present in the NC, etc. were determined with the help of XPS measurements. In **Chapters 3-6**, X-ray photoelectron spectra were recorded using a Thermo Scientific ESCALAB 250Xi (XR6 Microfocused Monochromator, $\text{Al K}\alpha$), utilizing $\text{Al K}\alpha$ X-rays (1486.6 eV). The binding energy (BE) calibration was done with respect to C 1s (284.5 eV). Casa XPS software was used for the deconvolution of spectra.

2.3.4 Liquid chromatography-mass spectrometry (LC-MS)

The ligands in **Chapters 3** and **4** were characterized by using Liquid chromatography-mass spectrometry (LC-MS). Waters Xevo TQD triple quadrupole mass spectrometer was used to perform the measurements.

2.3.5 Electrospray ionization-mass spectrometry (ESI-MS)

The NC formation and purity were confirmed by using Waters Synapt G2-Si high-definition mass spectrometer electrospray ionization-mass spectrometry.

Typical experimental parameters of ESI-MS were as follows: capillary voltage: 3 kV, cone voltage: 150 V, source offset: 150 V, source temperature: 100 °C, desolvation temperature: 100 °C, and desolvation gas flow: 400 L/h.

2.3.6 Infrared spectroscopy (IR)

Fourier transform infrared (FT-IR) measurements (attenuated total reflection (ATR) mode) in **Chapters 3** and **4** were carried out using a Bruker Tensor 27 spectrometer.

2.3.7 Fluorescence spectroscopy

The emissive property of NCs was characterized using Fluorescence spectroscopy. The PL spectra in **Chapter 5** were recorded using a Horiba Fluorolog 3 fluorescence spectrometer. The PL spectra in **Chapter 6** were recorded using a PerkinElmer LS55 fluorescence spectrometer.

2.3.8 Fluorescence lifetime measurements

The fluorescence lifetime measurements were carried out using a Horiba (model DeltaFlex) TCSPC (time-correlated single photon counting) system. The samples were excited using a 378 nm (Chapter 5) pulsed diode laser. The lifetime values (τ), normalized pre-exponential value (α) and average

lifetime (τ_{av}) were determined using EzTime decay analysis software. The equation used for the calculation of τ_{av} of multiexponential decay is $\alpha_1\tau_1 + \alpha_2\tau_2 + \dots + \alpha_n\tau_n$. The quality of the fit has been judged by the fitting parameters such as χ^2 (<1.1) as well as the visual inspection of the residuals. In Chapter 6, lifetimes were measured using a Hamamatsu compact fluorescence lifetime spectrometer C11367 Quantaaurus-Tau; an LED light source with excitation wavelength of 405 nm was used.

2.3.9 Quantum yield (QY) measurements

The fluorescence quantum yield was measured on a SPEX-Fluorolog-3 spectrofluorometer equipped with an integrating sphere.

2.3.10 Light source and monochromator

Photoisomerization of chromophores and NCs (Chapters 3 and 4) was performed using a Newport Mercury-Xenon light source (500 W) equipped with a monochromator (Oriel).

2.3.11 Contact angle

The Surface hydrophobicity of NC-PU and PU-alone films (Chapter 5) was examined using an AST VCA optima (S/N-1020041134) contact angle analyzer. Distilled water (5 μ L/drop) was used to measure the contact angle on NC-PU film-coated surfaces by dispensing water using a motorized syringe at 25 °C.

2.3.12 Universal testing machine

The stress-strain analysis (Chapter 5) was carried out at room temperature using a universal testing machine (Instron 3366; Instron Crop. USA). The printed band (50 mm length $\times$ 10 mm width) was fixed into the testing station and subjected to an extension rate of 10 mm/min.

2.3.13 Raman microscope

Optical images of crystalized NCs were recorded using a Horiba Jobin Yvon LabRAM HR Evolution laser Raman microscope.

2.3.14 Confocal fluorescence imaging

The confocal fluorescence image of crystalized NCs (Chapter 5) was recorded using a Carl Zeiss-LSM 880 confocal laser scanning microscope (458 nm laser).

2.3.15 Dark-field scattering imaging

Dark-field scattering imaging (Chapters 3 and 4) was performed on a Cytoviva hyperspectral imaging system (HSI) equipped with a Cytoviva high-resolution dark-field condenser (oil immersion). Here, a sample slide kept in an optical path was illuminated using a halogen lamp after passing through an oil immersion dark-field condenser. Scattering light was focused through a microscope objective (40x), and signals were collected with a colored CCD camera.

2.3.16 Dynamic light scattering (DLS) analysis

DLS measurements were performed using a Nanotracs Ultra NPA 253 from Microtrac (Chapter 3) and Malvern Zetasizer Nano S90 (Chapter 6). Particle size and distribution of self-assembled NC colloid solutions were obtained using the Microtrac Flex software.

2.3.17 Single-crystal X-ray diffraction (SCXRD)

SCXRD data collection of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs (Chapter 6) was performed with Bruker Kappa APEX III CMOS diffractometer with Mo $K\alpha$ ($\lambda = 0.71 \text{ \AA}$).

Identification code	[Au ₂ Cu ₆ (Sadm) ₆ (DPPEO) ₂]
Empirical formula	C112 H138 Au2 Cu6 O2 P4 S6
Formula weight	2607.63
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 16.3238(11) Å b = 18.3697(13) Å a = 99.376(3)° b = 102.663(2)° c = 24.5277(16) Å g = 110.645(2)°
Volume	6478.7(8) Å ³
Z	2
Density (calculated)	1.337 Mg/m ³
Absorption coefficient	3.407 mm ⁻¹
F(000)	2628
Crystal size	0.363 x 0.102 x 0.084 mm ³
Theta range for data collection	2.529 to 23.351°.
Index ranges	-18<=h<=18, -20<=k<=20, -27<=l<=27
Reflections collected	203284
Independent reflections	18680 [R(int) = 0.1540]
Completeness to theta = 23.351°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6365 and 0.3970
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	18680 / 210 / 1189
Goodness-of-fit on F ²	1.107
Final R indices [I>2sigma(I)]	R1 = 0.0749, wR2 = 0.1802
R indices (all data)	R1 = 0.1396, wR2 = 0.2342
Extinction coefficient	n/a
Largest diff. peak and hole	3.329 and -1.705 e.Å ⁻³

Table 2.1: Crystal data and structure refinement for [Au₂Cu₆(Sadm)₆(DPPEO)₂] NC.

2.3.18 Small-angle X-ray diffraction (SAXRD)

SAXRD measurement was (Chapter 3) performed using a third-generation Empyrean Malvern PANalytical X-ray diffractometer. The X-ray source was Cu K α (1.5418 Å). Dried powders of NC superstructures were used to measure the diffraction.

2.3.19 Field emission scanning electron microscopy (FESEM) and energy dispersive analysis of X-rays (EDAX)

FESEM images (Chapters 4 and 5) were recorded using a Carl-Zeiss SUPRA 55VP field emission scanning electron microscope equipped with EDAX. Samples were drop-casted on a silicon wafer or ITO glass. In Chapter 6, FESEM analysis was performed with a Verios G4 UC, FEI instrument. The samples were sputter-coated with Au/Pd mixture to produce better-quality images without charging.

2.3.20 Atomic force microscopy (AFM)

AFM images (Chapters 3, 4, and 6) were acquired using an Agilent Technologies 5500 series AFM/SPM microscope equipped with Pico View 1.14.1 software, and the images were processed using Gwyddion. The high-resolution tapping mode (AC mode) AFM measurements (Chapters 3 and 4) were performed on an Oxford Instruments Asylum Cypher ES.

2.3.21 High-resolution transmission electron microscopy (HRTEM)

HRTEM images were recorded on a FEI Talos F200S (200 kV) TEM and JEOL 3010 (300 kV) TEM. Scanning transmission electron microscopy (STEM) images with EDS and elemental mapping were recorded using a FEI Talos F200S (200 kV) TEM (Chapters 3 and 4) and Jeol F200 S/TEM (Chapter 6). The samples were prepared by drop-casting NC solution on carbon-coated copper grids and allowed to dry under ambient conditions.

2.3.22 Electron tomography

The transmission electron tomographic reconstruction and tilt series of 2D projections (Chapters 3, 4, and 6) were acquired with the Serial EM-software package.^[13,14] The specimen was tilted between ± 68 - 70° with 2 - 3° increment steps in low-dose mode.^[15] The acquired raw stack of images was first subjected to a series of preprocessing, coarse alignment, and final alignment and was further aligned using the IMOD software package.^[16] The final aligned file was then utilized for 3D reconstruction with a custom-made maximum entropy method (MEM) program with a regularization parameter value of $\lambda = 1.0 \times 10^{-3}$ on MacPro.^[17,18] The 3D isosurface and solid-colored images were produced using UCSF Chimera.

2.3.23 Density functional theory (DFT) calculations

Energy-minimized structures of NCs and ligands (Chapters 3, 4, and 5) were optimized using DFT as implemented in the grid-based projector-augmented wave (GPAW) software package.^[19,20] The following PAW setups were considered for Au(5d106s1), Ag(4d105s1), S(3s23p4), P(3s23p3), O(2s22p4), N(2s22p3), C(2s22p2), and H(1s1), with scalar-relativistic effects included for Au and Ag. The geometry optimizations were carried out using the PBE60 functional and DZP (double-zeta plus polarization) basis set in LCAO (Linear combination of atomic orbitals) mode^[21] with a grid spacing of $0.2 \text{ \AA}$ and the convergence condition that the residual forces be $0.05 \text{ eV/\AA}$, without imposing any symmetry constraints. All optimized structures were visualized using the visual molecular dynamics (VMD) software.^[22]

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CHAPTER 3

**LIGHT-TRIGGERED REVERSIBLE
SUPRACOLLOIDAL SELF-ASSEMBLY OF
PRECISION GOLD NANOCCLUSERS**

CHAPTER 3

LIGHT-TRIGGERED REVERSIBLE SUPRACOLLOIDAL SELF- ASSEMBLY OF PRECISION GOLD NANOCCLUSERS

3.1 Introduction

NCs show diverse applications in many fields owing to their quantum confinement, nanometric dimension, larger surface area, diverse functionalization, and stability towards chemicals and light.^[1-10] NCs with a varying number of metal atoms in the core and covalently bound functional ligands have been reported in the literature.^[11-26] Among these, functional thiolates tethered-NCs display important features, particularly Förster resonance energy transfer,^[27] optical chirality,^[28,29] and biocompatibility useful for the construction of bioconjugated protein machinery for extracellular labeling and intracellular delivery.^[30] Smart molecular imprinting on NC surfaces can also be extended to build self-assembled superstructures. Such novel materials can find applications in advanced optical materials due to their collective and enhanced optical properties that arise from the periodic organization. Recently, NC self-assemblies have been reported via dipole-induced van der Waals attraction,^[31] hydrogen bonding,^[32] C-H... π interactions,^[33] metal chelation,^[34] and aurophilic interactions.^[35] Importantly, self-assembled gold NC superstructures have been shown to alter the photoluminescence, catalytic activity, and bioavailability.^[34] Since NCs in such self-assembled structures interact with one another with local forces, the efficient reversibility of such static assemblies will be difficult. In this context, photoactive molecules offer a unique opportunity to achieve reversible molecular self-assembly and even for plasmonic nanoparticles.^[36] Therefore, it is relevant to investigate whether this approach can be implemented in NC self-assembly by

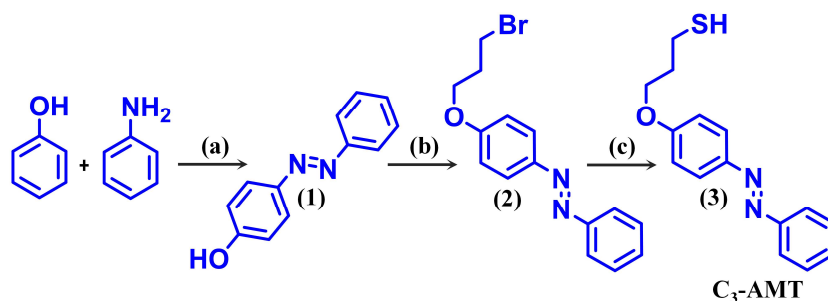
developing photo-isomerizing ligand^[37-42]-tethered NCs. As the photo-stability of NCs and their interactions with photons are significantly different from corresponding plasmonic nanoparticles, photon-assisted reversible self-assembly of NCs in solution at room temperature is still challenging. Furthermore, to achieve NC self-assembly in solution, it is crucial to overcome the thermal fluctuation of the surroundings, which is close to the inter-NC interaction.^[43] In the literature, two types of photo-switchable chromophores viz., azobenzene^[44] and spiropyran^[45] functionalized Au₂₅ NCs are known. However, the reported studies are limited to the spectroscopic investigation. A detailed understanding of the morphological changes and potential colloidal-level self-assembly has not been investigated. To address this challenge, we demonstrate the synthesis and photon-induced reversible self-assembly of azobenzene-alkyl monothiol (C₃-AMT)-tethered Au₂₅ NCs [Au₂₅(C₃-AMT)₁₈]⁻. We show that when a solution of [Au₂₅(C₃-AMT)₁₈]⁻ was irradiated with ultraviolet light (345 nm) disc-like superstructures (d~100-1000 nm) were formed. The stable structure obtained readily disassembled upon irradiating with visible light (435 nm), demonstrating the light-triggered assembly and disassembly. The temporal evolution of self-assembled superstructures was studied extensively by using various spectroscopic and microscopic techniques followed by correlating them with electron tomography reconstruction.

3.2 Result and discussion

3.2.1 Characterization of azobenzene monothiol (C₃-AMT)

The synthesis and characterization of azobenzene monothiol (AMT) ligand was carried out using a wet chemical method. The AMT with C₃-spacer was synthesized according to a reported procedure.^[46,47] The synthesis of C₃-AMT is given in the **Scheme 3.1**. The reaction was carried out from simple

starting molecules. The **molecule 1** was synthesized by the diazotization reaction between phenol and aniline. Further, it was treated with excess alkyl bromide to react with the phenol group and form a long alkyl chain. The resulting **molecule 2** was converted to thiol (**molecule 3**) using the HMDST-TBAF reaction. Details of reactions involved in the preparation of C₃-AMT are provided in **Chapter 2**. The ligand was thoroughly characterized in each step (**molecules 1, 2, and 3**) using NMR, FT-IR, and mass spectrometry (**Figure 3.1-3.6**) and corresponding values are shown in **Table 3.1**. Absorption spectra of C₃-AMT in DCM illuminated under ultraviolet (345 nm) and visible (435 nm) light is shown in **Figure 3.7A**. The *trans* isomer of AMT (a) has an absorption maximum in the UV region ($\lambda_{\text{max}} = 345 \text{ nm}$), whereas its *cis* isomer (b) absorbs more in the visible ($\lambda_{\text{max}} = 435 \text{ nm}$) domain. The energy-minimized structures of two geometrical isomers of C₃-AMT optimized using DFT are shown in inset A1. The time-dependent absorption spectra of C₃-AMT illuminated separately under 345 and 435 nm are given in **Figure 3.7B and C**. When illuminated under 345 nm, the absorption spectra of C₃-AMT show a gradual decrease in the optical density (OD) ca. 345 nm and an increased OD ca. 435 nm, whereas the opposite trend was observed under 435 nm wavelength (inset C1).



Scheme 3.1: (A) Scheme for the synthesis of C₃-AMT (**molecules 1-3**). (a) HONO, 0 °C (b) 1,3-dibromopropane, K₂CO₃/KI, acetone, 80 °C (c) HMDST/TBAF, Distilled THF, -10 °C.

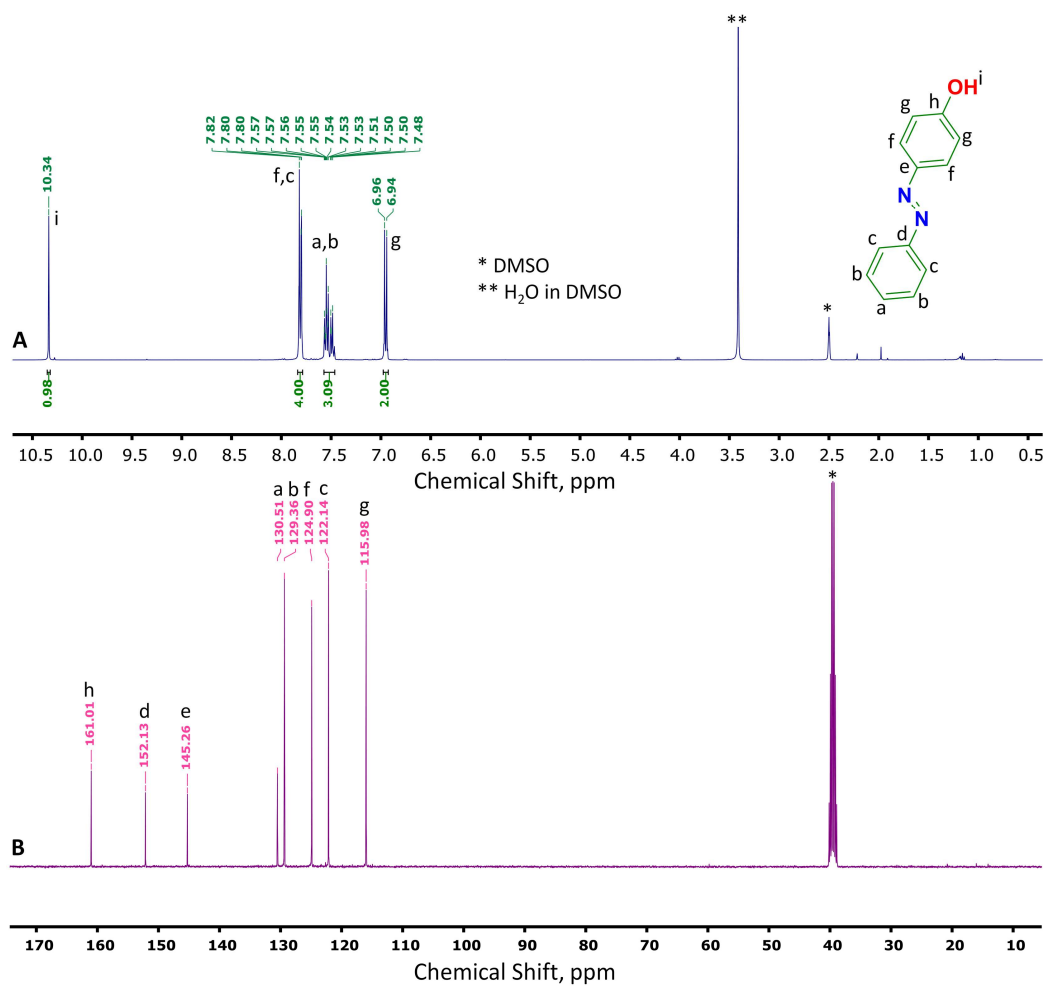


Figure 3.1: (A) ¹H NMR and (B) ¹³C NMR spectra of **molecule 1**.

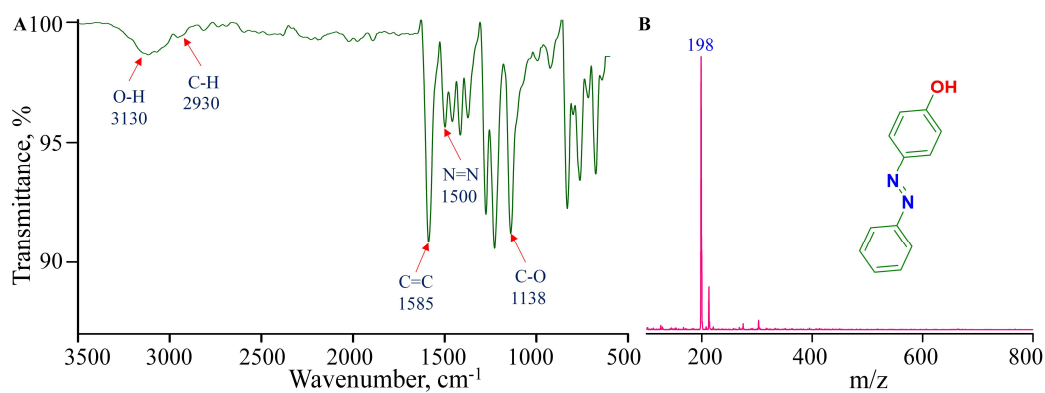


Figure 3.2: (A) FT-IR and (B) LC-MS of **molecule 1**.

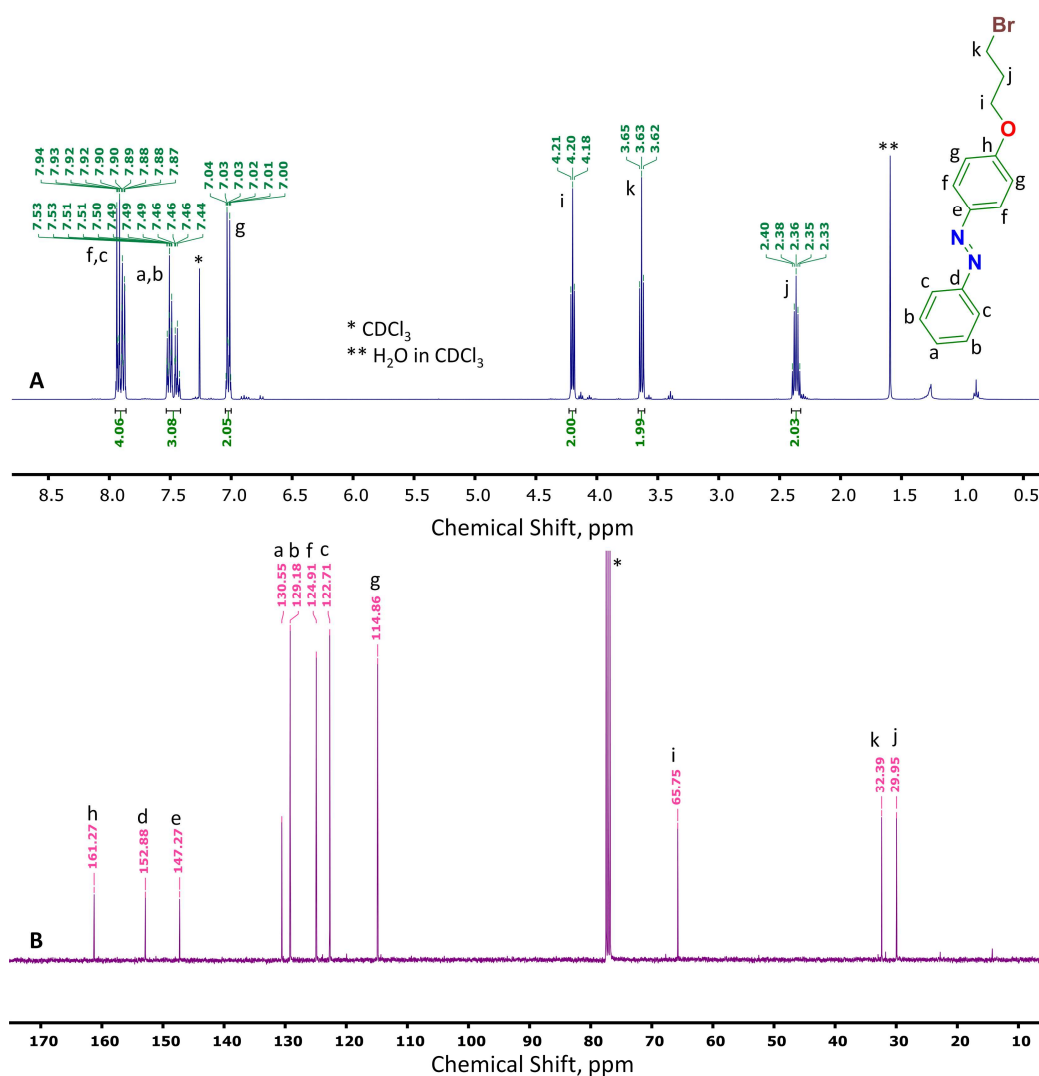


Figure 3.3: (A) ^1H NMR and (B) ^{13}C NMR spectra of molecule 2.

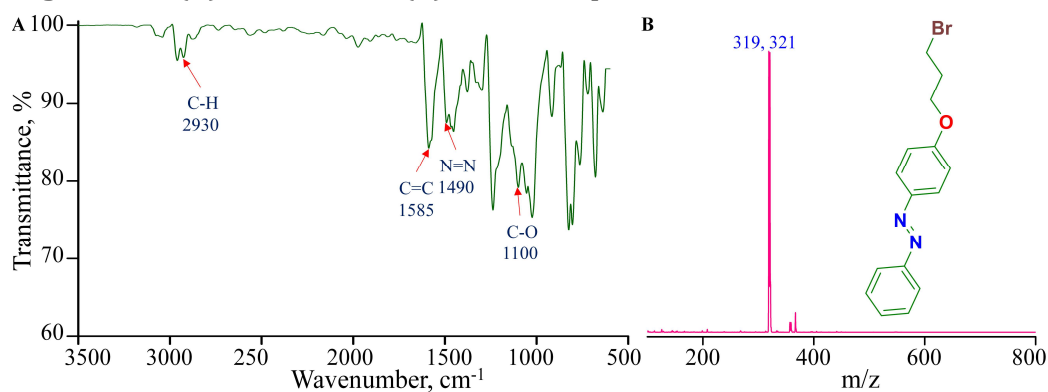


Figure 3.4: (A) FT-IR and (B) LC-MS of molecule 2.

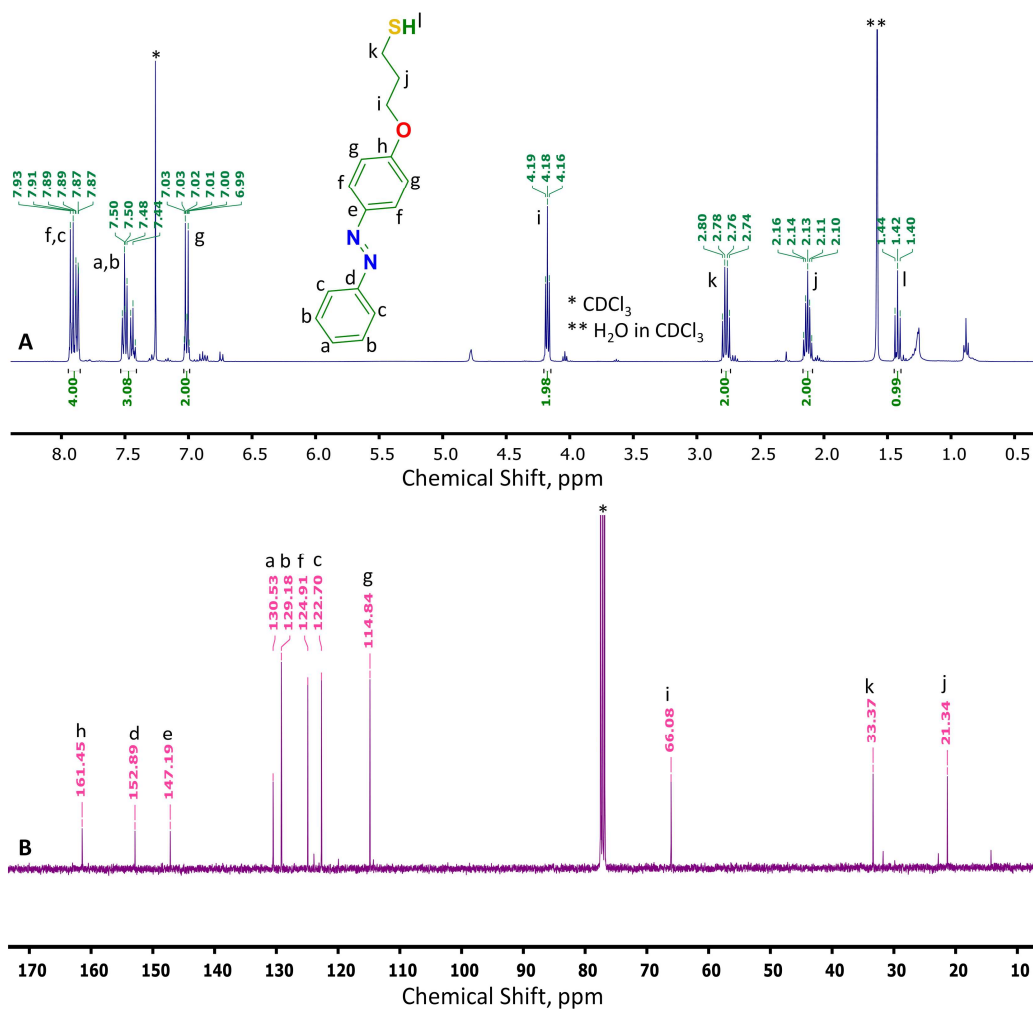


Figure 3.5: (A) ^1H NMR and (B) ^{13}C NMR spectra of molecule 3.

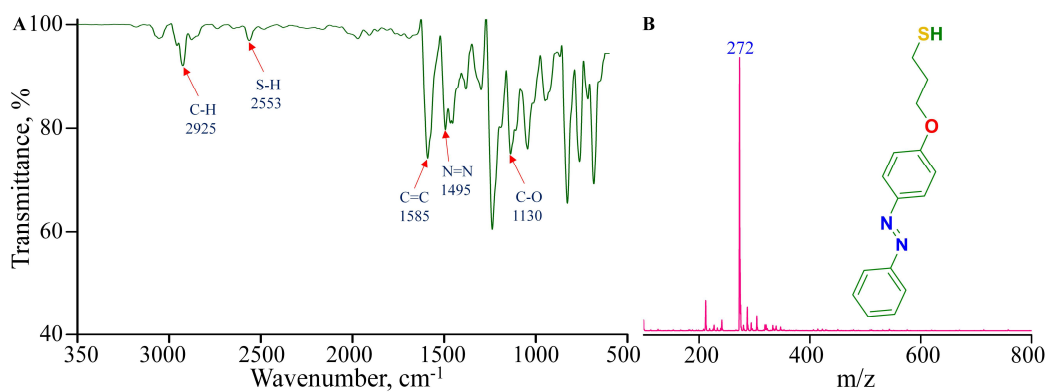


Figure 3.6: (A) FT-IR and (B) LC-MS of molecule 3.

Molecules	^1H NMR (ppm)	^{13}C NMR (ppm)	FT-IR(cm^{-1})	LC-MS
Molecule 1 (C₁₂H₁₀N₂O)	(400 MHz, DMSO- d_6) δ = 10.34 (s, 1H), 7.84 – 7.79 (m, 4H), 7.57 – 7.46 (m, 3H), 6.95 (d, J = 8.9 Hz, 2H)	(100 MHz, DMSO- d_6) δ = 161.4, 152.6, 145.7, 130.9, 129.8, 125.3, 122.6, and 116.4.	3117, 1587, 1500-1370, 1275, 1227, 1139, 831, and 762	190
Molecule 2 C₁₅H₁₅N₂OBr	(400 MHz, CDCl ₃) δ = 7.97–7.86 (m, 4H), 7.53–7.42 (m, 3H), 7.05–7.00 (m, 2H), 4.20 (t, J = 5.8 Hz, 2H), 3.63 (t, J = 6.4 Hz, 2H), 2.36 (p, J = 6.1 Hz, 2H).	(100 MHz, CDCl ₃) δ = 161.1, 152.7, 147.1, 130.4, 129.0, 124.8, 122.6, 114.7, 65.6, 32.2, and 29.8.	2960-2870, 1588, 1500-1370, 1237, 1100-1020, 916, 825-760, and 678 cm^{-1} .	319 and 321
Molecule 3 C₁₅H₁₆N₂OS	(500 MHz, CDCl ₃) δ = 7.95–7.85 (m, 4H), 7.53–7.41 (m, 3H), 7.04–6.99 (m, 2H), 4.18 (t, J = 5.9 Hz, 2H), 2.77 (q, J = 7.0 Hz, 2H), 2.13 (p, J = 6.5 Hz, 2H), 1.42 (t, J = 8.1 Hz, 1H).	(125 MHz, CDCl ₃) δ = 161.3, 152.8, 147.1, 130.4, 129, 124.8, 122.6, 114.7, 66, 33.2, and 21.2.	2930-2875, 2563, 1589, 1495-1380, 1298, 1237, 1137, 1044, 949, and 827 cm^{-1} .	273

Table 3.1: NMR, FT-IR, and mass spectrometry values of **Molecules 1, 2, and 3.**

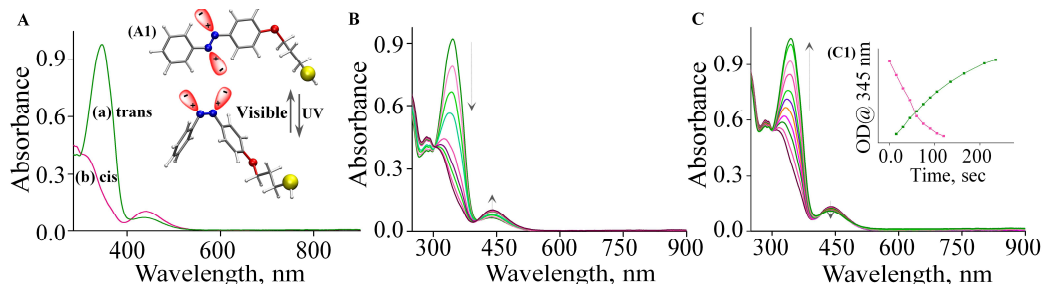


Figure 3.7: (A) Absorption spectra of C₃-AMT under (a) visible light and (b) UV light. Energy-minimized structures of the two geometrical isomers of C₃-AMT are shown in the inset (A1). (B and C) Temporal-absorption spectra of C₃-AMT illuminated under (B) 345 nm and (C) 435 nm light. A plot of OD at 345 nm vs. illumination time under 345 and 435 nm excitation shows reversible photo-switching is shown in the inset C1.

3.2.2 Characterization of [Au₂₅(C₃-AMT)₁₈]⁻

The synthesis of [Au₂₅(C₃-AMT)₁₈]⁻ NC was achieved using a modified Brust-Schiffrin single-phase method.^[48] To compare the optical absorption features of newly synthesized [Au₂₅(C₃-AMT)₁₈]⁻ NCs with reported 2-phenylethanethiol (PET) analog, [Au₂₅(PET)₁₈]⁻ was also synthesized and characterized.^[48] Detailed synthesis of [Au₂₅(PET)₁₈]⁻ and [Au₂₅(C₃-AMT)₁₈]⁻ NC are provided in **Chapter 2**. A schematic of the synthesis of [Au₂₅(C₃-AMT)₁₈]⁻ NC is given in **Figure 3.8A**. **Figure 3.8B** shows the absorption spectra of (a) [Au₂₅(PET)₁₈]⁻ and (b) [Au₂₅(C₃-AMT)₁₈]⁻ NCs. The peak ca. 680 nm (HOMO-LUMO), in the absorption spectra of [Au₂₅(C₃-AMT)₁₈]⁻ suggests the presence of monodisperse NCs. However, the peaks corresponding to HOMO-sp (ca. 450 nm) and d-sp transitions (ca. 400 nm) were merged with optical features of the azobenzene chromophore. The molecular composition of [Au₂₅(C₃-AMT)₁₈]⁻ was analyzed using electrospray ionization mass spectrometry (ESI-MS; negative ion mode), and the spectral patterns were compared with the PET analog. Peaks (inset B1) at *m/z* 7391 and 9808 represents [Au₂₅(PET)₁₈]⁻ and [Au₂₅(C₃-AMT)₁₈]⁻ NCs, respectively. The

appearance of a single peak ca. m/z 9808 in $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ in ESI-MS confirms the purity of NC. The photoisomerization efficiency of Au_{25} NCs in DCM was investigated in detail. Temporal absorption spectra of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC illuminated under 345 nm light (0.2 mW/cm^2 ; **Figure 3.8C**) exhibit a gradual decrease in the OD ca. 345 nm and an increased OD ca. 435 nm. Similar, but opposite photo-switching behavior was seen under 435 nm (0.5 mW/cm^2) excitation (**Figure 3.8D** and inset C1). The change in absorption spectra under UV and visible light is attributed to the *cis-trans* isomerization of surface azobenzene ligands as shown using DFT energy minimized structures of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ in **Figure 3.8A**. Photographs of NC solutions used for reversible switching are given in the inset D1. Here, the color of NC solution changed from yellowish-orange to reddish-orange under UV light and vice versa under visible light. The metal core of NCs and the nature of binding were evaluated in X-ray photoelectron spectroscopy. Binding energies (BE) of Au 4f levels in $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ were in good agreement with the reported values,^[49] with Au 4f_{7/2} ca 84.06 eV and Au 4f_{5/2} ca 87.75 eV (**Figure 3.9**). A slight change in the BE of these NCs is attributed to the different electron densities of ligands. The S2p B was in accordance with thiolate binding. The photo-switching ability of $\text{C}_3\text{-AMT}$ and $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC were further evaluated by analyzing their nuclear magnetic resonance (NMR) spectra (**Figure 3.10**). ^1H NMR spectrum of *trans* $\text{C}_3\text{-AMT}$ (**Figure 3.10B**) showed three sets of peaks in the aromatic region, ca. 7.97-7.84 (dd, 4H), 7.54-7.4 (m, 3H), and 7.05-6.96 ppm (d, 2H). The NMR spectrum of the *cis* isomer (**Figure 3.10D**) shows an upfield shift due to a larger shielding effect compared to *trans* counterparts. **Figure 3.10C** represents the NMR spectrum of a mixture of *cis* and *trans* isomers, recorded in between illumination. Similar photo-isomerization was also observed for surface $\text{C}_3\text{-AMT}$ ligands in Au_{25} NCs (**Figure 3.10E and F**). However, due to

their different possible conformations as well as the chemical and magnetic non-equivalent nature of ligands,^[50] ^1H NMR spectrum of AMT in $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ displays complex overlapping resonance peaks.

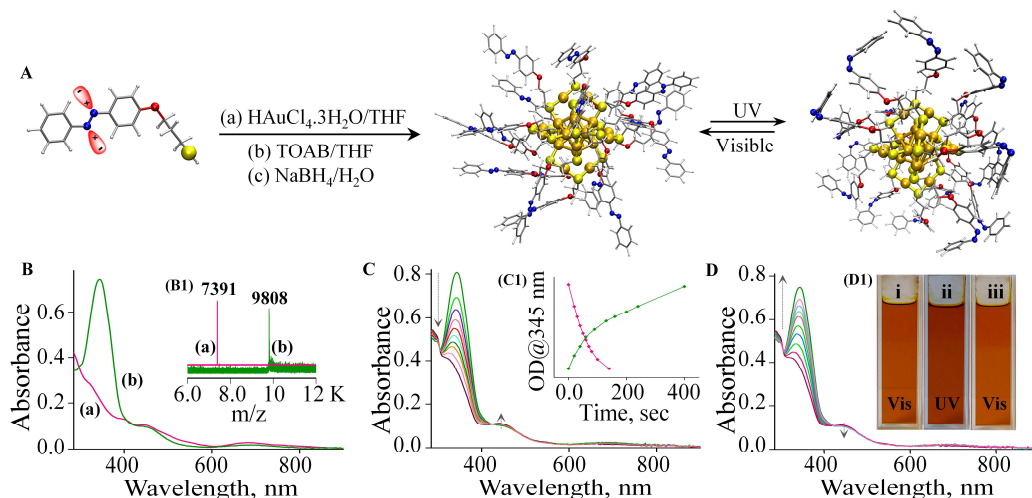


Figure 3.8: (A) Schematic representation showing the synthesis, the energy-minimized structures, and photoisomerization of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC. (B) Absorption spectra of (a) $[\text{Au}_{25}(\text{PET})_{18}]^-$ and (b) $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs. ESI-MS of both NCs are shown in the inset (B1). The temporal-absorption spectra of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ under (C) 345 nm and (D) 435 nm illumination. A plot of OD (ca. 345 nm) vs. illumination time under ultraviolet and visible light is shown in the inset C1. Inset D1 shows the photographs of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC solution during switchable self-assembly under (i) visible light (ii) UV light and (iii) visible light. The color of NC solution changed from yellowish-orange to reddish-orange under UV light and vice versa under visible light.

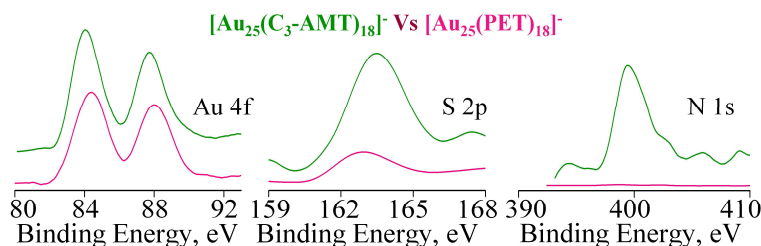


Figure 3.9: (A-C) XPS spectra of (A) Au 4f, (B) S 2p, and (C) N 1s levels of $[\text{Au}_{25}(\text{PET})_{18}]^-$ (pink), and $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ (green).

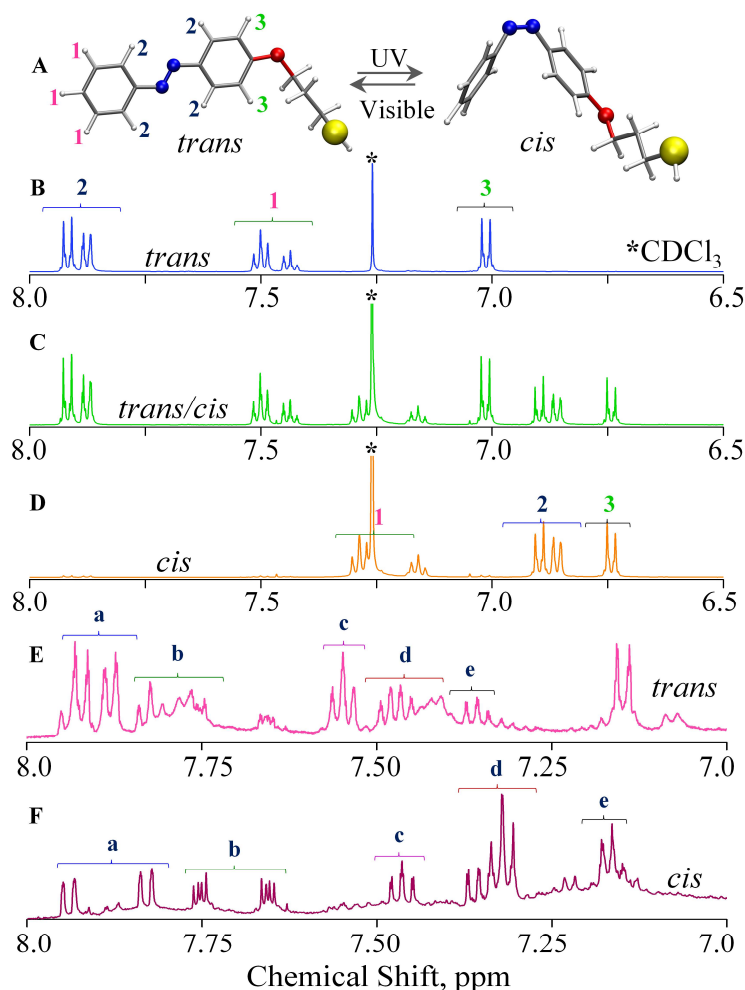


Figure 3.10: (A) Geometrical isomers of C₃-AMT. ¹H NMR spectra of (B) *trans*, (C) *trans/cis*, and (D) *cis* isomers of C₃-AMT in CDCl₃. (E and F) ¹H NMR spectra of *trans* and *cis* isomers of [Au₂₅(C₃-AMT)₁₈]⁻ in acetone-*d*₆, respectively. Resonance peaks are assigned and labelled above the traces.

3.2.3 Light-induced assembly of Au₂₅ NCs

Reversible photo-switching in NCs was further investigated by TEM imaging. At first, Au₂₅ NC was characterized using TEM by drop-casting and drying ~100 μM solution of [Au₂₅(C₃-AMT)₁₈]⁻ in DCM on a copper grid with carbon support film. However, due to electron beam damage, Au₂₅ NC undergoes rapid coalescence; therefore, high-resolution imaging of individual NCs

remained a challenge.^[45,49,51] Nevertheless, the non-aggregated nature of Au₂₅ NCs is evident from the TEM micrographs (**Figure 3.11A**). To monitor the light-induced self-assembly, ~100 μ M solution of NC in DCM at room temperature was illuminated under 345 nm light (0.2 mW/cm²) for 120 minutes in a temperature-controlled bath. The solution was continuously stirred during the photo-isomerization process to avoid the possibility of thermally induced aggregation. Illuminated NC solution was drop-casted on a grid and dried under the dark. Remarkably, TEM images of [Au₂₅(C₃-AMT)₁₈]⁻ NCs show the formation of circular superstructures (**Figure 3.11B**) with an average diameter of ~100 to 200 nm. The evolution of self-assembled superstructures was investigated in detail by shining the same NC solution under 345 nm light for a longer illumination time. Similar trends were observed in the TEM analysis of samples illuminated for 240 min (**Figure 3.11C**). However, there is no regular order of NCs within the layer or between the layers. More interestingly, photo-activation of such self-assembled superstructures in solution at room temperature under 435 nm light (0.5 mW/cm²; 300 min) shows the formation of well-separated NCs by disassembly (**Figure 3.11D**). High-resolution TEM images (**Figure 3.11E** and **G**) clearly show the presence of individual NCs. The above results suggest that the superstructure formation is facilitated by inter-NC interaction through surface ligands. Attractive dipole-dipole interaction^[39] between nearby NCs in *cis* arrangement facilitates the self-assembly in NCs. A cartoon representation for the dipole-induced attraction of NCs (**Figure 3.11F**), self-assembly of NCs, and their possible arrangements within the circular superstructure is shown in **Scheme 3.2**. The overall diameter of the superstructures was increased from ~200 nm to ~1000 nm. The increase in width and thickness suggests extended self-assembly of Au₂₅ NCs. Larger area TEM micrographs of self-assembled NC superstructures obtained by

illuminating the NC solution for 120 min and 240 min are shown in **Figure 3.12A** and **B**. Based on the observations from the time-dependent TEM micrographs, we found that the formation of a circular monolayer aggregates of NCs is the early stage of the assembly. Accumulation of more *cis* NCs on such monolayer aggregates under continuous UV illumination helps to enhance the thickness and diameter of superstructures. Large area TEM images representing the stepwise disassembly of superstructures are given in **Figure 3.12 C** and **D**. A decrease in the diameter of the superstructures with illumination time, and the presence of individual NCs suggest the controlled disassembly.

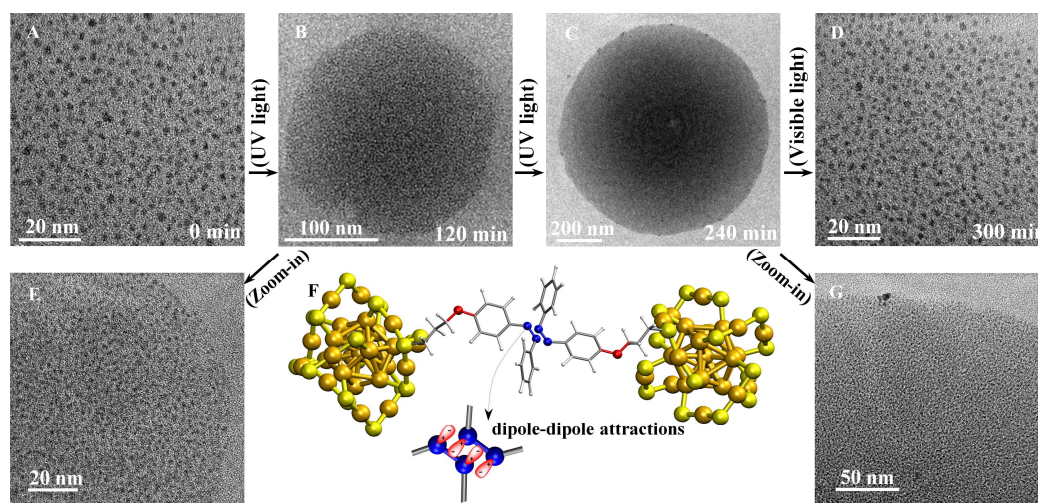
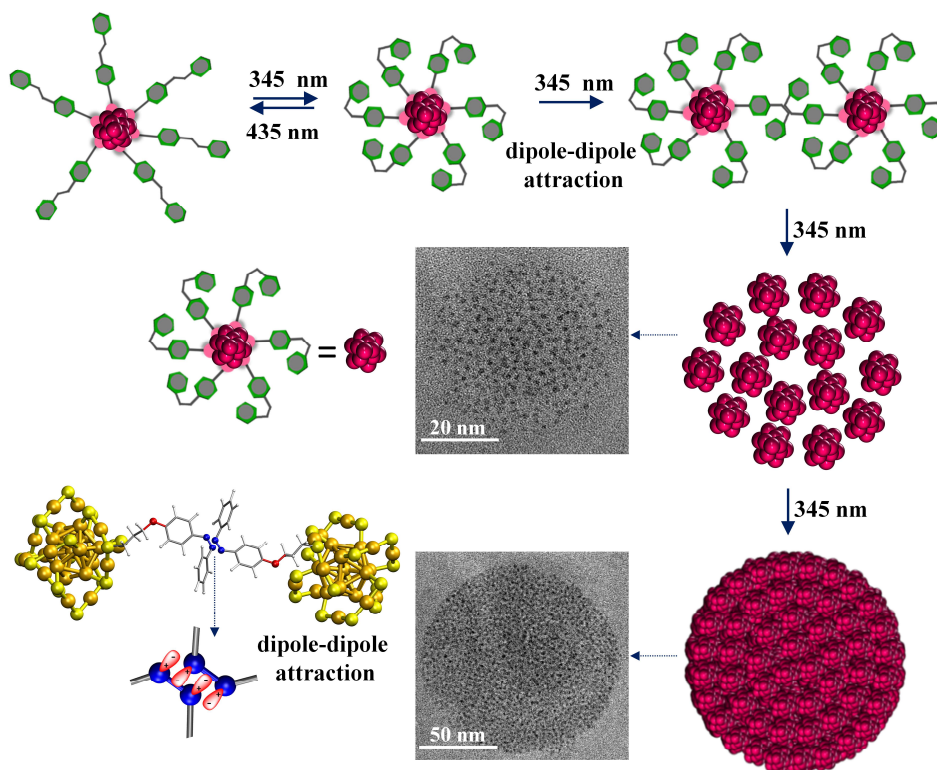


Figure 3.11: TEM images of (A) *trans* [Au₂₅(C₃-AMT)₁₈]⁻ NCs and (B and C) *cis* [Au₂₅(C₃-AMT)₁₈]⁻ NC assembly captured during (B) 120 min, and (C) 240 min of light illumination (345 nm). The TEM image of [Au₂₅(C₃-AMT)₁₈]⁻ NC self-assembled superstructures after 435 nm illumination is shown in Figure 3.11D, clearly shows their disassembly. Zoom-in and focused HRTEM images taken from the edges are shown in Figure 3.11E and G, respectively. Cartoon representation of dipole-induced self-assembly in [Au₂₅(C₃-AMT)₁₈]⁻ NCs is shown in F.



Scheme 3.2: The mechanism for dipole-induced self-assembly of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs and their possible arrangements in the superstructure are represented. Corresponding TEM micrographs are shown.

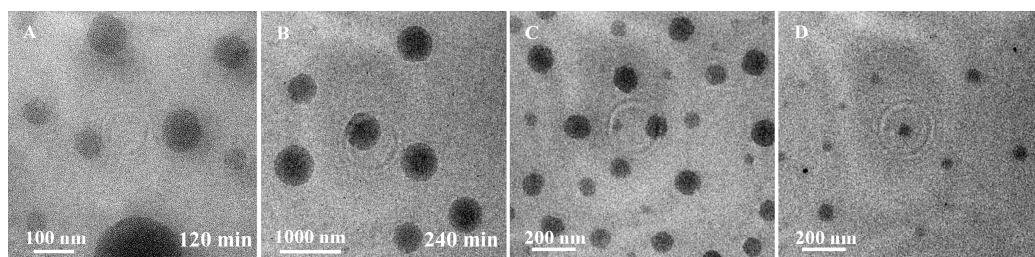


Figure 3.12: Larger area TEM images of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC self-assembly illuminated under 345 nm light for (A) 120 min and (B) 240 min and disassembly illuminated under 435 nm light for (C) 150 min and (D) 240 min.

To further check the stability of self-assembled NCs in dark conditions, we have recorded and analyzed the time-dependent absorption spectra of superstructures stored in the dark room. Absorption spectra (**Figure 3.13A**)

of NC assembly do not show any changes in their optical absorption features, suggesting the stability of superstructures under dark. In other words, disassembly of superstructures can trigger only in the presence of visible (435 nm) light. Additionally, we have analyzed the time-dependent absorption spectra of *trans* $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC solution under dark conditions. As there were no changes in the optical absorption features of NCs, the possibility of NC self-assembly in the dark has been ruled out (**Figure 3.13B**). To check the importance of AMT in the light-induced assembly, the PET analog, $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs solution was illuminated under 345 nm light for 240 min. TEM images of $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs before and after the illumination were similar (**Figure 3.14A and B**), which shows the inability of $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs for the light-induced self-assembly. These two control experiments validate the role of AMT and light for the switchable assembly and disassembly in $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs. Apart from the circular structures, dimers were also formed during self-assembly (**Figure 3.14C**). Electron microscopic analysis at the interface of the dimer shows well-organized NCs (**Figure 3.14D**).

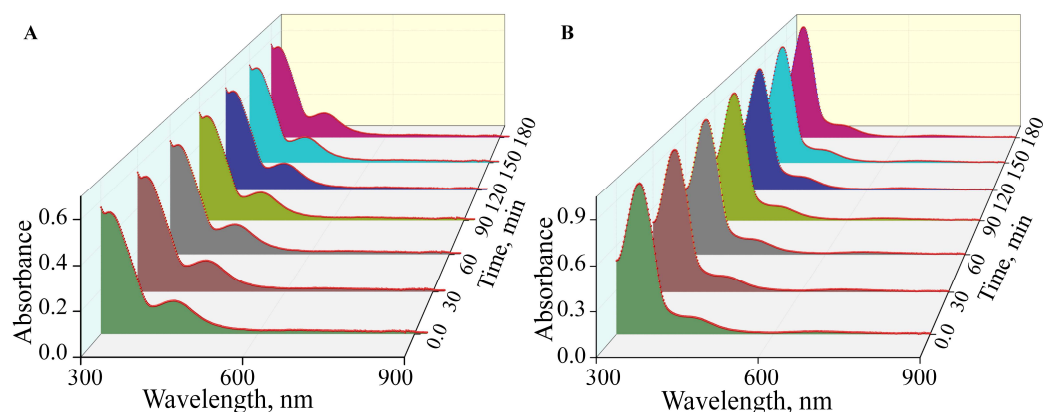


Figure 3.13: (A) Temporal absorption spectra of self-assembled NCs recorded under dark conditions (30-180 min) (B) Temporal absorption spectra of *trans* NCs recorded under dark conditions (30-180 min).

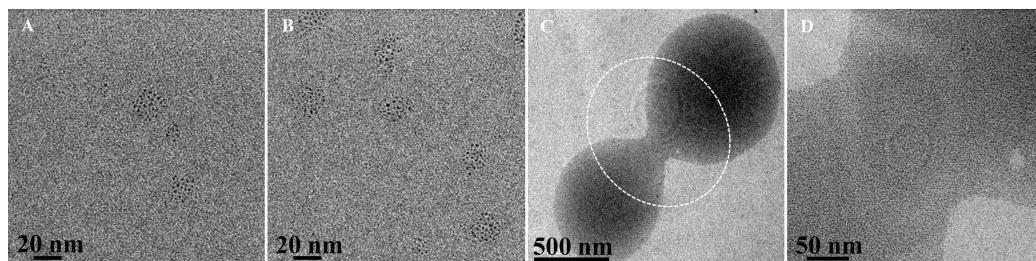


Figure 3.14: TEM images of $[\text{Au}_{25}(\text{PET})_{18}]^-$ (A) before and (B) after 240 min light illumination (345 nm). (C) TEM image of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ self-assembled dimer. (D) Zoom-in and focused HRTEM image taken from the interface of the dimer shows periodic self-assembly of NC.

The morphology and thickness of the superstructures were further evaluated by atomic force microscopy (AFM). Self-assembled NC solution drop cast and dried on a silicon substrate was used for AFM measurements. Tapping mode AFM image (topography) of a single self-assembled superstructure (240 min illumination) shows an average thickness and diameter of 50 nm and 800 nm (**Figure 3.15A-C**), respectively. The morphology of the superstructures shown in the AFM image is similar to TEM analysis. The above results suggest that self-assembly occurs in solution in the presence of light, which helps us to rule out the possibility of electron beam-induced self-organization of NCs on the TEM grid.

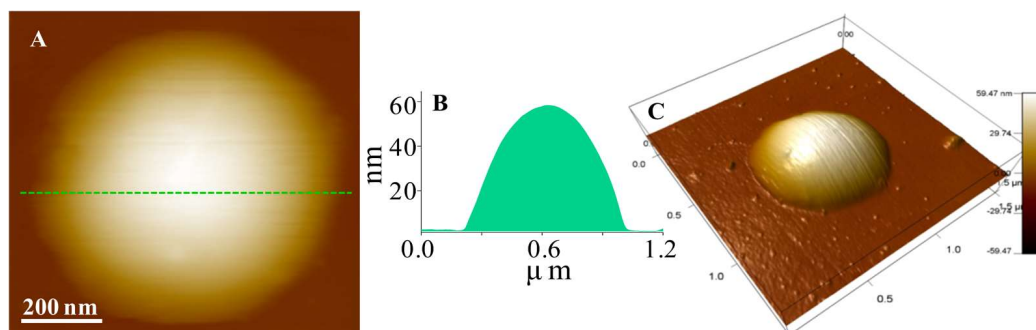


Figure 3.15: (A and C) AFM images of (A-topography and C-amplitude) *cis* $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ self-assembled single super-structure captured after 240 min of illumination. The height profile is shown in (B).

The elemental composition of self-assembled superstructures analyzed by using energy dispersive analysis of X-rays (EDS) has shown the presence of gold, sulfur, nitrogen, oxygen, and carbon. Elemental mapping and corresponding spectrum are shown in **Figure 3.16**. To further evaluate the light-induced assembly of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$, time-dependent dynamic light scattering (DLS) spectra of NC solution illuminated under 345 nm light were measured. DLS measurements show an increment in the size of superstructures with illumination time. The average particle size within 120 min illumination (345 nm) was ~ 250 nm, which was increased to ~ 550 nm upon continuous illumination, and finally to ~ 1.5 μm (**Figure 3.17A-C**). On the other hand, a gradual decrease in the diameter of superstructures was observed under 435 nm illumination (**Figure 3.17D and E**).

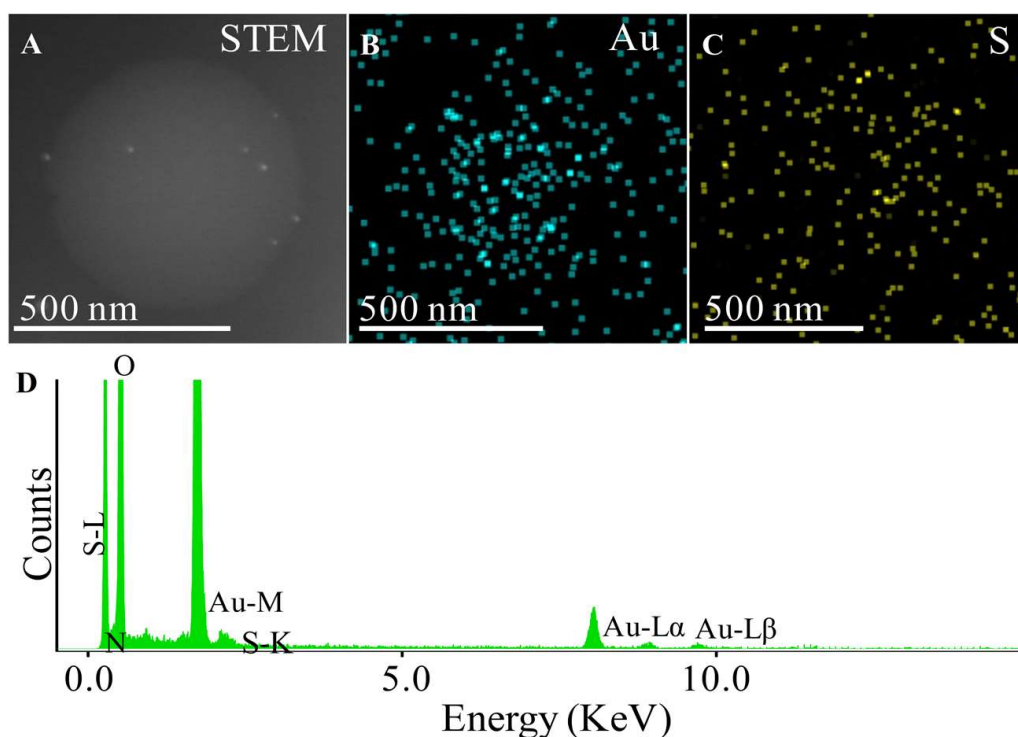


Figure 3.16: (B and C) Elemental maps (B-gold and C-sulfur), and (D) EDS spectrum of a single $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ superstructure (A) using STEM.

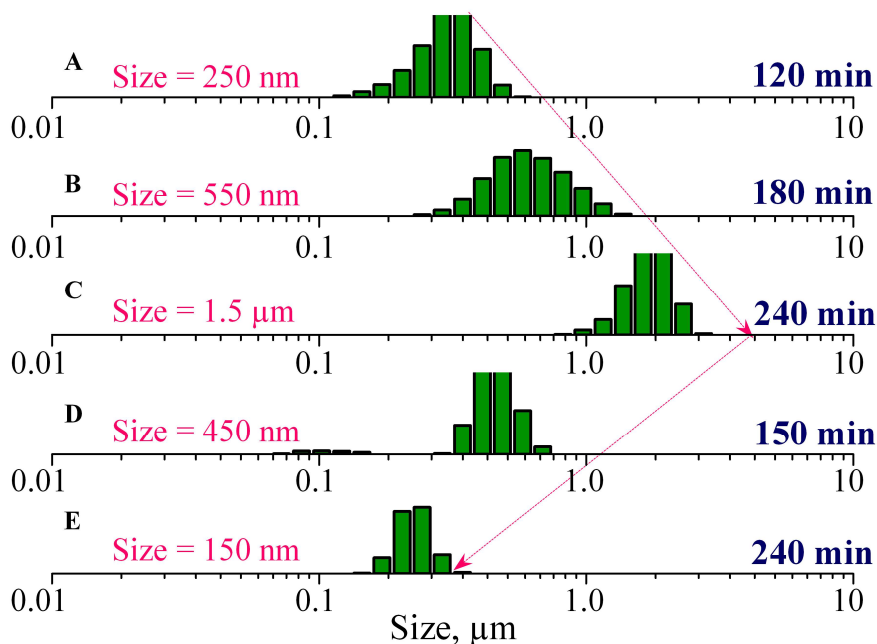


Figure 3.17: DLS spectra of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs during the light-induced (A-C) self-assembly (under 345 nm), and (D and E) disassembly (under 435 nm) at different time intervals. Particle size distribution of self-assembled superstructures is in good agreement with TEM micrographs.

Further, dark-field scattering microscopy was utilized to image the self-assembled structures in the solution state. Accordingly, ~ 100 nM solution of self-assembled superstructures in DCM was drop-casted on a 1 mm thick glass slide and sandwiched with a 0.14 mm thick glass coverslip. Golden-yellow scattering spots represent the individual self-assembled superstructures of NC (**Figure 3.18A**). Whereas, no such scattering spots were observed in the control sample (**Figure 3.18B**). An increase in the particle size under 345 nm and a decrease in the size of superstructures under 435 nm illuminations, respectively, confirm the switchable assembly in NCs. DLS data is in good agreement with TEM micrographs.

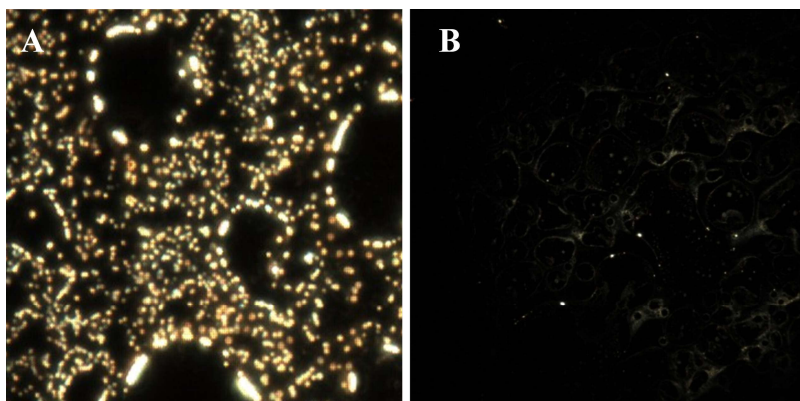


Figure 3.18: Dark-field scattering images collected from (A) $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ superstructures and (B) control sample (solvent alone).

Transmission electron tomography (ET) reconstruction was carried out to gain information on the internal structural details of self-assembled superstructures. Accordingly, the specimen prepared from a solution of NCs after irradiating for 240 min was used to acquire a series of 2D projections between $\pm 69^\circ$ with an increment angle of 2° . **Figure 3.19A-C** shows TEM images of a superstructure tilted at -60° , 0° , and $+60^\circ$. The tilt series and corresponding 3D reconstruction (**Figure 3.19D-F**) suggest that the superstructures are disc-like colloidal particles. It is important to note that the disc-like structures can also be partly due to the deformation resulting from solvent evaporation upon drying. However, these 3D superstructures are composed of densely packed NCs (**Figure 3.20**). The results obtained from electron tomography reconstruction is in good agreement with the AFM analysis.

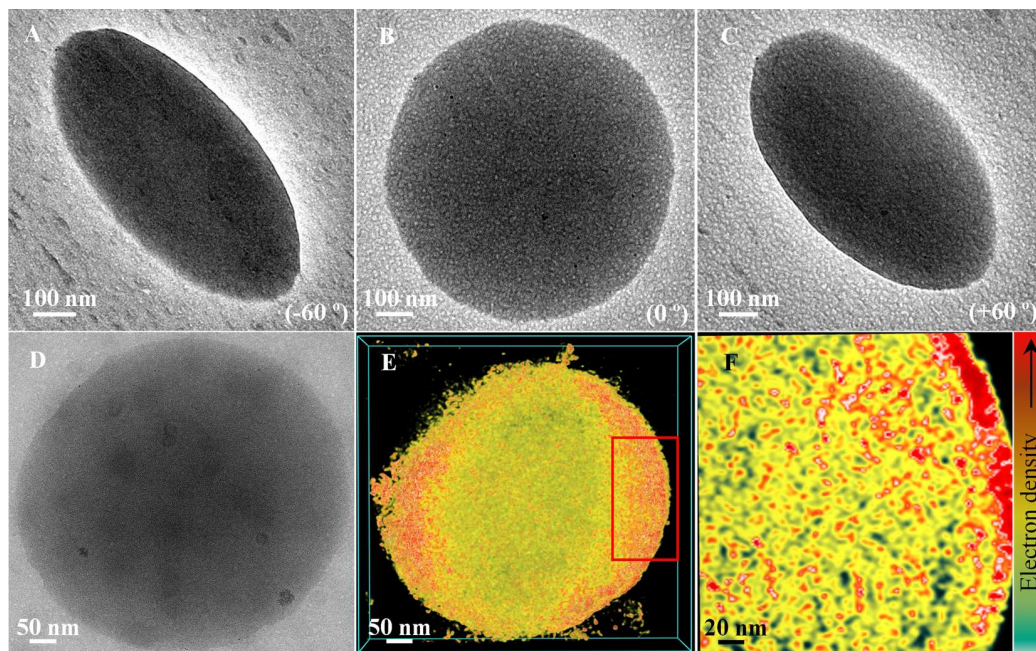


Figure 3.19: (A-C) TEM micrographs of a tilted self-assembled $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ disc-like superstructure collected at -60° , 0° and $+60^\circ$. (D) TEM micrograph of a superstructure, (E) shows an electron tomography reconstruction image, and (F) the cross-sectional view of a self-assembled superstructure.

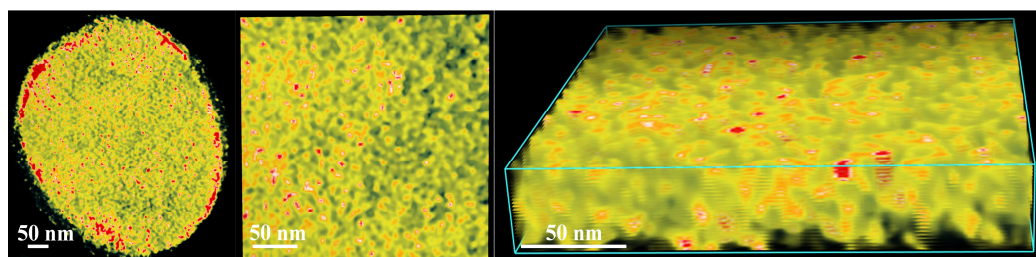


Figure 3.20: Cross-sectional views of the 3D reconstructed disc-like superstructure of NC.

The self-assembled superstructures were further characterized by using small-angle powder X-ray diffraction (SAXRD). A dried self-assembled NC powder was used to measure SAXRD. **Figure 3.21A** shows the SAXRD pattern collected from the disc-like colloidal superstructures. The calculated

d-spacing value suggests an inter-particle distance of 3.27 nm, which is in good agreement with the inter-NC distance measured from TEM micrographs (3.3 ± 0.5 nm) shown in **Figure 3.21B-F**. The cross-sectional view of the 3D reconstructed disc-like structure also supports the above observation (**Figure 3.20**).

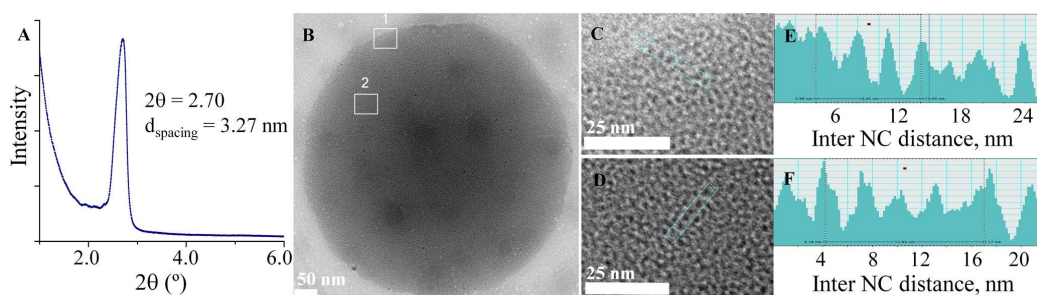


Figure 3.21: (A) Small-angle powder X-ray diffraction pattern of disc-like superstructures. (B) TEM micrograph of a disc-like superstructure. Zoom-in and focused HRTEM images (C and D) from an area marked as 1 and 2 in B, and corresponding size distribution profiles (E and F) are shown.

3.3 Conclusion

In summary, we have successfully demonstrated reversible self-assembly in atomically precise Au_{25} NC. Using light as an external stimulus, we introduced a simple strategy to self-assemble NCs. To achieve this goal, photo-switchable NC was designed and synthesized using a thiol derivative of azobenzene chromophore with a suitable spacer length. Photo-isomerization of the chromophore and analogs NC under ultraviolet and visible light were studied through systematic changes in the electronic absorption bands, and chemical shifts in NMR spectra. Microscopic techniques were employed to understand reversible photo-switching in NC. The time-dependent evolution of light-mediated self-assembly was monitored using DLS, AFM, TEM, and subsequent electron tomography reconstruction. Detailed investigations of self-assembled superstructures have shown the long-range periodic organization of individual NCs. The

stacking of NCs in the self-assembly was evaluated using SAXRD. The calculated d-spacing value was in good agreement with TEM micrographs. The development of such smart self-assembled architectures will create new materials for electrochemistry, biology, photocatalysis, and light-harvesting technology owing to their collective and enhanced optical and electronic properties. Especially, switchable NCs with appropriate molecular functionalities will be a potential cargo system to load and unload drug molecules by a light-triggered mechanism. Also, such self-assembled superstructures will be a suitable probe for the fabrication of electrochemical and photochemical devices.

3.4 References

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CHAPTER 4

**ROLE OF CHROMOPHORE-SPACER LENGTH
IN THE LIGHT-INDUCED SELF-ASSEMBLY OF
GOLD NANOCCLUSERS**

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ROLE OF CHROMOPHORE-SPACER LENGTH IN THE LIGHT-INDUCED SELF-ASSEMBLY OF GOLD NANOCCLUSERS

4.1 Introduction

NCs offer atomic-scale control over the metal core and exhibit remarkable photophysical and electrochemical properties.^[1–10] Even minor modifications to a single metal atom can have a major influence on the behavior and functionality of NCs.^[11–16] This characteristic makes NCs ideal building blocks for constructing two-dimensional and three-dimensional self-assembled superstructures with collective and enhanced properties.^[17–20] The delicate balance between non-covalent interactions (van der Waals interactions, hydrogen bonding, C-H $\cdots$ π / $\pi\cdots\pi$ interactions, electrostatic interactions, aurophilic interactions, amphiphilic interactions, or light-induced dipole-dipole attractions) and thermodynamics control the generation of self-assembled superstructures, emphasizing the complexity of the assembly process.^[21–30] Such assembled materials find applications in device fabrication,^[31–34] green catalysis,^[35–39] toxin/metal ion screening,^[40] gas sensing,^[41,42] bioimaging, and therapeutics.^[43–47] Among the different non-covalent interactions, the light-induced dipolar interaction is promising as it allows reversible assembly by changing the wavelength of light. Studies on photoswitching properties of azobenzene functionalized gold NPs are well documented in the literature for over two decades.^[48–51] Recently, twenty-five atom gold (Au₂₅) NCs functionalized with thiolated-spiropyran or -azobenzene ligands demonstrated the feasibility of light-induced reversible self-assembly for hierarchical structure formation across length scales.^[29,52,53] These studies have shown that when azobenzene molecules are attached to the surface of NCs, their dipole moments play a significant

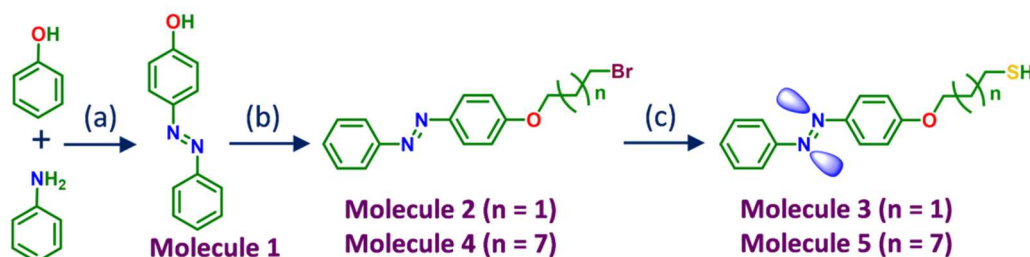
role in the assembly process. Light irradiation triggers the *trans-to-cis* isomerization, resulting in an induced dipole moment. This leads to attractive interactions between neighboring NCs, and forms assembled superstructures. Similar photochemistry has been utilized in systems containing other metal clusters and inorganic nanocages.^[54–56] However, the extent of assembly largely depends on the photoswitching efficiency of the chromophores attached to the NC surface. This efficiency is influenced by the chemical structure of the chromophore and its proximity to the NC surface. Thus, NCs functionalized with photoswitchable ligands offer facile control over self-assembly kinetics and structural diversity of self-assembled structures. Here, we show the interplay between the spacer length and photoswitching ability of azobenzene alkyl monothiol (AMT) capped Au NCs. We used, AMT-protected NCs (C₃-NCs and C₉-NCs) with two different spacer lengths (C₃-AMT and C₉-AMT). The assembly process of both NCs in a dichloromethane (DCM) solution at ambient temperature under 345 nm light was investigated using different spectroscopic studies and microscopic imaging. The C₉-NCs showed quick self-assembly compared to the C₃ analog due to negligible steric hindrance experienced at the NC-chromophore interface resulting from their safer separation. The less nonbonding steric interactions allow more favorable orientation and arrangement to the surface chromophores, forming self-assembled superstructures *via* attractive dipoles. The prolonged illumination of C₉-NCs showed a chain-like assembly due to the dipolar attractions between nearby superstructures. These findings highlight the importance of rational design and control over the spatial arrangement of chromophores in precision NCs. By carefully tuning the spacer length and considering the steric effects, it becomes feasible to optimize the self-assembly process and achieve desired

supramolecular structures with enhanced photophysical and electrochemical properties.

4.2 Result and discussion

4.2.1 Characterization of azobenzene monothiol (C₃ and C₉-AMT)

To investigate the role of chromophore-spacer length in the light-induced assembly of NCs, we first covalently linked the azobenzene core with the C₃-carbon chain (short; C₃-AMT) and C₉-carbon chain (long; C₉-AMT) thiols. The AMT with C₃ and C₉-spacer was synthesized according to a reported literature procedure.^[57,58] The synthesis and characterization of short chain C₃-AMT (**molecules 1, 2, and 3**) is already given in **Chapters 2 and 3** respectively. The synthesis of long chain C₉-AMT is carried out similar to C₃-AMT and details are given in **Scheme 4.1**.



Scheme 4.1: Scheme for the synthesis of C₃-AMT and C₉-AMT (**molecules 1-5**). (a) HONO, 0 °C (b) 1,3-dibromopropane or 1,9-dibromononane, K₂CO₃/KI, acetone, 80 °C (c) HMDST/TBAF, Distilled THF, -10 °C.

Herein, the azophenol (**molecule 1**) formed in the first step of diazotization reaction was treated with excess alkyl bromide (C₉-spacer) to react with the phenol group and form a C₉ alkyl chain. The resulting **molecule 4** was converted to thiol (**molecule 5**) using the HMDST-TBAF reaction. Details of reactions involved in the preparation of C₉-AMT are provided in **Chapter 2**. The ligand was thoroughly characterized in each step (**molecules 4 and 5**)

using NMR, FT-IR, and mass spectrometry (**Figure 4.1-4.6**) and corresponding values are shown in **Table 4.1**.

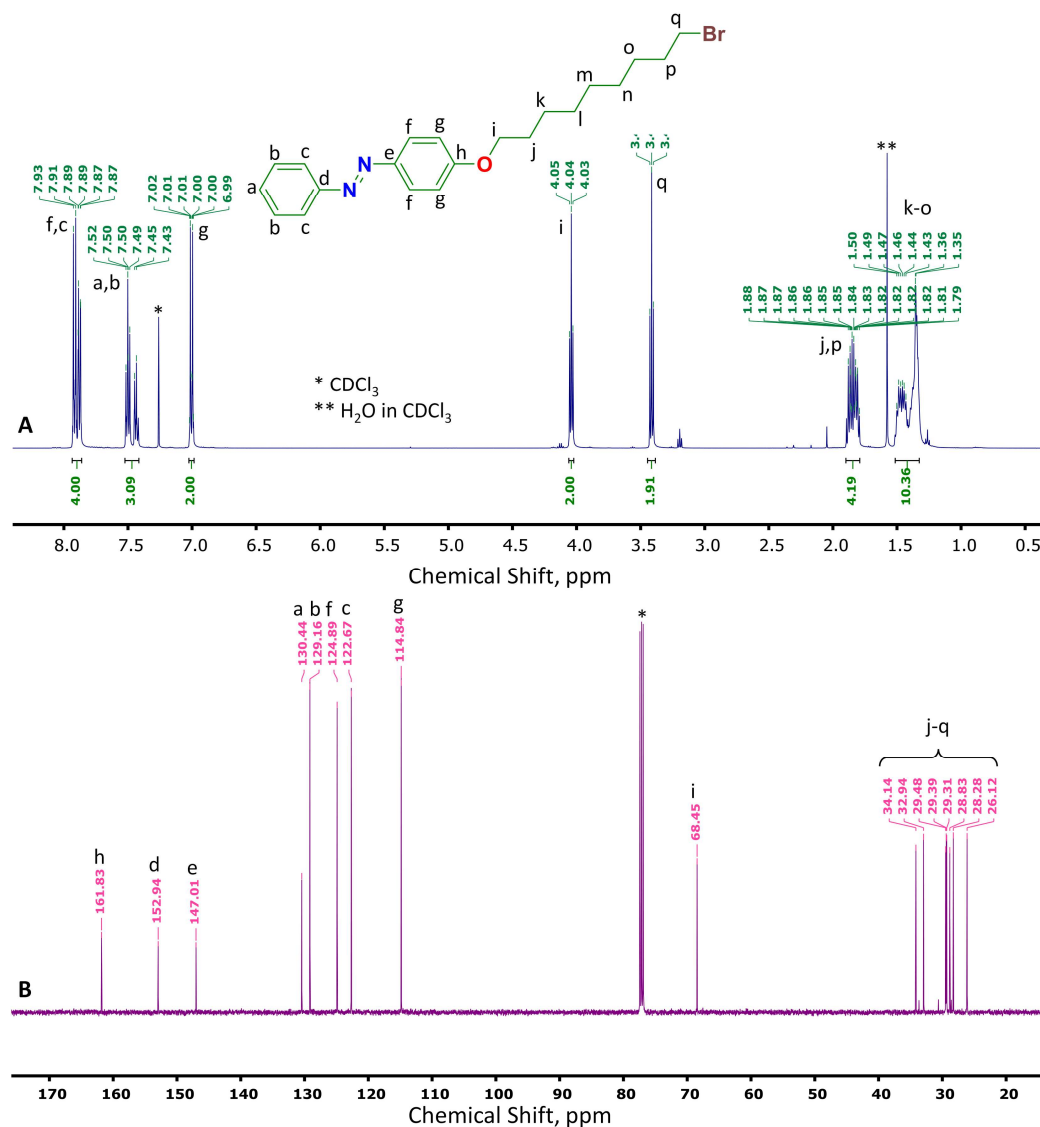


Figure 4.1: (A) ^1H NMR and (B) ^{13}C NMR spectra of **molecule 4**.

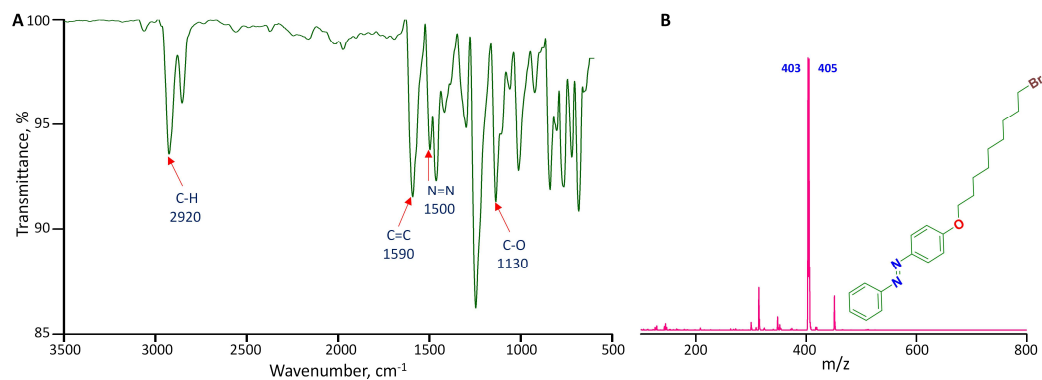


Figure 4.2: (A) FT-IR and (B) LC-MS of **molecule 4**.

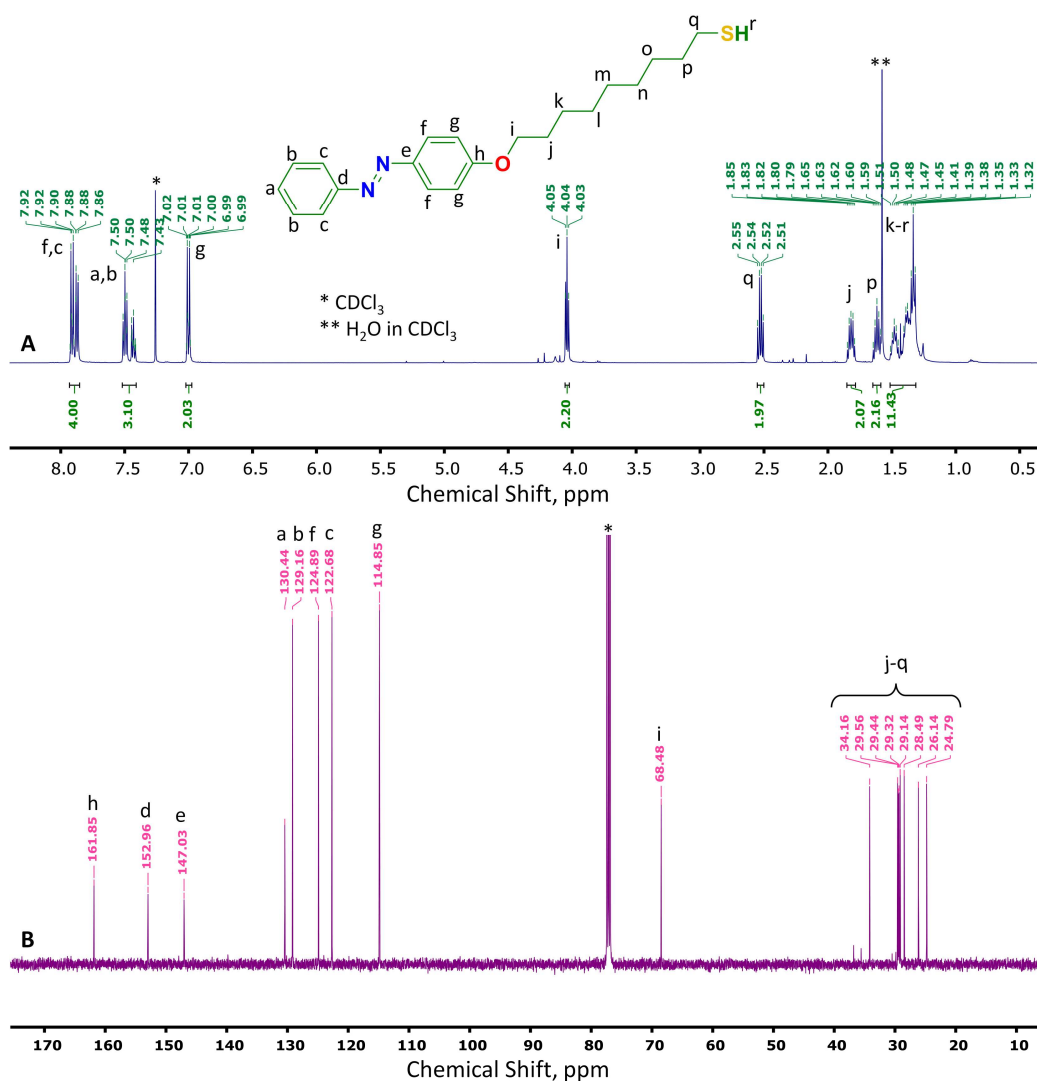


Figure 4.3: (A) ^1H NMR and (B) ^{13}C NMR spectra of **molecule 5**.

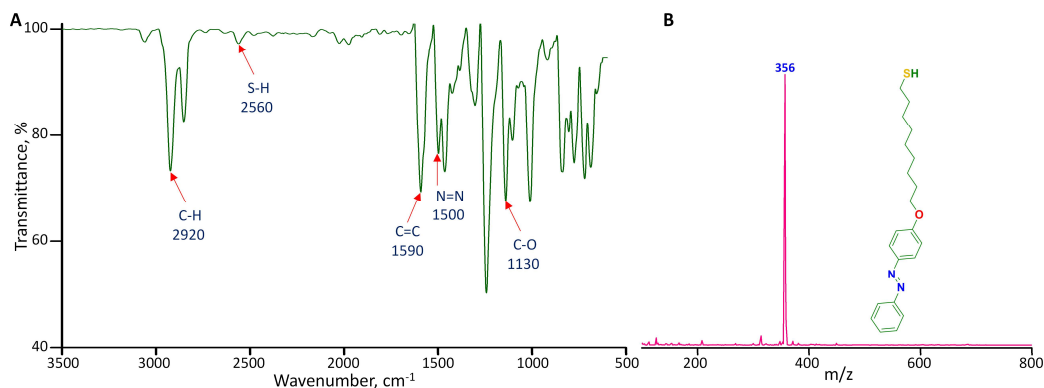


Figure 4.4: (A) FT-IR and (B) LC-MS of **molecule 5**.

Molecules	^1H NMR (ppm)	^{13}C NMR (ppm)	FT-IR (cm^{-1})	LC-MS
Molecule 4 C₂₁H₂₇N₂O Br	(500 MHz, CDCl ₃) δ = 7.94-7.86 (m, 4H), 7.52-7.41 (m, 3H), 7.02-6.98 (m, 2H), 4.04 (t, J = 6.5 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 1.90-1.79 (m, 4H), 1.51-1.33 (m, 10H).	(125 MHz, CDCl ₃) δ = 161.83, 152.94, 147.01, 130.44, 129.16, 122.67, 114.84, 68.45, 34.14, 32.94, 29.48, 29.39, 29.31, 28.83, 28.28, and 26.12	2930-2850, 1591, 1500-1410, 1298, 1246, 1137, 1012, 839, 764, 720, and 682 cm^{-1}	403 and 405
Molecule 5 C₂₁H₂₈N₂O S	(500 MHz, CDCl ₃) δ = 7.93-7.85 (m, 4H), 7.52-7.41 (m, 3H), 7.02-6.97 (m, 2H), 4.04 (t, J = 6.5 Hz, 2H), 2.53 (q, J = 7.5 Hz, 2H), 1.82 (dt, J = 14.5, 6.6 Hz, 2H), 1.62 (p, J = 7.3 Hz, 2H), 1.51-1.31 (m, 11H).	(125 MHz, CDCl ₃) δ = 161.85, 152.96, 147.03, 130.44, 129.16, 124.89, 122.68, 114.85, 68.48, 34.16, 29.56, 29.44, 29.32, 29.14, 28.49, 26.14, and 24.79	2925-2850, 2560, 1591, 1500-1380, 1302, 1242, 1140-1100, 1010, and 840-770 cm^{-1}	357

Table 4.1: NMR, FT-IR, and LC-MS values of **Molecules 4** and **5**.

The time-dependent absorption spectrum obtained from both C₃-AMT and C₉-AMT dispersed in DCM and irradiated separately using UV light (345 nm) are shown in **Figure 4.5A** and **B**, respectively. The systematic drop in optical density (OD) at 345 nm and simultaneous gradual growth in OD around 435 nm indicate the occurrence of *trans-to-cis* photoswitching. The energy-minimized structures of *cis-trans* geometrical isomers of C₃ and C₉-AMT obtained through DFT are shown in the inset of **Figure 4.5A** and **B**, respectively. The temporal absorption spectra recorded from both C₃-AMT and C₉-AMT show reverse photoswitching (*cis-to-trans*) under 435 nm light (**Figures 4.6A** and **B**). From the combined plot of OD@345 nm vs. lighting time of C₃-AMT and C₉-AMT recorded under 345 nm and 435 nm lights, it is well clear that the time required for *trans-to-cis* (~140 sec) or *cis-to-trans* (~260 sec) photoswitching in AMT is almost same, irrespective of the spacer length (**Figure 4.6C**). However, the *cis* to *trans* conversion was not complete due to the overlap of n- π^* transition of *cis* and *trans* isomers.^[59]

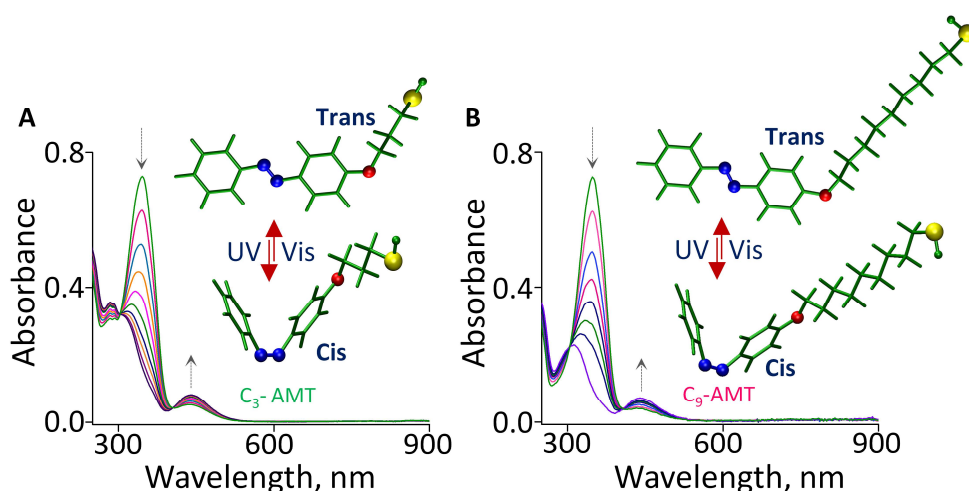


Figure 4.5: The temporal optical absorption spectra of (A) C₃-AMT and (B) C₉-AMT under 345 nm illumination. Energy-minimized structures of *trans/cis* isomers of C₃-AMT and C₉-AMT are shown in the inset.

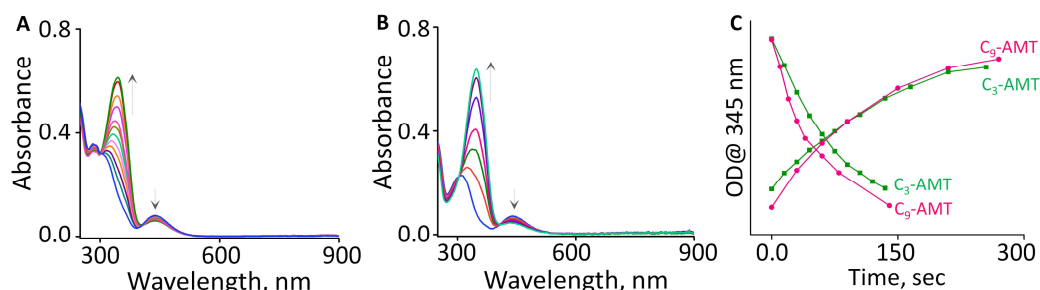


Figure 4.6: The temporal absorption spectra recorded from both (A) C₃-AMT and (B) C₉-AMT show the reverse photoswitching (*cis*-to-*trans*) under 435 nm light (C) Combined plots of OD (*ca.* 345 nm) vs. illumination time recorded from C₃ and C₉-AMT under 345 nm and 435 nm.

4.2.2 Characterization of C₃ and C₉ -NCs

To evaluate the role of chromophore-spacer length in the light-induced assembly of NCs, photoswitchable gold NCs with two different spacer lengths (C₃-NC and C₉-NC) were synthesized and purified using the procedure reported for [Au₁₄₄(PET)₆₀] NCs (abbreviated as PET-NC; here PET represents 2-phenylethanethiol).^[60] Detailed synthesis of PET-NC, C₃-NC, and C₉-NC NC are provided in **Chapter 2**. A schematic representation of the synthesis of C₃-NC and C₉-NC is given in **Figure 4.7A**. The optical absorption features of C₃ and C₉ NCs were recorded and compared with the PET analog (PET-NC; **Figure 4.7B**). The presence of two weak humps *ca.* 520 nm and 700 nm similar to PET-NC and an overlapping absorption maximum at 345 nm equivalent to the optical absorption characteristics of AMT confirms the formation of C₃ and C₉ NCs. Since the ESI and MALDI mass spectrometry trials were not successful, we further recorded and compared the XPS of these two NCs with that of PET-NC. The well-matching BE values of gold 4f electron orbitals in C₃-NC and C₉-NC compared to the reported values of PET-NC (inset in **Figure 4.7B**) suggest similar core for all the three NCs (C₃-NC, C₉-NC, and PET-NC). A trivial shift in the BE of these NCs is mostly due to the difference in the electron densities of the organic counterparts. The BE

values of C 1s, N 1s, O 1s, and S 2p levels of all three NCs are shown in **Figures 4.8A-D**.

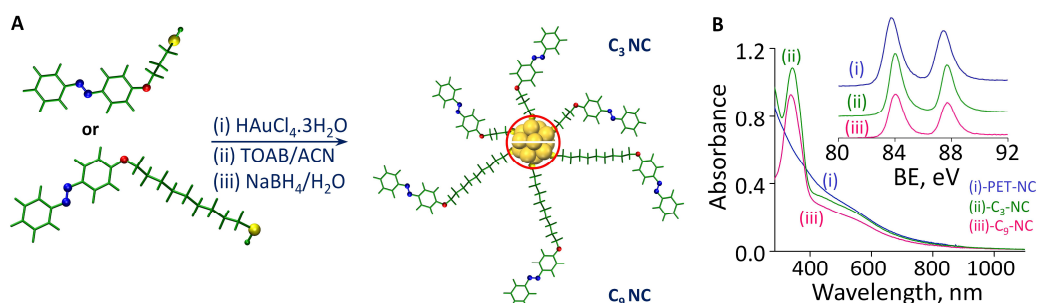


Figure 4.7: (A) Schematic shows the synthesis of C₃ and C₉-NC. (B) UV-Vis absorption spectra of (i) PET-NC, (ii) C₃-NC and (iii) C₉-NC recorded in DCM. The XPS spectra (gold 4f levels) of all three NCs are shown in the inset.

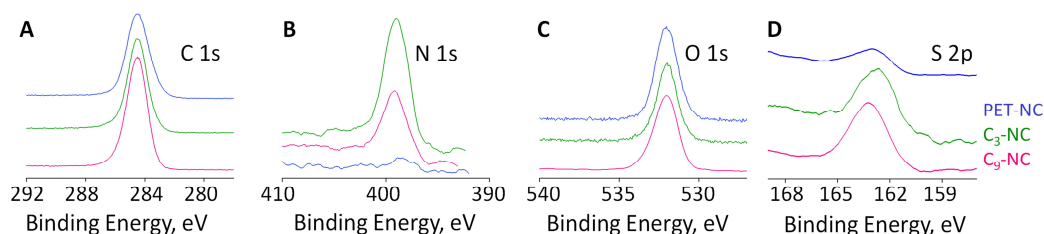


Figure 4.8: XPS spectra of (A) C 1s, (B) N 1s, (C) O 1s, and (D) S 2p levels of PET-NC (blue), C₃-NC (green), and C₉-NC (pink).

Next, we evaluated the photoisomerization efficiency of C₃ and C₉ NC solutions (prepared separately in DCM) under two different wavelengths of light. Temporal absorption spectra recorded from C₃ and C₉ NCs illuminated under 345 nm light are shown in **Figures 4.9A** and **B**, respectively. The time-dependent absorption spectra of C₃ and C₉ NCs recorded separately during the reverse (*cis-to-trans*) photoswitching (435 nm) are shown in **Figures 4.9C** and **D**. The combined plots of OD@345 nm vs. illumination time recorded during the photoisomerization (*trans-to-cis* and *cis-to-trans*) of C₃ and C₉ NCs are shown in the inset of **Figure 4.9D**.

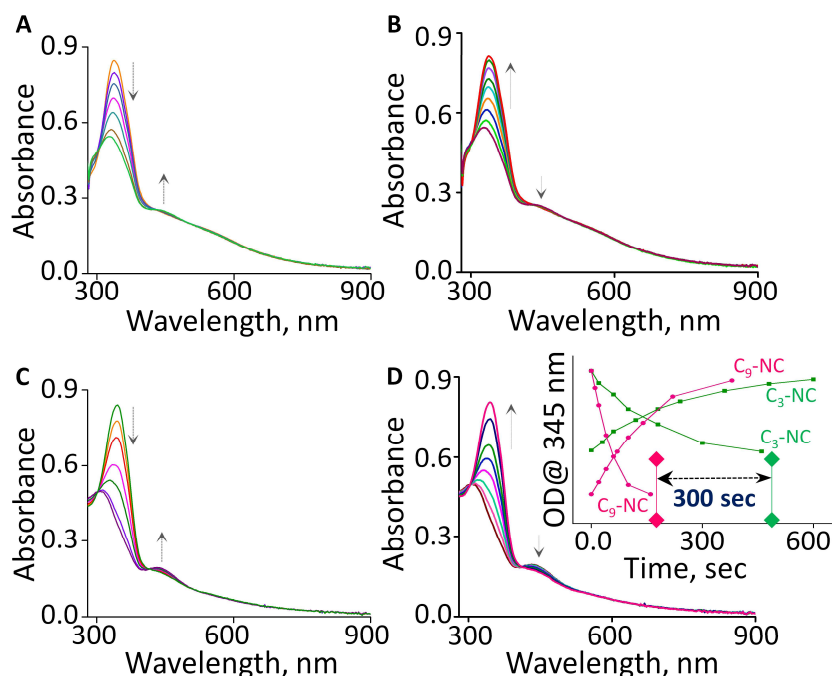


Figure 4.9: The temporal optical absorption spectra of (A) C₃-NC and (B) C₉-NC under 345 nm illumination. The reverse photoswitching (*cis*-to-*trans*) of (C) C₃-NC and (D) C₉-NC under 435 nm illumination. The combined plots of OD (*ca.* 345 nm) vs. irradiation time, using 345 nm and 435 nm lights recorded from C₃-NC and C₉-NC are shown in the inset of Figure 4.9D.

Notably, the time required for *trans*-to-*cis* photoswitching in C₃ and C₉ NCs (same concentration) under a similar intensity of light (0.2 mW/cm²) is found to be different. More precisely, the *trans*-to-*cis* photoswitching in C₃-NC could accomplish only 65% even after 460 seconds of illumination. Beyond this point, there was no change in their absorbance. On the other hand, C₉-NC completed this process within 160 seconds of illumination. Though the time scale for *trans*-to-*cis* photoswitching in C₉-NC is comparable to AMTs (140 sec), which is three times slower in the case of C₃-NCs. This means that the photoswitching of NCs is as fast as pure AMT when the chromophore is away from the NC surface (longer spacer length; C₉-NC). However, the photoswitching slows down when AMT places very close to the

NC surface (shorter spacer length; C₃-NC). From the above experimental data, it is clear that the steric hindrance experienced at the NC-chromophore interface could slow down and finally freeze the photoswitching process.

4.2.3 Light-induced assembly of C₃ and C₉-NCs

The core size of C₃-NC and C₉-NC was examined using TEM analysis. TEM micrographs captured from C₃- and C₉-NCs (**Figure 4.10A** and **B**, respectively) show nearly uniform size distributions (1.9 ± 0.14 nm and 1.87 ± 0.12 nm). The core sizes of C₃- and C₉-NCs are in good agreement with that of the PET-NC. We further investigated the role of chromophore spacer length in the self-organization of NCs by recording and analyzing the TEM micrographs. For this, ~ 100 μ M solutions of C₃ and C₉ NCs in DCM were irradiated under 345 nm light for 90 min in a dark room. A constant stirring of NC solutions in a temperature-controlled bath helped to reduce thermal aggregation. The large area TEM micrographs captured from the illuminated C₃ and C₉ NCs are shown in **Figures 4.10C** and **D**, respectively. Though C₃ and C₉ NCs underwent light-induced self-assembly and formed circular superstructures, the extent of assembly is found to be different in both cases. Well-organized and thick arrangements were seen in the case of C₉-NCs. On the other hand, an incomplete assembly is formed from C₃-NCs. The magnified and focused TEM micrographs of a single superstructure assembled from C₃ and C₉ NCs are shown in **Figures 4.10E** and **F**, respectively. The C₃-NCs slowly self-assembled into disc-like superstructures with a few layers of upcoming organized NCs at the top surface (enlarged view of top surface is shown in **Figure 4.10G**). An enlarged view from the edge of the C₉-NC superstructure (**Figure 4.10H**) showed a nearly uniform and thick assembly. The slow assembly in C₃-NCs helped to capture the intermediates of assembly. From the above spectroscopic and

microscopic studies, it is obvious that the time scale of the light-induced self-assembly largely depends on the suitable separation between chromophores and NCs. The prompt and complete self-assembly in C₉-NC compared to the C₃ analog is attributed to the negligible steric hindrance experienced at the NC-chromophore interface. The schematic shows the distant-dependent self-assembly in C₃ and C₉ NCs and the possible mechanism for their slow and quick assembly is shown in **Figure 4.10I**.

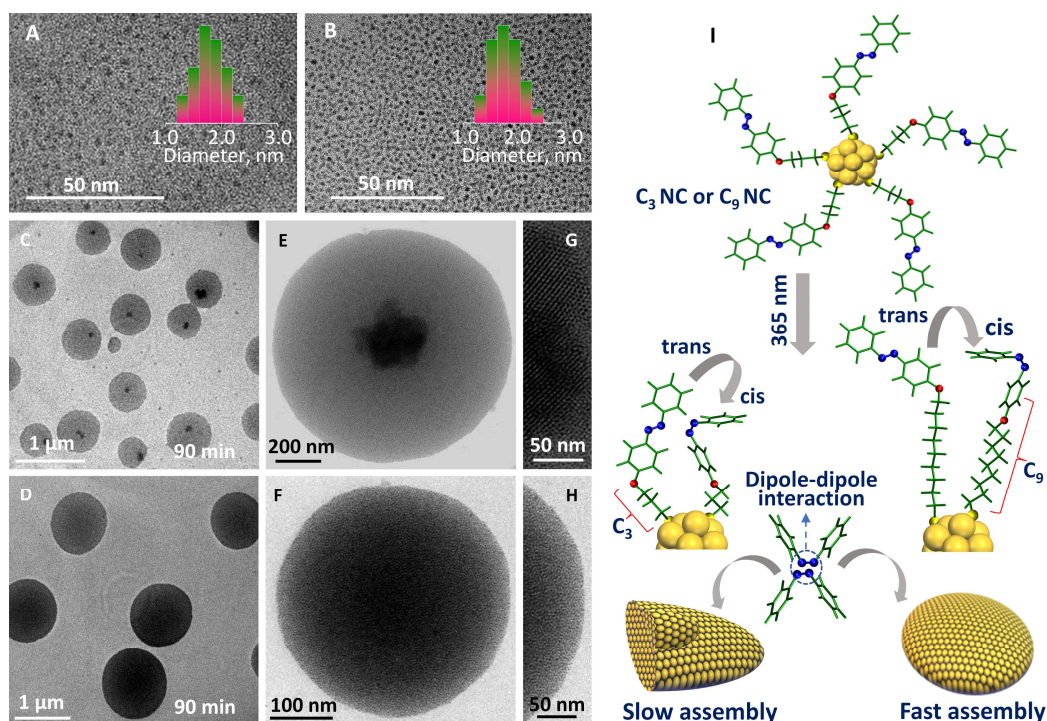


Figure 4.10: (A and B) The TEM micrograph of (A) C₃-NC and (B) C₉-NC before irradiation. (C and D) Large area TEM images captured from (C) C₃-NC and (D) C₉-NC assembly after 90 min of illumination under 345 nm light. (E and F) Magnified and tight-focused TEM micrographs of a single superstructure derived from (E) C₃-NC and (F) C₉-NC. (G and H) An enlarged view captured from (G) the centre dark spot of C₃-NC and (H) the edge of C₉-NC assemblies. (I) The schematic shows the distant-dependent self-assembly in C₃-NC and C₉-NC and the possible mechanism for their slow and quick assembly.

The structural details of self-assembled superstructures were further explored using dark-field STEM imaging and elemental mapping. The large-area STEM micrographs captured from C₃- and C₉-NC assemblies are shown in **Figure 4.11A** and **B**, respectively. A contrast difference in the STEM micrograph captured from the C₃-NC assembly shows the existence of crystallized aggregates encapsulated within the disc-like structures (**Figure 4.11C**). The STEM micrograph recorded from the C₉-NC assembly showed uniform contrast all over the surface (**Figure 4.11D**). The STEM measurements align well with the TEM images displayed in **Figures 4.10E** and **F**. The chemical composition assessment of both self-assembled superstructures using energy-dispersive X-ray analysis (EDS), verifies the existence of gold, sulfur, nitrogen, oxygen, and carbon. The gold (yellow) and sulfur (green) mapping of single superstructures derived from C₃- and C₉-NCs are shown in **Figure 4.11E-H**. The contrast difference in the elemental maps (E and G) helped to distinguish the upcoming layers at the top surface of the C₃-NC assembly. The large area STEM images, elemental maps (gold, sulfur, and nitrogen), and EDS spectra recorded from C₃- and C₉-NCs assemblies are shown in **Figure 4.12**.

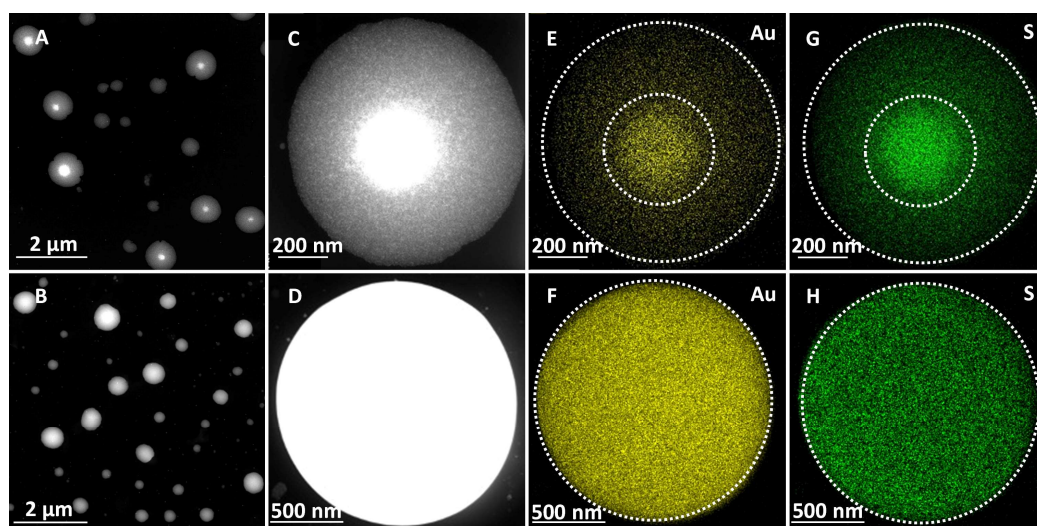


Figure 4.11: (A and B) Large area STEM images captured from (A) C₃-NC and (B) C₉-NC assembly. (C and D) A single STEM image from (C) C₃-NC and (D) C₉-NC assembly. The elemental maps of a single superstructure derived from (E and G) C₃-NC and (F and H) C₉-NC demonstrate the presence of (E and F) gold and (G and H) sulfur.

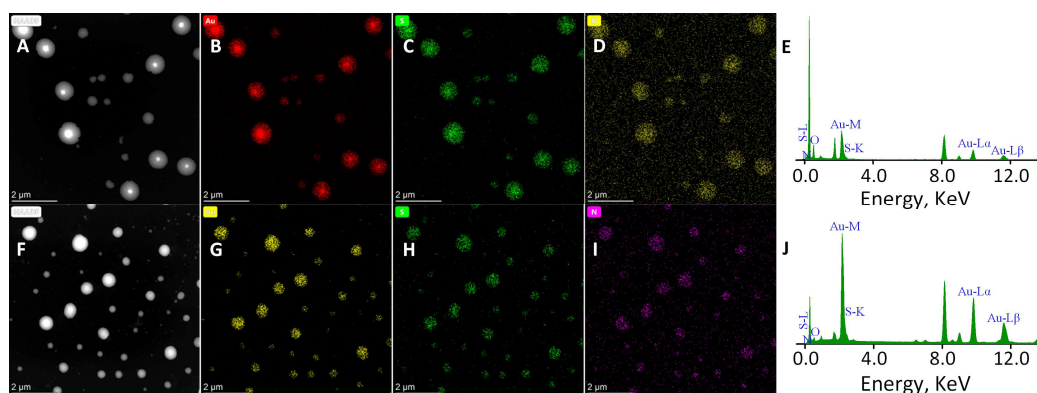


Figure 4.12: (A and F) STEM, (B-D and G-I) elemental maps (B and G-gold; C and H-sulfur; D and I-nitrogen), and (E and J) EDS spectra recorded from (A-E) C₃-NC and (F-J) C₉-NC assemblies.

Further, field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) images were utilized to investigate the structural details of assembled superstructures. **Figures 4.13A and B** show the FESEM micrographs captured from C₃- and C₉-NC assemblies. The disc-like

superstructures with a few layers of upcoming assemblies on the top surface are seen in the case of the C₃-NC assembly. The C₉-NC assembly shows densely packed disc-like superstructures similar to the TEM image shown in **Figure 4.10D**. The morphology of assembled superstructures was further examined using AFM imaging. **Figures 4.13C and D** show the large area AFM images captured from C₃- and C₉-NC assemblies, in which the upcoming assemblies are visible in the case of C₃-NC. The AFM images of single superstructures derived from C₃- and C₉-NCs are shown in **Figure 4.13E-J**. The AFM data is consistent with TEM, STEM, and FESEM results. The high-resolution AFM images captured from a single superstructure derived from C₃-NC (**Figures 4.14A-E**) show the periodic assembly of NCs. The zig-zag patterns represent the NC directions in the assembly (**Figures 4.14B and C**).

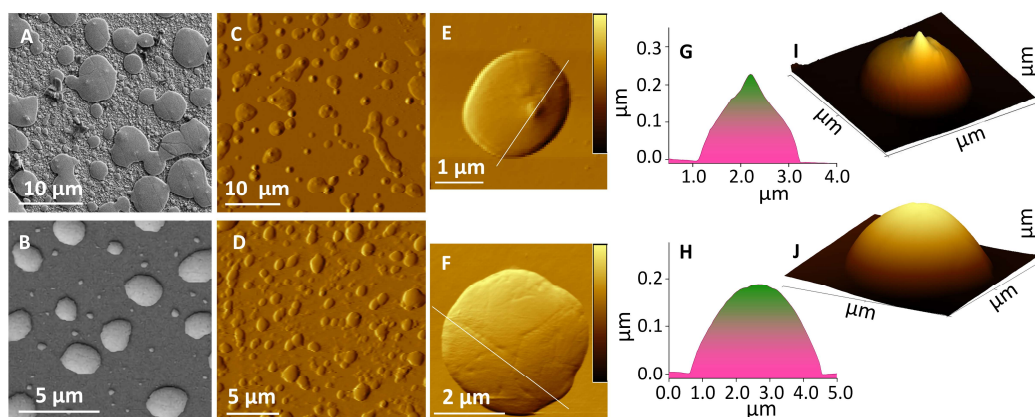


Figure 4.13: (A and B) FESEM images of (A) C₃-NC and (B) C₉-NC assemblies. (C and D) Large area AFM images of (C) C₃-NC and (D) C₉-NC assemblies. (E and F) AFM images of single superstructure derived from (E) C₃-NC and (F) C₉-NC. Corresponding (G and H) height profiles and (I and J) 3D images.

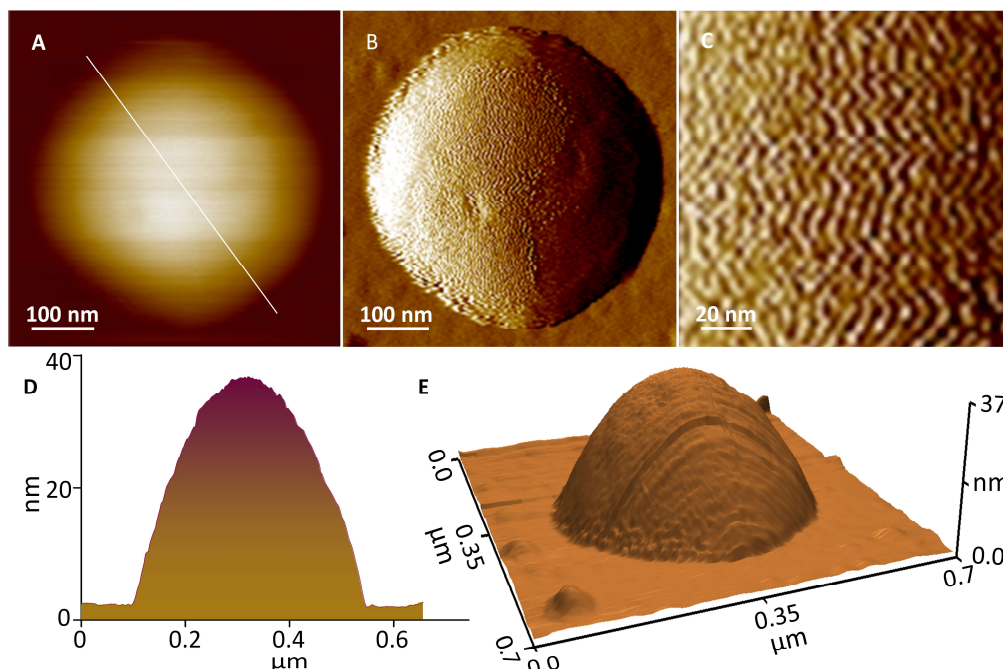


Figure 4.14: (A and B) High-resolution tapping mode AFM (A-topography and B-amplitude) images of a single superstructure derived from C₃-NC. (C) A zoomed and focused AFM image captured from the top surface of the C₃-NC assembly showed the NC direction in the assembly. (D and E) The height profile and 3D AFM image of the same assembly.

Transmission electron tomography (ET) reconstruction was executed to obtain a comprehensive understanding of the 3D structural attributes of the assembled superstructures.^[61] Accordingly, the 2D projections were collected between $\pm 70^\circ$ with an increment angle of 2° . The corresponding TEM images (**Figures 4.15A and B**) and the 3D reconstruction images of C₃- and C₉-NC assemblies (**Figures 4.15C and D**) revealed the disc-like morphology of the superstructures. The cross-sectional view suggests that the superstructures are composed of densely packed NC networks. However, there is a significant difference in the overall disc thickness. As observed in 2D projections, the C₃ NCs contain crystalline aggregates within the discs that are protruding outside the discs (**Figures 4.15C, E and F**). On the other hand,

uniform array of NCs was observed in the case of C₉ NC-based assemblies (**Figures 4.15D and G**). It is important to note that deformed shapes and flattening are commonly observed in such assemblies due to solvent evaporation and drying artifacts during specimen preparation. However, we observed a clear difference in 3D reconstructed structures obtained from C₃ NCs and C₉ NCs. Superstructures obtained from C₃ NCs display uniform thickness across the particle. This suggests that the superstructures are disc-like assemblies. On the other hand, in the case of C₉ NCs, the deformation and flattening of the structure is evident due to non-uniform thickness between the center and the periphery. NCs were also assembled into dimer and trimer superstructures during the light-induced self-assembly. However, the percentage of dimer and trimer formed is significantly less compared to monomer assembly. The early stages of monomer, dimer, and trimer assemblies derived from C₉-NCs are shown in **Figures 4.16A-C**, in which the dimer and the trimer showed well-connected interfaces with periodic assembly. Eventually, they transformed into densely packed superstructures with constant illumination under 345 nm light.

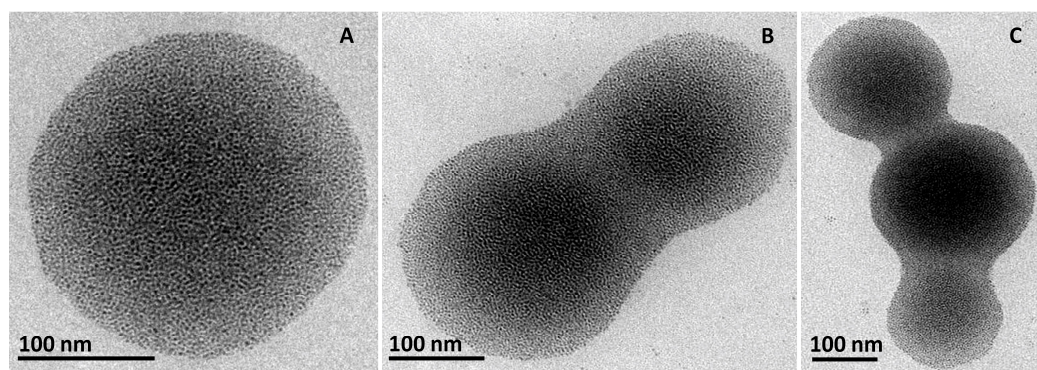


Figure 4.15: (A and B) TEM images and (C and D) corresponding ET reconstruction images of (A and C) C₃- and (B and D) C₉-NC superstructures. (E-G) The 3D-reconstructed tomograms of (E and F) C₃- and (G) C₉-NC superstructures in different orientations.

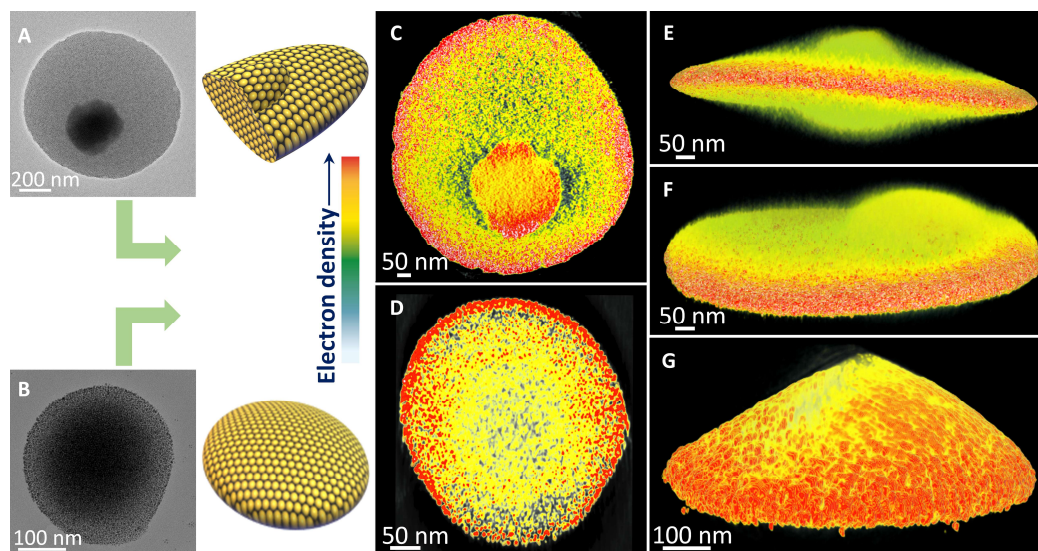


Figure 4.16: (A-C) The early-stage TEM micrographs captured from (A) monomer, (B) dimer, and (C) trimer superstructures of C₉-NCs.

Subsequently, we investigated the long-term stability of assembled superstructures using TEM imaging of the same grid stored at low temperature. Notably, the morphology of assembly was intact even after one year (**Figure 4.17**). To understand the formation of disc-like assembly, TEM imaging was performed for samples prepared using a solution of C₉-NC in DCM under 345 nm illumination at different time intervals. The TEM images revealed the formation of disc-like superstructures, that evolved from the short circular assembly (**Figure 4.18**). The consequence of the long-term illumination on the structural transformation of assembled superstructures was investigated in detail. For this, a solution of C₉-NC in DCM was irradiated with UV (345 nm) light for 5 h. The sustained illumination resulted in the solidification of NCs due to the formation of bulky superstructures. To understand the structural rearrangements, the solid material was further examined by redissolving them in DCM. The FESEM image (**Figure 4.19A**) shows a chain-like assembly formed by fusing the individual superstructures due to dipole-dipole interactions between them. A similar chain-like

framework seen in the dark-field scattering microscope (**Figure 4.19B**) is in good agreement with the FESEM data. The TEM micrographs captured from the surface and edge of the chain-like structures (**Figure 4.19C and D**) showed highly ordered multilayer assembly throughout. A scheme for the formation of a chain-like assembly is shown in **Figure 4.19E**, in which the individual NCs initially self-assembled into spherical superstructures and then into chain-like assembly due to the extended dipolar interactions between them during the course of illumination. The above-demonstrated idea will be useful to fulfill industrial needs, especially in the development of molecular photoswitches.

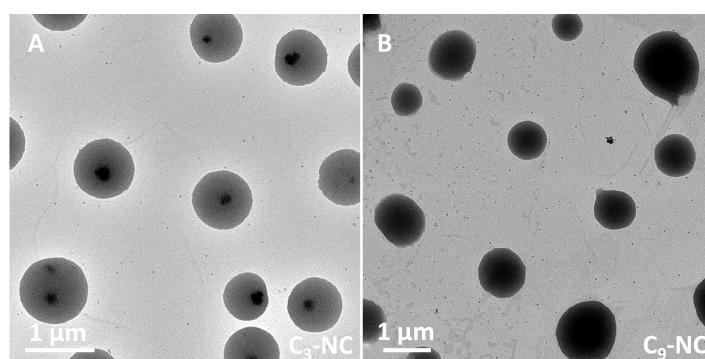


Figure 4.17: TEM micrographs of (A) C₃-NC and (B) C₉-NC assembly recorded after one year.

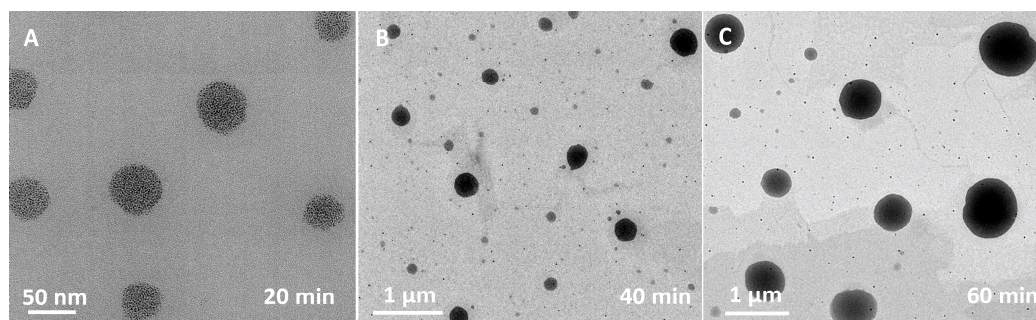


Figure 4.18: The mechanism for the formation of disc-like assembly. The temporal TEM micrographs of C₉-NC solution under 345 nm illumination for (A) 20 min, (B) 40 min, and (C) 60 min.

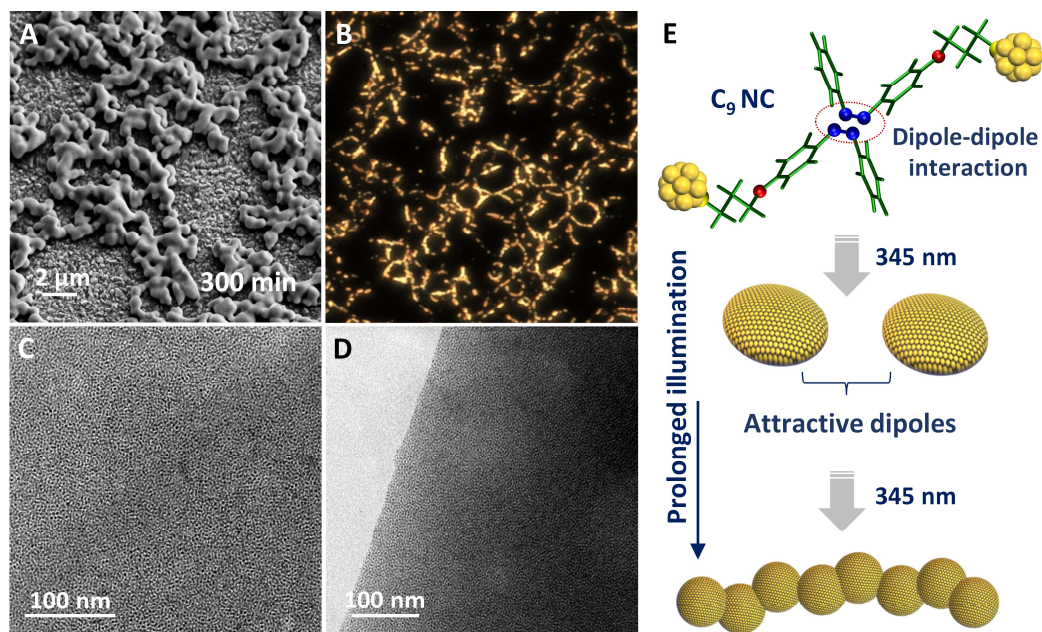


Figure 4.19: (A) FESEM and (B) dark-field scattering images of the chain-like assembly. (D and E) TEM micrographs from the surface and edge of the chain-like assembly. (E) The schematic depicts the formation of a chain-like assembly.

4.3 Conclusion

The reversible self-assembly of NCs using external stimuli such as light, heat, and magnetic field is tremendously evolving research area. In the recent past, light has been identified as an efficient probe to demonstrate the supramolecular self-assembly of chromophore-tethered NCs. However, the magnitude of assembly in chromophore-tethered NCs largely depends on its photoswitching efficiency. We have successfully demonstrated this concept by introducing two photoswitchable NCs fabricated using the thiolated-azobenzene molecule with different spacer lengths. The core and molecular information of both NCs were investigated in detail using various spectroscopic and microscopic techniques. Photoactivation of both NC solutions at ambient temperature using 345 nm light resulted in the generation of self-assembled superstructures. FESEM, AFM, TEM, ET

reconstruction, STEM, and dark field scattering microscopic studies showed the presence of densely packed NCs in self-assembled superstructures. By introducing the idea of distance dependency, we successfully demonstrated the prompt self-assembly in NCs. This was evident from the fast assembly observed in C₉-NCs due to their improved photoswitching efficiency resulting from the negligible steric hindrance experienced at the NC-chromophore interface. Such molecular control over the self-assembly of NCs by placing the chromophores suitably away from the nanosurface are useful tools to develop next-generation switchable sensors, especially in biological, electrochemical, and electronic devices.

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CHAPTER 5

**LIGHT-EMITTING ATOMICALLY PRECISE
NANOCLUSTER-BASED FLEXIBLE QR CODES FOR
ANTI-COUNTERFEITING**

CHAPTER 5

LIGHT-EMITTING ATOMICALLY PRECISE NANOCUSTER-BASED FLEXIBLE QR CODES FOR ANTI-COUNTERFEITING

5.1 Introduction

Counterfeiting of any official documents, especially currency, passports, stamps, etc. is a global concern that affects the security and revenue of a country. Though many of these are protected with anti-counterfeiting techniques, estimated global economic loss due to duplication has increased significantly and reached up to multi-billion US dollars per annum.^[1] Conventional anti-counterfeiting technology is mainly based on the printing of a security label using ink developed from luminescent materials that can glow under ultraviolet light. Different materials used or proposed to fabricate the printing ink include organic dyes,^[2-6] semiconductor quantum dots,^[7-9] inorganic perovskites,^[10,11] rare-earth metals,^[12-16] up-conversion nanoparticles,^[17] carbon dots,^[18,19] polymer dots,^[20] and so on. Yet, the moderate photostability, sizable elemental toxicity, expensive precursors, or hard synthetic protocols rarely limit their attention. Non-toxic luminescent ink fabricated from NCs is another possible candidate. In the recent past, an attempt to make the NC-based luminescent printing ink was reported.^[21] NCs have been considered as a class of materials made up of about ten to a few hundred atoms in their cores.^[22,23] Precise atomic combinations, discrete electronic energy levels, characteristic optical absorption features, bright photoluminescence, stability under a range of chemicals and photons, and moderate toxicity due to less metallic contents are the strengths of individual NCs.^[24,25] NCs are known for diverse potential applications, which include, catalysis,^[26,27] solar energy conversion,^[28,29] LED fabrication,^[30,31] sensing,^[32-35] bioimaging,^[36-39] drug screening,^[40] and therapeutics.^[41,42] A

large variety of gold and silver NCs with different combinations of cores and ligands are reported.^[23-25,43-53] Some of these NCs emit in the solid state owing to their strong interparticle electronic coupling.^[52,53] Stable solid-state emitting NCs with better PLQY are promising materials for developing large-area printable electronics, mainly for security prints, wearable LEDs, and healthcare sensors. To achieve this goal, the key criteria is to fabricate a smart luminescent NC-based ink having adequate consistency for printing, preserved PL and molecular stability, and flexibility for multiple usages. The development of such NC-based luminescent printing ink is still in its infancy. To address this challenge, we have fabricated a stable, flexible, non-toxic, and low-cost NC-based luminescent ink by integrating solid-state emitting NCs in an elastic matrix. Different spectroscopic and microscopic studies show that intercalated NCs in printing ink are highly stable as their optical absorption features, PL, and molecular compositions are analog to the pristine NCs. This elastic ink has been efficiently used to print the text and Quick Response (QR) code using the stencil-printing technique. A QR code is a machine-readable two-dimensional barcode, which can encrypt data such as name, URL (Uniform Resource Locator), address, phone number, location details, and so on. The information encoded on these optical labels can be accessed by scanning with a camera-enabled mobile device having a QR code scanner application. In the recent past, the QR code fabricated from up-conversion nanoparticle-based ink has been used to demonstrate pharmaceutical anti-counterfeiting.^[54] Herein, we have successfully demonstrated the printing and electronic reading of a QR code encrypted with confidential information on a currency. Notably, the printed security labels are stable over a range of temperatures, under a spectrum of lights, humidity, and mechanical stress. The elastomeric binder-based luminescent ink facilitates flexible and stretchable solid-state patterns, which helps to hold the printed security

code on the currency even after multiple foldings. By using this stretchable ink, we can stamp any authentic security codes (2.5 cm x 2.5 cm) at the cost of 0.013 US per stamp. This methodology can be further extended to encrypt more details about the currency, such as serial numbers or any other pieces of information to validate its authenticity.

5.2 Result and discussion

5.2.1 Characterization of Ag₂₉ NCs

To address the development of a stable, non-toxic, and low-cost NC-based luminescent ink, different gold and silver NCs were scrutinized. We have synthesized and studied photophysical properties of a variety of NCs, including [Au₂₂(SG)₁₈], [Au₂₅(PET)₁₈]⁻, [Ag₂₉(LA)₁₂]³⁻, [Ag₂₉(BDT)₁₂](TPP)]₄³⁻, [Au₁₀₂(*p*-MBA)₄₄], and [Au₁₄₄(PET)₆₀]; (LA= Alpha-lipoic acid). The procedure for the synthesis of these NCs are given in **Chapter 2**. To check the suitability of these NCs for printing applications, we have recorded and compared the optical absorption and emission spectra of all six NCs (**Figure 5.1**).

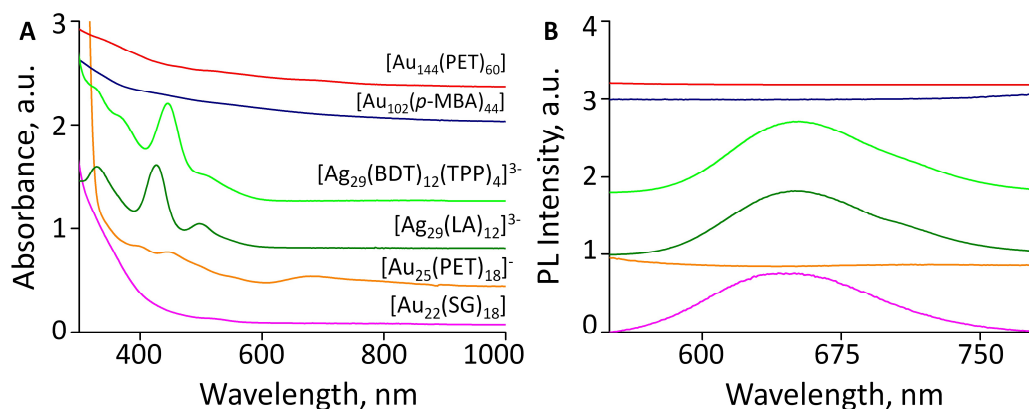


Figure 5.1: (A) UV-Vis absorption and (B) PL spectra of [Au₂₂(SG)₁₈], [Au₁₀₂(*p*-MBA)₄₄], and [Ag₂₉(LA)₁₂]³⁻ in water, [Ag₂₉(BDT)₁₂](TPP)]₄³⁻ in DMF, [Au₂₅(PET)₁₈]⁻ and [Au₁₄₄(PET)₆₀] NCs in DCM.

In the first set of screening, $[\text{Au}_{25}(\text{PET})_{18}]^-$, $[\text{Au}_{102}(p\text{-MBA})_{44}]$, and $[\text{Au}_{144}(\text{PET})_{60}]$ were eliminated due to their poor PL. Though $[\text{Au}_{22}(\text{SG})_{18}]$ NC showed better PL, their solubility in water reduced the importance. In this case, there is a chance to leach out NCs from the printed documents while wetting. Finally, two different twenty-nine-atom silver NCs (Ag_{29}) have been selected to fabricate the printing ink due to their bright red emission and better PLQY. Among $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ and $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$, the second one showed better photostability and solid-state PL compared to $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NC. $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs were synthesized^[53,55] and characterized by using optical absorption and PL spectroscopy. **Figure 5.2A** and **B** show the UV-Vis absorption (I), excitation (II), and emission (III) spectra of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs in DMF. Different absorption humps *ca* 265, 365, 445, and 510 nm represent different possible molecular electronic transitions, which are more prominent in the excitation spectra. PL spectra of these NCs show an emission maximum *ca* 650 nm at 450 nm excitation. Photographs of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NC solutions under visible (*c*₁ and *e*₁) and UV light (*c*₂ and *e*₂), and the energy-minimized structure of the ligands used to synthesize NCs are shown in **Figure 5.2C** and **E**, respectively. Among two NCs, $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ shows bright solid-state emission, a fundamental requirement for the luminescent-based printing ink. Photographs of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC powder under visible (*d*₁) and UV light (*d*₂) are shown in **Figure 5.2D**. To evaluate the photostability of NCs, we have recorded and compared the time-dependent PL spectra of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NC solutions illuminated at 365 nm excitation at different time intervals. Photostability experiments show extended stability for $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NCs compared to $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs (**Figure 5.2F**). Illumination of $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NC solution (365 nm light)

underwent photobleaching within 15 min, which is evident from the plot of (b) I/I_0 vs. illumination time (I_0 represents the PL intensity at $t=0$). At the same time, $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC shows (a) robust I/I_0 values even for a couple of hours of photoexcitation. The photographs (under UV light) of (a) $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and (b) $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NC solutions illuminated under 365 nm light are given in the inset (**Figure 5.2F**). Due to the exceptional photostability, easy synthetic protocol, solid-state emission, and lower cost of raw materials, we have chosen $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ as the potential ingredient for the fabrication of luminescent-ink. Before that, a comprehensive picture of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NCs was investigated in detail using various spectroscopic and microscopic techniques. PL lifetime of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC solution was recorded using time-resolved spectroscopy. **Figure 5.2G** (a) represents the PL decay profile (TCSPC) of NC at their emission maximum *ca* 650 nm using 378 nm excitation. $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC shows a bi-exponential luminescence relaxation with a faster component of 88 ns and a slower component of 245 ns. The fast and slow components of NCs presumably originated from the prompt and thermally activated delayed emission, similar to the other NCs reported.^[39,56] The average lifetime of NC is found to be 117 ns,^[57] which was estimated using the equation $\tau_{\text{av}} = (\tau_1 A_1 + \tau_2 A_2) / (A_1 + A_2)$, where τ_1 and τ_2 are the individual lifetime values, and A_1 and A_2 are the corresponding amplitudes.

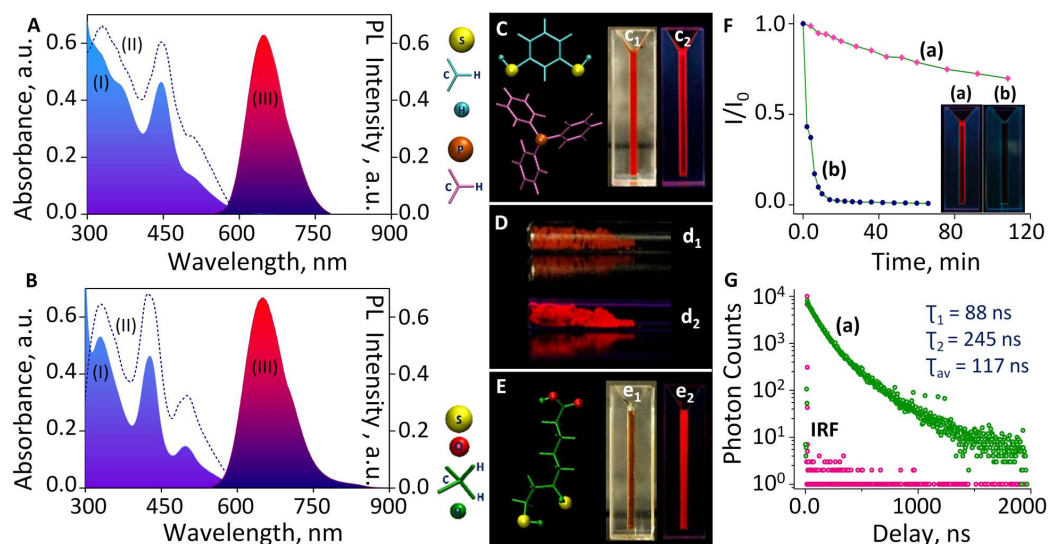


Figure 5.2: (A and B) UV-Vis absorption (I), excitation (II), and emission (III) spectra of (A) $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and (B) $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs. (C and E) Photographs of (C) $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and (E) $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NC solutions under visible (c_1 and e_1) and UV light (c_2 and e_2). Energy-minimized structure of the ligands used to synthesize NCs are shown. (D) Photographs of solid $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC under visible (d_1) and UV (d_2) light. (F) A plot of I/I_0 vs. illumination time for (a) $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and (b) $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs show their photostability. The photographs (under UV light) of illuminated NC solutions are given in the inset. PL decay profile of (a) $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC and instrument response factor (IRF) are shown in Figure 5.2G.

The molecular composition of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC was recorded and analyzed using electrospray ionization-mass spectrometry (ESI-MS, negative mode). ESI-MS of purified $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC in DMF is shown in **Figure 5.3A**, which is comparable to the reported spectrum.^[53,57] Single molecular ion peak *ca* 1603 represents pure $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$. The molecular weight of TPP is not accounted for in the mass spectrum owing to their easy dissociation during ionization.^[57] Expansion of the peak *ca* 1603 shows the characteristic isotopic distribution, in which separation between nearby peaks is found to be 0.33 (inset in **Figure 5.3A**, a_1). The corresponding

theoretical isotopic distribution is shown in the inset (**Figure 5.3A**, a₂). The structure of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC consists of Ag_{13} icosahedral core with twelve Ag atoms capped in the external shell. These twelve Ag atoms form four tetrahedrally oriented trigonal prisms and another four Ag atoms face-cap the thirteen-atom core at four tetrahedral positions.^[53] The energy-minimized structure of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC optimized using the DFT is shown in **Figure 5.3B**. The core of NC and the nature of binding were studied by recording and analyzing the XPS. BE values of Ag 3d levels in $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC are in good agreement with reported values,^[57,58] with Ag 3d_{5/2} *ca* 368.4 eV and Ag 3d_{3/2} *ca* 374.4 eV (**Figure 5.3C**). The deconvoluted spectrum shows the presence of P 2p_{3/2} and 2p_{1/2} peaks *ca* 130.8 eV and 131.8 eV, which confirm the presence of bound TPP in NC. The BE of S 2p was in accordance with thiolate binding, in which sulfur 2p_{3/2} and 2p_{1/2} peaks appear around 162 eV and 163.2 eV, respectively. By comparing the ESI-MS and XPS, the molecular composition of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC is confirmed.

To further confirm the presence of bound ligands in the purified NC, we have recorded and analyzed ¹H and ³¹P nuclear magnetic resonance (NMR) spectra in DMSO-d₆. ¹H and ³¹P NMR spectra of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC solution were assigned and labeled (**Figure 5.3D** and **E**), by comparing the proton-proton interactions in the correlation NMR (COSY; **Figure 5.3F**). The peaks *ca* δ = 8.22-8.20, 6.72-6.69, 6.10-6.05, 5.98-5.92 ppm were assigned to BDT, whereas the other peaks (δ = 7.34-7.29, 7.24-7.16, 6.84-6.74) were originated from TPP. The proton in between the thiol groups (**Figure 5.3D**, a) has shown a downfield shift owing to the electron-withdrawing nature of the silver core. The environmental changes around NCs resulted in two different sets of peaks for identical protons (**Figure 5.3D**, b, and c). The

appearance of all the aromatic protons in ^1H NMR and a single broad peak (**Figure 5.3E, b**) *ca* -1.44 ppm (slight changes will be expected according to TPP amount present) in ^{31}P NMR suggest the presence of bound BDT and TPP in the purified NC.^[57,59] A small hump *ca* 25.6 ppm (**Figure 5.3E, b**) arises from the oxidized TPP due to air oxidation of NCs.^[60] The ^{31}P NMR spectrum of the parent TPP molecule shows a single narrow peak *ca* -6.818 ppm (**Figure 5.3E, a**). NC was further characterized using TEM by drop-casting and drying ~ 100 μM solution of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC in DMF on a copper grid with a carbon-supported film. TEM image (**Figure 5.3G**) shows a nearly uniform size distribution (1.5 ± 0.2 nm; inset in **Figure 5.3G**) in the grid, which indicates the monodispersity of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC. As extreme purity is recommended in printing gadgets, NCs were further purified by crystallization using a slow solvent evaporation technique.^[53] Optical (white-light) and confocal fluorescence images of rhombohedral crystals are shown in **Figure 5.3H** and **J**, respectively. Resemblances in the optical absorption (I) and PL (II) features (**Figure 5.3I**) of NC crystals redissolved in DMF verify Ag_{29} core.

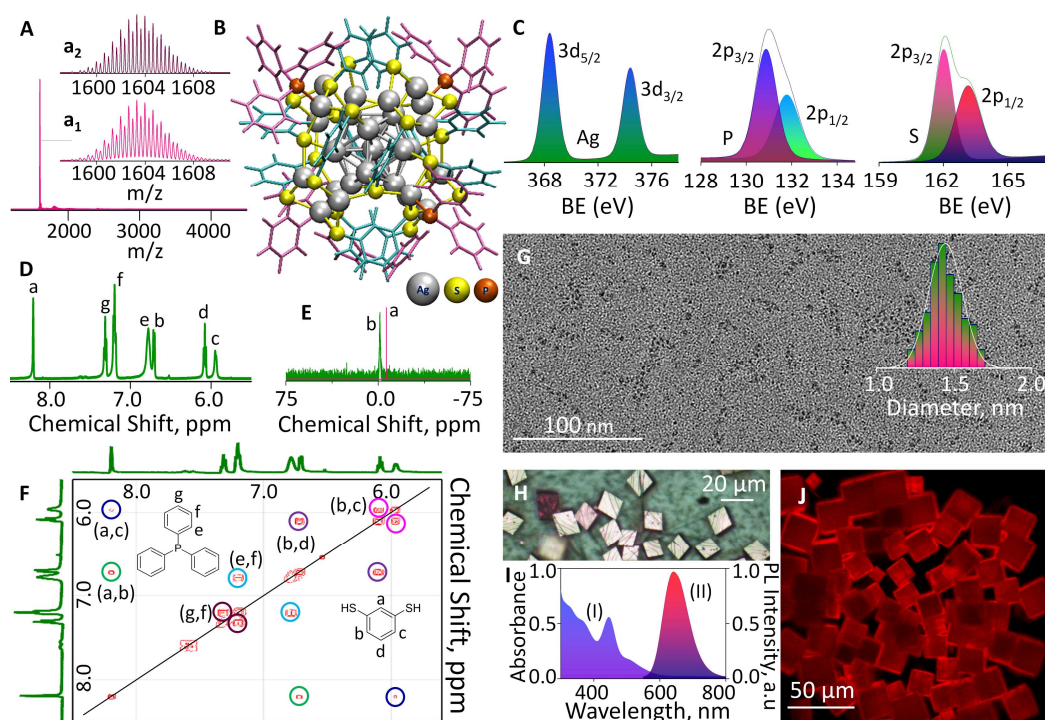


Figure 5.3: (A and B) ESI-MS and energy-minimized structure of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC. An expanded view of (a₁) experimental and (a₂) theoretical isotopic patterns are shown in the inset. (C) XPS spectra of NC show the presence of silver, phosphorus, and sulfur. (D) ^1H , (E) ^{31}P , and (F) ^1H - ^1H correlation (COSY) NMR spectra of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC. All the peaks are assigned and labelled above the traces. (G) Larger area TEM image shows monodisperse NCs. The size distribution of NC is shown in the inset. (H and J) Optical and confocal fluorescence images of crystallized NC show rhombohedral crystals. (I) Absorption (I) and PL (II) spectra of redissolved crystals recorded in DMF.

5.2.2 Characterization of NC-based printing ink and films

To develop a flexible NC-based printing ink, we have chosen thermoplastic polyurethane (PU) polymer as a matrix to intercalate NCs. The elastic and transparent natures of PU help to adopt the flexibility and visibility for NC-based ink. Details of ink preparation are given in **Chapter 2**. Photographs (under visible and UV light) demonstrating the different steps involved in the

fabrication of NC-based ink are shown in **Figure 5.4A**. The addition of crystallized NCs into the PU dispersion previously prepared in THF followed by constant stirring at room temperature ensured high-quality printing ink with the required consistency. To check the competence of the above-prepared ink, we have printed luminescent letters and bands using a stencil-printing technique.^[61-64] Details of the stencil printing technique are provided in **Chapter 2**. **Figure 5.4B** shows the photographs (under visible and UV light) of a word (CECRI) and a band stencil printed on tattoo paper. The perfect texture of the ink helped to print the letters without any diffusion.

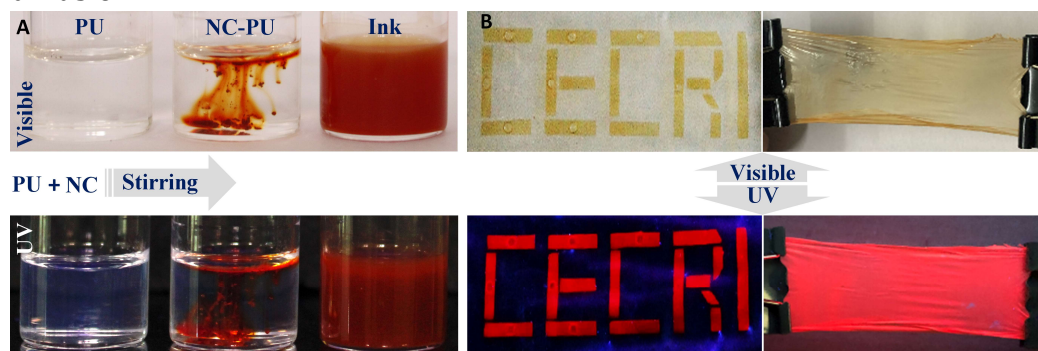


Figure 5.4: Photographs represent (A) different steps involved in the fabrication of ink and (B) stencil-printed luminescent word (CECRI) and band under visible and UV light.

To ensure the stability of NCs in the printed patterns, their optical features were probed using different spectroscopic and microscopic techniques. One-to-one correspondence in the UV-Vis absorption (I) and PL (II) spectra recorded from the printed band (**Figure 5.5A**) with NC solution (**Figure 5.2A**) suggests that NCs are stable in ink as well as in the printed patterns. PL decay profile (TCSPC) recorded from the printed band (378 nm excitation) shows a prolonged lifetime (727 ns; **Figure 5.5B**) compared to the parent NC crystals (280 ns) due to their least collisional quenching in the excited state. The longer lifetime of NCs in the printed band rules out their

direct interactions with atmospheric oxygen because of the polymer coating. The thickness of the printed materials is essential, especially in high-security documents. To measure the thickness of the printed band, we have recorded and analyzed SEM micrographs. FESEM images of the printed band captured from different areas are given in **Figure 5.5C** (rolled) and **D** (flat), which show nearly uniform thickness ($\sim 8.75 \pm 0.85 \mu\text{m}$) and surface morphology. The elemental composition of the printed band (**Figure 5.5E**) shows the presence of Ag, N, and O. Moreover, the printed band is highly transparent, which allows us to see the background (**Figure 5.5F**).

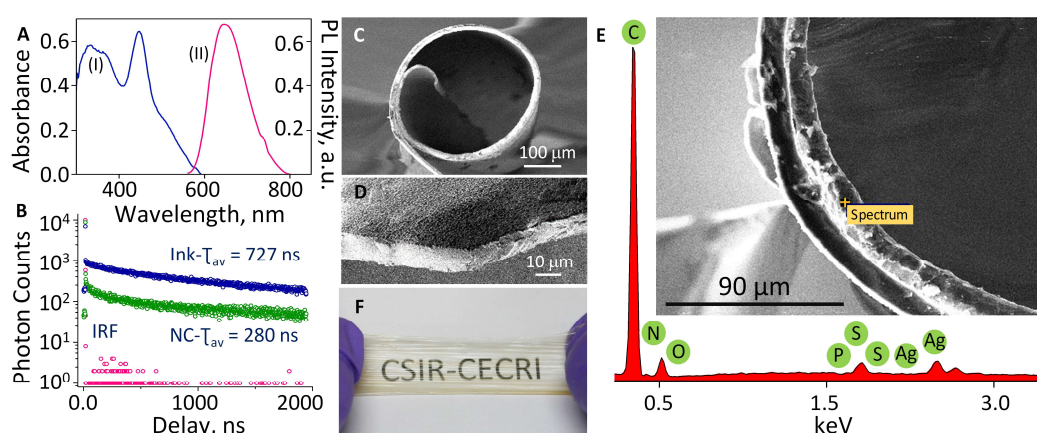


Figure 5.5: (A) UV-Vis absorption (I) and PL (II) spectra and (B) PL decay profile recorded from luminescent ink/band. (C and D) FESEM images were taken from the (C) rolled and (D) flat printed band. (E) The EDAX spectrum collected from the printed band (shown in the inset). The elemental composition is also shown. (F) The photograph shows the transparency of the printed band. Low-concentration ink (7mg NC/24 mL PU) has been used in this case.

Subsequently, we investigated the morphology of NCs in the printed band by recording and analyzing the TEM images of ink coated on a carbon-supported copper grid. TEM image of NCs dispersed in ink or printed band is shown in **Figure 5.6A**, which suggests the unaltered size of NCs. However, we could observe the random organization of NCs in the grid, marked by blue

circles. Detailed TEM investigation shows a circular assembly of NCs in the polymer matrix (**Figure 5.6B**). Such organization is mostly due to the C-H $\cdots\pi/\pi\cdots\pi$ interactions between the BDT/TPP and PU moieties, similar to the assembly reported in [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NCs.^[65] Further, we have recorded and compared the PL spectra of an equimolar concentration of parent NCs and ink. Notably, the PL spectrum recorded from the ink shows a four-fold enhancement compared to the NC solution (**Figure 5.6C**) under similar experimental conditions. The enhanced PL and extended lifetime of NCs in ink and the printed band seemingly originated from their assembly. The earlier reports on the self-organization of NCs in a polymer matrix^[66] and enhanced PL in the assembled NCs^[66,67] support the above results. The XPS spectra recorded and analyzed from the printed band provided BE values of Ag 3d (**Figure 5.6D**; Ag 3d_{5/2} *ca* 368.4 eV and 3d_{3/2} *ca* 374.4 eV) and S 2p (**Figure 5.6E**; S 2P_{3/2} *ca* 162.3 eV and 2P_{1/2} *ca* 163.5 eV), which are in good agreement with pristine NCs^[57,58] (**Figure 5.3C**). Slight broadening in the BE of P 2p (**Figure 5.6F**) is probably due to the presence of unbound^[57] or oxidized TPP^[60] in the film. Though a small amount of TPP separated from the NC surface during the ink fabrication, NCs were found to be highly stable in ink. The XPS spectra representing the BE of O 1s and N 1s (polymer) are shown in **Figure 5.6G** and **H**, respectively. All the above experiments confirm the presence of stable NCs in ink as well as in the printed bands. The stability of the printed materials is indispensable, especially for authorized documents.

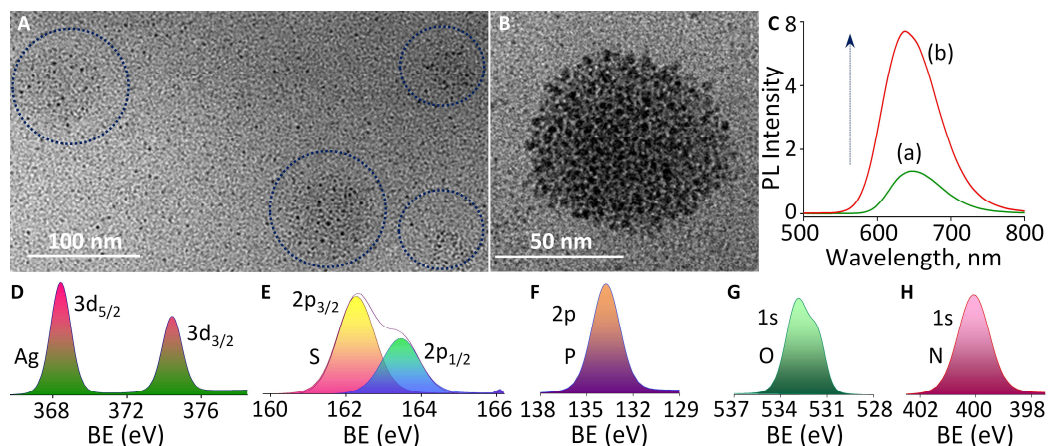


Figure 5.6: (A) Large area TEM image and (B) Zoom-in and focused TEM image captured from the NC-based ink shows the self-assembly of NCs. (C) PL spectra recorded from (b) NC-based ink and (a) NC solution (same concentration) shows a four-fold enhancement for NC-based ink. (D-H) XPS spectra (D) Ag 3d, (E) S 2p, (F) P 2p, (G) O 1s, and (H) N 1s recorded from the printed band.

5.2.3 Stability studies of printed bands

We have systematically investigated the photostability, thermal stability, moisture effect, and mechanical strength of the printed bands. To study their photostability, we have recorded and analyzed the PL spectra from the printed band illuminated at 365 nm excitation at different time intervals. A plot of I/I_0 (**Figure 5.7A**) vs. illumination time shows an exceptional photostability for (b) NCs embedded in the printed band compared to (a) NC solution (**Figure 5.2F-a**) under similar experimental conditions. To test their thermal stability, PL spectra were recorded from the printed band kept at different temperatures. A range of temperatures from $-70\text{ }^{\circ}\text{C}$ to $50\text{ }^{\circ}\text{C}$ was achieved by soaking the printed band in liquid nitrogen, cold water, and warm water, respectively. A plot of PL intensity vs. the number of temperature cycles (**Figure 5.7B**) shows switchable PL under variable

temperatures, which suggests the stability of NCs in the printed band over a range of temperatures.

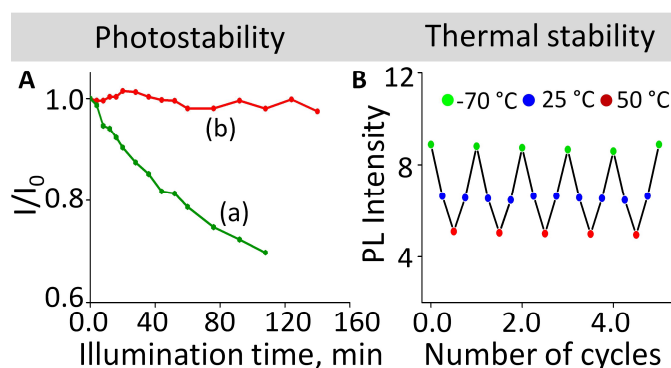


Figure 5.7: (A) Plot of I/I_0 vs. illumination time recorded from (a) NC solution and (b) printed band illuminated at 365 nm. (B) Plot of PL intensity vs. number of temperature cycles recorded from the printed band kept at -70 °C, 25 °C, and 50 °C.

Additionally, the unaltered optical absorption features of NCs (**Figure 5.8A**) recorded after dipping the printed band in liquid nitrogen, cold water, and warm water proved the stability of NCs in different temperatures. As expected, PL intensity was maximum at low temperatures owing to the least rotational and vibrational movements of bound ligands on the NC surface. The photograph showing the enhanced PL from the printed band before and after dipping in liquid nitrogen is shown in **Figures 5.8B** and **C**. The above set of experiments also suggests the durability of printed materials in a wet environment. To further study the moisture effect, we have recorded and compared the PL spectra of the printed band after wetting (**Figure 5.9A**). The analog PL spectra recorded from the printed band under dry and wet conditions confirm their stability in humid settings. Photographs of a wet band under visible and UV lights (inset in **Figure 5.9A**) show their hydrophobicity. The integrity of NCs in the printed band was tested by keeping them in a water (Millipore) bath for three days. A robust PL from the

printed band showed exceptional stability of NCs in water (**Figure 5.9B and C**). The hydrophobicity of the printed band was also studied by using contact angle measurements. The experimental details are given in **Chapter 2**. The water drop profile used to determine the water contact angle on the printed band is shown in **Figure 5.10A and B**. The measured contact angle from the NC-PU printed band ($93.72 \pm 0.85^\circ$) is comparable to the PU-alone printed band ($95.78 \pm 0.5^\circ$). A slight decrease in the contact angle of the NC-PU printed band is attributed to the polar nature of NCs.

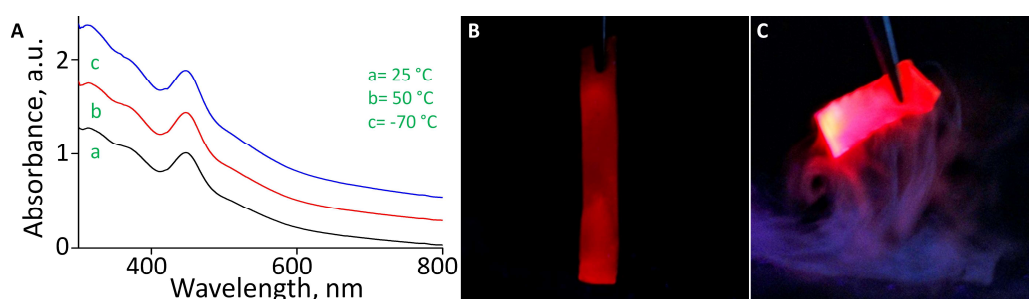


Figure 5.8: (A) UV-Vis absorption spectra recorded from the printed band kept at different temperatures. (B and C) The photographs of the printed band under UV light (B) before and (C) after dipping in liquid nitrogen.

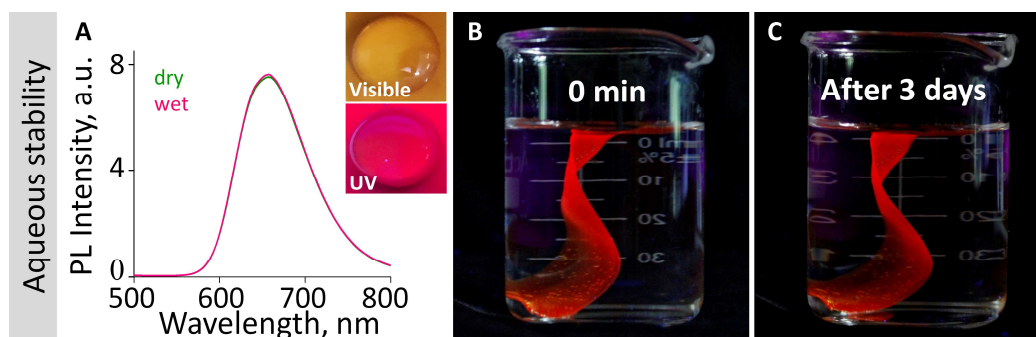


Figure 5.9: (A) PL spectra recorded from the printed band under wet and dry conditions. Photographs of a wet band under visible and UV light are shown in the inset. (B and C) The photographs show the long-term stability of the printed band under water.

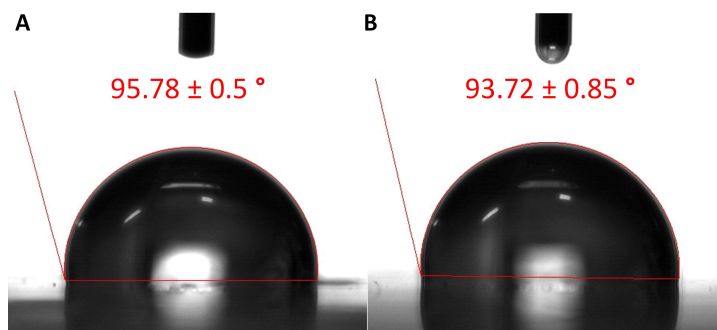


Figure 5.10: The water drop-profiles on (A) PU-alone and (B) NC-PU printed bands.

Further, we have tested the elasticity of printed free-standing bands (3 cm x 1 cm x 0.01 mm) by stretching and relaxing them multiple times. Photographs (under UV light) captured during the different sequences of stretching and wincing (**Figure 5.11A and B**) demonstrate the flexibility and mechanical strength of the printed bands. We also tested the restoring ability of the printed band after stretching. The photographs captured before and after the stretching are shown in **Figure 5.11C**. This suggests a nearly complete recovery in the size and shape of the printed band. Later, tensile strength and elongation at the breaking point of the printed band were tested and compared with the PU band. The stress-strain curve recorded from the NC-PU and PU-alone printed bands is shown in **Figure 5.11D**. Notably, consistent data points were observed from different sets of measurements. The tensile strength of the NC-PU band was slightly decreased from 28.4 ± 2.1 MPa to 25.32 ± 0.6 MPa. This could probably be due to the molecular interactions between NCs and PU moieties discussed earlier. NC-PU band withstood 229 ± 16 % strain, comparable to the PU band (253 ± 10 %). All the above spectroscopic information suggests that NC in ink is stable and reliable for printing any relevant documents.

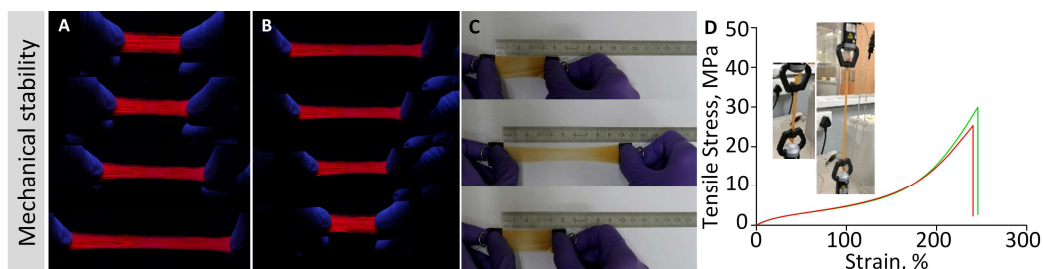


Figure 5.11: Photographs of the printed band captured during the (A) stretching and (B) wincing test under UV light. (C) The photographs show the restoring ability of NC-based printed band after stretching. (D) The stress-strain curves recorded from the NC-PU (red) and PU-alone (green) printed bands. The photographs taken during the measurement are shown in the inset.

5.2.4 Fabrication of QR codes on currency

Proven by the stability of NC-based luminescent ink, we have further employed them to fabricate an electronic security label on the currency. The schematic representation of the stencil-printing technique used to print a static QR code is shown in **Figure 5.12A**. The QR code-stencil pattern previously encrypted with confidential text has been used to print security labels. The photographs (under visible and UV light) of a QR code printed on an A4 paper are shown in **Figure 5.12B**. Here, the blue background (under UV light) is because of the fluorescence coming from the optical brightener (OB) used in the paper. As a result, the red emission of NC was merged with OB emission. Interestingly, we found that the printed QR code is readable only under UV light. This is due to the optical contrast illusion created by the combination of blue and red emissions from OB and NCs, respectively. Later, we extended the same strategy to print high-security QR codes on a currency. Since the raw materials vary from currency to currency during their manufacture, it is very essential to ensure a homogeneous surface on the currency as a background for QR code printing. Also, the QR code recognition and decryption necessitate a significant difference in the background-to-

foreground color contrast. To address such challenges, we have selected thiophene-based OB (BBOT; inset **Figure 5.12C**), which is extensively used in printed electronics and laser applications. The absorbance spectrum of thiophene-based OB is shown in **Figure 5.12C**. The better solubility of this molecule in THF helped to make highly uniform OB-PU dispersion. An interface layer of OB-PU was initially printed on the currency, which helps to ensure a uniform surface and durable adhesion of the QR code. Subsequently, the QR code has been printed on top of the OB-PU layer using the previously prepared NC-based luminescent ink. Printing details are given in **Chapter 2**. The combined PL spectrum of OB and NCs under 365 nm excitation is recorded and shown in **Figure 5.12D**.

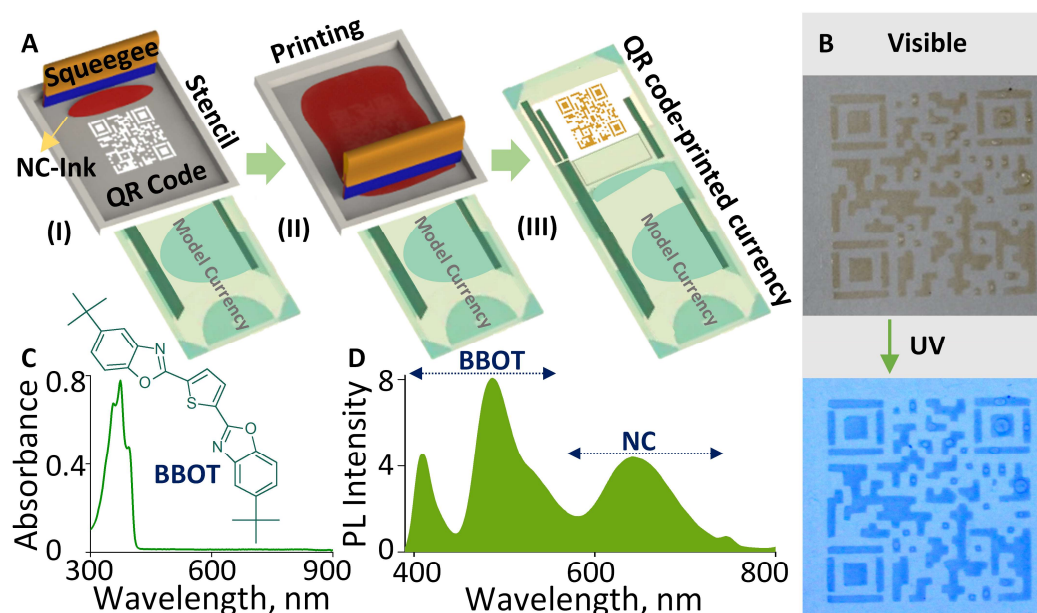


Figure 5.12: (A) Schematic representation of the screen-printing technique used to print QR code on the currency. (B) Photographs (under visible and UV light) of the printed QR code on A4 paper. (C) The UV absorption spectrum of thiophene-based OB (chemical structure is shown in the inset) and (D) combined PL spectrum recorded from a mixture of NCs and OB.

After printing the QR codes on the surface of fifty rupees currency, we tried to decrypt the data using the QR code reader in the smartphone. **Figure 5.13A** shows the photograph representing the QR code decryption process using a smartphone. The QR code printed currency was kept under UV light during the data decryption. The presence of OB helped to enhance the optical contrast between the interface layer (OB-PU) and the NC layer, which indeed supports the decryption of a security label specifically under UV light. Additionally, the OB-PU layer allows facile decryption of the QR codes printed on any universal currencies preloaded with unspecified UV-sensitive interfering inks. Though the combined emission of OB and NCs under 365 nm excitation (**Figure 5.12D**) reduced the PL brightness of NCs in ink (**Figure 5.13B**), we could successfully demonstrate the printing and electronic reading of a QR code on currency *via* the optical contrast illusion process. The printed security label is optically unclonable as its electronic absorption bands and PL features are highly precise. The photograph of QR code-printed currency captured under UV and visible lights is shown in **Figure 5.13B** and **C**. It is evident from the photograph that the printed security label is spotless and electronically readable without any destruction. The printed QR code is readable only under UV light. Later, we tested the mechanical stability of the QR code-printed currency by a folding assay. The photographic evidence shows (**Figure 5.13D**; under UV light) that the printed security label is stable even after multiple folding. Finally, we tested the aqueous stability of QR code-printed currency by dipping them in water (**Figure 5.13E**). The poor solubility of NCs and OB in water prevents their leaching. The data decryption was successful after both folding and wetting trials. The exceptional mechanical, thermal, photo, and aqueous stability of the printed documents suggest that NC-based luminescent ink can be further extended to develop the next-level security codes.

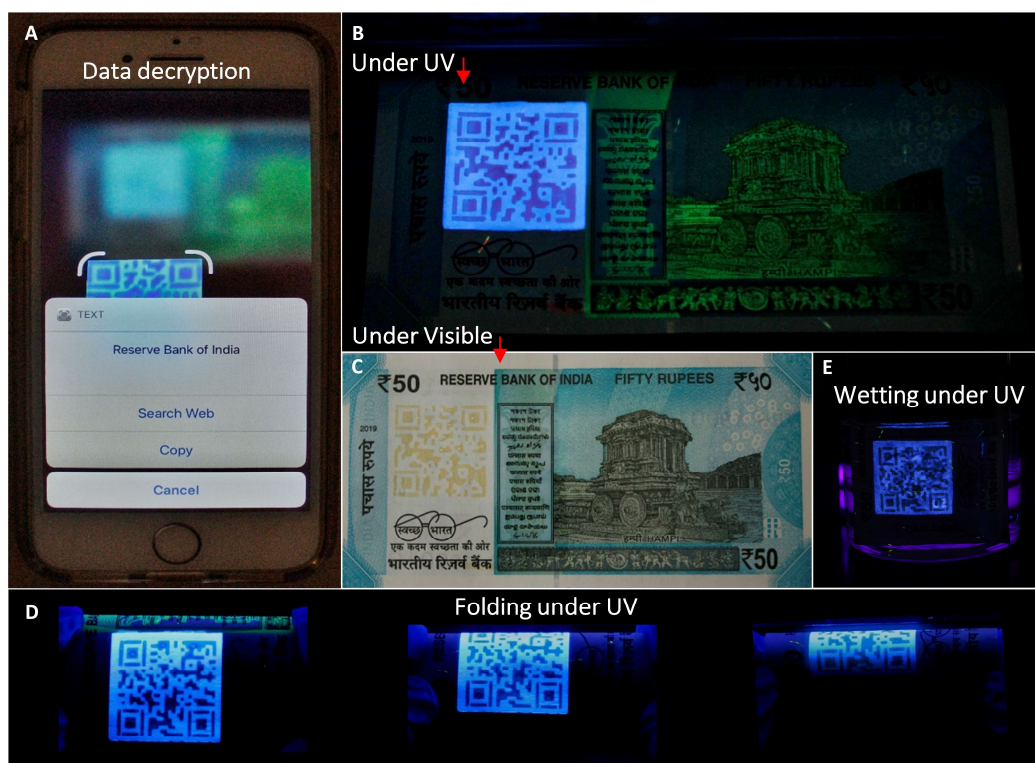


Figure 5.13: (A) Data decryption process using a smartphone under UV light. (B and C) QR code printed currency under UV and visible light. (D and E) Photographs captured during the folding and wetting assay of the QR code printed currency under UV light.

5.3 Conclusion

In summary, we have successfully demonstrated the room temperature fabrication of non-toxic, cost-effective, reliable, and optically unclonable luminescent security labels. Such security labels are fabricated through stencil-printing technology using near NIR-emitting precise NCs as the primary component in ink. The successful intercalation of NCs into the PU matrix helped to develop light-emitting and flexible ink. NC-based ink displayed brilliant PL owing to their strong $C-H \cdots \pi/\pi \cdots \pi$ interactions. Spectroscopic and microscopic techniques were employed to study the stability of NCs in ink and the printed band. The robust optical absorption,

PL, and molecular composition of NCs suggest their extended stability in ink. Detailed investigation of the printed security labels disclosed their unique mechanical, thermal, photo, and aqueous stability. This information helped to demonstrate the printing and electronic reading of QR codes on a currency using a smartphone. Encryption and decryption of a security label under a defined spectrum of light were demonstrated by creating an optical contrast illusion on the currency. The elastomeric binder helped to hold the printed QR code on currency even after multiple folding and wetting. The overall cost of a security label has been estimated to be approximately 0.013 US per stamp. The anti-counterfeiting technology can be further upgraded by printing the dynamic QR codes that enable us to update the encrypted data even after printing. In the future, this particular low-cost and non-toxic luminescent-based ink can be extended to develop wearable LEDs, healthcare sensors, pharmaceuticals, and food technology.

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CHAPTER 6

BIMETALLIC GOLD-COPPER NANOCCLUSERS FOR EFFICIENT ELECTROLUMINESCENT LIGHT- EMITTING DEVICES

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6.1 Introduction

Self-emissive light-emitting diodes (LEDs) have received significant attention in recent years due to their reduced energy consumption, environmental compatibility, and cost-effectiveness compared to conventional cathode-ray tube (CRT) and liquid crystal display (LCD) technologies.^[1,2] In the past few decades, organic (OLED), polymer (PLED), quantum dot (QLED), and emerging perovskites (PeLEDs)- based LEDs have been successfully developed using emissive organic molecules, polymers, inorganic nanocrystals, and organic/inorganic hybrid materials, respectively.^[3-8] Though all these emissive materials offer unique advantages, they face challenges such as laborious and high-temperature synthetic steps, minimal structural selection, resource sustainability, toxicity, requirement of passivating agents, and instability under light, heat, and moisture. In this context, the precision metal NCs could be another promising materials for both non-doped and simple solution processing devices due to their easy synthetic routes, less-toxicity, well-defined crystal structure, unique excited state characteristics, photo/thermal stability, environmental compatibility, and solid-state PL.^[9-18] Although the external quantum efficiency (EQE) of NC-based LED (NC-LED) was initially below 0.1%,^[19] a significant improvement has been made by combining them with a variety of host materials.^[15,20-29] The low PL quantum yield (QY) and poor device compatibility due to the bulky ligands still limit their applications in NC-LED.^[30] Recent developments in metal core engineering, ligand engineering, self-assembly techniques, and advanced synthetic procedures significantly helped to overcome such

issues.^[31–35] The solid-state emitting NCs with improved PL properties have been recently developed using a combination of rigid ligands and multiple metal precursors.^[36–38] Here, the metal core/ligand engineering has been utilized to reduce the PLQY gap between NCs and traditional luminescent materials by precisely controlling the core size, composition, and crystal structure.^[36–44] However, the development of an ideal blend of solid-state emitting NCs holding improved EQE is still in its infancy. To address this challenge, herein, we have designed and synthesized, highly stable and solid-state emitting gold-copper bimetallic NCs ($[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPE})_2]$) using adamantane thiol (HSadm) and 1,2-bis(diphenylphosphino)ethane (DPPE) as the primary and secondary ligands, respectively. $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPE})_2]$ NCs crystalized very quickly (within 30 min) when compared to its analog ($[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{TPP})_2]$) NC reported earlier.^[45,46] The spectroscopic data suggest that only one phosphine is bound to the gold and the second one is oxidized to phosphine oxide ($[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$). The strong hydrogen bonding established between $\text{P} = \text{O}$ and the hydrogen atoms of adamantane moieties facilitated strong inter-NC interaction and the rapid crystallization of NCs upon solvent evaporation. The existence of strong hydrogen bonding due to the *in situ* formation of $\text{P} = \text{O}$ strongly helped to enhance the overall stability and solid-state luminescence of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs. Due to the excellent photo/thermal stability of solid-state emitting $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs, we fabricated LEDs using this NC as an emitter. The solution-processed and non-doped NC-LEDs showed a maximum luminance of 1246 cd/m^2 and EQE of 12.60 % without using any host materials. The electroluminescence (EL) maximum of the fabricated device *c.a.* 668 nm with the International Commission on Illumination (CIE) coordinates of 0.70, 0.30, respectively. The CIE values at the edge of the chromaticity diagram represent an extremely saturated pure red

emission. These NCs with enhanced PL, high photo/thermal stability, and high performance are expected to offer new directions in the design and fabrication of efficient, non-toxic, and sustainable NC-LEDs for future sustainable technology.

6.2 Results and discussion

6.2.1 Synthesis and characterization of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPE})_2]$ NCs

The bimetallic gold-copper $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPE})_2]$ NC was synthesized using the modified one-pot chemical reduction method reported for the synthesis of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{TPP})_2]$ NCs. The detailed synthetic procedure is given in **Chapter 2**. The $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPE})_2]$ NCs were initially characterized by optical absorption and PL spectroscopy. **Figure 6.1A** shows the (i) UV-Vis absorption, (ii) excitation, and (iii) emission spectra of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPE})_2]$ NCs recorded in toluene. Multiple broad absorption humps *ca.* 325 nm, 515 nm, and 595 nm and a tail band at 390 nm represent different possible molecular electronic transitions of NCs. Notably, the excitation spectrum and the absorption spectrum are identical. PL spectrum of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPE})_2]$ NC shows an emission maximum *ca.* 668 nm at 515 nm excitation. Photographs of the NC solution and powder with violet color under visible light [**Figure 6.1B (b₁ and b₃)**], and displayed strong red emission under UV light irradiation [**Figure 6.1B (b₂ and b₄)**]. The diffuse reflection spectra (DRS, i) and PL (ii) spectra recorded from $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPE})_2]$ NC powder (**Figure 6.1C**) showed an inverse relationship with solution state spectra, which suggests that rather stable, highly luminescent, and solid-state emitting NC is a suitable material for LED fabrication. The chemical structure of ligands used for the preparation of NC ($\text{L}_1 = \text{Sadm}$ and $\text{L}_2 = \text{DPPE}$) is shown in the inset **Figure 6.1C**.

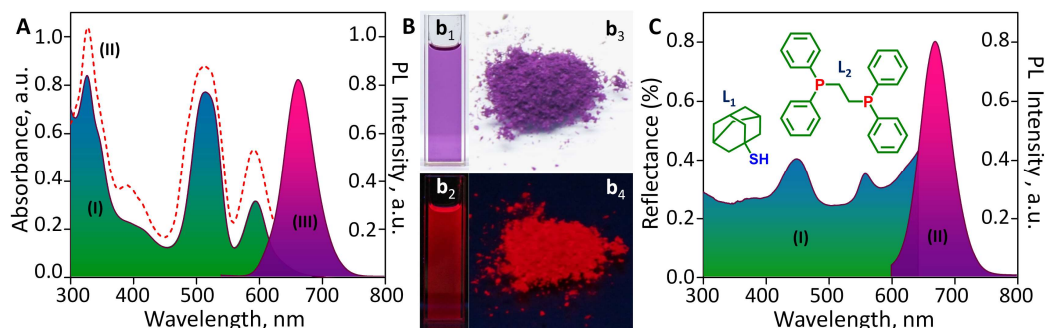


Figure 6.1: (A) UV-Vis absorption (i), excitation (ii), and PL (iii) spectra of [Au₂Cu₆(Sadm)₆(DPPEO)₂] NC recorded in DCM. (B) Photographs of a highly concentrated NC solution and powder captured under visible (b₁ and b₃) and UV (b₂ and b₄) lights respectively. (C) DRS (i) and PL (ii) spectra of NC powder showed an inverse relationship with the solution state. The chemical structure of both DPPE and HSadm is shown in the inset of Figure 6.1C.

The molecular composition of [Au₂Cu₆(Sadm)₆(DPPE)₂] NC was confirmed by using ESI-MS. The molecular ion peak *ca.* 2608 represents the parent [Au₂Cu₆(Sadm)₆(DPPE)₂] NC (**Figure 6.2A**, ii; pink = experimental and green = theoretical), in which one unbound phosphine from each DPPE molecule was oxidized and formed a P = O bond ([Au₂Cu₆(Sadm)₆(DPPEO)₂]). This clearly shows that only one phosphine from each DPPE has been directly bound to Au and the second one was oxidized during the synthesis of NC. The peak *ca.* 2377 represents the daughter ion peak after the dissociation of one [Cu(Sadm)] from the parent NC ([Au₂Cu₅(Sadm)₅(DPPEO)₂]; **Figure 6.2A**, i]. Molecular ion peaks *ca.* 2631 and 2647 represent the Na and Na/O adducts of [Au₂Cu₆(Sadm)₆(DPPEO)₂] NCs ([Au₂Cu₆(Sadm)₆(DPPEO)₂]Na; **Figure 6.2A** (iii) and [Au₂Cu₆(Sadm)₆(DPPEO)₂]NaO; **Figure 6.2A** (iv)). NCs were characterized using TEM by drop-casting and drying a DCM solution of [Au₂Cu₆(Sadm)₆(DPPEO)₂] NC on a carbon-supported copper grid. Although the TEM micrograph (**Figure 6.2B**) showed a nearly uniform size

distribution, a few bigger particles were also formed due to electron beam-induced fusion of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs.

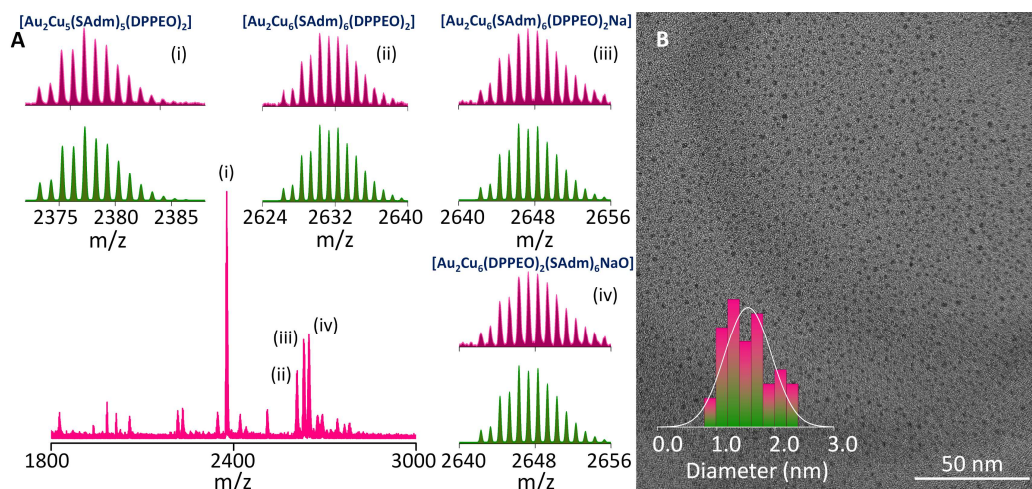


Figure 6.2: (A) ESI-MS of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NC with all possible fragmentation and addition. (B) TEM micrograph of NC with size distribution in the inset.

To further confirm the presence of bound ligands in the purified $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NC, ^1H and ^{31}P NMR spectra were recorded and analyzed in $\text{DCM}-d_2$ (**Figure 6.3**). The peaks *ca.* $\delta = 7.88\text{--}7.81$, $7.69\text{--}7.61$, $7.52\text{--}7.44$, $7.43\text{--}7.35$, $7.34\text{--}7.28$, 2.91 , and 2.82 ppm represent DPPEO ligand and $2.04\text{--}1.47$ ppm represents adamantane moieties. The splitting and downfield shift of aromatic broad peak *ca.* $\delta = 7.39\text{--}7.26$ ppm and aliphatic triplet *ca.* 1.9 ppm in the ^1H NMR spectrum of DPPE ligand confirms the transformation of unbound phosphine to $\text{P}=\text{O}$ bond. At the same time, the presence of two types of phosphines (bound and $\text{P}=\text{O}$) was more visible in the ^{31}P NMR spectrum of NCs (**Figure 6.4**). Though DPPE showed only a single peak *ca.* -13.6 ppm, a clear splitting and downfield shift (33.3 and 60.2 ppm) were observed in the case of NCs owing to the presence of anchored phosphine on the NC surface and free-standing phosphine bound to an electronegative oxygen atom.

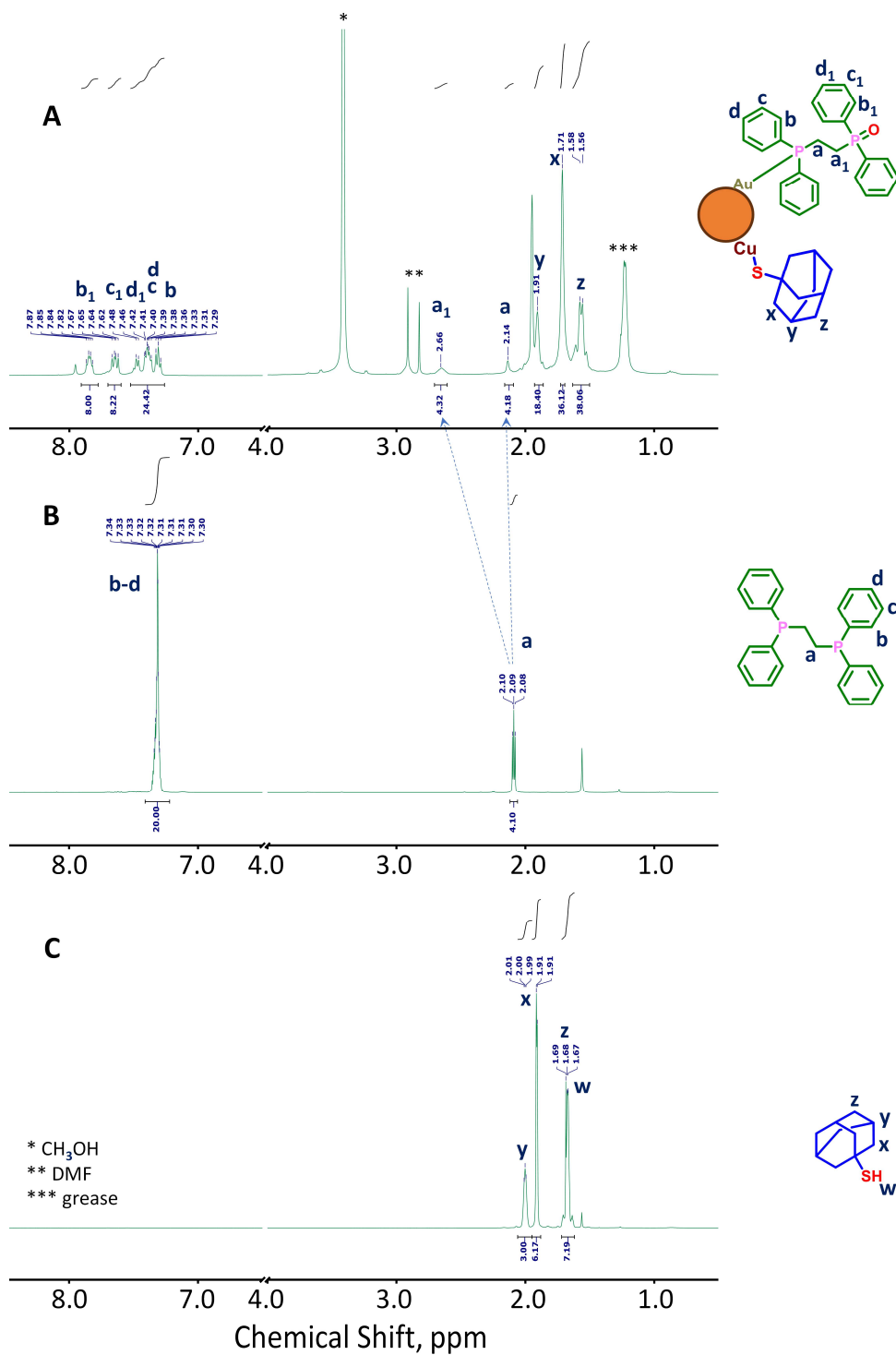


Figure 6.3: ^1H NMR spectra of (A) $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]\text{NC}$, (B) DPPE, (C) HSadm recorded in $\text{DCM-}d_2$.

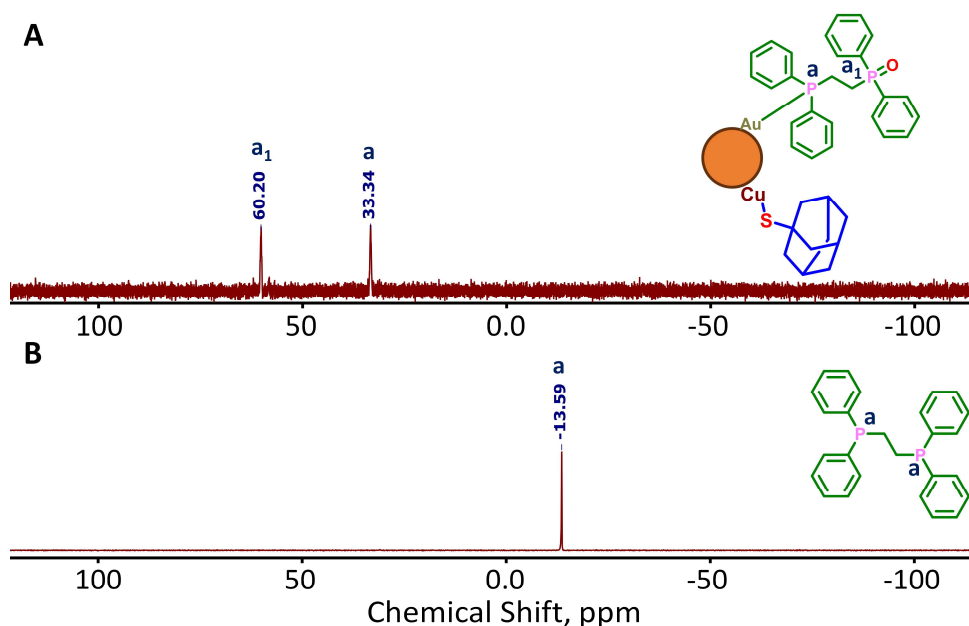


Figure 6.4: ^{31}P NMR spectra of (A) $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NC and (B) DPPE recorded in $\text{DCM-}d_2$.

Further, the core of NC and the nature of binding were studied in detail using XPS (**Figure 6.5**). The BE values of Au 4f and Cu 2p levels closely match with the previous report,^[45] which showed the presence of zero valence state gold (84.2 eV and 87.9 eV for Au 4f_{7/2} and Au 4f_{5/2}) and +1 valence state copper (952.5 eV and 932.7 eV for Cu 2p_{3/2} and 2p_{1/2}). Further analysis unveiled P 2p_{3/2} and 2p_{1/2} peaks at 131.5 eV and 132.38 eV, confirming the presence of bound DPPE within the NC. Though the two P atoms in each DPPE are different, it was difficult to differentiate as the BEs of Au-bound phosphine and P = O bonds are nearly close. The BE value of O 1s is *ca.* 531.5 eV. The S 2p BE values (161.7 eV and 162.8 eV for 2p_{3/2} and 2p_{1/2}) were consistent with thiolate binding, providing insights into the role of sulfur in the structure of NC.

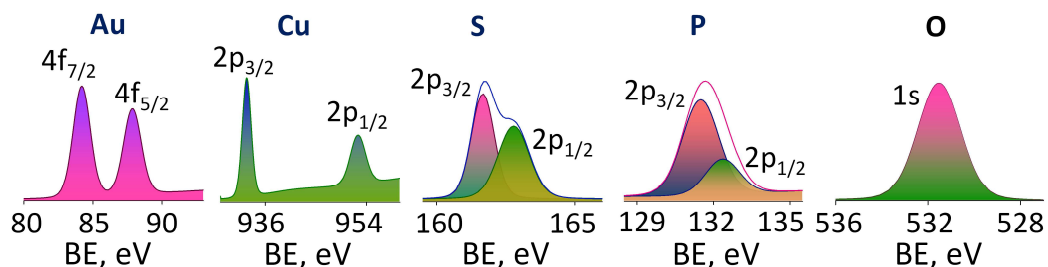


Figure 6.5: XPS spectra of the $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NC show the presence of gold, copper, sulfur, phosphorus, and oxygen.

Strict purity standards must be fulfilled when employing solid-state emitting NCs for the device fabrication. Crystallization is one of the best methods to produce extremely pure NCs despite its difficulty. Solvent (DCM) evaporation from the supersaturated solution of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NC (at room temperature) resulted in the formation of rod-shaped cuboid single crystals. Optical micrographs of crystals under white light and UV illumination are shown in **Figures 6.6A** and **B**, respectively. The single crystal was subjected to X-ray diffraction (XRD) analysis. The NCs crystallized in a Triclinic crystal system with the space group of P-1. The core structure was found to be similar to that of earlier reported $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{TPP})_2]$ NC (**Figure 6.6C-E**).^[45] From **Figure 6.6C**, it is evident that the central kernel of the NC consists of a benzenoid-like hexagonal planar copper (Cu_6) framework having an average intermetallic Cu-Cu distance of 2.67 Å. Two isolated gold atoms were capped on the top and bottom of the Cu_6 , giving rise to a hexagonal-bipyramidal geometry resembling the unidentified flying object (UFO)-like shape. The Cu-Au distance ranges from 2.8 to 3.0 Å and the distance between two Au atoms is 2.5 Å. Six adamantane-thiolate bonded with the hexagonal Cu_6 , where each Adm-S tied with the Cu-Cu edge of the hexagon through 'V-shaped' Cu-S-Cu motifs (**Figure 6.6D**). The average Cu-S distance is 2.1 Å and the Cu-S-Cu angle ranges from 73.87° to 76.03°. The overall arrangement of the six S

atoms can be visualized as a chair-shaped S_6 unit, where alternative S atoms are placed up and down the hexagonal Cu_6 unit. 3D adamantane units are placed in the central body of the NC in a planar fashion and sterically protect the NCs. Furthermore, two secondary DPPE ligands were independently anchored on each gold atom (**Figure 6.6E**), where one phosphine was connected with the Au atom having an Au-P bond distance of 2.34 Å and another phosphine underwent oxidation to form a robust P = O bond, known for its role as a potent hydrogen bond acceptor. This newly formed P = O bond was found to establish hydrogen bonds with the hydrogen atoms of adamantane moiety present in the nearby NCs. This strong hydrogen bond interaction played a crucial role in expediting the assembly of the $[Au_2Cu_6(Sadm)_6(DPPEO)_2]$ NCs and led to their rapid crystallization upon solvent evaporation. The distances measured between oxygen and adamantane hydrogen atoms were approximately 2.38 and 2.6 Å, which strongly supports the existence of hydrogen bonding in the present system (**Figure 6.6F**). Notably, the observed fast crystallization of the NC could be attributed to the remarkable strength of these hydrogen bonds. The presence of such strong hydrogen bonding interactions in the DPPE ligand-modified $[Au_2Cu_6(Sadm)_6(DPPEO)_2]$ opens new avenues for controlled NC assembly and crystal growth. The extended supramolecular packing (**Figure 6.7**) reveals a slanted layer-like lamellar arrangement of NCs. The distance between two adjacent layers is 16.32, 9.18 Å along a and b crystallographic directions, respectively.

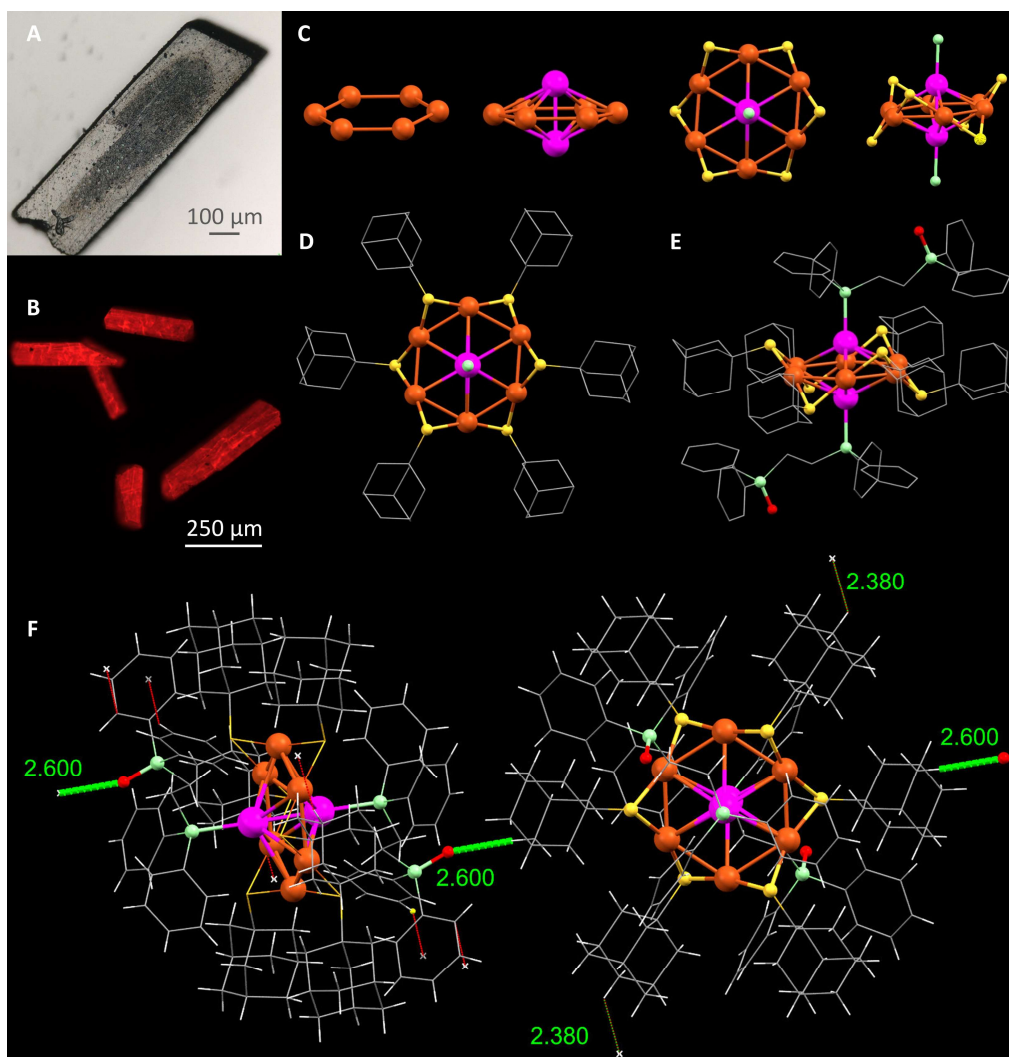


Figure 6.6: (A) Micrographs of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ crystal under (A) white light and (B) UV illumination. (C-E) The crystal structure of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NC, in which the central kernel of NC was made of a benzenoid-like planar hexagonal copper (Cu_6) framework. Two isolated gold atoms were connected on both the top and bottom of the Cu_6 kernel. The six adamantane-thiolates were bonded to the hexagonal Cu_6 framework. Finally, two secondary DPPE ligands were independently anchored on each gold atom, where one phosphine was directly connected to the Au atom and another phosphine underwent oxidation to form a robust $\text{P} = \text{O}$ bond. (F) DPPE-centered hydrogen bonding interaction between two adjacent NCs resulted in one-dimensional lamellar assembly of NCs. Cu (orange), Au (magenta), P (green), S (yellow), O (red), C (grey), and H (white).

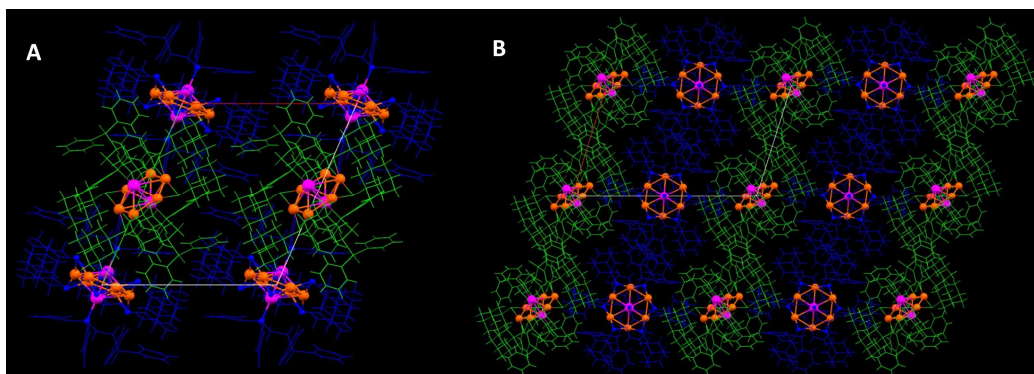


Figure 6.7: The extended supramolecular packing shows a slanted layer-like lamellar arrangement of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs.

6.2.2 Stability of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs

It is important to ensure the stability of NCs before looking at their possible real-world applications. We evaluated the stability of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs in solution, solid, and crystalized forms under a combination of light and different gases. The UV-Vis absorption spectra (**Figure 6.8A**) of NC solution (toluene) in the presence of inert gas (argon, i) and oxygen (ii) exhibited comparable optical absorption features to those of the same solution at ambient conditions (iii). At the same time, the PL intensity of the NC solution purged in argon increased (**Figure 6.8B**, i) compared to ambient conditions (**Figure 6.8B**, ii), but decreased in the presence of oxygen (**Figure 6.8B**, iii). Though the PL intensity was dropped in the presence of oxygen, it increased when argon was purged once more. The recovery in the PL intensity of NC solution in the presence of argon and unaltered optical absorption features proved the stability of NCs under different gases. The photostability of NCs in both solution and solid-state (film) was examined by comparing their PL intensity before and after exposure to UV light (345 nm; low power) at different time intervals. A plot of I/I_0 (I_0 represents the initial PL intensity) vs. illumination time shows better photostability for NC film (**Figure 6.9A**, i) compared to its solution

(**Figure 6.9A**, ii). Though the NC solution photobleached within 60 min of illumination, the NC film withstood for a longer time, which is more evident from the photographs captured after the UV light exposure (inset in **Figure 6.9A**). The temporal PL (**Figure 6.9B** and **C**) and absorption (**Figure 6.9D** and **E**) spectra recorded from the solution and film are given in **Figure 6.9B-E**, respectively. The absorption spectra of NC solution (**Figure 6.9E**) clearly show the decomposition of NCs after illumination under UV light. At the same time, the film sample showed all the characteristic features of NCs (**Figure 6.9D**). The intact optical absorption features of NC film recorded after the UV exposure revealed the photostability of NC in the ensemble solid-state. The photostability of single crystals derived from NC is also evaluated in detail under different gases. Before being exposed to a high-power CW laser (512 nm), the single crystals placed inside a plastic petri dish were sealed and purged with argon gas *via* a syringe needle. The PL intensity trajectory of a single crystal recorded *in situ* under an argon atmosphere showed stable photon counts (**Figure 6.9F** i). However, the crystals photobleached quickly when the argon was replaced with oxygen or air (**Figure 6.9F** ii). The photograph of a single crystal used for the experiment is shown in the inset of **Figure 6.9F**. The overall data suggest that the photostability of NC is better when the crystals are stored under an inert atmosphere.

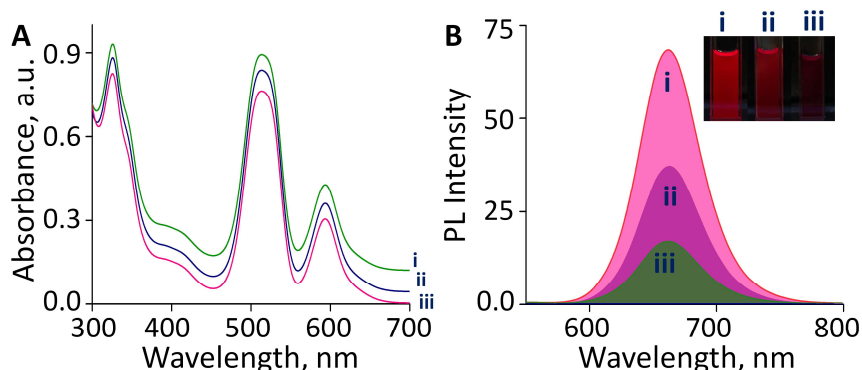


Figure 6.8: (A) UV-Vis absorption and (B) PL spectra of NC solution recorded under (i) inert, (ii) ambient, and (iii) oxygen conditions. The photographs of corresponding solutions are shown in the inset of Figure 6.8B.

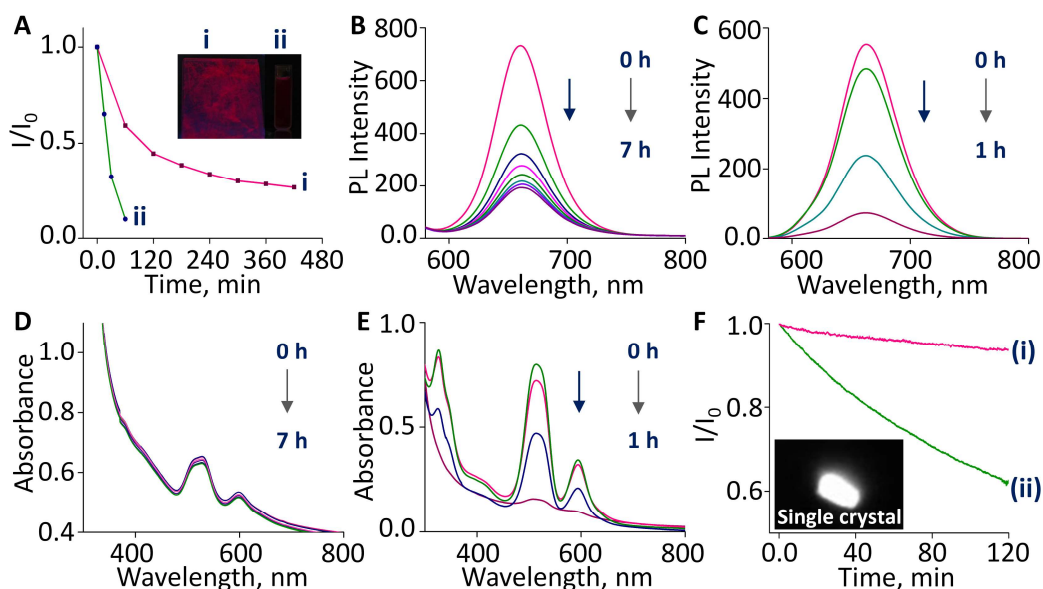


Figure 6.9: (A) Plot of I/I_0 vs illumination time for (i) NC film and (ii) solution shows the photostability. The inset in Figure 6.9A shows the photographs of NC film and solution after the illumination. (B and C) Temporal PL spectra recorded from the NC (B) film and (C) solution under UV illumination. (D and E) Temporal UV-Vis spectra recorded from the NC (D) film and (E) solution under UV illumination. (F) Plot of I/I_0 vs illumination time for a NC crystal under (i) inert and (ii) oxygen atmosphere.

The PL lifetime of NC solution and film was recorded and analyzed using time-resolved spectroscopy. **Figure 6.10A** (i and ii) shows the PL decay profile (time-correlated single-photon counting, TCSPC) of NC solution recorded under (i) ambient and (ii) argon atmosphere using 405 nm excitation. In both cases, the NC solution showed a biexponential relaxation with one fast and one slow component. The average lifetime of NC solution increased from 1292 ns to 4392 ns in the presence of argon gas. The average lifetime of NC film under inert settings has also increased from 2186 ns to 2697 ns (**Figure 6.10B**) due to its reduced excited state interactions in the solid state.

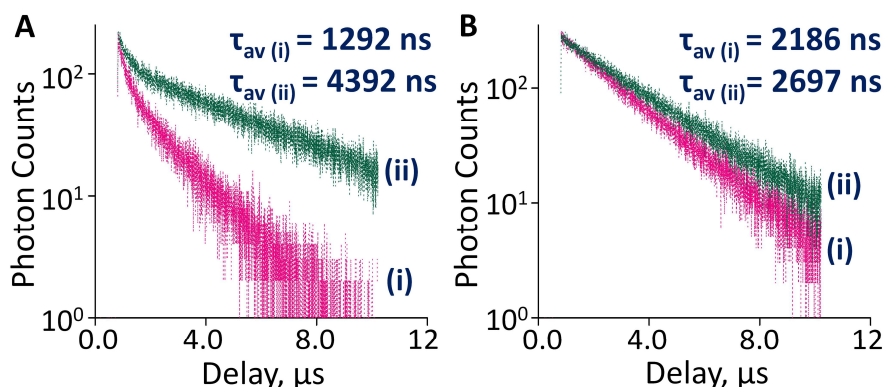


Figure 6.10: PL decay profile of (A) NC solution and (B) film under (i) ambient and (ii) inert conditions.

6.2.3 Solvent induced aggregation behaviour of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs

We investigated the aggregation behavior of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NC solution (THF) in the presence of poor solvents such as H_2O . The addition of water into the NC solution in 1:1 volume ratio resulted in the formation of a cloudy solution with enhanced PL. To understand this phenomenon in detail, the morphology and PL intensity changes of NC solutions after the consecutive addition of water are recorded and analyzed. Remarkably, the

transparent purple NC solution preserved its transparency until the volume fraction of water ($f_w = \text{vol}_{\text{water}}/\text{vol}_{\text{THF+water}}$) reached 50%. The solution became cloudy when the f_w increased from 50% to 90%, suggesting aggregation of NCs with an enhancement in the PL intensity. **Figure 6.11A** shows the photographs of NC solutions (under visible and UV lights) prepared in different f_w (0%, 20%, 40%, 50%, 60%, 70%, 80% and 90%). From the PL spectra of NC solutions at different f_w (**Figure 6.11B**), it is found that PL intensity increased till 60% of f_w and started to decrease up to 90% with a maximum intensity at 60%. The TEM images of NC solution at different f_w are shown in **Figure 6.11 C-F** (50%, 60%, 70%, and 90%). Though spherical assemblies are formed in all cases, the average diameter (size of the spheres) is found to be different in each case. To further confirm the discrepancy in size, FESEM images of NC solutions at different f_w (50%, 60%, 70%, and 90%) are captured (**Figure 6.11 G-J**). Similar to TEM micrographs, FESEM also shows the spherical assembly with an average diameter increased from 50% (~160 nm) to 60% (~190 nm) and then decreased systematically from 70% (~150 nm) to 90% (~70 nm). The changes in the size of NC assembly is more evident in the DLS data (**Figure 6.12A**). The size of the assembly is found to be maximum when f_w is 60%, which is in good agreement with maximum intensity in the PL spectra (**Figure 6.11B**) and the scattering in the UV-Vis absorption spectra of NC solution at different f_w (**Figure 6.12B**). Since the best assembly happened at 60%, we further evaluated the morphology of assembled spheres ($f_w = 60\%$) using AFM. From the larger area AFM topography image (**Figure 6.12C**), the average thickness and diameter of a single sphere is found to be $\cong 200$ nm and 250 nm, respectively. Since the AFM image is in good agreement with TEM and FESEM micrographs, the possibility of electron beam-induced assembly could be avoided.

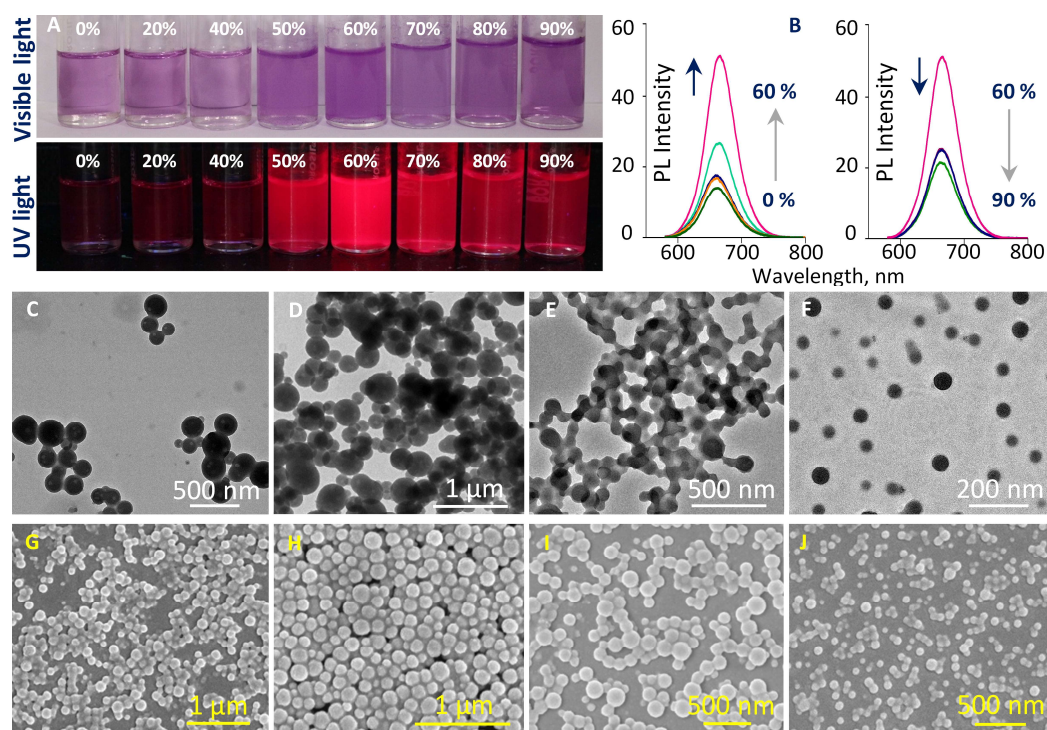


Figure 6.11: (A) Photographs of NC solution (under visible and UV light) prepared in different f_w . (B) Corresponding PL spectra (C-F) TEM and (G-J) FESEM micrographs of NC assembly fabricated at (C & G) 50%, (D & H) 60%, (E & I) 70%, and (F & J) 90% f_w .

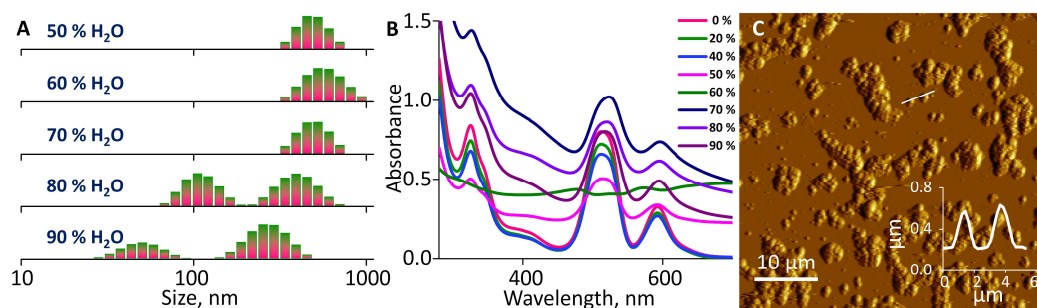


Figure 6.12: (A) DLS and (B) UV-Vis absorption spectra of a THF solution of $[Au_2Cu_6(Sadm)_6(DPPEO)_2]$ NC at different f_w . (C) Large area AFM image of NC assembly formed at 60% f_w .

The STEM image and elemental mapping of a single assembled sphere shows the presence of gold, copper, sulfur, phosphorus, and oxygen (**Figure 6.13**

A-F). Low and high-magnification bright-field (BF) and dark-field (DF) STEM images are given in **Figure 6.13 G-L**. To further understand the internal morphology and 3D view of the assembly, 3D reconstruction using transmission electron tomography (ET) was performed (**Figure 6.14D** and **E**). Accordingly, TEM micrographs were collected at different tilt angles between $\pm 70^\circ$ with an increment angle of 2° (**Figure 6.14A-C**). The 3D reconstruction and cross-sectional views show the presence of densely packed NCs in the assembled spheres. ET reconstruction data is in agreement with AFM, FESEM, and TEM, as shown above. Importantly, a slight deformation is observed in all spherical particles due to drying artifacts and strong adhesion to the support film.

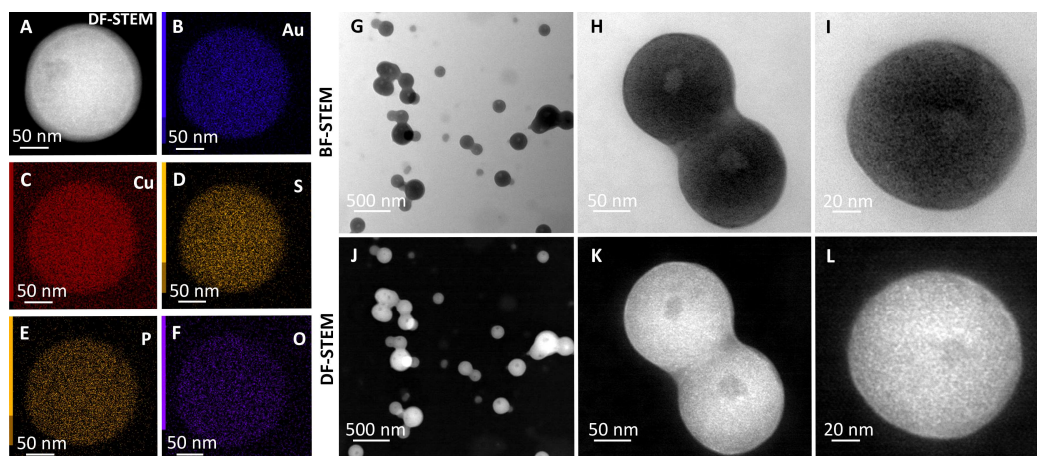


Figure 6.13: (A-F) (A) STEM image (60%) and elemental maps of a single sphere show the presence of (B) gold, (C) copper, (D) sulfur, (E) phosphorus, and (F) oxygen. (G-L) Bright-field and dark-field STEM images captured from larger area assembly, and assembled monomer and dimer.

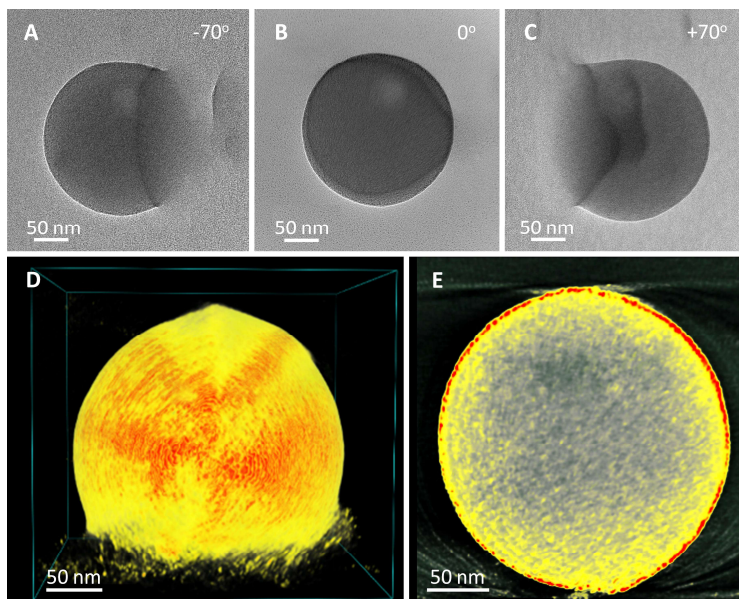


Figure 6.14: (A-C) TEM micrographs of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NC assembly at different tilt angles. (D) 3D reconstruction electron tomogram, and (E) the cross-sectional view shows the presence of densely packed NCs.

6.2.4 Electroluminescent light-emitting device fabrication

To investigate the EL performance of $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs, non-doped device was fabricated with following device architecture: Glass/ITO/PEDOT: PSS (40 nm)/PVK (30 nm)/ $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs (25 nm)/TPBi (50 nm)/LiQ (2 nm)/Al (100 nm) (**Figure 6.15A**). The structures of the organic materials used in the device fabrication are shown in **Chapter 2**. The device performance characteristics are shown in **Figure 6.15B-F** and summarized in **Table 2**. The EQE vs Luminance curve shows a maximum external quantum efficiency (EQE_{max}) of 12.6 % with a turn-on voltage of 3. The J-V-L curve shows a maximum current density of 387 mA/cm^2 and a maximum Luminance of 1246 cd/m^2 . The device shows the maximum current efficiency (CE_{max}) and power efficiency (PE_{max}) of 3.66 cd/A and 3.84 lm/W , respectively. The EL spectra show a maximum EL wavelength (λ_{EL}) of 668 nm with the CIE chromaticity coordinates of (0.70,

0.30) at 7 V. The EL spectra show the FWHM (full-width half maximum) of the $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs-based device to be 72 nm. The CIE coordinates of the $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs-based device are located at the edge of the chromaticity diagram, which represents the most saturated red color light. The EL spectra of the $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs-based device were also taken at various voltages (5–10 V; **Figure 6.15B**), and no significant residual emission peak was observed. This indicates that the fabricated $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$ NCs-based device is very stable under different operating voltages and the electron-hole recombination occurs within the emissive layer at different operating voltages.

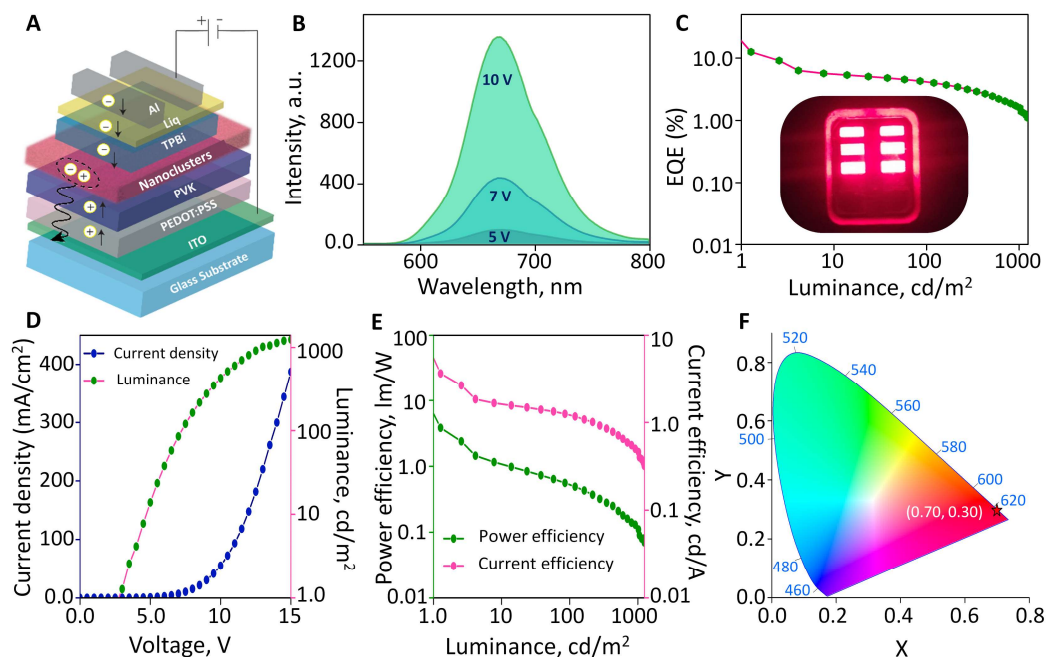


Figure 6.15: (A) Schematic of device structure. (B) EL spectra of the device at 5V, 7V, and 10V. (C) EQE vs Luminance curve. The inset shows a photograph of the fabricated LED device. (D) Current density-voltage-luminance curve of the device. (E) Power efficiency-luminance-current efficiency curve of the device. (F) Chromaticity diagram of the device.

Emit ting layer	Turn-on Voltage (V) @ 1 cd/ m ²	L _{max} (cd/ m ²) @ 15V	EQE _{max} (%)	CE _{max} (cd/ A)	PE _{max} (lm/ W)	λ(EL) _{max} (nm) @ 11V	CIE @ 7V (x, y)	FWHM (nm)
NC	3.00	1246.06	12.57	3.66	3.84	668.0	0.70, 0.30	72.62

Table 6.1: The summary of device characteristics.

L_{max} = maximum luminance, EQE_{max} = maximum external quantum efficiency, CE_{max} = maximum current efficiency, PE_{max} = maximum power efficiency, λ(EL)_{max} = electroluminescent maximum wavelength.

6.3 Conclusion

In summary, we have successfully demonstrated the fabrication of an EL-LED using the solid-state emitting [Au₂Cu₆(Sadm)₆(DPPEO)₂] NCs. The bimetallic copper-gold NCs stabilized using a magical combination of HSadm and DPPE crystalized rapidly during solvent evaporation. Oxidation of one phosphine into P = O during the synthesis of NCs helped to establish a strong hydrogen bonding with the adamantane hydrogen from neighboring NCs. These NCs showed exceptional photostability when their crystals/films were preserved in inert conditions. The solvent-induced aggregation behavior of NC solution was studied in detail by changing the volume fraction of water. NCs were self-assembled into spherical superstructures with enhanced PL. Multiple spectroscopic and microscopic techniques have been employed to study the assembly and morphology of superstructures. The average diameter of assembled superstructures was found to be maximum at 60% volume fraction, which systematically reduced with increasing the volume fraction. DLS data was in good agreement with TEM and FESEM micrographs. HRTEM, ET reconstruction, AFM, and FESEM data revealed the presence of thickly packed

NCs in the assembled superspheres. Finally, the fabricated LED display achieved a maximum brightness of 1246 cd/m² and an external quantum efficiency of 12.6% without using any additional host materials. These NCs are anticipated to be a suitable class of materials for the fabrication of sustainable, non-toxic, and efficient LEDs in the future.

6.4 References

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CHAPTER 7

SUMMARY AND FUTURE DIRECTIONS

CHAPTER 7

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7.1 Summary

This thesis investigated the synthesis of different functional NCs, their self-assembly, and the fabrication of advanced devices. Each chapter highlights the importance of molecular interactions and functional ligands in the process of fabricating self-assembled superstructures and devices. **Chapter 1** provided a comprehensive overview of the synthesis, isolation, properties, and applications of diverse NCs. The second half of this chapter discussed in detail about the hierarchical self-assembly of NCs, their properties, and the broad scope of their applications. Chapter **2** outlines the materials and experimental methods used in the investigations. **Chapters 3-6** extensively discuss the key findings and outcomes of the research work. The core of these investigations is summarized as follows. In **Chapter 3**, we have successfully demonstrated the reversible self-assembly of Au₂₅ NCs using light as the external stimulus. Thiolated-azobenzene chromophore synthesized using organic transformation reactions has been used to make Au₂₅ NCs. Photoisomerization of chromophore-functionalized Au₂₅ NCs under ultraviolet and visible light was studied systematically. The detailed spectroscopic and microscopic studies successfully demonstrated the reversible self-assembly of Au₂₅ NCs under two different spectra of lights. In **Chapter 4**, we discussed the role of chromophore-spacer length in the light-induced self-assembly of NCs. The self-assembly of gold NCs were studied in detail by introducing two photoswitchable NCs (C₃-NC and C₉-NC) fabricated using the thiolated-azobenzene molecule with different spacer lengths (C₃-AMT and C₉-AMT). The core and molecular information of both NCs were explored using various spectroscopic and microscopic techniques.

Photoactivation of C₃-NC and C₉-NC solutions separately at ambient temperature using 345 nm light resulted in the formation of self-assembled superstructures. The fast assembly was observed in C₉-NCs due to their improved photoswitching efficiency resulting from the negligible steric hindrance experienced at the NC-chromophore interface.

In **Chapter 5**, we have successfully demonstrated the fabrication of non-toxic, cost-effective, reliable, and optically unclonable luminescent security labels through a stencil-printing technology using the NIR-emitting Ag₂₉ NCs as the luminous component in the ink. Using this flexible and luminescent ink, we demonstrated the printing and electronic reading of QR codes on a currency using a smartphone. Encryption and decryption of a security label under a defined spectrum of light were demonstrated by creating an optical contrast illusion on the currency. The overall cost of a security label was only 0.013 USD per stamp.

In **Chapter 6**, we have successfully demonstrated the fabrication of electroluminescent light-emitting diodes (EL-LEDs) using highly stable bimetallic copper-gold NCs synthesized using adamantane thiol and 1,2-bis(diphenylphosphino)ethane ligands. Oxidation of one phosphine into P = O during the synthesis of NCs helped to establish a strong hydrogen bonding with the adamantane hydrogen from the neighboring NCs, which resulted in the rapid crystallization of NCs. [Au₂Cu₆(Sadm)₆(DPPEO)₂] NC under different volume fractions of water showed the periodic self-assembly and formation of spherical superstructures with enhanced PL. The exceptional photo and thermal stability of NCs in the solid-state enabled the fabrication of EL-LEDs without any additional host materials, with a maximum brightness of 1246 cd/m² and an external quantum efficiency of 12.6%.

7.2 Future directions

This thesis comprehensively discussed the self-assembly of functional NCs and their applications. In the initial working chapter, we successfully demonstrated the reversible assembly of NCs using different spectra of lights. Subsequent research efforts in this domain helped to understand the mechanism behind the controlled self-assembly of NCs using different molecular interactions established by the functional ligands tethered on the NC surface. The fabricated smart self-assembled architectures are expected to be ideal materials for electrochemistry, biology, photocatalysis, and light-harvesting technology owing to their collective and enhanced optical and electronic properties. Especially, the switchable NCs with appropriate molecular functionalities will be a potential cargo system to load and unload drug molecules by a light-triggered mechanism. Further, molecular control over the self-assembly of NCs by placing the chromophores suitably away from the nanosurface will be useful tools for developing next-generation switchable sensors, especially in biological, electrochemical, and electronic devices. In the last two chapters, we used the luminescent NCs for the fabrication of luminescent-based devices. Notably, we used these NCs for the fabrication of anticounterfeiting ink and EL-LEDs. We expected to improve the anticounterfeiting technique to the next level by printing the dynamic QR codes that enable to update the encrypted data even after printing. The low-cost and non-toxic luminescent-based ink will be useful for the development of wearable LEDs, healthcare sensors, pharmaceuticals, and food technology. The demonstrated NC-based EL-LEDs showcased the potential of these materials in this research field. The development of new LEDs using the chiral-luminescent NCs will be useful for brighter, efficient, and environmentally sustainable display technology. Further investigations into the scalable methods of NC synthesis and device fabrication are expected to

facilitate the large-scale manufacturing and commercialization of NC-based products. In addition, investigating new functionalities and advanced applications of NC-based assembled materials apart from those addressed in this thesis may lead to revolutionary technologies. For example, exploring the potential of assembled NCs in catalysis, energy, and biomedical fields is expected to address many unsolved societal and technological challenges. Finally, the interdisciplinary collaborations across chemistry, physics, materials science, engineering, and biology will eventually lead to the development of novel materials, tools, and technologies with significant societal and economic benefits.

CHAPTER 8

RECOMMENDATIONS

CHAPTER 8

RECOMMENDATIONS

- Develop scalable methods for the synthesis of NCs and introduce new functionalities to produce NC-based assembled materials.
- Explore advanced applications of NC-based assembled materials in catalysis, energy, and biomedical fields to address societal and technological challenges.
- Improve anticounterfeiting techniques by developing dynamic as well as invincible next-generation QR codes that allow updating encrypted data post-printing.
- Develop low-cost, non-toxic, luminescent NC-based polymer ink for applications in wearable LEDs, healthcare sensors, pharmaceuticals, and food technology.
- Innovate ligand and metal core design to produce new LEDs with higher EQE. Also introducing chirality using chiral-luminescent NCs for brighter, more efficient, and environmentally sustainable display technology.
- Develop scalable methods for the synthesis of NCs and fabrication of NC-based devices to enable large-scale manufacturing and commercialization.
- Foster interdisciplinary collaborations across chemistry, physics, materials science, engineering, and biology to develop novel NC-based nanomaterials, tools, and technologies with significant societal and economic benefits.

LIST OF PUBLICATIONS

- [1] Jose V. Rival, Nonappa, Edakkattuparambil Sidharth Shibu* Role of Chromophore Spacer-Length in the Light-Induced Self Assembly of Gold Nanoclusters. *Nanoscale* **2024** (Just Accepted).
<https://doi.org/10.1039/D4NR01954G>
- [2] Paloli Mymoona, Jose V. Rival, Nonappa, Edakkattuparambil Sidharth Shibu*, Chinnaiah Jeyabharathi* Platinum-Grafted Twenty-Five Atom Gold Nanoclusters for Robust Hydrogen Evolution. *Small* **2023**, 2308610.
<https://doi.org/10.1002/sml.202308610>
- [3] Jose V Rival^f, Jeladhara Sobhanan^f, Abdulaziz Anas*, Edakkattuparambil Sidharth Shibu*, Yuta Takano, and Vasudevanpillai Biju* Luminescent Quantum Dots: Synthesis, Optical Properties, Bioimaging and Toxicity. *Adv. Drug Deliv. Rev.* **2023**, 197, 114830.
<https://doi.org/10.1016/j.addr.2023.114830>
- [4] Jose V. Rival^f, Kavalloor Murali Lakshmi^f, Pakath Sreeraj, Sindhu R. Nambiar, Chinnaiah Jeyabharathi, Nonappa, and Edakkattuparambil Sidharth Shibu* Precision Nanocluster-Based Toroidal and Supertoroidal Frameworks Using Photocycloaddition-Assisted Dynamic Covalent Chemistry. *Small* **2023**, 19, 2207119.
<https://doi.org/10.1002/sml.202207119>
- [5] Jose V. Rival, Paloli Mymoona, Rajendran Vinoth, A. M. Vinu Mohan, and Edakkattuparambil Sidharth Shibu* Light-Emitting Atomically Precise Nanocluster-Based Flexible QR Codes for Anticounterfeiting. *ACS Appl. Mater. Interfaces* **2021** 13 (8), 10583-10593.
<https://doi.org/10.1021/acsami.0c21127>
- [6] Jose V. Rival, Paloli Mymoona, Kavalloor Murali Lakshmi, Nonappa*, Thalappil Pradeep*, and Edakkattuparambil Sidharth Shibu* Self-Assembly of Precision Noble Metal Nanoclusters: Hierarchical Structural

Complexity, Colloidal Superstructures, and Applications. *Small* **2021**, 17, 2005718. <https://doi.org/10.1002/sml.202005718>

- [7] Jose V. Rival, Nonappa, and Edakkattuparambil Sidharth Shibu* Light-Triggered Reversible Supracolloidal Self-Assembly of Precision Gold Nanoclusters. *ACS Appl. Mater. Interfaces* **2020**, 12 (12), 14569-14577. <https://doi.org/10.1021/acsami.0c00328>

Book chapter

- [1] Jose V. Rival, Paloli Mymoona, and Edakkattuparambil Sidharth Shibu Chapter 8 - Precision Nanoclusters: Promising Materials for Sensing, Optoelectronics, and Biology Editor(s): M. K. Jayaraj, P. P. Subha, Shibi Thomas, Nanomaterials for Sensing and Optoelectronic Applications, Elsevier, **2022**, 149-199. <https://doi.org/10.1016/B978-0-12-824008-3.00009-6>

Manuscript in preparation

- [1] Jose V. Rival, Savita, Jana Arijit, Nonappa, Vasudevanpillai Biju, Pachaiyappan Rajamalli, Thalappil Pradeep, and Edakkattuparambil Sidharth Shibu* Bimetallic Gold-Copper Nanoclusters for Efficient Electroluminescent Light-Emitting Devices.

CONFERENCE PRESENTATIONS

- [1] The paper entitled “From Nanoscale Precision to Macroscopic Impact: Self-Assembled Nanoclusters and Luminescence-Driven Device Fabrication” in the “International Conference on Advanced Materials for Sustainability, ICAMS 2023” held at the School of Physical Sciences, University of Calicut, Kerala. Received Best Paper Award for Poster.
- [2] The paper entitled “Precision Nanocluster-Based Toroidal and Supertoroidal Frameworks Using Photocycloaddition-Assisted Dynamic Covalent Chemistry” in the national conference, “Emerging Frontiers in Chemical Sciences, EFCS 2022” held at Farook College, Calicut, Kerala. Received Best Paper Award for Poster.
- [3] The paper entitled “Light-Emitting Atomically Precise Nanocluster-Based Flexible QR Codes for Anticounterfeiting” in the international conference, “Frontiers in Chemical Sciences, FCS 2021” held at the Department of Chemistry, University of Calicut, Kerala. Received Best Paper Award for Poster.
- [4] The paper entitled “Light-Emitting Atomically Precise Nanocluster-Based Flexible QR Codes for Anticounterfeiting” in the international conference, “Emerging Frontiers in Chemical Sciences, EFCS 2021” held at Farook College, Calicut, Kerala. Received Best Paper Award for Oral.
- [5] The paper entitled “Light-Triggered Reversible Supracolloidal Self-Assembly of Precision Gold Nanoclusters” in “National Science Day Competitions 2021” held at CSIR-CECRI, Karaikudi, Tamil Nadu. Received Best Paper Award for Poster.

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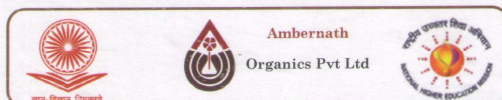
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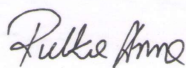
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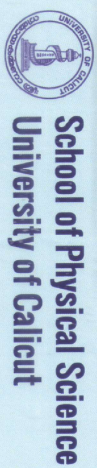
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Light-Triggered Reversible Supracolloidal Self-Assembly of Precision Gold Nanoclusters

Jose V. Rival, Nonappa, and Edakkattuparambil Sidharth Shibu*

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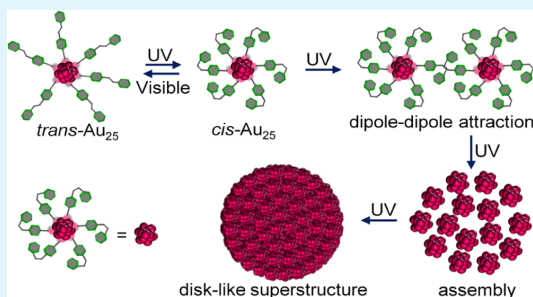
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Supporting Information

ABSTRACT: Monolayer thiol-protected noble metal nanoclusters are attractive nanoscale building blocks for well-defined colloidal superstructures. However, achieving facile reversible self-assembly of nanoclusters using external stimuli is still in its infancy. Herein, we report the synthesis and photon-assisted reversible self-assembly of thiolated azobenzene-stapled Au_{25} nanoclusters. Photoactivation of functionalized nanoclusters in dichloromethane by irradiating ultraviolet light at 345 nm results in a visual change and formation of disc-like colloidal superstructures ($d \sim 100\text{--}1000$ nm). The superstructures readily disassemble into individual nanoclusters upon irradiating with visible light at 435 nm. Systematic changes in both the electronic absorption bands and nuclear magnetic resonance spectra of chromophores in solution suggest that the photoisomerization of surface ligands drives the self-assembly. High-resolution transmission electron microscopy, electron tomographic reconstruction, dynamic light scattering, and small-angle X-ray powder diffraction show that the disc-like superstructures contain densely packed nanoclusters. Long-range self-assembly and disassembly under ultraviolet and visible light, respectively, demonstrate reversible photoswitching in nanoclusters.

KEYWORDS: photoisomerization, switchable Au_{25} nanoclusters, light-stimulated reversible assembly, electron tomography, superstructures



■ INTRODUCTION

Atomically precise noble metal nanoclusters (NCs) show diverse applications in many fields owing to their quantum confinement, nanometric dimensions, larger surface area, diverse functionalization, and stability toward chemicals and light.^{1–10} NCs with a varying number of metal atoms in the core and covalently bound functional ligands have been reported in the literature.^{11–26} Among them, functional thiolate-tethered NCs display important features, particularly Förster resonance energy transfer,²⁷ optical chirality,^{28,29} and biocompatibility useful for the construction of bioconjugated protein machinery for extracellular labeling and intracellular delivery.³⁰ Smart molecular imprinting on NC surfaces can also be extended to build self-assembled superstructures. Such novel materials can find applications in advanced optical materials due to their collective and enhanced optical properties that arise from the periodic organization. Recently, NC self-assemblies have been reported *via* dipole-induced van der Waals attraction,³¹ hydrogen bonding,³² C–H... π interactions,³³ metal chelation,³⁴ and aurophilic interactions.³⁵ Importantly, self-assembled gold NC superstructures have been shown to alter the luminescence, catalytic activity, and bioavailability.³⁴ Since NCs in such self-assembled structures interact with one another with local forces, the efficient reversibility of such static assemblies will be difficult. In this

context, photoactive molecules offer a unique opportunity to achieve reversible molecular self-assembly and even for plasmonic nanoparticles.³⁶ Therefore, it is relevant to investigate whether this approach can be implemented to NC self-assembly by developing photoisomerizing ligand^{37–42} tethered NCs. As the photostability of NCs and their interactions with photons are significantly different from those of the corresponding plasmonic nanoparticles, photon-assisted reversible self-assembly of NCs in solution at room temperature is still challenging. Furthermore, to achieve NC self-assembly in solution, it is crucial to overcome the thermal fluctuation of the surroundings, which is close to the inter-NC interaction.⁴³ In the literature, Au_{25} NCs functionalized with two types of photoswitchable chromophores, *viz.*, azobenzene⁴⁴ and spiropyran,⁴⁵ are known. However, the reported studies are limited to their spectroscopic investigations. A detailed understanding of the morphological changes and potential colloidal-level self-assembly is still lacking. To address

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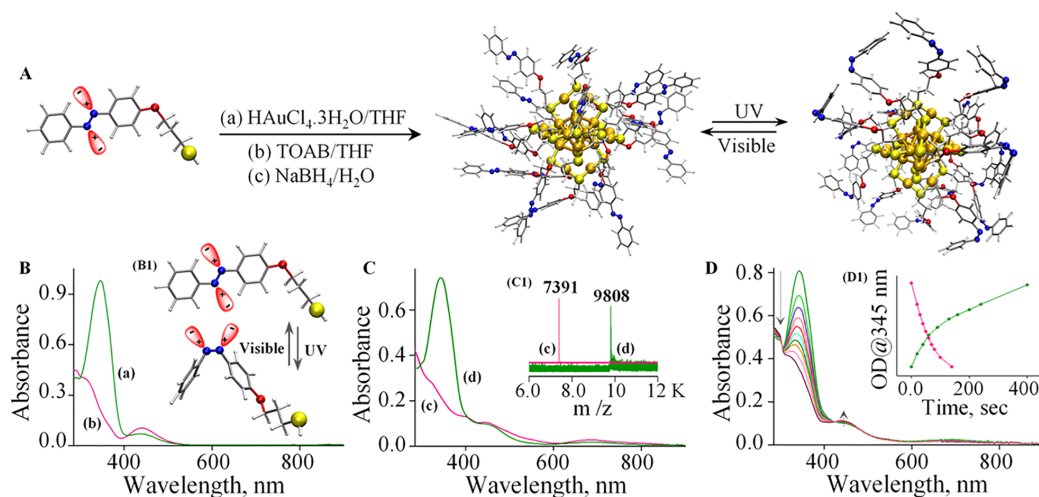


Figure 1. Synthesis and photophysical properties. (A) Schematic representation showing the synthesis, energy-minimized structures, and photoisomerization of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs. (B) Absorption spectra of $\text{C}_3\text{-AMT}$ under (a) visible light and (b) UV light. Energy-minimized structures of the two geometrical isomers of $\text{C}_3\text{-AMT}$ are shown in the inset (B1). (C) Absorption spectra of (d) $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ and (c) $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs. ESI-MS of both NCs are shown in the inset (C1). (D) Temporal absorption spectra of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ at 345 nm illumination. A plot of OD (ca. 345 nm) vs illumination time under ultraviolet and visible light is shown in the inset (D1).

this challenge, we demonstrate the synthesis and photon-induced reversible self-assembly of azobenzene-alkyl monothiol ($\text{C}_3\text{-AMT}$)-tethered Au_{25} NCs $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$. We show that when a solution of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ was irradiated with ultraviolet light (345 nm) disc-like superstructures ($d \sim 100\text{--}1000$ nm) were formed. The stable structure obtained readily disassembled upon irradiating with visible light (435 nm), demonstrating the light-triggered assembly and disassembly. The temporal evolution of the self-assembled superstructures was studied extensively using various spectroscopic and microscopic techniques followed by their correlation with electron tomography reconstruction.

First, we discuss the synthesis and characterization of $\text{C}_3\text{-AMT}$ ligand and $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs. AMT with a C_3 -spacer (Figure 1A) was synthesized according to a reported literature procedure.^{46,47} Details of reactions involved in the preparation of $\text{C}_3\text{-AMT}$ and its characterization (Scheme S1 and Figures S1–S3 in the Supporting Information (SI)) are provided in the Experimental Section. Absorption spectra of $\text{C}_3\text{-AMT}$ in dichloromethane (DCM) illuminated under ultraviolet (345 nm) and visible (435 nm) light are shown in Figure 1B. The trans isomer of $\text{C}_3\text{-AMT}$ (a) has an absorption maximum in the UV region ($\lambda_{\text{max}} = 345$ nm), whereas its cis isomer (b) absorbs more in the visible ($\lambda_{\text{max}} = 435$ nm) domain. Energy-minimized structures of the two geometrical isomers of $\text{C}_3\text{-AMT}$ optimized using density functional theory (DFT) are shown in inset B1. The time-dependent absorption spectra of $\text{C}_3\text{-AMT}$ illuminated separately at 345 and 435 nm are given in the SI (Figure S4A,B). When illuminated at 345 nm, the absorption spectra of $\text{C}_3\text{-AMT}$ show a gradual decrease in the optical density (OD) ca. 345 nm and an increased OD ca. 435 nm, whereas the opposite trend was observed when illuminated at 435 nm wavelength (inset in Figure S4B).

The synthesis of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs were achieved using a modified Brust–Schiffrin single-phase method.⁴⁸ To

compare the optical absorption features of the newly synthesized $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs, a phenylethanethiol (PET) analogue, $[\text{Au}_{25}(\text{PET})_{18}]^-$, was also synthesized and characterized.⁴⁸ Details are provided in the Experimental Section. Figure 1C shows the absorption spectra of (d) $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ and its comparison with that of (c) $[\text{Au}_{25}(\text{PET})_{18}]^-$. The peak ca. 680 nm (highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO)) in the absorption spectra of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ suggests the presence of monodisperse NCs. However, the peaks corresponding to HOMO–sp (ca. 450 nm) and d–sp transitions (ca. 400 nm) were merged with optical features of the azobenzene chromophore. The molecular composition of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ was analyzed using electrospray ionization-mass spectrometry (ESI-MS; negative ion mode), and the spectral patterns were compared with those of the PET analogue. The peaks (inset C1) at m/z 7391 and 9808 represent $[\text{Au}_{25}(\text{PET})_{18}]^-$ and $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs, respectively.

The appearance of a single peak ca. m/z 9808 in $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ in ESI-MS confirms the purity of the NCs. The metal core of NCs and the nature of binding were evaluated using X-ray photoelectron spectroscopy. Binding energies of Au 4f levels in $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ were in agreement with the reported values,⁴⁹ with Au 4f_{7/2} having ca. 84.06 eV and Au 4f_{5/2} ca. 87.75 eV (Figure S5). A slight change in the BE of these clusters is attributed to the different electron density of ligands. The S 2p binding energy was in accordance with thiolate binding.

We then studied the photoisomerization of Au_{25} NCs in DCM. Temporal absorption spectra of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs illuminated at 345 nm light (0.2 mW/cm²; Figure 1D) exhibits a gradual decrease in the OD ca. 345 nm and an increased OD ca. 435 nm (inset D1). Similar, but opposite, photoswitching behavior was seen at 435 nm (0.5 mW/cm²) excitation (Figure S6). The change in absorption spectra under

UV and visible light is attributed to the cis–trans isomerization of the surface azobenzene ligands, as shown using DFT energy-minimized structures of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ in Figure 1A.

Photoswitching aspects of $\text{C}_3\text{-AMT}$ and $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs were further evaluated by analyzing their

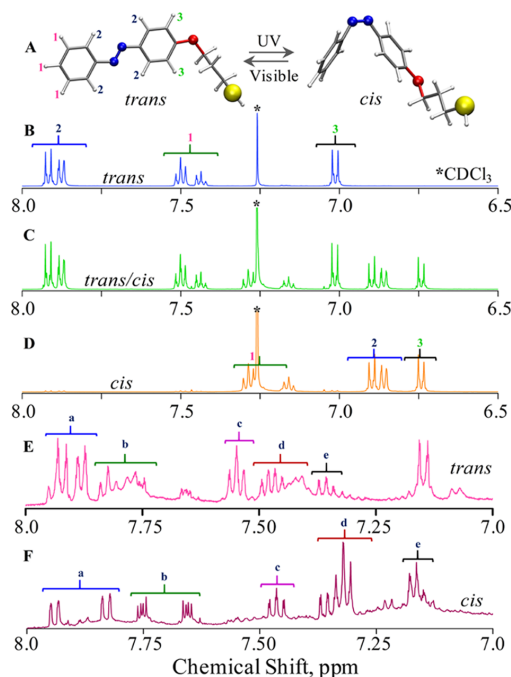


Figure 2. (A) Geometrical isomers of $\text{C}_3\text{-AMT}$. ^1H NMR spectra of (B) *trans*, (C) *trans/cis*, and (D) *cis* isomers of $\text{C}_3\text{-AMT}$ in CDCl_3 . (E, F) ^1H NMR spectra of *trans* and *cis* isomers of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ in $\text{acetone-}d_6$, respectively. Resonance peaks are assigned and labeled above the traces.

nuclear magnetic resonance (NMR) spectra (Figure 2). The ^1H NMR spectrum of *trans* $\text{C}_3\text{-AMT}$ (Figure 2B) shows three sets of peaks in the aromatic region, ca. 7.97–7.84 (dd, 4H), 7.54–7.4 (m, 3H), and 7.05–6.96 ppm (d, 2H). The NMR spectrum of the *cis* isomer (Figure 2D) shows an upfield shift due to a larger shielding effect compared to its *trans* counterpart. Figure 2C represents the NMR spectrum of a mixture of *cis* and *trans* isomers, recorded in between illumination. A similar photoisomerization was also observed for the surface $\text{C}_3\text{-AMT}$ ligands in Au_{25} NCs (Figure 2E,F). However, due to their different possible conformations as well as the chemical and magnetic nonequivalent nature of ligands,⁵⁰ the ^1H NMR spectrum of $\text{C}_3\text{-AMT}$ in $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ displays complex overlapping resonance peaks.

Reversible photoswitching in NCs was further investigated by transmission electron microscopy (TEM) imaging. First, Au_{25} NCs were characterized using TEM by drop-casting and drying $\sim 100 \mu\text{M}$ solution of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ in DCM on a copper grid with a carbon support film. However, due to electron beam damage, Au_{25} NCs underwent rapid coalescence; therefore, high-resolution imaging of individual NCs remained a challenge.^{45,49,51} Nevertheless, the nonaggregated

nature of Au_{25} NCs is evident from the TEM micrographs (Figure 3A). To monitor the light-induced self-assembly, $\sim 100 \mu\text{M}$ solution of NC in DCM at room temperature was illuminated at 345 nm light ($0.2 \text{ mW}/\text{cm}^2$) for 120 minutes in a temperature-controlled bath. The solution was continuously stirred during the photoisomerization process to avoid the possibility of thermally induced aggregation. The illuminated NC solution was drop-casted onto TEM grid and dried in the dark. Remarkably, TEM images of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs show the formation of circular superstructures (Figure 3B) with an average diameter of ~ 100 – 200 nm . The evolution of the self-assembled superstructures was investigated in detail by illuminating the same NC solution with 345 nm light for a longer illumination time. Similar trends were observed in the TEM analysis of samples illuminated for 240 min (Figure 3C). The overall diameter of the superstructures was increased from ~ 200 – 1000 nm . The increase in width and thickness suggests extended self-assembly of Au_{25} NCs. Large-area TEM micrographs of the self-assembled NC superstructures obtained by illuminating the NC solution for 120 and 240 min are shown in Figure S7. High-resolution TEM (HRTEM) images (Figure 3E,G) clearly show the presence of individual NCs. The above results suggest that the superstructure formation is facilitated by inter-NC interactions through the surface ligands.

Attractive dipole–dipole interactions³⁹ between nearby NCs in the *cis* arrangement facilitate the self-assembly in NCs. A cartoon representation of the dipole-induced attraction of NCs (Figure 3F), self-assembly of NCs, and their possible arrangements within the circular superstructure is shown in the SI (Scheme S2). Based on the observations from the time-dependent TEM micrographs, we found that the formation of circular monolayer aggregates of NCs is the early stage of the assembly. Accumulation of more *cis* NCs on such monolayer aggregates under continuous UV illumination helps to enhance the thickness and diameter of the superstructures. However, there is no regular order of NCs within the layer or between the layers. More interestingly, photoactivation of such self-assembled superstructures in solution at room temperature under 435 nm light ($0.5 \text{ mW}/\text{cm}^2$; 300 min) shows the formation of well-separated NCs by disassembly (Figure 3D). Large-area TEM images representing the stepwise disassembly of superstructures are given in the SI (Figure S8). A decrease in the diameter of the superstructures with illumination time and the presence of individual NCs suggest controlled disassembly.

Photographs of NC solutions used for reversible switching are given in the SI (Figure S9). Notably, there was no precipitation of NCs during assembly and disassembly. To further check the stability of the self-assembled NCs under dark conditions, we have recorded and analyzed the time-dependent absorption spectra of superstructures stored in a dark room. Absorption spectra (Figure S10) of assembled NCs do not show any changes in their optical absorption features, suggesting the stability of the superstructures in the dark. In other words, disassembly of superstructures can be triggered only in the presence of visible (435 nm) light.

To check the importance of $\text{C}_3\text{-AMT}$ in the light-induced assembly, the PET analogue, $[\text{Au}_{25}(\text{PET})_{18}]^-$ NC solution was illuminated at 345 nm light for 240 min. TEM images of $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs before and after the illumination are similar (Figure S11), which shows the inability of $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs for light-induced self-assembly. Addi-

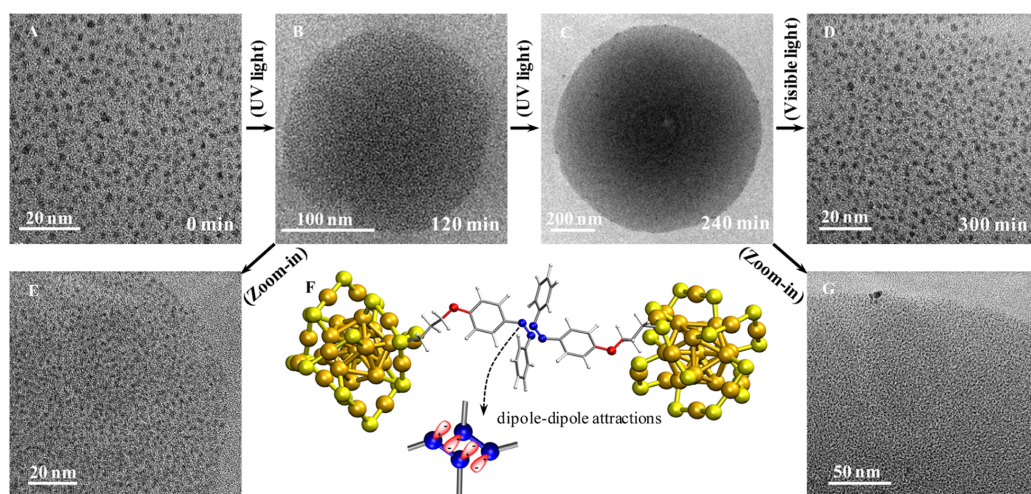


Figure 3. TEM micrographs of (A) trans $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs and (B, C) cis $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC assembly captured during (B) 120 min and (C) 240 min of light illumination (345 nm). The TEM image of self-assembled $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC superstructures after 435 nm illumination is shown in (D), clearly showing their disassembly. Zoom-in and focused HRTEM images taken from the edges are shown in (E) and (G), respectively. A cartoon representation of dipole-induced self-assembly in $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs is shown in (F).

tionally, we have analyzed the time-dependent absorption spectra of trans $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC solution under dark conditions. As there were no changes in the optical absorption features of NCs, the possibility of NC self-assembly in the dark was ruled out (Figure S12). These two control experiments validate the role of $\text{C}_3\text{-AMT}$ and light for the switchable assembly and disassembly in $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs. Apart from the circular structures, dimers were also formed during self-assembly (Figure S13A). Electron microscopic analysis at the interface of dimers shows well-organized NCs (Figure S13B).

The morphology and thickness of the superstructures were further evaluated by atomic force microscopy (AFM). A solution of self-assembled NCs drop-casted and dried on a silicon substrate was used for AFM measurements. The tapping mode AFM image (topography) of a single self-assembled superstructure (240 min illumination) shows an average thickness and diameter of 50 and 800 nm (Figure 4A,C), respectively. The morphology of the superstructures shown in the AFM image is similar to that obtained from the TEM analysis. The above results suggest that self-assembly occurs in solution in the presence of light, which helps us to rule out the possibility of electron-beam-induced self-organization of NCs on the TEM grid. The elemental

composition analysis of the self-assembled superstructures using energy-dispersive X-ray analysis (EDS) shows the presence of gold, sulfur, nitrogen, oxygen, and carbon. Elemental mapping and the corresponding spectrum are shown in Figure S14.

To further evaluate the light-induced assembly of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$, time-dependent dynamic light scattering (DLS) spectra of NC solutions illuminated at 345 nm light were measured. DLS measurements showed an increase in the size of the superstructures with illumination time. The average particle size within 120 min of illumination (345 nm) was ~ 250 nm, which was increased to ~ 550 nm upon continuous illumination, and finally to $\sim 1.5 \mu\text{m}$ (Figure S15A–C). On the other hand, a gradual decrease in the diameter of the superstructures was observed at 435 nm illumination (Figure S15D,E). An increase in the size of superstructures at 345 nm illumination and a decrease in the size of the superstructures at 435 nm illumination, respectively, confirm the switchable assembly in NCs. DLS data are in good agreement with TEM micrographs.

Transmission electron tomography (ET) reconstruction was carried out to gain information on the internal structural details of the self-assembled superstructures. Accordingly, the specimen prepared from a solution of NCs after irradiating for 240 min was used to acquire a series of two-dimensional (2D) projections between $\pm 69^\circ$ with an increment angle of 2° (details are provided in the Experimental Section). Figure 5A–C shows the TEM images of a superstructure tilted at -60° , 0° , and $+60^\circ$. Tilt series and corresponding three-dimensional (3D) reconstruction (Figure 5D–F) suggest that the superstructures are disc-like colloidal particles. It is important to note that the disc-like structures can also be partly due to the deformation resulting from solvent evaporation upon drying. However, these 3D superstructures are composed of densely packed NCs (Video S1). The results obtained from electron tomography reconstruction are in agreement with the AFM analysis results.

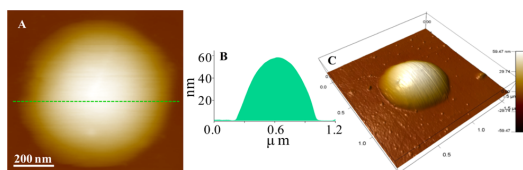


Figure 4. (A, C) AFM images of ((A) topography and (C) amplitude) a cis $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ self-assembled single superstructure captured after 240 min of illumination. The height profile is shown in (B).

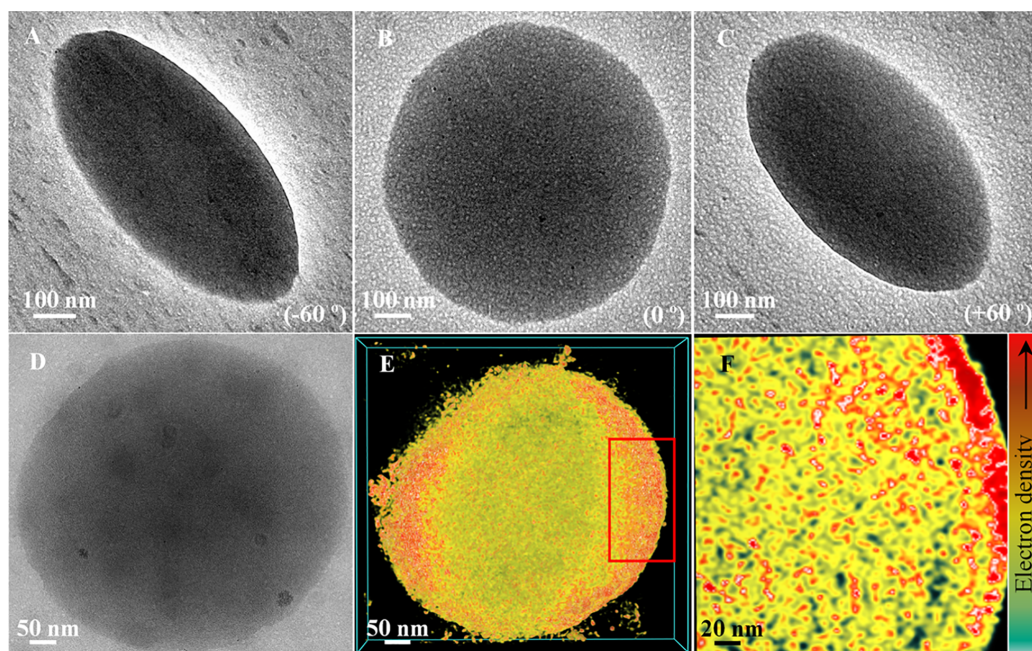


Figure 5. (A–C) TEM micrographs of a tilted self-assembled $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ disc-like superstructure collected at -60 , 0 , and $+60^\circ$. (D) TEM micrograph of a superstructure, (E) electron tomography reconstruction image, and (F) cross-sectional view of a self-assembled superstructure.

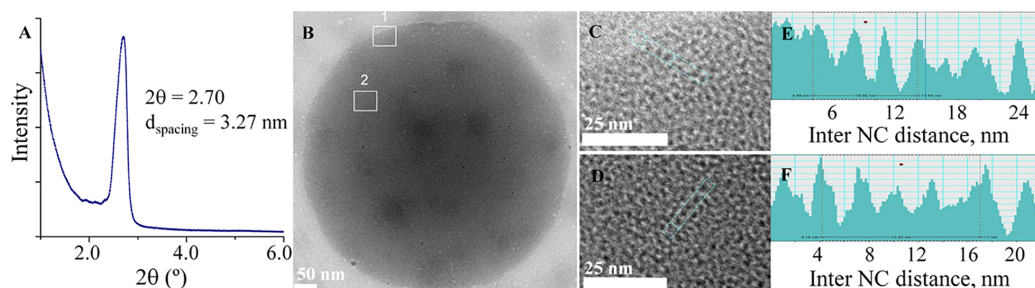


Figure 6. (A) Small-angle powder X-ray diffraction pattern of disc-like superstructures. (B) TEM micrograph of a disc-like superstructure. Zoom-in and focused HRTEM images (C, D) from areas 1 and 2 from TEM micrograph in (B) and corresponding line profiles showing inter-NC distances (E, F).

The self-assembled superstructures were further characterized using small-angle powder X-ray diffraction (SAXRD). Dried self-assembled NC powders were used to measure SAXRD. Figure 6A shows the SAXRD pattern collected from the disc-like colloidal superstructures. The calculated d -spacing value suggests an interparticle distance of 3.27 nm, which is in good agreement with the inter-NC distance measured from TEM micrographs (3.3 ± 0.5 nm) shown in Figure 6B–F. The cross-sectional view of the 3D reconstructed disc-like structure also supports the above observation (Figure S16). Finally, dark-field scattering microscopy was utilized to image the self-assembled structures in the solution state. Accordingly, an ~ 100 nM solution of self-assembled superstructures in DCM was drop-casted on a 1 mm thick glass slide and sandwiched with a 0.14 mm thick glass coverslip. Golden-yellow scattering spots represent the individual self-assembled superstructures of

NCs (Figure S17A). However, no such scattering spots were observed in the control sample (Figure S17B).

CONCLUSIONS

In summary, we have successfully demonstrated reversible self-assembly in atomically precise Au_{25} NCs. Using light as an external stimulus, we introduced a simple strategy to self-assemble NCs. To achieve this goal, photoswitchable NCs were designed and synthesized using a thiol derivative of the azobenzene chromophore with a suitable spacer length. Photoisomerization of the chromophore-functionalized and PET analogue NCs under ultraviolet and visible light was studied through systematic changes in the electronic absorption bands and chemical shifts in NMR spectra. Microscopic techniques were employed to understand the reversible photoswitching in NCs. The time-dependent

evolution of light-mediated self-assembly was monitored using DLS, AFM, TEM, and subsequent electron tomography reconstruction. Detailed investigations of self-assembled superstructures have shown the long-range periodic organization of individual NCs. The stacking of NCs in the self-assembly was evaluated using SAXRD. The calculated *d*-spacing value was in good agreement with TEM micrograph values. The development of such smart self-assembled architectures will create new materials for electrochemistry, biology, photocatalysis, and light-harvesting technology owing to their collective and enhanced optical and electronic properties. In particular, switchable NCs with appropriate molecular functionalities will be a potential cargo system to load and unload drug molecules by a light-triggered mechanism. Also, such self-assembled superstructures will be a suitable probe for the fabrication of electrochemical and photochemical devices.

■ EXPERIMENTAL SECTION

Reagents and Materials. All chemicals and solvents were of analytical grade and used without any further purification. Phenol, aniline, potassium nitrite (KNO_2), 1,3-dibromopropane, hexamethyldisilathiane (HMDST), tetrabutylammonium fluoride (TBAF), tetraoctylammonium bromide (TOAB), ammonium chloride (NH_4Cl), ammonia solution (25%), potassium carbonate (K_2CO_3), potassium iodide (KI), 2-phenylethanethiol (PET), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), and sodium borohydride (NaBH_4) were purchased from Sigma-Aldrich.

Characterization. ^1H and ^{13}C NMR measurements were carried out using Bruker AVANCE III HD 400/500 MHz spectrometers. UV/Vis absorbance spectra were recorded on a VARIAN Cary 500 Scan spectrometer. Fourier transform infrared (FT-IR) measurements (attenuated total reflection (ATR) mode) were carried out using a Bruker Tensor 27 spectrometer. Liquid chromatography–mass spectrometry (LC–MS) was performed using a Waters Xevo TQD triple quadrupole mass spectrometer. Electrospray ionization–mass spectrometric (ESI–MS) measurements were carried out on a Waters Synapt G2-Si high-definition mass spectrometer. Typical experimental parameters of ESI–MS were as follows: capillary voltage: 3 kV, cone voltage: 150 V, source offset: 150 V, source temperature: 100 °C, desolvation temperature: 100 °C, and desolvation gas flow: 400 L/h. HRTEM images were recorded on a JEOL 3010 (300 kV) transmission electron microscope. Scanning transmission electron microscopy (STEM) images with EDS and elemental mapping were recorded using a FEI Talos F200S (200 kV) transmission electron microscope. Transmission electron tomographic reconstruction and tilt series of 2D projections were acquired with the Serial EM-software package.^{52,53} The specimen was tilted between $\pm 69^\circ$ with 2–3° increment steps in low-dose mode.⁵⁴ The acquired raw stack of images was first subjected to a series of preprocessing, coarse alignment, and final alignment and was further aligned using the IMOD software package.⁵⁵ The final aligned file was then utilized for 3D reconstruction with a custom-made maximum entropy method (MEM) program with a regularization parameter value of $\lambda = 1.0 \times 10^{-3}$ on MacPro.^{56,57} The 3D isosurface and solid-colored images were produced using UCSF Chimera. High-resolution tapping mode (AC mode) AFM measurements were performed on an Oxford Instruments Asylum Cypher ES. X-ray photoelectron spectra were recorded using a Thermo Scientific ESCALAB 250Xi. Photoisomerization of chromophores and NCs was performed using a Newport Mercury–Xenon light source (500 W) equipped with a monochromator (Oriel). DLS measurements were performed using a Nanotrack Ultra NPA 253 from Microtrac. Particle size and distribution of self-assembled NC colloid solutions were obtained using the Microtrac Flex software. Dark-field scattering imaging was performed on a Cytoviva hyperspectral imaging system (HSI) equipped with a Cytoviva high-resolution dark-field condenser (oil immersion). Here, a sample slide kept in an optical path was illuminated using a halogen lamp after passing through an oil-

immersion dark-field condenser. Scattering light was focused through a microscope objective (40X), and signals were collected with a colored CCD camera. SAXRD measurement was performed using a third-generation Empyrean Malvern PANalytical X-ray diffractometer. The X-ray source was Cu $K\alpha$ (1.5418 Å). Dried powders of NC superstructures were used to measure the diffraction. Energy-minimized structures of NCs were optimized using density functional theory (DFT) as implemented in the grid-based projector-augmented wave (GPAW) software package.^{58,59} The following PAW setups were considered for Au($5d^{10}6s^1$), S($3s^23p^4$), O($2s^22p^4$), N($2s^22p^3$), C($2s^22p^2$), and H($1s^1$), with scalar-relativistic effects included for Au. The geometry optimizations were carried out using the PBE⁶⁰ functional and DZP (double-zeta plus polarization) basis set in LCAO mode⁶⁰ with a grid spacing of 0.2 Å and the convergence condition that the residual forces be 0.05 eV/Å, without imposing any symmetry constraints. All optimized structures were visualized using the visual molecular dynamics (VMD) software.⁶¹

Different steps involved in the synthesis of molecules 1–3 are shown in Scheme S1 (SI).

Synthesis of Molecule 1. Molecule 1 was synthesized using a reported protocol.⁴⁶ Aniline (4.6 mL; 50 mmol) was dissolved in 15 mL of conc. HCl and cooled to 0 °C. An aqueous solution (15 mL) of KNO_2 (4.4 g; 52 mmol) was added dropwise to the above solution under constant stirring. A clear solution of freshly prepared diazonium salt was added dropwise into phenol (4.7 g; 50 mmol) dissolved in 400 mL of $\text{NH}_3\text{--NH}_4\text{Cl}$ buffer solution (pH $\sim$ 9) at 0 °C. The reaction was carried out at ice-cold temperature for another 3 h followed by addition of excess conc. HCl. The precipitated product was washed and collected by vacuum filtration. Washing was repeated multiple times to remove excess reagents and starting materials. ^1H NMR (400 MHz, DMSO- d_6); δ = 10.3 (s, 1H), 7.85–7.78 (broad-d, 4H), 7.59–7.45 (m, 3H), and 6.98–6.93 (broad-d, 2H); ^{13}C NMR (100 MHz, DMSO- d_6); δ = 161.4, 152.6, 145.7, 130.9, 129.8, 125.3, 122.6, and 116.4; LC–MS ($\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}$), m/z + 1 = 199; FT-IR (ν_{max}) = 3117, 1587, 1500–1370, 1275, 1227, 1139, 831, and 762 cm^{-1} . ^1H and ^{13}C NMR, LC–MS, and FT-IR spectra of molecule 1 are shown in SI (Figure S1).

Synthesis of Molecule 2. A suspension of molecule 1 (1.98 g; 10 mmol), 1,3-dibromopropane ($\sim$ 10 mL; 100 mmol), K_2CO_3 (1.66 g; 12 mmol), and a catalytic amount of KI was refluxed in acetone (50 mL) for 5 h at 80 °C.⁴⁷ The reaction mixture was cooled and filtered. Excess 1,3-dibromopropane was removed by pumping in a rotary evaporator. The crude product was chromatographed over silica gel and eluted with a 2% ethyl acetate/hexane mixture. ^1H NMR (400 MHz, CDCl_3); δ = 7.95–7.85 (m, 4H), 7.53–7.4 (m, 3H), 7.04–6.99 (dd, 2H), 4.2–4.17 (t, 2H), 3.65–3.60 (t, 2H), and 2.4–2.32 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3); δ = 161.1, 152.7, 147.1, 130.4, 129.0, 124.8, 122.6, 114.7, 65.6, 32.2, and 29.8; LC–MS ($\text{C}_{15}\text{H}_{15}\text{N}_2\text{OBr}$), m/z + 1 = 319 and 321; FT-IR (ν_{max}) = 2960–2870, 1588, 1500–1370, 1237, 1100–1020, 916, 825–760, and 678 cm^{-1} . ^1H and ^{13}C NMR, LC–MS, and FT-IR spectra of molecule 2 are shown in SI (Figure S2).

Synthesis of Molecule 3. A stirred solution of molecule 2 (0.319 g; 1 mmol) in freshly distilled tetrahydrofuran (THF) (4 mL) was cooled to -10 °C followed by addition of a mixture of HMDST (255 μL ; 1.2 mmol) and TBAF (0.35 g; 1.1 mmol) dissolved in THF (1 mL).⁴⁷ The mixture was warmed to room temperature while being stirred. After 1 h, the reaction mixture was diluted with dichloromethane and washed with saturated NH_4Cl solution. The crude product was chromatographed over silica gel and eluted with a 2% ethyl acetate/hexane mixture. ^1H NMR (500 MHz, CDCl_3); δ = 7.95–7.85 (m, 4H), 7.53–7.4 (m, 3H), 7.04–6.99 (dd, 2H), 4.2–4.15 (t, 2H), 2.8–2.73 (q, 2H), 2.17–2.08 (m, 2H), and 1.44–1.39 (t, 1H); ^{13}C NMR (125 MHz, CDCl_3); δ = 161.3, 152.8, 147.1, 130.4, 129, 124.8, 122.6, 114.7, 66, 33.2, and 21.2; LC–MS ($\text{C}_{15}\text{H}_{16}\text{N}_2\text{OS}$), m/z + 1 = 273; FT-IR (ν_{max}) = 2930–2875, 2563, 1589, 1495–1380, 1298, 1237, 1137, 1044, 949, and 827 cm^{-1} . ^1H and ^{13}C NMR, LC–MS, and FT-IR spectra of molecule 3 are shown in SI (Figure S3).

Synthesis of $[\text{Au}_{25}(\text{PET})_{18}]^-$. $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs were synthesized using a reported protocol.⁴⁸ To a solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (20 mg/2 mL THF), TOAB (33 mg/1.75 mL THF) was added and stirred until the color turned dark red. Then, PET (34 μL ; 5 mol equivalents w.r.t. gold) was added and stirred at 400 rpm for 1 h. The Au–thiolate solution formed was further reduced by injecting a freshly prepared ice-cold aqueous NaBH_4 solution (19 mg/1.25 mL; 10 mol equivalents w.r.t. gold). The mixture was stirred at room temperature for another 8–9 h to complete the reaction. Using a separating funnel, the organic and aqueous layers were separated (toluene was added for good separation), and the organic layer was washed several times with Millipore water. Excess thiol and other impurities were removed by precipitating NCs by adding methanol. This washing step was repeated three times. Insoluble Au–S polymers were removed from the crude mixture by extracting NCs in DCM. Finally, NCs were re-dispersed in acetone to remove byproducts (Au_{144} NCs). Dried $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs were stored at 4 °C for further characterizations.

Synthesis of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$. A modified Brust–Schiffrin single-phase procedure was used for the synthesis of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$.⁴⁸ To a solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (20 mg/2 mL THF), TOAB (33 mg/1.75 mL THF) was added and stirred until the color turned dark red. Then, $\text{C}_3\text{-AMT}$ (69 mg; 5 mol equivalents w.r.t. gold) was added and stirred at 400 rpm for 1 h. The Au–thiolate solution formed was further reduced by injecting a freshly prepared ice-cold aqueous NaBH_4 solution (19 mg/1.25 mL; 10 mol equivalents w.r.t. gold). The mixture was stirred at room temperature for another 8–9 h to complete the reaction. Using a separating funnel, the organic and aqueous layers were separated (toluene was added for good separation), and the organic layer was washed several times with Millipore water. Excess thiol and other impurities were removed by precipitating NCs by adding methanol. This washing step was repeated three times. Insoluble Au–S polymers were removed from the crude mixture by extracting NCs in DCM. Finally, NCs were re-dispersed in acetone to remove byproducts (Au_{144} NCs). Dried $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs were stored at 4 °C for further characterizations.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c00328>.

Scheme for the synthesis of molecules 1–3 ($\text{C}_3\text{-AMT}$); ^1H and ^{13}C NMR, LC–MS, and FT-IR spectra of molecules; temporal absorption spectra of $\text{C}_3\text{-AMT}$ and $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$; XPS spectra of NCs; mechanism for the dipole-induced self-assembly; photographs of NC solution during the course of assembly and disassembly; large-area TEM micrographs of assembly and disassembly; Temporal absorption spectra of self-assembled superstructures and trans NCs under dark; TEM images of $[\text{Au}_{25}(\text{PET})_{18}]^-$ before and after light illumination; TEM images of self-assembled dimer; elemental maps and EDS spectrum of superstructure; temporal DLS spectra of assembly and disassembly; dark-field scattering image of superstructures; cross-sectional views of 3D-reconstructed disc-like superstructures (PDF) Three-dimensional superstructures are composed of densely packed NCs (MOV)

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Author Contributions

The project was designed and supervised by E.S.S. J.V.R. synthesized the chromophore and nanoclusters. J.V.R. and E.S.S. conducted experiments. Nonappa performed electron tomography data acquisition and reconstruction. The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS USED

NC, atomically precise noble metal nanocluster
 $\text{C}_3\text{-AMT}$, azobenzene-alkyl monothiol

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Light-Emitting Atomically Precise Nanocluster-Based Flexible QR Codes for Anticounterfeiting

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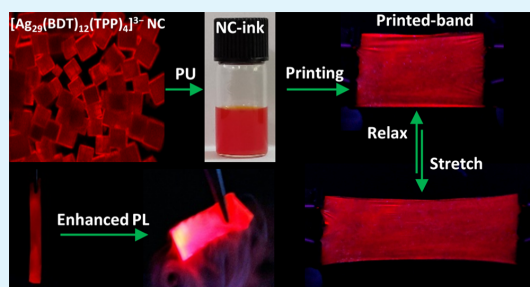
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Supporting Information

ABSTRACT: Despite tremendous progress in the field of fluorescence-based anticounterfeiting, the advanced anticounterfeiting techniques are still posing challenges all over the world due to their cost and reliability. Recently, light-emitting atomically precise nanoclusters have emerged as attractive building blocks because of their well-defined structure, function, and stable photoluminescence. Herein, we report the room temperature fabrication of a stable, flexible, nontoxic, and low-cost precision nanocluster-based luminescent ink for the stencil printing of an optically unclonable security label. Nanocluster-based printing ink shows brilliant photoluminescence owing to its extended C–H... π/π ... π interactions. Spectroscopic and microscopic investigations show that intercalated nanoclusters in the printed security labels are highly stable as their optical features and molecular compositions are unaffected. The exceptional mechanical, thermal, photo, and aqueous stabilities of the printed security labels endorse to demonstrate the printing and smartphone-based electronic reading of the quick response code on a currency. Finally, confidential information protection and decryption under a precise window of light have been achieved by adopting the optical contrast illusion. The overall cost of the security label is found to be approximately 0.013 USD per stamp.

KEYWORDS: light-emitting nanoclusters, luminescent inks, stencil printing, self-assembly, flexible QR codes, anticounterfeiting, optical contrast illusion



INTRODUCTION

Counterfeiting of any official documents, especially currency, passport, stamp, and so forth, is a global concern that affects the security and revenue of a country. Although many of these are protected with anticounterfeiting techniques, the estimated global economic loss due to duplication has been increased significantly and reached up to multibillion USD per annum.¹ Conventional anticounterfeiting technology is mainly based on the printing of a security label using an ink developed from luminescent materials that can glow under ultraviolet light. Different materials used or proposed to fabricate the printing ink include organic dyes,^{2–6} semiconductor quantum dots,^{7–9} inorganic perovskites,^{10,11} rare-earth metals,^{12–16} upconversion nanoparticles,¹⁷ carbon dots,^{18,19} polymer dots,²⁰ and so on. However, the moderate photostability, sizable elemental toxicity, expensive precursors, or hard synthetic protocols rarely limit their attention. Nontoxic luminescent ink fabricated from the atomically precise nanocluster (NC) is another possible candidate. In the recent past, an attempt to make the NC-based luminescent printing ink was reported.²¹ NCs have been considered as a class of materials made up of about ten to a few hundred atoms in their cores.^{22,23} Precise

atomic combinations, discrete electronic energy levels, characteristic optical absorption features, bright photoluminescence (PL), stability under a range of chemicals and photons, and moderate toxicity due to less metallic contents are the strengths of individual NCs.^{24,25} NCs are known for diverse potential applications, which include catalysis,^{26,27} solar energy conversion,^{28,29} light-emitting diode (LED) fabrication,^{30,31} sensing,^{32–35} bioimaging,^{36–39} drug screening,⁴⁰ and therapeutics.^{41,42} A large variety of gold and silver NCs with different combinations of cores and ligands are reported.^{23–25,43–53} Some of these NCs emit in the solid-state owing to their strong interparticle electronic coupling.^{52,53} Stable solid-state emitting NCs with better PL quantum yield are promising materials for developing large-area printable electronics, mainly for security prints, wearable LEDs, and

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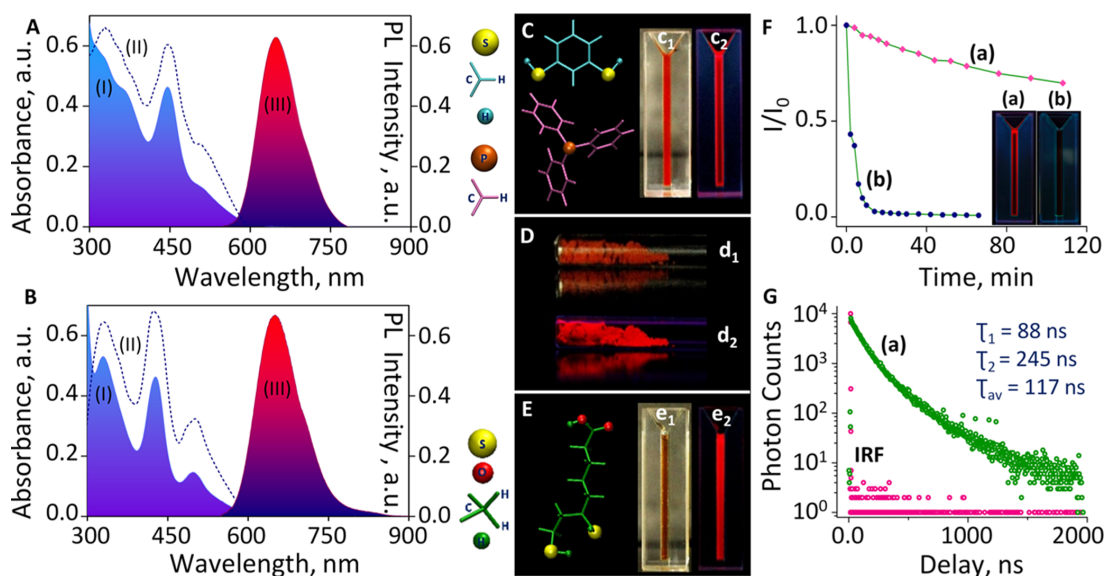


Figure 1. (A,B) UV/vis absorption (I), excitation (II), and PL (III) spectra of (A) $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and (B) $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs. (C,E) Photographs of (C) $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and (E) $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NC solutions under visible (c_1 and e_1) and UV light (c_2 and e_2). Energy-minimized structures of the ligands used to synthesize NCs are shown. (D) Photographs of the solid $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC under visible (d_1) and UV (d_2) light. (F) Plot of I/I_0 vs illumination time for (a) $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and (b) $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs shows their photostability. The photographs (under UV light) of illuminated NC solutions are given in the inset. The PL decay profile of (a) $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC and instrument response factor (IRF) are shown in (G).

healthcare sensors. To achieve this goal, the key criterion is to fabricate a smart luminescent NC-based ink having adequate consistency for printing, preserved PL and molecular stability, and flexibility for multiple usages. The development of such a NC-based luminescent printing ink is still in its infancy. To address this challenge, we have fabricated a stable, flexible, nontoxic, and low-cost NC-based luminescent ink by integrating solid-state emitting NCs in an elastic matrix. Different spectroscopic and microscopic studies show that intercalated NCs in the printing ink are highly stable as their optical absorption features, PL, and molecular compositions are analogue to the pristine NCs. This elastic ink has been efficiently used to print the text and quick response (QR) code using the stencil printing technique. A QR code is a machine-readable two-dimensional barcode, which can encrypt data such as name, uniform resource locator (URL), address, phone number, location details, and so on. The information encoded on these optical labels can be accessed by scanning with a camera-enabled mobile device having a QR code scanner application. In the recent past, the QR code fabricated from upconversion nanoparticle-based ink has been used to demonstrate the pharmaceutical anticounterfeiting.⁵⁴ Herein, we have successfully demonstrated the printing and electronic reading of a QR code encrypted with “confidential information” on a currency. Notably, the printed security labels are stable over a range of temperatures, under a spectrum of lights, humidity, and mechanical stress. The elastomeric binder-based luminescent ink facilitates flexible and stretchable solid-state patterns, which helps to hold the printed security code on the currency even after multiple folding and wetting. Using this stretchable luminescent ink, we can print any authentic security codes (2.5 cm × 2.5 cm) at the

cost of 0.013 USD per stamp. This methodology can be further extended to encrypt more details about the currency, such as serial numbers, or any other pieces of information to validate its authenticity.

RESULTS AND DISCUSSION

To address the development of a stable, nontoxic, and low-cost NC-based luminescent ink, different gold and silver NCs were scrutinized. Among these, twenty-nine-atom silver NCs (Ag_{29}) have been selected to fabricate the printing ink. Details are provided in the Supporting Information (Figure S1). Two different Ag_{29} NCs, viz., $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$, were synthesized and purified according to protocols reported elsewhere.^{53,55} Details are given in the Experimental Section. Both of these NCs were characterized using optical absorption and PL spectroscopy. Figure 1A,B shows the UV/vis absorption (I), excitation (II), and PL (III) spectra of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs in *N,N*-dimethylformamide (DMF). Different absorption humps, *ca.* 265, 365, 445, and 510 nm, represent different possible molecular electronic transitions, which are more prominent in the excitation spectra. PL spectra of these NCs show an emission maximum *ca.* 650 nm at 450 nm excitation. Photographs of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NC solutions under visible (c_1 and e_1) and UV light (c_2 and e_2) and the energy-minimized structure of the ligands used to synthesize NCs are shown in Figure 1C,E, respectively. Among two NCs, $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ shows bright solid-state emission, a fundamental requirement for the luminescent-based printing ink. Photographs of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC powder under visible (d_1) and UV light (d_2) are shown in Figure 1D. To evaluate the photostability of NCs, we have

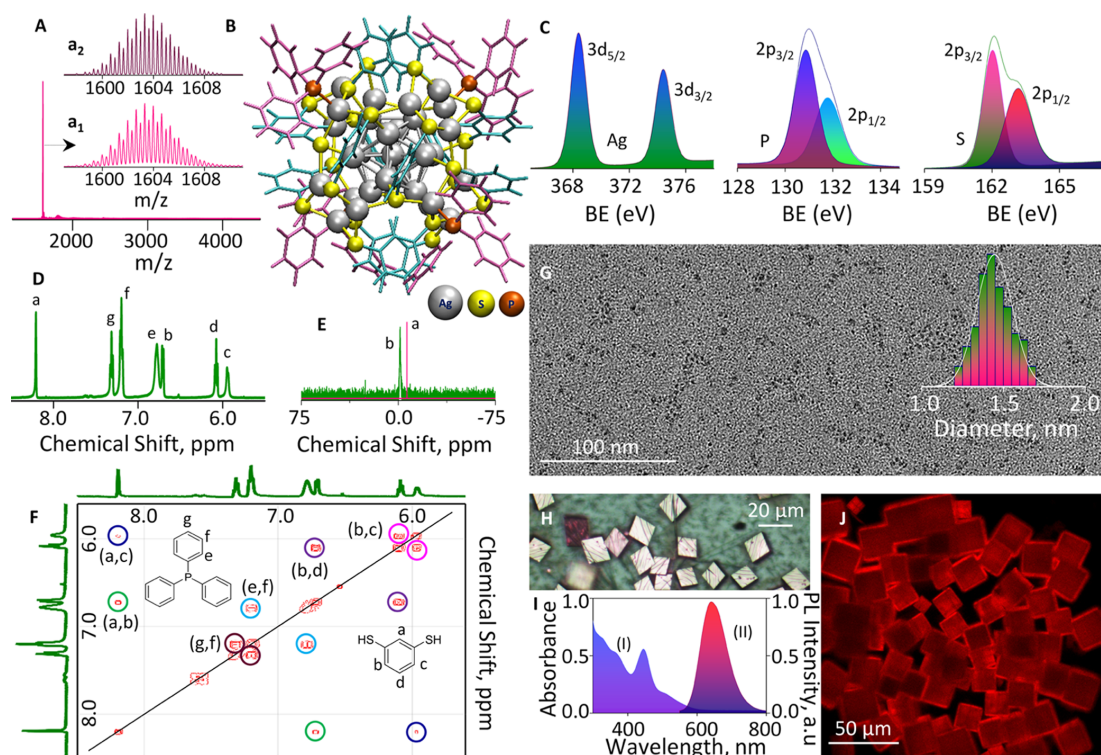


Figure 2. (A,B) ESI-MS and energy-minimized structure of the [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NC. An expanded view of (a_1) experimental and (a_2) theoretical isotopic patterns are shown in the inset. (C) XPS spectra of the NC show the presence of silver, phosphorus, and sulfur. (D) ¹H, (E) ³¹P, and (F) ¹H–¹H correlation (COSY) NMR spectra of the [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NC. All the peaks are assigned and labeled above the traces. (G) Larger area TEM image shows monodisperse NCs. The size distribution of the NC is shown in the inset. (H,I) Optical and confocal fluorescence images of the crystallized NC show rhombohedral crystals. (I) Absorption (I) and PL (II) spectra of redissolved crystals recorded in DMF.

recorded and compared the time-dependent PL spectra of [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ and [Ag₂₉(LA)₁₂]³⁻ NC solutions illuminated at 365 nm excitation at different time intervals. Photostability experiments show extended stability for [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NCs compared to [Ag₂₉(LA)₁₂]³⁻ NCs (Figure 1F). Illumination of [Ag₂₉(LA)₁₂]³⁻ NC solution (365 nm light) underwent photobleaching within 15 min, which is evident from the plot of (b) I/I_0 vs illumination time (I_0 represents the PL intensity at $t = 0$). At the same time, the [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NC shows (a) robust I/I_0 values even for a couple of hours of photoexcitation. The photographs (under UV light) of (a) [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ and (b) [Ag₂₉(LA)₁₂]³⁻ NC solutions illuminated under 365 nm light are given in the inset (Figure 1F). Temporal PL spectra recorded from both of these NCs under 365 nm illumination are given in the Supporting Information (Figure S2). Due to the exceptional photostability, easy synthetic protocol, solid-state emission, and less cost of raw materials, we have chosen [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ as the potential ingredient for the fabrication of luminescent ink. Before that, a comprehensive picture of [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NCs was investigated in detail using various spectroscopic and microscopic techniques. The PL lifetime of [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NC solution was recorded using time-resolved spectroscopy. Figure 1G (a) represents the PL decay profile (time-correlated single-photon

counting, TCSPC) of the NC at its emission maximum *ca.* 650 nm using 378 nm excitation. The [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NC shows a biexponential luminescence relaxation with a faster component of 88 ns and a slower component of 245 ns. The fast and slow components of NCs presumably originated from the prompt and thermally activated delayed emission, similar to the other NCs reported.^{39,56} The average lifetime of NC is found to be 117 ns,⁵⁷ which was estimated using the equation $\tau_{av} = (\tau_1 A_1 + \tau_2 A_2) / (A_1 + A_2)$, where τ_1 and τ_2 are the individual lifetime values and A_1 and A_2 are the corresponding amplitudes.

The molecular composition of [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NC was recorded and analyzed using electrospray ionization-mass spectrometry (ESI-MS, negative mode). ESI-MS of the purified [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NC in DMF is shown in Figure 2A, which is comparable to the reported spectrum.^{53,57} Single molecular ion peak *ca.* 1603 represents pure [Ag₂₉(BDT)₁₂]³⁻. The molecular weight of TPP is not accounted in the mass spectrum owing to its easy dissociation during ionization.⁵⁷ Expansion of the peak *ca.* 1603 shows the characteristic isotopic distribution, in which separation between nearby peaks is found to be 0.33 (inset in Figure 2A, a_1). The corresponding theoretical isotopic distribution is shown in the inset (Figure 2A, a_2). The structure of the [Ag₂₉(BDT)₁₂(TPP)₄]³⁻ NC consists of a Ag₁₃ icosahedral

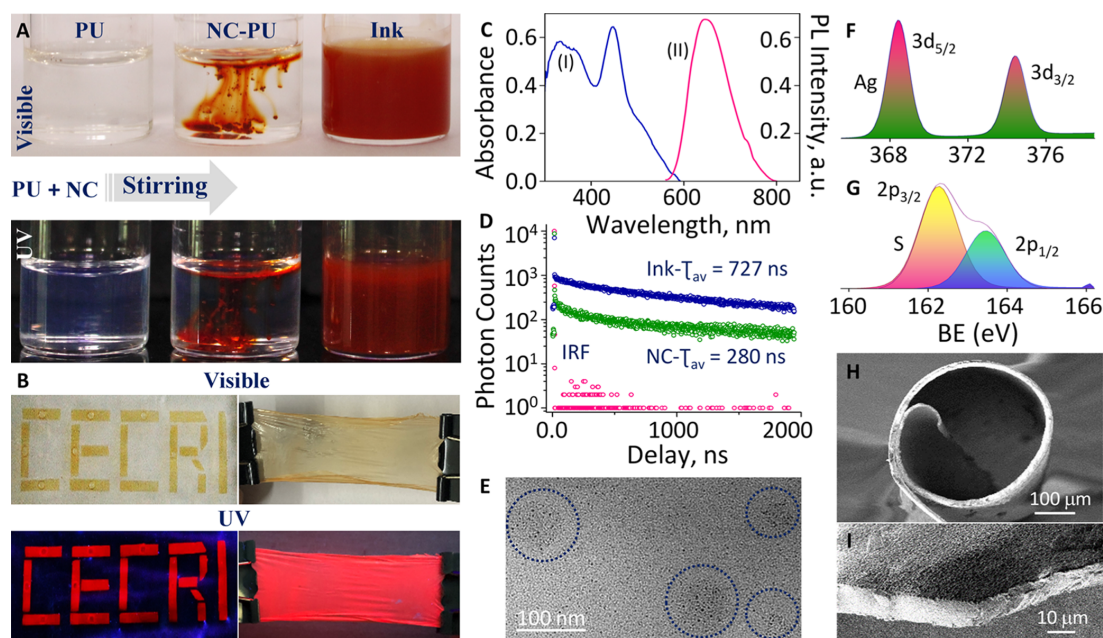


Figure 3. Photographs represent (A) different steps involved in the fabrication of ink and (B) stencil-printed luminescent word (CECRI) and band under visible and UV light. (C) UV/vis absorption (I) and PL (II) spectra, (D) PL decay profile, (E) TEM image, and (F,G) XPS spectra (Ag 3d and S 2p) recorded from the luminescent ink/band. Peaks are assigned and labeled above the traces. (H,I) FESEM images taken from the (H) rolled and (I) flat printed band.

core with 12 Ag atoms capped in the external shell. These twelve Ag atoms form four tetrahedrally oriented trigonal prisms, and another four Ag atoms face-cap the thirteen-atom core at four tetrahedral positions.⁵³ The energy-minimized structure of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC optimized using the density functional theory (DFT) is shown in Figure 2B. The core of the NC and the nature of binding were studied by recording and analyzing the X-ray photoelectron spectrum. Binding energy (BE) values of Ag 3d levels in the $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC are in good agreement with reported values,^{57,58} with Ag 3d_{5/2} ca. 368.4 eV and Ag 3d_{3/2} ca. 374.4 eV (Figure 2C). The deconvoluted spectrum shows the presence of P 2p_{3/2} and 2p_{1/2} peaks ca. 130.8 and 131.8 eV, which confirm the presence of bound TPP in the NC. The BE of S 2p was in accordance with thiolate binding, in which sulfur 2p_{3/2} and 2p_{1/2} peaks appear around 162 and 163.2 eV, respectively. By comparing ESI-MS and X-ray photoelectron spectroscopy (XPS), the molecular composition of the $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC is confirmed.

To further confirm the presence of bound ligands in the purified NC, we have recorded and analyzed ¹H and ³¹P nuclear magnetic resonance (NMR) spectra in DMSO-*d*₆. ¹H and ³¹P NMR spectra of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC solution were assigned and labeled (Figure 2D,E), by comparing the proton–proton interactions in the correlation NMR (COSY; Figure 2F). The peaks ca. δ = 8.22–8.20, 6.72–6.69, 6.10–6.05, and 5.98–5.92 ppm were assigned to BDT, whereas the other peaks (δ = 7.34–7.29, 7.24–7.16, and 6.84–6.74) were originated from TPP. The proton in between the thiol groups (Figure 2D, a) has shown a downfield shift owing to the electron-withdrawing nature of the silver core. The environ-

mental changes around NCs resulted in two different sets of peaks for identical protons (Figure 2D, b and c). Appearance of all the aromatic protons in ¹H NMR and a single broad peak (Figure 2E, b) ca. –1.44 ppm (slight changes will be expected according to the TPP amount present) in ³¹P NMR suggests the presence of bound BDT and TPP in the purified NC.^{57,59} A small hump ca. 25.6 ppm (Figure 2E, b) arises from the oxidized TPP due to air oxidation of NCs.⁶⁰ The ³¹P NMR spectrum of the parent TPP molecule shows a single narrow peak ca. –6.818 ppm (Figure 2E, a). The NC was further characterized using transmission electron microscopy (TEM) by drop-casting and drying ~100 μM solution of the $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC in DMF on a copper grid with a carbon-supported film. The TEM image (Figure 2G) shows nearly uniform size distribution (1.5 ± 0.2 nm; inset in Figure 2G) in the grid, which indicates the monodispersity of the $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC. As an extreme purity is recommended in the printing gadgets, NCs were further purified by the crystallization using a slow solvent evaporation technique.⁵³ Optical (white light) and confocal fluorescence images of rhombohedral crystals are shown in Figure 2H,J, respectively. Resemblances in the optical absorption (I) and PL (II) features (Figure 2I) of NC crystals redissolved in DMF verify the Ag₂₉ core.

To develop a flexible NC-based printing ink, we have chosen thermoplastic polyurethane (PU) polymer as a matrix to intercalate NCs. The elastic and transparent natures of PU help to adopt the flexibility and visibility for NC-based ink. Details of ink preparation are given in the Experimental Section. Photographs (under visible and UV light) demonstrating the different steps involved in the fabrication of NC-

based ink are shown in Figure 3A. The addition of crystallized NCs into the PU dispersion previously prepared in tetrahydrofuran (THF) followed by constant stirring at room temperature ensured high-quality printing ink with the required consistency. To check the competence of the above-prepared ink, we have printed luminescent letters and bands using a stencil printing technique.^{61–64} Details are provided in the Experimental Section. Figure 3B shows the photographs (under visible and UV light) of a word (CECRI) and a band stencil-printed on a tattoo paper. The perfect texture of the ink helped to print the letters without any diffusion. Moreover, the printed band is highly transparent, which allows us to see the background (Figure S3). To ensure the stability of NCs in the printed patterns, their optical features were probed using different spectroscopic and microscopic techniques. One-to-one correspondence in the UV/vis absorption (I) and PL (II) spectra recorded from the printed band (Figure 3C) with Figure 1A suggests that NCs are stable in ink and in the printed patterns. The PL decay profile (TCSPC) recorded from the printed band (378 nm excitation) shows a prolonged lifetime (727 ns; Figure 3D) compared to the parent NC crystals (280 ns) due to their least collisional quenching in the excited state. The longer lifetime of NCs in the printed band rules out their direct interactions with atmospheric oxygen because of the polymer coating. Subsequently, we have investigated the morphology of NCs in the printed band by recording and analyzing the TEM images of ink coated on a carbon-supported copper grid. The TEM image of NCs dispersed in ink or printed band is shown in Figure 3E, which suggests the unaltered size of NCs. However, we could observe random organization of NCs in the grid, marked by blue circles. Detailed TEM investigation shows a circular assembly of NCs in the polymer matrix (Figure S4A). Such an organization is mostly due to the C–H... π / π ... π interactions between the BDT/TPP and PU moieties, similar to the assembly reported in [Ag₂₉(BDT)₁₂(TPP)₄]^{3–} NCs.⁶⁵ Furthermore, we have recorded and compared the PL spectra of an equimolar concentration of parent NCs and ink. Notably, the PL spectrum recorded from the ink shows fourfold enhancement compared to the NC solution (Figure S4B) under similar experimental conditions. The enhanced PL and extended lifetime of NCs in ink and the printed band seemingly originated from their assembly. The earlier reports on the self-organization of NCs in a polymer matrix⁶⁶ and enhanced PL in the assembled NCs^{66,67} support the above-mentioned results. The XPS spectra recorded and analyzed from the printed band provided BE values of Ag 3d (Figure 3F; Ag 3d_{5/2} ca. 368.4 eV and 3d_{3/2} ca. 374.4 eV) and S 2p (Figure 3G; S 2p_{3/2} ca. 162.3 eV and 2p_{1/2} ca. 163.5 eV), which are in good agreement with pristine NCs^{57,58} (Figure 2C). Slight broadening in the BE of P 2p (Figure S5A) is probably due to the presence of unbound⁵⁷ or oxidized TPP⁶⁰ in the film. Although a small amount of TPP separated from the NC surface during the ink fabrication, NCs were found to be highly stable in ink. The XPS spectra representing the BE of O 1s and N 1s (polymer) are shown in Figure S5B,C, respectively. The thickness of the printed materials is essential, especially in high-security documents. To measure the thickness of the printed band, we have recorded and analyzed scanning electron microscopy (SEM) micrographs. Field emission (FE) SEM images of the printed band captured from different areas are given in Figure 3H (rolled) and I (flat), which show nearly uniform thickness ($\sim 8.75 \pm 0.85 \mu\text{m}$) and surface

morphology. The elemental composition of the printed band is given in the Supporting Information (Figure S6). All the abovementioned experiments confirm the presence of stable NCs in ink and in the printed bands.

Stability of the printed materials is indispensable, especially for the authorized documents. We have systematically investigated photostability, thermal stability, moisture effect, and mechanical strength of the printed bands. To study their photostability, we have recorded and analyzed the PL spectra from the printed band illuminated at 365 nm excitation at different time intervals. A plot of I/I_0 (Figure 4A) vs

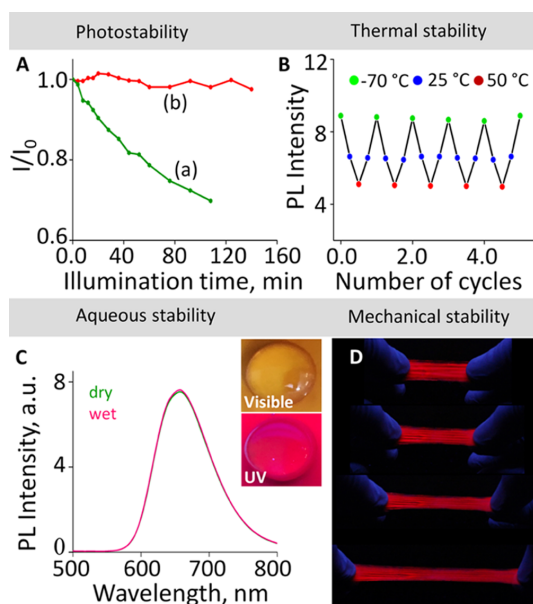


Figure 4. (A) Plot of I/I_0 vs illumination time recorded from (a) NC solution and (b) printed band illuminated at 365 nm. (B) Plot of PL intensity vs number of temperature cycles recorded from the printed band kept at -70 , 25 , and 50 °C. (C) PL spectra recorded from the printed band under wet and dry conditions. Photographs of a wet band under visible and UV light are shown in the inset. (D) Photographs of the printed band captured during the stretching test under UV light.

illumination time shows an exceptional photostability for (b) NCs embedded in the printed band compared to (a) NC solution (Figure 1F-a) under similar experimental conditions. The temporal PL spectra recorded from the printed band are given in the Supporting Information (Figure S7). To test their thermal stability, PL spectra were recorded from the printed band kept at different temperatures. A range of temperatures from -70 to 50 °C were achieved by soaking the printed band in liquid nitrogen, cold water, and warm water. A plot of PL intensity vs the number of temperature cycles (Figure 4B) shows switchable PL under variable temperatures, which suggests the stability of NCs in the printed band over a range of temperatures. Additionally, the unaltered optical absorption features of NCs (Figure S8A) recorded after dipping the printed band in liquid nitrogen, cold water, and warm water proved the stability of NCs at different temperatures. As expected, PL intensity was maximum at low

temperature owing to the least rotational and vibrational movements of bound ligands on the NC surface. The photograph showing the enhanced PL from the printed band while dipping in liquid nitrogen is shown in the Supporting Information (Figure S8C). Five cycles of PL spectra recorded from the printed band soaked at different temperatures are provided in the Supporting Information (Figure S9). The abovementioned set of the experiment also suggests the durability of printed materials in a wet environment. To further study the moisture effect, we have recorded and compared the PL spectra of the printed band after wetting (Figure 4C). The analogue PL spectra recorded from the printed band under dry and wet conditions confirm their stability in humid settings. Photographs of a wet band under visible and UV lights (inset in Figure 4C) show their hydrophobicity, which was further confirmed by contact angle measurements. Details are provided in the Experimental Section. The water drop profile used to determine the water contact angle on the printed band is shown in Figure S10. The measured contact angle from the NC–PU printed band ($93.72 \pm 0.85^\circ$) is comparable to the PU-alone printed band ($95.78 \pm 0.5^\circ$). A slight decrease in the contact angle of the NC–PU printed band is attributed to the polar nature of NCs. The integrity of NCs in the printed band was tested by keeping them in a water (Millipore) bath for a long time. A robust PL from the printed band showed exceptional stability of NCs in water (Figure S11).

Furthermore, we have tested the elasticity of the printed free-standing band ($3 \text{ cm} \times 1 \text{ cm} \times 0.01 \text{ mm}$) by stretching and relaxing them multiple times. Photographs (under UV light) captured during the different sequences of stretching (Figure 4D) and wincing (Figure S12A) demonstrate the flexibility and mechanical strength of the printed bands. We also tested the restoring ability of the printed band after stretching. The photographs captured before and after the stretching are shown in Figure S12B. This suggests a nearly complete recovery in the size and shape of the printed band. Later, tensile strength and elongation at the breaking point of the printed band were tested and compared with the PU band. The stress–strain curve recorded from the NC–PU and PU-alone printed bands are shown in the Supporting Information (Figure S13). The tensile strength of the NC–PU band was slightly decreased from 28.4 ± 2.1 to $25.32 \pm 0.6 \text{ MPa}$. This could probably be due to the molecular interactions between NCs and PU moieties discussed earlier. The NC–PU band withstood $229 \pm 16\%$ strain, comparable to the PU band ($253 \pm 10\%$). All the abovementioned spectroscopic information suggests that NC in ink is stable and reliable to print any relevant documents.

Proven after the stability of NC-based luminescent ink, we have further employed them to fabricate an electronic security label on the currency. The schematic representation of the stencil printing technique used to print a static QR code is shown in Figure 5A. The QR code-stencil pattern previously encrypted with the “confidential information” has been used to print security labels. The photographs (under visible and UV light) of a QR code-printed on an A4 paper are provided in the Supporting Information (Figure S14A,B). Here, the blue background (under UV light) is because of the fluorescence coming from the optical brightener (OB) used in the paper. As a result, the red emission of the NC was merged with OB emission. Interestingly, we found that the printed QR code is readable only under UV light. This is due to optical contrast illusion created by the combination of blue and red emissions

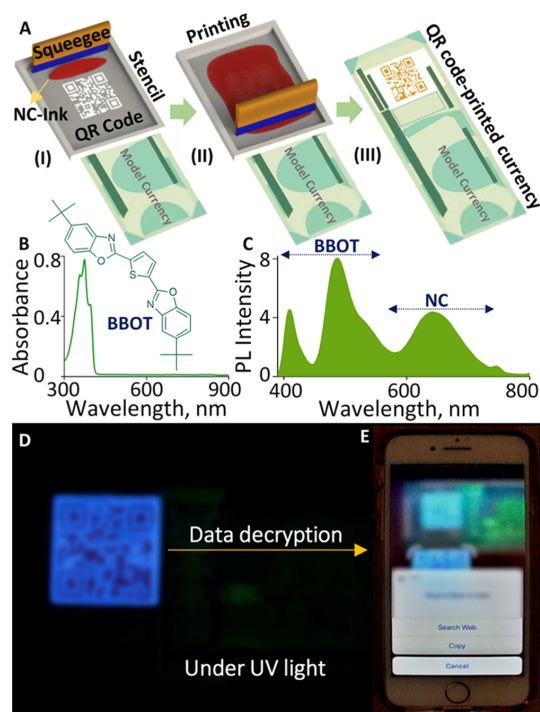


Figure 5. (A) Schematic representation of the stencil printing technique used to print QR code on a currency. (B) Absorption spectrum and chemical structure of BBOT. (C) Combined PL spectrum recorded from a mixture of NCs and BBOT. Photographs of the (D) QR code-printed currency and (E) data decryption process using a smartphone under UV light. The photograph of the QR code-printed original currency has been blurred to avoid copyright issues.

from OB and NCs, respectively. Later, we have extended the same strategy to print high-security QR code on a currency. The raw materials vary from currency to currency during their manufacture. Hence, it is essential to ensure a homogeneous surface on the currency as a background for QR code printing. Also, the QR code recognition and decryption necessitate a significant difference in the background to foreground color contrast. To address such challenges, we have selected thiophene-based OB [2,5-bis-(5-*tert*-butyl-benzoxazol-2-yl)-thiophene (BBOT)], which is extensively used in printed electronics and laser applications. The optical absorption spectrum and chemical structure of BBOT are given in Figure 5B. The better solubility of this molecule in THF helped to make highly uniform BBOT–PU dispersion. An interface layer of BBOT–PU was initially printed on the currency, which helps to ensure uniform surface and durable adhesion of the QR code. Subsequently, the QR code has been printed on top of the BBOT–PU layer using the previously prepared NC-based luminescent ink. Printing details are provided in the Experimental Section. The schematic representation is shown in Figure 5A. The photographs of the QR code-printed currency captured under visible and UV lights are provided in Figures S14C and 5D, respectively. Similar to the previous case, the printed QR code is readable only under UV light. Figure 5E shows the photograph representing the QR code

decryption process using a smartphone. Due to copyright issues, the photographs of the original currency and QR code were blurred. The QR code-printed currency was kept under UV light during the data decryption. The presence of BBOT helped to enhance the optical contrast between the interface layer (BBOT-PU) and the NC layer, which indeed supports the decryption of a security label specifically under UV light. Additionally, the BBOT-PU layer allows facile decryption of the QR codes-printed on any universal currencies preloaded with unspecified UV sensitive interfering inks. Although the combined emission of BBOT and NCs under 365 nm excitation (Figure 5C) reduced the PL brightness of NCs in ink (Figure 5D), we could successfully demonstrate the printing and electronic reading of a QR code on currency via the optical contrast illusion process. The printed security label is optically unclonable as their electronic absorption bands and PL features are highly precise (Figure 3C). Later, we have tested the mechanical stability of the QR code-printed currency by a folding assay. The photographic evidence shows (Figure S15A; under UV light) that the printed security label is stable even after multiple folding. Finally, we have tested aqueous stability of QR code-printed currency by dipping them in water (Figure S15B). The poor solubility of NCs and BBOT in water prevents their leaching. The data decryption was successful after both folding and wetting trials. The exceptional mechanical, thermal, photo, and aqueous stability of the printed documents suggest that NC-based luminescent ink can be further extended to develop the next-level security codes.

CONCLUSIONS

In summary, we have successfully demonstrated the room temperature fabrication of nontoxic, cost-effective, reliable, and optically unclonable luminescent security labels. Such security labels are fabricated through the stencil printing technology using near NIR-emitting precise NCs as the primary component in ink. The successful intercalation of NCs into the PU matrix helped to develop light-emitting and flexible ink. NC-based ink displayed brilliant PL owing to their strong C-H $\cdots\pi/\pi\cdots\pi$ interactions. Spectroscopic and microscopic techniques were employed to study the stability of NCs in ink and the printed band. Robust optical absorption, PL, and molecular composition of NCs suggest their extended stability in ink. Detailed investigation of the printed security labels disclosed their unique mechanical, thermal, photo, and aqueous stability. This information helped to demonstrate the printing and electronic reading of the QR code on a currency using a smartphone. Encryption and decryption of a security label under a defined spectrum of light were demonstrated by creating an optical contrast illusion on the currency. The elastomeric binder helped to hold the printed QR code on currency even after multiple folding and wetting. The overall cost of a security label has been estimated to be approximately 0.013 USD per stamp. The anticounterfeiting technology can be further upgraded by printing the dynamic QR codes that enable us to update the encrypted data even after printing. In the future, this particular low-cost and nontoxic luminescent-based ink can be extended to develop wearable LEDs, healthcare sensors, pharmaceuticals, and food technology.

EXPERIMENTAL SECTION

Reagents and Materials. All the chemicals and solvents are of analytical grade and used without any further purification. Silver nitrate (AgNO_3), 1,3-benzenedithiol (BDT), sodium borohydride (NaBH_4), potassium hydroxide (KOH), BBOT, methanol, acetone, THF, dichloromethane (DCM), DMF, gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), glutathione (GSH), 2-phenylethanethiol (PET), *p*-mercaptobenzoic acid (*p*-MBA), tetraoctylammonium bromide (TOAB), toluene, and hydrochloric acid (HCl) were purchased from Sigma-Aldrich. α -Lipoic acid (LA) and triphenylphosphine (TPP) were purchased from Tokyo Chemicals Industry (TCI). Sodium hydroxide (NaOH) and ammonium acetate (NH_4OAc) were purchased from Fisher Scientific. DMSO- d_6 was purchased from Sisco Research Laboratories (SRL). Medical grade thermoplastic PU (TECOFLEX EG-93A) was received from Lubrizol Advanced Materials India.

Characterization. ^1H and ^{31}P NMR measurements were carried out using Bruker AVANCE III HD 400/500 MHz spectrometers. UV/vis absorbance spectra were recorded on a Varian Cary 500 Scan spectrometer. PL spectra were recorded using a Horiba Fluorolog 3 spectrometer. The fluorescence lifetime measurements were carried out using a Horiba (model DeltaFlex) TCSPC system. The samples were excited using a 378 nm pulsed diode laser (NanoLED-375L; <100 ps pulse duration). ESI-MS measurements were carried out on a Waters Synapt G2-Si high-definition mass spectrometer. Typical experimental parameters of ESI-MS were as follows: capillary voltage: 3 kV, cone voltage: 20 V, source offset: 20 V, source temperature: 100 $^\circ\text{C}$, desolvation temperature: 150 $^\circ\text{C}$, and desolvation gas flow: 400 L/h. HR-TEM images were recorded on a FEI Talos F200S (200 kV) TEM. FESEM images were recorded using a Carl-Zeiss SUPRA 55VP field emission scanning electron microscope. XPS spectra were recorded using a Thermo Scientific ESCALAB 250Xi (XR6 Micro-focused Monochromator, Al $K\alpha$). Optical images of crystallized NCs were recorded using a Horiba Jobin Yvon LabRAM HR Evolution laser Raman microscope. The confocal fluorescence image of crystallized NCs was recorded using a Carl Zeiss-LSM 880 confocal laser scanning microscope (458 nm laser). Surface hydrophobicity of NC-PU and PU-alone films was examined using an AST VCA optima (S/N-1020041134) contact angle analyzer. Distilled water (5 $\mu\text{L}/\text{drop}$) was used to measure the contact angle on NC-PU film-coated surfaces by dispensing water using a motorized syringe at 25 $^\circ\text{C}$. The stress-strain analysis was carried out at room temperature using a universal testing machine (Instron 3366; Instron Crop. USA). The printed band (50 mm length $\times$ 10 mm width) was fixed into the testing station and subjected to an extension rate of 10 mm/min. Energy-minimized structures of NCs were optimized using DFT as implemented in the grid-based projector augmented wave (GPAW) software package.⁶⁸ The structures were optimized in real space having a grid spacing of 0.2 $\text{\AA}$ for the electron density with the PBE⁶⁹ functional in the FD mode. The convergence criterion for residual forces was set to be 0.05 eV/ $\text{\AA}$, without imposing any symmetry constraints. The following PAW setups were considered for Ag($4d^{10}5s^1$), S($3s^23p^4$), P($3s^23p^3$), O($2s^22p^4$), C($2s^22p^2$), and H($1s^1$), with scalar-relativistic effects included for Ag. The visual molecular dynamics (VMD) software⁷⁰ was used for the visualization of the structures.

Synthesis of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NCs. $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NCs were synthesized using a reported protocol.⁵³ Briefly, in a glass tube, 13.5 μL of BDT was added to 10 mL of DCM. AgNO_3 (20 mg) was separately dissolved in 5 mL of methanol by ultrahigh sonication. The addition of AgNO_3 solution into the above-prepared reaction mixture resulted in a turbid yellow solution, indicating the formation of an insoluble silver-thiolate complex. The mixture was cooled to ice-cold temperature. The addition of TPP (200 mg/1 mL DCM) into the turbid yellow solution resulted in the formation of a colorless solution. The reaction mixture was allowed to stir for another 10 min before adding a freshly prepared aqueous ice-cold NaBH_4 solution (10.5 mg/500 μL). The color of the solution turned dark brown immediately, which gradually

changed (over a period of 5 h) to dark orange, indicating the formation of Ag_{29}NCs . NCs were purified by the ultrahigh centrifugation method (8000 rpm for 2 min). Residual dark orange NCs were washed several times with ethanol to remove all the unreacted materials. Purified NCs were dried under vacuum and stored at 4 °C for further characterizations. Photographs representing the different stages of NCs synthesis are given in the Supporting Information (Figure S16).

Synthesis of $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs. $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs were synthesized using a protocol reported elsewhere.⁵⁵ Briefly, an aqueous solution of KOH (1 M) was added to LA (19 mg/1 mL) until it dissolves completely. An aqueous solution of NaBH_4 (7 mg/100 μL) was added into the abovementioned lipate solution and stirred for another 15 min. Followed by this, an aqueous AgNO_3 (2.9 mg/200 μL) solution was injected and stirred for 30 min at room temperature. The addition of ice-cold NaBH_4 (10 mg/100 μL) solution into the abovementioned reaction mixture resulted in a color change from black to dark orange (over a period of 4 h), indicating the formation of NCs. NCs were purified by adding an equal volume of acetone followed by ultrahigh centrifugation (8000 rpm for 2 min). Furthermore, the residual dark orange supernatant solution was precipitated by adding excess acetone. The precipitate was washed several times with ethanol to remove all the unreacted materials. Purified NCs were dried under vacuum and stored at 4 °C for further characterizations.

Fabrication of Luminescent NC-Based Printing Ink. PU was used as an elastomeric binder for the development of stretch-enduring luminescent printing ink. A typical synthesis of ink consists of mixing crystallized NCs (7 or 40 mg) in PU suspension (24 mL) in a shaker for 30 min, followed by constant stirring for another 5 h. The PU suspension was previously prepared by dispersing PU (2 g) in THF (24 mL) using the ultrasonication (30 min) method, followed by continuous stirring (overnight). Similarly, the BBOT–PU suspension was prepared by dispersing PU (2 g) and BBOT (1.25 mg) in THF (24 mL). To print QR codes, we have used low concentration NC–PU (7 mg NC/24 mL PU) dispersion.

Fabrication of the Printed QR Code. The luminescent ink was manually printed on the desired area of the currency using a stencil printing technique. Initially, a static QR code image encrypted with “confidential information” was generated using free available software (<https://www.the-qrcode-generator.com>). The stencil pattern corresponding to the QR code image was designed using AutoCAD software. The stencil was created on a polyester sheet (100 μm thickness) by engraving the intended sketch using an electronic cutter (Silhouette Cameo, US). The BBOT–PU interface layer was initially printed (2.5 $\times$ 2.5 cm) to facilitate the luminescent ink adhesion on the currency substrate and cured at 65 °C for 20 min in a convection oven. Subsequently, the QR code was patterned by printing the luminescent ink on the BBOT–PU layer and cured at 65 °C for 30 min. The luminescent ink movement over the stencil using a squeegee facilitates printing the QR code pattern on the underlying currency substrate. The freestanding stretchable film was prepared by directly printing the luminescent ink on the temporary transfer paper (tattoo paper). The transfer paper was prepared by coating a water-soluble starch layer on the copier paper (80 gsm).⁶⁴ Typically, 55% starch was dispersed in water by heating at 95 °C for 15 min and cross-linked with D-sorbitol (45%) under stirring for 1 h. The cross-linked starch was printed on the paper substrate and cured at 70 °C for 30 min. The process was repeated twice to get the homogenous water-soluble film on the paper substrate. The printed luminescent film on the tattoo paper can be released by moisturizing it for 1 min.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c21127>.

Synthetic procedure for $[\text{Au}_{22}(\text{SG})_{18}]^-$, $[\text{Au}_{25}(\text{PET})_{18}]^-$, $[\text{Au}_{102}(\text{p-MBA})_{44}]$, and $[\text{Au}_{144}(\text{PET})_{60}]$ NCs; UV/vis absorption and PL spectra of $[\text{Au}_{22}(\text{SG})_{18}]^-$,

$[\text{Au}_{25}(\text{PET})_{18}]^-$, $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$, $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$, $[\text{Au}_{102}(\text{p-MBA})_{44}]$, and $[\text{Au}_{144}(\text{PET})_{60}]$ NCs; time-dependent PL spectra of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ and $[\text{Ag}_{29}(\text{LA})_{12}]^{3-}$ NCs under 365 nm illumination; photograph shows transparency of the printed band; TEM image and PL spectrum recorded from NC-based ink; XPS spectra of P 2p, O 1s, and N 1s recorded from the printed band; EDAX spectrum and elemental composition of the printed band; temporal-PL spectra recorded from the printed band under 365 nm illumination; UV/vis absorption spectra recorded from the printed band kept at different temperatures; photographs of the printed band under UV light before and after dipping in liquid nitrogen; five cycles of PL spectra recorded from the printed band at different temperatures; water drop profiles on PU-alone and NC–PU printed bands; photographs showing the long-term stability of the printed band under water; photographs of the printed band captured during the wincing under UV light; photographs showing the restoring ability of the printed band after stretching; stress–strain curves recorded from the NC–PU and PU-alone printed band; photographs of the printed QR code on A4 paper under visible and UV light; photograph of QR code-printed currency under visible light; photographs of QR code-printed currency captured during folding and wetting assay under UV light; photographs captured during the synthesis of $[\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_4]^{3-}$ NC; and references (PDF)

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Author Contributions

J.V.R. and P.M. contributed equally. The project was designed and supervised by E.S.S. Nanoclusters and ink were synthesized by J.V.R. and P.M. Stencil printing was designed by A.M.V.M. Stencil printing was performed by R.V. and A.M.V.M. All the spectroscopy and microscopy were performed by J.V.R., P.M., and E.S.S. The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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■ ABBREVIATIONS

NC, atomically precise noble metal nanocluster
 PU, polyurethane
 QR, quick response

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ARTICLE

The interplay of chromophore-spacer length in light-induced gold nanocluster self-assembly

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The light-induced self-assembly of chromophore-tethered precision nanoclusters (NCs) has received significant attention recently due to their facile control over structure, function, and reversibility under ambient conditions. However, the magnitude of assembly depends on the photoswitching efficiency, chemical structure, and proximity of the chromophore to the NC surface. Herein, using azobenzene alkyl monothiol (AMT)-capped gold NCs with two different spacer lengths (denoted as C₃-NC and C₉-NC), we show that reversible *cis* ↔ *trans* isomerization efficiency can be readily tuned to control the self-assembly kinetics of NCs. Irrespective of the chain length, the time required for *trans*-*cis* (140 s) and *cis*-*trans* (260 s) isomerization of individual C₃-AMT and C₉-AMT are identical in dichloromethane solution. When a similar experiment was performed using a solution of C₃-NCs and C₉-NCs, it resulted in self-assembled disc-like superstructures. Notably, the *trans*-*to*-*cis* photoswitching in C₃-NC could accomplish only 65% even after 460 seconds of irradiation. On the other hand, C₉-NC completed this process within 160 seconds of irradiation. The low photoswitching efficiency of the C₃-NC analog is due to the short and rigid spacer length of C₃-AMT ligands, which is in close proximity to the NC surface, resulting in steric hindrance experienced at the NC-chromophore interface. Importantly, the slow photoswitching in C₃-NCs helps to isolate and investigate the intermediates of assembly. Using high-resolution electron microscopy, atomic force microscopy, and 3D reconstruction, we show that the discs are made up of densely packed arrays of NCs. The prolonged illumination of C₉-NCs results in a chain-like assembly due to the dipolar attractions between the previously assembled superstructures. The efficient photoisomerization of chromophores located away from the nanocluster surface has been identified as the key element to speed up the light-induced assembly in chromophore-tethered nanoclusters. Such information will be useful while developing nanoscale photoswitches for electrochemistry, biosensors, and electronic devices.

Introduction

Precision nanoclusters (NCs) offer atomic-scale control over the metal core and exhibit remarkable photophysical and electrochemical properties.^{1–10} Even minor modifications to a single metal atom can have a major influence on the behavior and functionality of NCs.^{11–16} This characteristic makes NCs ideal building blocks for constructing two-dimensional and three-dimensional self-assembled superstructures with collective and enhanced properties.^{17–20} The delicate balance between non-covalent interactions (van der Waals interactions, hydrogen bonding, C–H...π/π...π interactions, electrostatic interactions, aurophilic interactions, amphiphilic interactions, or light-induced dipole-dipole attractions) and thermodynamics control the generation of self-assembled superstructures, emphasizing the complexity of the assembly process.^{21–30} Such assembled materials find applications in device fabrication,^{31–34} green catalysis,^{35–39} toxin/metal ion screening,⁴⁰ gas sensing,^{41,42}

bioimaging, and therapeutics.^{43–47} Among the different non-covalent interactions, the light-induced dipolar interaction is promising as it allows reversible assembly by changing the wavelength of light. Studies on photoswitching properties of azobenzene functionalized gold nanoparticles are well documented in the literature for over two decades.^{48–51} Recently, twenty-five atom gold (Au₂₅) NCs functionalized with thiolated-spiropyran or -azobenzene ligands demonstrated the feasibility of light-induced reversible self-assembly for hierarchical structure formation across length scales.^{29,52,53} These studies have shown that when azobenzene molecules are attached to the surface of NCs, their dipole moments play a significant role in the assembly process. Light irradiation triggers the *trans*-*to*-*cis* isomerization, resulting in an induced dipole moment. This leads to attractive interactions between neighboring NCs, and forms assembled superstructures. Similar photochemistry has been utilized in systems containing other metal clusters and inorganic nanocages.^{54–56} However, the extent of assembly largely depends on the photoswitching efficiency of the chromophores attached to the NC surface. This efficiency is influenced by the chemical structure of the chromophore and its proximity to the NC surface. Thus, NCs functionalized with photoswitchable ligands offer facile control over self-assembly kinetics and structural diversity of self-assembled structures. Here, we show the interplay between the

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spacer length and photoswitching ability of azobenzene alkyl monothiol (AMT) capped Au NCs. We used, AMT-protected NCs (C_3 -NCs and C_9 -NCs) with two different spacer lengths (C_3 -AMT and C_9 -AMT). The assembly process of both NCs in a dichloromethane (DCM) solution at ambient temperature under 345 nm light was investigated using different spectroscopic studies and microscopic imaging. The C_9 -NCs showed quick self-assembly compared to the C_3 analog due to negligible steric hindrance experienced at the NC-chromophore interface resulting from their safer separation. The less nonbonding steric interactions allow more favorable orientation and arrangement to the surface chromophores, forming self-assembled superstructures *via* attractive dipoles. The prolonged illumination of C_9 -NCs showed a chain-like assembly due to the dipolar attractions between nearby superstructures. These findings highlight the importance of rational design and control over the spatial arrangement of chromophores in precision NCs. By carefully tuning the spacer length and considering the steric effects, it becomes feasible to optimize the self-assembly process and achieve desired supramolecular structures with enhanced photophysical and electrochemical properties.

Result and Discussion

To investigate the role of chromophore-spacer length in the light-induced assembly of NCs, we first covalently linked the azobenzene core with the C_3 -carbon chain (short; C_3 -AMT) and C_9 -carbon chain (long; C_9 -AMT) thiols (Fig. 1a). The synthesis and characterization of ligands are presented in the supplementary information (Fig. S1-S15[†]). The time-dependent absorption spectra obtained from C_3 -AMT and C_9 -AMT dispersed in DCM and irradiated separately using UV light (345 nm) are shown in Fig. 1b and c, respectively. The systematic decrease in optical density (OD) at 345 nm and simultaneous gradual growth in OD around 435 nm indicate the *trans*-to-*cis* isomerization of azobenzene moieties. The absorption spectra of C_3 -AMT and C_9 -AMT show the *cis*-to-*trans* isomerization when irradiated at 435 nm (Fig. S16a and b[†]). The energy-minimized structures of *cis*-*trans* geometrical isomers of C_3 and C_9 -AMT obtained through density functional theory (DFT) are illustrated in the inset of Fig. 1b and Fig. S17[†], respectively. From the combined plot of OD@345 nm vs. irradiation time of C_3 -AMT and C_9 -AMT recorded under 345 nm and 435 nm lights, it is evident that the time required for *trans*-to-*cis* (~140 sec) or *cis*-to-*trans* (~260 sec) isomerization in AMT is nearly identical, irrespective of the spacer length (inset in Fig. 1c). However, the *cis* to *trans* conversion was not complete due to the overlap of n - π^* transition of *cis* and *trans* isomers.⁵⁷

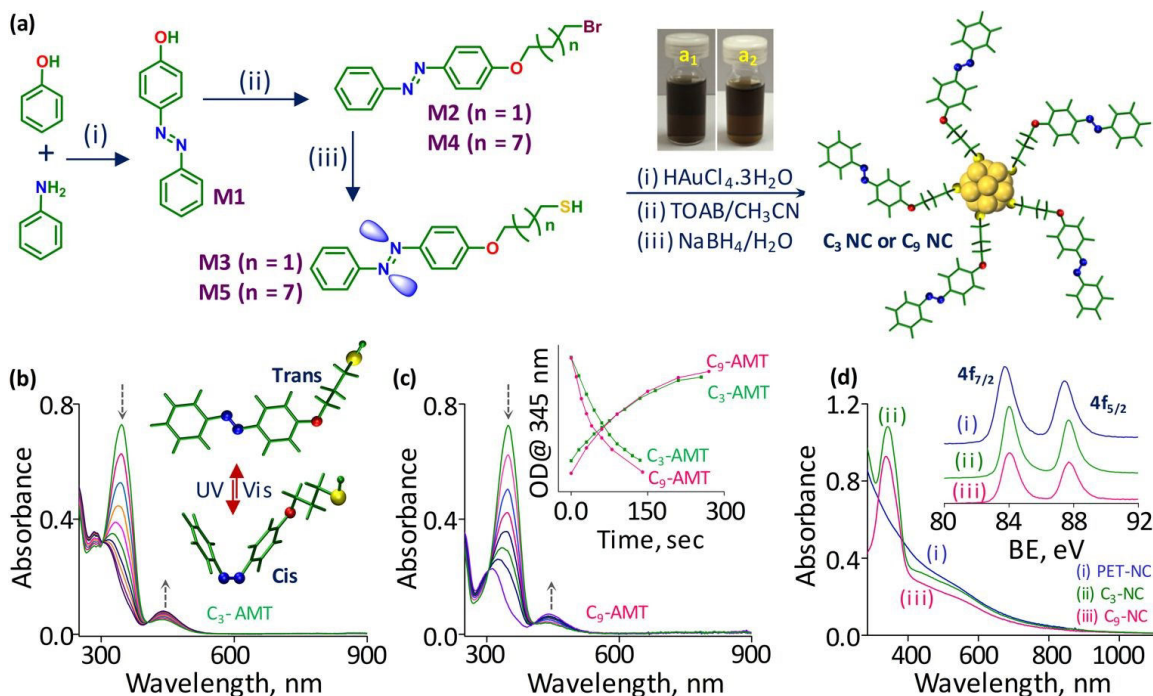


Fig. 1 (a) Synthesis scheme of C_3 -AMT and C_9 -AMT (M1-M5), C_3 -NC, and C_9 -NC; (i) Conc. HCl, NaNO₂, 0 °C (ii) 1,3-dibromopropane or 1,9-dibromononane, K₂CO₃, KI, acetone, 80 °C (iii) HMDST and TBAF, distilled THF, -10 °C. The photographs of C_3 and C_9 NC solutions are shown in a₁ and a₂. (b and c) The temporal optical absorption spectra of (b) C_3 -AMT and (c) C_9 -AMT under 345 nm illumination. Energy-minimized structures of *trans* and *cis* isomers of C_3 -AMT are shown in the inset of Fig. 1b. Combined plots of OD (ca. 345 nm) vs. illumination time recorded from C_3 -AMT and C_9 -AMT under 345 nm and 435 nm are given in the inset of Fig. 1c. (d) UV-Vis absorption spectra of (i) PET-NC, (ii) C_3 -NC and (iii) C_9 -NC recorded in DCM. The XPS spectra (Au 4f levels) of all three NCs are shown in the inset of Fig. 1d.

To evaluate the role of chromophore-spacer length in the light-induced assembly of NCs, photoswitchable gold NCs with two different spacer lengths (C_3 -NC and C_9 -NC) were synthesized and purified using the procedure reported for $[Au_{144}(PET)_{60}]$ NCs (abbreviated as PET-NC; Fig. 1a, see SI for details; here PET represents 2-phenylethanethiol). The optical absorption features of C_3 and C_9 NCs were compared with the PET analog (PET-NC; Fig. 1d). The presence of two weak humps *ca.* 520 nm and 700 nm, similar to PET-NC, and an overlapping absorption maximum at 345 nm equivalent to the optical absorption characteristics of AMT confirms the formation of C_3 and C_9 NCs. Since the electrospray ionization mass spectrometry (ESI-MS) and matrix-assisted laser desorption ionization (MALDI) mass spectrometry trials were not successful, we compared the X-ray photoelectron spectra (XPS) of these C_3 -NC and C_9 -NC with that of PET-NC. The well-matching binding energy (BE) values of gold 4f electron orbitals in C_3 -NC and C_9 -NC compared to the reported values of PET-NC (inset in Fig. 1d) suggest similar metal core for all the three NCs (C_3 -NC, C_9 -NC, and PET-NC). A small shift in the BE of the NCs is presumably due to the difference in the electron densities of the organic counterparts. The BE values of C1s, N1s, O1s, and S2p levels of all three NCs are

shown in Fig. S18a-d†. The core size of C_3 -NC and C_9 -NC was examined using TEM (transmission electron microscopy) analysis. TEM images from C_3 - and C_9 -NCs (inset in Fig. 2a and Fig. S19†, respectively) show nearly uniform size distributions (1.9 ± 0.14 nm and 1.87 ± 0.12 nm). The core sizes of C_3 - and C_9 -NCs are in agreement with that of the PET-NC.⁵⁸ Next, we evaluated the photoisomerization efficiency of C_3 and C_9 NC solutions in DCM under two different wavelengths of light. The absorption spectra of C_3 and C_9 NCs illuminated under 345 nm are shown in Fig. 2a and b, respectively. The time-dependent absorption spectra of C_3 and C_9 NCs recorded separately during the reverse (*cis*-to-*trans*) photoswitching (435 nm) are shown in Fig. S20a and b†. The combined plots of OD@345 nm vs. irradiation time recorded during the photoisomerization (*trans*-to-*cis* and *cis*-to-*trans*) of C_3 and C_9 NCs are shown in the inset of Fig. 2b. Notably, the time required for *trans*-to-*cis* photoswitching in C_3 and C_9 NCs (same concentration) under a similar intensity of light (0.2 mW/cm²) was found to be different. More precisely, the *trans*-to-*cis* photoswitching in C_3 -NC could accomplish only 65% even after 460 seconds of illumination. Beyond this point, there was no change in their absorbance.

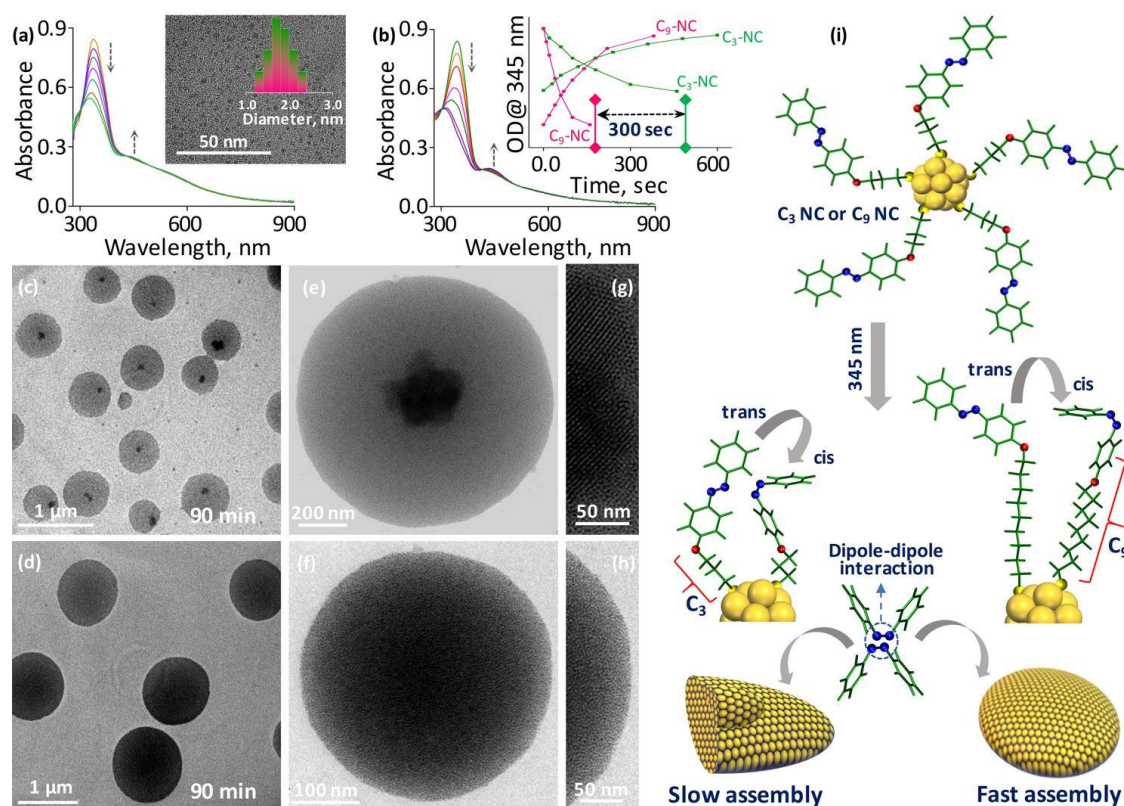


Fig. 2 (a and b) Temporal optical absorption spectra recorded from (a) C_3 -NC and (b) C_9 -NC under 345 nm illumination. The TEM micrograph of C_3 -NC is shown in the inset of Fig. 2a. The combined plots of OD (*ca.* 345 nm) vs. irradiation time, using 345 nm and 435 nm lights recorded from C_3 -NC and C_9 -NC are shown in the inset of Fig. 2b. (c and d) Large area TEM images captured from (c) C_3 -NC and (d) C_9 -NC assembly after 90 min of illumination under 345 nm light. (e and f) Magnified and tight-focused TEM micrographs of a single superstructure derived from (e) C_3 -NC and (f) C_9 -NC. (g and h) An enlarged image captured from (g) the centre dark spot of C_3 -NC and (h) the edge of C_9 -NC assemblies. (i) The schematic shows the distant-dependent self-assembly in C_3 -NC and C_9 -NC and the possible mechanism for their slow and quick assembly.

On the other hand, C₉-NC completed the isomerization process within 160 seconds of illumination. Importantly, the *trans*-to-*cis* isomerization in C₉-NC is comparable to free AMT molecules (inset in Fig. 1c; 140 sec). While the isomerization is three times slower in the case of C₃-NCs. This suggests the effect of chromophore proximity on photoswitching. In C₉-NCs, the chromophore is located far from the metal surface. Furthermore, the spacer is flexible, allowing less steric crowding. However, in C₃-NCs the short spacer is rigid, and the chromophore is in close proximity to the NC surface, resulting in steric crowding of surface ligands. Therefore, the steric hindrance experienced at the NC-chromophore interface finally restricts the photoswitching process. To understand the role of chromophore spacer length in the self-assembly of NCs and investigate the resulting superstructures, we used TEM imaging. For this, ~100 μM solutions of C₃ and C₉ NCs prepared in DCM separately were irradiated at 345 nm for 90 min in a dark room. A constant stirring of NC solutions in a temperature-controlled bath helped to reduce thermal aggregation. The TEM images from the illuminated C₃ and C₉ NCs are shown in Fig. 2c and d, respectively. Though C₃ and C₉ NCs underwent light-induced self-assembly and formed disc-like superstructures, there are some morphological differences for the superstructures formed from both NCs. TEM images of individual superstructures from C₃ and C₉ NCs are shown in Fig. 2e and f, respectively. The C₃-NCs are self-assembled into disc-like superstructures with some crystallized array of NCs encapsulated in each superstructure (Fig. 2g). This is presumably due to the slow assembly and rigid nature of ligands, which promote a well-ordered array of NCs. Furthermore, an incomplete and slow isomerization may also affect the assembly kinetics resulting in heterogeneous

structures. On the other hand, C₉-NC superstructure (Fig. 2h) showed a nearly uniform assembly of densely packed structures. From the above spectroscopic and microscopic studies, it is obvious that the time scale of the light-induced self-assembly largely depends on the suitable distance between chromophores and NCs. The uniform assembly in C₉-NC compared to the C₃ analog is attributed to the negligible steric hindrance experienced at the NC-chromophore interface. The schematic shows the distant-dependent self-assembly in C₃ and C₉ NCs and the possible mechanism for their slow and quick assembly is shown in Fig. 2i. The structural details of self-assembled superstructures were further explored using dark-field scanning transmission electron microscopy (STEM) imaging and elemental mapping. The STEM images from C₃- and C₉-NC assemblies are shown in Fig. S21a and b†, respectively. A contrast difference in the STEM image for C₃-NC assembly shows the existence of crystallized aggregates encapsulated within the disc-like structures (Fig. S21c†). The STEM micrograph recorded from the C₉-NC assembly showed uniform contrast all over the surface (Fig. S21d†). The chemical composition assessment of both self-assembled superstructures using energy-dispersive X-ray analysis (EDS), verifies the existence of gold, sulfur, nitrogen, oxygen, and carbon. The gold (yellow) and sulfur (green) mapping of single superstructures derived from C₃- and C₉-NCs are shown in Fig. S21e-h†. The large area STEM images, elemental maps (gold, sulfur, and nitrogen), and EDS spectra recorded from C₃- and C₉-NCs assemblies are shown in the SI (Fig. S22†). Further, field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) images were utilized to investigate the structural details of assembled superstructures.

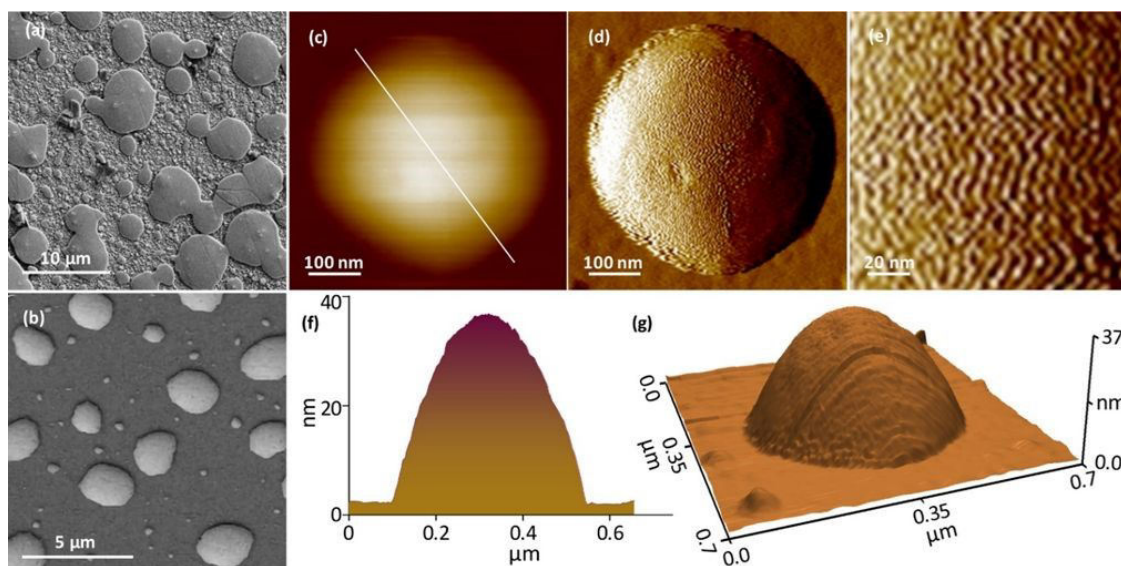


Fig. 3 (a and b) FESEM images of (a) C₃-NC and (b) C₉-NC assemblies. (c and d) High-resolution tapping mode AFM (c-topography and d-amplitude) images of single superstructure derived from C₃-NC. (e) A zoomed and focused AFM image captured from the top surface of the C₃-NC assembly showed the NC direction in the assembly. (f and g) The height profile and three-dimensional (3D) AFM image of the same assembly.

Fig. 3a and b show the FESEM micrographs captured from C_3 - and C_9 -NC assemblies. The disc-like superstructures with a few layers of upcoming assemblies on the top surface are seen in the case of the C_3 -NC assembly. The C_9 -NC assembly shows densely packed disc-like superstructures similar to the TEM image shown in Fig. 2d. The morphology of assembled superstructures was further examined using AFM imaging. Fig. S23a and b[†] show the large area AFM images captured from C_3 - and C_9 -NC assemblies, in which the upcoming assemblies are visible in the case of C_3 -NC. The AFM images of single superstructures derived from C_3 - and C_9 -NCs are shown in Fig. S24[†]. The AFM data is consistent with TEM, STEM, and FESEM results. The high-resolution AFM images captured from a single superstructure derived from C_3 -NC (Fig. 3c-g) show the periodic assembly of NCs. The zig-zag patterns represent the NC directions in the assembly (Fig. 3d-e).

To further gain insights into 3D internal structures of self-assembled structures, we used electron tomography (ET).⁵⁹ Detailed are provided in the SI. Accordingly, the 2D projections were collected between $\pm 70^\circ$ with an increment angle of 2° (Fig. S25[†]). The corresponding TEM images (Fig. 4a and b) and the 3D reconstruction images of C_3 - and C_9 -NC assemblies (Fig. 4c-g, Videos S₁ and S₂[†]) revealed the disc-like morphology of the superstructures. The cross-sectional view suggests that the superstructures are composed of densely packed NC networks. However, there is a significant difference in the overall disc thickness. As observed in 2D projections, the C_3 NCs contain crystalline aggregates within the discs that are protruding outside the discs (Fig. 4c, e, and f). On the other hand, uniform array of NCs was observed in the case of C_9 NC-based assemblies (Fig. 4d and g). It is important to note that deformed

shapes and flattening are commonly observed in such assemblies due to solvent evaporation and drying artifacts during specimen preparation. However, we observed a clear difference in 3D reconstructed structures obtained from C_3 NCs and C_9 NCs. Superstructures obtained from C_3 NCs display uniform thickness across the particle. This suggests that the superstructures are disc-like assemblies. On the other hand, in the case of C_9 NCs, the deformation and flattening of the structure is evident due to non-uniform thickness between the center and the periphery.

NCs were also assembled into dimer and trimer superstructures during the light-induced self-assembly. However, the percentage of dimer and trimer formed is significantly less compared to monomer assembly. The early stages of monomer, dimer, and trimer assemblies derived from C_9 -NCs are shown in Fig. S26[†], in which the dimer and the trimer showed well-connected interfaces with periodic assembly. Eventually, they transformed into densely packed superstructures with constant illumination under 345 nm light (Fig. S27[†]). The early stages of dimer and trimer assemblies fabricated from C_3 -NCs with a few layers of incomplete assemblies similar to the monomer are shown in Fig. S28[†]. Subsequently, we investigated the long-term stability of assembled superstructures using TEM imaging of the same grid stored at low temperature. Notably, the morphology of assembly was intact even after one year (Fig. S29[†]). To understand the formation of disc-like assembly, TEM imaging was performed for samples prepared using a solution of C_9 -NC in DCM under 345 nm illumination at different time intervals. The TEM images revealed the formation of disc-like superstructures, that evolved from the short circular assembly (Fig. S30[†]).

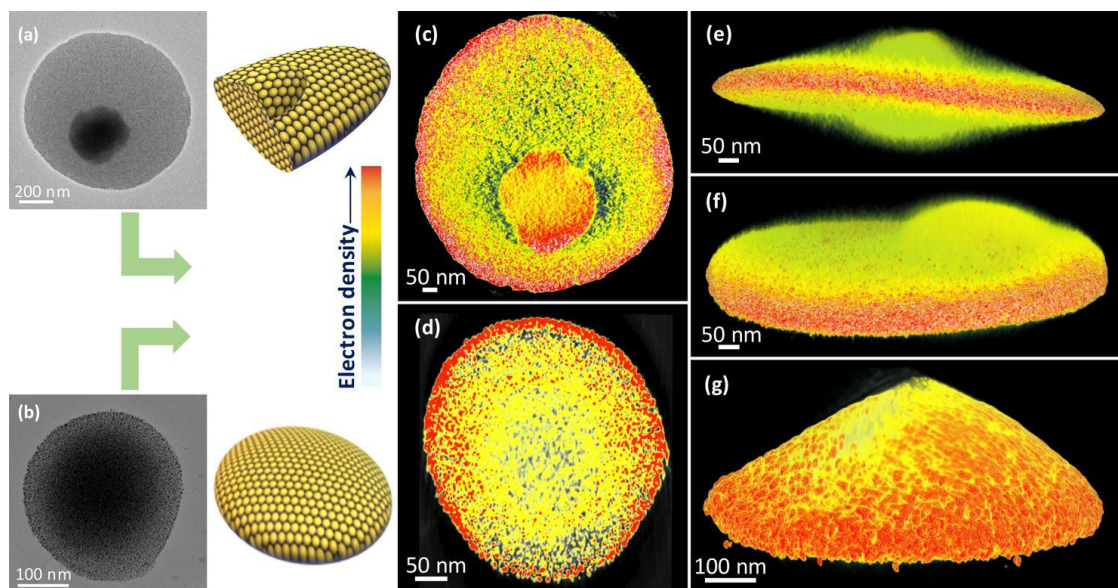


Fig. 4. (a and b) TEM images and (c and d) corresponding ET reconstruction images of (a and c) C_3 - and (b and d) C_9 -NC superstructures. (e-g) The 3D-reconstructed tomograms of (e and f) C_3 - and (g) C_9 -NC superstructures in different orientations.

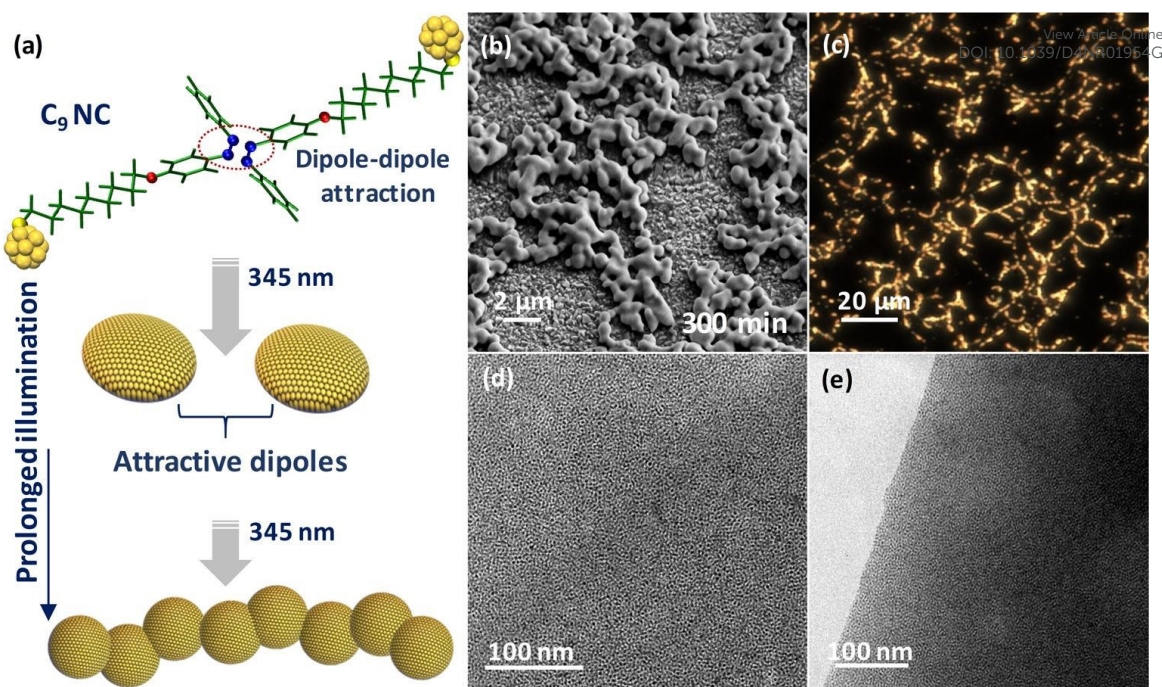


Fig. 5 (a) The schematic depicts the formation of a chain-like assembly. (b) FESEM and (c) dark-field scattering images of the chain-like assembly. (d and e) TEM micrographs from the surface and edge of the chain-like assembly.

We finally investigated the impact of prolonged illumination on the structural transformation of assembled superstructures. For this, a solution of C_9 -NC in DCM was UV irradiated at 345 nm for 5 h. The sustained illumination resulted in the solidification of NCs due to the formation of bulky superstructures. To understand the structural rearrangements, the solid material was further examined by redissolving them in DCM. The FESEM image (Fig. 5b) shows a chain-like assembly formed by fusing the individual superstructures due to dipole-dipole interactions between them. A similar chain-like framework seen in the dark-field scattering microscope (Fig. 5c) is in good agreement with the FESEM data. The TEM micrographs captured from the surface and edge of the chain-like structures (Fig. 5d and e) showed highly ordered multilayer assembly throughout. A scheme for the formation of a chain-like assembly is shown in Fig. 5a, in which the individual NCs initially self-assembled into disc-like superstructures and then into chain-like assemblies due to the extended dipolar interactions between them during the course of illumination. The above-demonstrated idea will be useful in fulfilling industrial needs, especially in the development of molecular photoswitches.

Conclusions

The reversible self-assembly of NCs using external stimuli such as light, heat, and magnetic fields is a tremendously evolving research area. In the recent past, light has been identified as an efficient probe to demonstrate the supramolecular self-assembly of chromophore-tethered NCs. However, the

magnitude of assembly in chromophore-tethered NCs largely depends on their photoswitching efficiency. We have successfully demonstrated this concept by introducing two photoswitchable NCs fabricated using the thiolated-azobenzene molecule with different spacer lengths. The core and molecular information of both NCs were meticulously explored using various spectroscopic and microscopic techniques. Photoactivation of both NC solutions at ambient temperature using 345 nm light resulted in the formation of self-assembled superstructures. FESEM, AFM, TEM, ET reconstruction, STEM, and dark field scattering microscopic studies showed the presence of densely packed NCs in self-assembled superstructures. By introducing the idea of distance dependency, we successfully demonstrated the prompt self-assembly in NCs. This was evident from the fast assembly observed in C_9 -NCs due to their improved photoswitching efficiency resulting from the negligible steric hindrance experienced at the NC-chromophore interface. Such molecular control over the self-assembly of NCs by placing the chromophores suitably away from the nanosurface are useful tools for developing next-generation switchable sensors, especially in biological, electrochemical, and electronic devices.

Data availability

The ESI contains experimental details, ^1H , ^{13}C , FT-IR, and LC-MS of molecules; Energy-minimized structures and temporal absorption spectra of M3 and M5 molecules; XPS spectra of PET-NC, C_3 -NC, and C_9 -NC; HR-TEM images and temporal absorption spectra of C_3 -NC,

and C₉-NC; STEM micrographs and elemental maps of C₃-NC and C₉-NC assemblies; AFM images of C₃-NC and C₉-NC assemblies; TEM images of C₃-NC and C₉-NC self-assembled monomer, dimer, and trimer; TEM images of C₃-NC and C₉-NC assembly after one year; Temporal TEM images of C₉-NC assembly demonstrate the formation of disc-like assembly; Three-dimensional superstructures are composed of densely packed NCs (MOV)

Author Contributions

The project was designed and supervised by E.S.S. The chromophores and nanoclusters were synthesized by J.V.R. All the experiments were performed by E.S.S. and J.V.R. The electron tomography data acquisition and reconstruction were performed by N. The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Self-Assembly of Precision Noble Metal Nanoclusters: Hierarchical Structural Complexity, Colloidal Superstructures, and Applications

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Ligand protected noble metal nanoparticles are excellent building blocks for colloidal self-assembly. Metal nanoparticle self-assembly offers routes for a wide range of multifunctional nanomaterials with enhanced optoelectronic properties. The emergence of atomically precise monolayer thiol-protected noble metal nanoclusters has overcome numerous challenges such as uncontrolled aggregation, polydispersity, and directionalities faced in plasmonic nanoparticle self-assemblies. Because of their well-defined molecular compositions, enhanced stability, and diverse surface functionalities, nanoclusters offer an excellent platform for developing colloidal superstructures via the self-assembly driven by surface ligands and metal cores. More importantly, recent reports have also revealed the hierarchical structural complexity of several nanoclusters. In this review, the formulation and periodic self-assembly of different noble metal nanoclusters are focused upon. Further, self-assembly induced amplification of physicochemical properties, and their potential applications in molecular recognition, sensing, gas storage, device fabrication, bioimaging, therapeutics, and catalysis are discussed. The topics covered in this review are extensively associated with state-of-the-art achievements in the field of precision noble metal nanoclusters.

1. Introduction

1.1. Precision Noble Metal Nanoclusters

Atomically precise monolayer thiol-protected noble metal nanoclusters (NCs) emerged as a fascinating area of nanoscience research for the past two decades.^[1–10] NCs are distinct pieces of matter, possess ultrasmall metal cores (<2 nm), composed of a few to hundreds of atoms protected with a definite number of ligand shells.^[11–19] The electronic stability of NCs was well-explained using the superatom model,^[12,20,21] according to which NCs display better stability when the number of free electrons falls in the magic number series.^[13,22–24] NCs prepared from gold and silver metals have received substantial attention in recent past due to their size-dependent electronic,^[3,9,17] optical absorption,^[6,9] photoluminescence (PL),^[25–32] and magnetic properties.^[33,34] The specific

geometry and intrinsic photophysical properties of NCs have been efficiently used to probe catalytic reactions,^[35–50] toxic metal ions/molecules,^[51–55] biological events,^[56–68] solar energy conversion,^[69–73] and light-emitting device fabrication.^[74,75] A large number of NCs stapled with thiols,^[6,7] phosphenes,^[76–84] and selenols^[85–89] have been synthesized in liquid,^[6,7] solid,^[90] and interface layers.^[91,92] Later on, new and improved protocols were developed to fabricate monodisperse NCs.^[93–102] Advanced chromatographic techniques have been employed to separate and purify NCs.^[103–108] The molecular composition of several NCs has been determined using mass-spectrometry and single-crystal X-ray diffraction studies.^[109–132] Important milestones were the successful characterization of Au₁₈(SR)₁₄,^[109,110] Au₂₀(SR)₁₆,^[111] Au₂₃(SR)₁₆,^[112] Au₂₄(SR)₁₆,^[113] Au₂₅(SR)₁₈,^[114,115] Au₂₈(SR)₂₀,^[116] Au₃₀(SR)₁₈,^[117] Au₃₆(SR)₂₄,^[118] Au₃₈(SR)₂₄,^[119] Au₁₀₂(SR)₄₄,^[120] Au₁₄₄(SR)₆₀,^[121,122] Ag₂₅(SR)₁₈,^[123] Ag₂₉(S₂R)₁₂,^[124] and Ag₄₄(SR)₃₀.^[133] NCs. The chemical reactivity of NCs has been utilized to prepare doped and alloy NCs with altered optical and electrochemical properties.^[134–159] Furthermore, the organic synthetic toolbox has allowed the rational design of a variety of NCs with specific functional moieties on their surfaces. Among them, functional thiol-protected NCs have been extensively studied for photoinduced electron or energy

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Luminescent quantum dots: Synthesis, optical properties, bioimaging and toxicity

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ABSTRACT

Luminescent nanomaterials such as semiconductor nanocrystals (NCs) and quantum dots (QDs) attract much attention to optical detectors, LEDs, photovoltaics, displays, biosensing, and bioimaging. These materials include metal chalcogenide QDs and metal halide perovskite NCs. Since the introduction of cadmium chalcogenide QDs to biolabeling and bioimaging, various metal nanoparticles (NPs), atomically precise metal nanoclusters, carbon QDs, graphene QDs, silicon QDs, and other chalcogenide QDs have been infiltrating the nano-bio interface as imaging and therapeutic agents. Nanobioconjugates prepared from luminescent QDs form a new class of imaging probes for cellular and *in vivo* imaging with single-molecule, super-resolution, and 3D resolutions. Surface modified and bioconjugated core-only and core-shell QDs of metal chalcogenides (MX; M = Cd/Pb/Hg/Ag, and X = S/Se/Te), binary metal chalcogenides (MInX₂; M = Cu/Ag, and X = S/Se/Te), indium compounds (InAs and InP), metal NPs (Ag, Au, and Pt), pure or mixed precision nanoclusters (Ag, Au, Pt), carbon nanomaterials (graphene QDs, graphene nanosheets, carbon NPs, and nanodiamond), silica NPs, silicon QDs, etc. have become prevalent in biosensing, bioimaging, and phototherapy. While heavy metal-based QDs are limited to *in vitro* bioanalysis or clinical testing due to their potential metal ion-induced toxicity, carbon (nanodiamond and graphene) and silicon QDs, gold and silica nanoparticles, and metal nanoclusters continue their *in vivo* voyage towards clinical imaging and therapeutic applications. This review summarizes the synthesis, chemical modifications, optical properties, and bioimaging applications of semiconductor QDs with particular references to metal chalcogenide QDs and bimetallic chalcogenide QDs. Also, this review highlights the toxicity and pharmacokinetics of QD bioconjugates.

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