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

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KEYWORDS: Photoisomerization, switchable Au₂₅ NCs, light-stimulated reversible assembly, electron tomography, superstructures

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 Au₂₅ nanoclusters. Photoactivation of functionalized nanoclusters in dichloromethane by irradiating ultraviolet light at 345 nm resulted in a visual change and formation of disc-like colloidal superstructures ($d \sim 100$ –1000 nm). The superstructures readily disassembled into individual nanoclusters 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 self-assembly is driven by the photoisomerization of surface ligands. 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 photo-switching in nanoclusters.

INTRODUCTION

Atomically precise noble metal nanoclusters (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 thiols 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-assembly was realized *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 these self-assemblies are bonded to one another with local

forces, the efficient reversibility of such static assemblies will be difficult. In this setting, 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 by developing photo-isomerizing ligand^{37–42}-tethered NCs. As the photo-stability of NCs and their interactions with photons are largely 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.*, azobenzene⁴⁴ and spiropyran⁴⁵ 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 ($d \sim 100\text{--}1000\text{ nm}$) 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.

First, we discuss the synthesis and characterization of azobenzene monothiol ligand and $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC. AMT with C_3 -spacer (Figure 1A) was synthesized according to a reported literature procedure.^{46,47} Details of reactions involved in the preparation of C_3 -AMT, and their characterizations (Scheme S1 and Figures S1-S3 in Supporting Information; SI) are given in the experimental section. Absorption spectra of C_3 -AMT in dichloromethane (DCM) illuminated under ultraviolet (345 nm) and visible (435 nm) light is shown in Figure 1B. *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. Energy minimized structures of two geometrical isomers of C_3 -AMT optimized using density functional theory (DFT) is shown in the inset B1. Time-dependent absorption spectra of C_3 -AMT illuminated separately under 345 and 435 nm are given in the SI (Figure S4A and B). When illuminated under 345 nm the absorption spectra of C_3 -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 in Figure S4B).

plot of OD (*ca.* 345 nm) vs. illumination time under ultraviolet and visible light is shown in the inset D1.

The synthesis of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC was achieved using a modified Brust-Schiffrin single-phase method.⁴⁸ To compare the optical absorption features of newly synthesized $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NCs, phenylethanethiol (PET) analog, $[\text{Au}_{25}(\text{PET})_{18}]^-$ 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) $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$. The peak *ca.* 680 nm (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 the PET analog. Peaks (inset C1) at m/z 7391 and 9808 represents $[\text{Au}_{25}(\text{PET})_{18}]^-$ 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 NC. Metal core of NCs and the nature of binding were evaluated in 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} *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 S2p binding energy was in accordance with thiolate binding.

Figure 1. Synthesis and photophysical properties. (A) Schematic representation showing the synthesis, energy minimized structures and photoisomerization of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC (B) Absorption spectra of C_3 -AMT under visible light and UV light. Energy minimized structures of two geometrical isomers of C_3 -AMT is shown in the inset B1. (C) Absorption spectra of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ and $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs. ESI-MS of both NCs are shown in the inset (C1). (D) Temporal-absorption spectra of $[\text{Au}_{25}(\text{AMT})_{18}]^-$ under 345 nm illumination. A

We then studied the photoisomerization of Au_{25} NCs in DCM. 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 1D) exhibits a-

ligands,⁵⁰ ^1H NMR spectrum of the AMT in $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ display complex overlapping resonance peaks.

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

Figure 3.

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

gradual decrease in the OD *ca.* 345 nm and an increased OD *ca.* 435 nm (inset D1). Similar, but opposite photo-switching behavior was seen under 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 surface azobenzene ligands as shown using DFT energy minimized structures of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ in Figure 1A.

Photo-switching aspects 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 2). ^1H NMR spectrum of *trans* $\text{C}_3\text{-AMT}$ (Figure 2B) 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 2D) shows an upfield shift due to a larger shielding effect compared to *trans* counterparts. Figure 2C 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 2E and F). However, due to their different possible conformations as well as the chemical and magnetic non-equivalent nature of the

Reversible photo-switching in NCs was further investigated by transmission electron microscopy (TEM) imaging. At first, Au_{25} NC was 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 carbon support film. However, due to electron beam damage Au_{25} NC undergo rapid coalescence therefore, high-resolution imaging of individual NCs remained a challenge (Figure 3A).^{45,49,51} Nevertheless, the non-aggregated nature of Au_{25} NCs is evident from the TEM micrographs. To examine the light-induced self-assembly, $\sim 100 \mu\text{M}$ solution of NC in DCM at room temperature was illuminated under 345 nm light ($0.2 \text{ mW}/\text{cm}^2$) for 120 minutes in a temperature-controlled bath. The solution was stirred constantly during the photoisomerization process to avoid the possibility of thermally induced aggregation. Illuminated NC solution was drop-casted on a grid and dried under 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 to 200 nm . The evolution of self-assembled superstructures was investigated in detail by shining the same NC solution under 345 nm light for longer illumination time. Similar trends were observed in the TEM analysis of samples illuminated for 240 min (Figure 3C). The overall

diameter of the circular superstructures was increased from $\sim 200 \text{ nm}$ to $\sim 1000 \text{ nm}$. Enlargement in width and thickness of these circles suggests extended self-assembly in Au_{25} NCs. Large area TEM images of self-assembled NCs fabricated by illuminating them for 120 min and 240 min are shown in Figure S7. Zoom-in and focused high-resolution TEM images (Figure 3E and G) clearly show the presence of individual NCs. This suggests that the superstructure formation is facilitated by inter-NC interaction through the surface ligands.

Attractive dipole-dipole interaction³⁹ between nearby NCs in *cis* arrangement facilitates the self-assembly in NCs. A cartoon representation for the dipole-induced attraction of NCs (Figure 3F), self-assembly of NCs, and their possible arrangements within the disc-like superstructure are shown in the supporting information (Scheme 2). 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. 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 ($0.5 \text{ mW}/\text{cm}^2$; 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 the controlled disassembly.

Figure 4. (A and C) AFM images of (A-topography and C-amplitude) *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 Figure 4B.

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, (E) electron tomography reconstruction image, and (F) cross-sectional view of the self-assembled disc-like superstructure are shown.

Photographs of NC solution used for reversible switching is given in the SI (Figure S9). Notably, there was no precipitation of NCs during assembly and disassembly. To further check the stability of self-assembled NCs under dark conditions, we have recorded and analyzed the time-dependent absorption spectra of superstructures stored in the dark room. Absorption spectra (Figure S10) of NC assembly do not show any changes in their optical absorption features, suggest the stability of superstructures under dark. In other words, disassembly of superstructures can trigger only in the presence of visible (435 nm) light. 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 S11), which show the inability of $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs for the light-induced self-assembly. Additionally, we have analyzed the time-dependent absorption spectra of *trans* $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$ NC solution under dark condition. 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 S12). 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 S13A). Electron microscopic analysis at the interface of dimer shows well-organized NCs (Figure S13B).

To further evaluate the light-induced assembly of $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$, we have recorded and analyzed the time-dependent dynamic light scattering (DLS) spectra of NC solution illuminated under 345 nm light. Before that, the NC solution was filtered using a 0.22-micron nylon syringe. DLS measurements show an increment in the size of superstructures with illumination time. The average particle size of the self-assembled sphere within 120 min illumination (345 nm) was ~ 250 nm. Upon continuous illumination of NC solution, the particle size of the self-assembled sphere was increased from 250 nm to 550 nm and finally to $\sim 1.5 \mu\text{m}$ (Figure S14A-C). At the same time, a gradual decrease in the diameter of superstructures was observed under 435 nm illumination (Figure S14 D and E).

An increase and decrease in the size of self-assembled superstructures during 345 and 435 nm illuminations, respectively confirm the switchable assembly in NCs. DLS data is in good agreement with TEM micrographs.

Morphology and thickness of circular superstructures were further evaluated by atomic force microscopy. Self-assembled NC solution drop casted 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 4A and C), respectively. The morphology of the superstructures shown in the AFM image is similar to TEM analysis. This clearly suggests that self-assembly is occurring 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 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 S15.

To gain more information on three-dimensional structural details and internal structure of self-assembled superstructures, electron tomography reconstruction was carried out. Accordingly, the specimen prepared from a solution after irradiating for 240 min was used to acquire a series of 2D projections between $\pm 69^\circ$ with an increment angle of 2° (Details are provided

Figure 6. (A) Small-angle powder X-ray diffraction pattern of disc-like superstructures. (B) TEM micrograph of a self-assembled NC 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.

in the experimental section). Figure 5A-C shows TEM images of a tilted disc-like superstructures at -60° , 0° and $+60^\circ$. Tilt series and corresponding 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 results from solvent evaporation upon drying. However, these 3D superstructures are composed of densely packed NCs (Video S1). The results obtained from electron tomography reconstruction is in agreement with the AFM analysis.

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 6A shows SAXRD pattern collected from the disc-like colloidal superstructures. Calculated d-spacing value provides the inter-particle distances (3.27 nm) in the reversible self-assembly, which is in good agreement with inter-NC distance measured from TEM micrographs (3.3 ± 0.5 nm) shown in Figure 6B-F. Cross-sectional views of 3D reconstructed disc-like structure were also supported the above observation (Figure S16). Finally, the dark-field scattering microscopy was utilized to image the self-assembled structures in the solution state. Here, ~ 100 nM solution of self-assembled superstructures in DCM was drop-casted on a 1 mm thick glass slide and sandwiched with 0.14 mm thick glass coverslip. Golden-yellow scattering spots represent the individual self-assembled superstructures of NC (Figure S17).

CONCLUSIONS

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 suitable spacer length. Photo-isomerization of the chromophore and analogous 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.

EXPERIMENTAL SECTION

Reagents and Materials: All the chemicals and solvents are 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.

Characterizations: ^1H and ^{13}C NMR measurements were carried out using Bruker, AVANCE III HD 400/500 MHz spectrometers. UV/Vis absorbance spectra were recorded in VARIAN, Cary 500 Scan spectrometer. FT-IR measurements (ATR mode) were carried out by using Bruker, Tensor 27 spectrometer. Liquid chromatography-mass spectrometry (LC-MS) was performed by using Waters, Xevo TQD Triple Quadrupole Mass Spectrometry. Electrospray ionization-mass spectrometric (ESI-MS) measurements were carried out in Waters, Synapt G2-Si high-definition mass spectrometer. Typical experimental parameters of ESI-MS were: 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 in JEOL 3010 (300 kV) transmission electron microscope. Scanning transmission electron microscopy (STEM) images with EDS and elemental mapping were recorded using 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} Specimen was tilted between $\pm 69^\circ$ angles with $2\text{--}3^\circ$ increment steps under low dose mode.⁵⁴ The acquired raw stack of images was first subjected for a series of pre-processing, coarse alignment, final alignment, and further aligned using IMOD software package.⁵⁵ The final aligned file was then utilized for 3D reconstruction with 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 in Oxford Instruments, Asylum Cypher ES. X-ray photoelectron spectra were recorded using Thermo Scientific, ESCALAB 250Xi. Photoisomerization of chromophores and NCs were performed using a Newport, Mercury-Xenon light source (500 W) equipped with a monochromator (Oriel). **DLS measurements were performed by using Nanotracs 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 in Cytoviva hyperspectral imaging system (HSI) equipped with CytovivaTM high-resolution dark-field

condenser (oil immersion). Here, 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 (40 x), and signals were collected with a colored CCD camera. **SAXD measurement was performed by using 3rd generation Empyrean, Malvern Panalytical X-ray diffractometer. X-ray source was Cu K α (1.5418 Å). A dried powder of NC superstructures were used to measure the diffraction.** Energy minimum structures of NCs were optimized using density functional theory (DFT) as implemented in grid based projector augmented waves (GPAW) software package.^{58,59} The following PAW set-ups were considered for Au(5d¹⁰6s¹), S(3s²3p⁴), O(2s²2p⁴), N(2s²2p³), C(2s²2p²) and H(1s¹), 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 to be 0.05 eV/Å, without imposing any symmetry constraints. All the optimized structures were visualized using the visual molecular dynamics (VMD) software.⁶¹

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 con. 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 $\text{NH}_3\text{--NH}_4\text{Cl}$ buffer solution (pH ~9) at 0 °C. 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. ^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 ($\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$), $m/z +1$ = 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 (~10 mL; 100 mmol), K_2CO_3 (1.66 g; 12 mmol) and catalytic amount of KI were refluxed in acetone (50 mL) for 5 h at 80 °C.⁴⁷ Reaction mixture was cooled and filtered. Excess 1,3-dibromopropane were removed by pumping in a rotary operator. The crude product was chromatographed over silica gel and eluted with 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 (d-d, 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 THF (4 mL) was cooled to -10 °C followed by adding 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, reaction mixture was diluted with dichloromethane and washed with saturated NH₄Cl solution. The crude product was chromatographed over silica gel and eluted with 2% ethyl acetate/hexane mixture. ¹H NMR (500 MHz, CDCl₃); δ= 7.95-7.85 (m, 4H), 7.53-7.4 (m, 3H), 7.04-6.99 (d-d, 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).; ¹³C NMR (125 MHz, CDCl₃); δ= 161.3, 152.8, 147.1, 130.4, 129, 124.8, 122.6, 114.7, 66, 33.2, and 21.2.; LC-MS (C₁₅H₁₆N₂OS), 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 ¹³C NMR, LC-MS, and FT-IR spectra of molecule 3 are shown in SI (Figure S3). Different steps involved in the synthesis of molecules 1-3 are shown in Scheme S1.

Synthesis of [Au₂₅(PET)₁₈]⁻: [Au₂₅(PET)₁₈]⁻ NCs were synthesized by using a reported protocol.⁴⁸ To a solution of HAuCl₄·3H₂O (20 mg/2 mL THF), TOAB (33 mg/1.75 mL THF) was added and stirred until color turned to dark red. Followed by this, PET (34 µL; 5 mol equivalents w.r.t. gold) was added and stirred at 400 rpm for 1 h. Au-thiolate solution formed was further reduced by injecting a freshly-prepared ice-cold aqueous NaBH₄ 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 separating funnel organic and aqueous layer were separated (toluene was added for good separation), 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 by extracting NCs in dichloromethane (DCM). Finally, NCs were re-dispersed in acetone to remove byproducts (Au₄₄ NCs). Dried [Au₂₅(PET)₁₈]⁻ NCs were stored at 4 °C for further characterizations.

Synthesis of [Au₂₅(C₃-AMT)₁₈]⁻: Modified Brust-Schiffrin single-phase procedure was used for the synthesis of [Au₂₅(C₃-AMT)₁₈]⁻.⁴⁸ To a solution of HAuCl₄·3H₂O (20 mg/2 mL THF), TOAB (33 mg/1.75 mL THF) was added and stirred until color turned to dark red. Followed by this, C₃-AMT (69 mg; 5 mol equivalents w.r.t. gold) was added and stirred at 400 rpm for 1 h. Au-thiolate solution formed was further reduced by injecting a freshly-prepared ice-cold aqueous NaBH₄ 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 separating funnel organic and aqueous layer were separated (toluene was added for good separation), 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 by extracting NCs in DCM. Finally, NCs were re-dispersed in acetone to remove byproducts (Au₄₄

NCs). Dried [Au₂₅(C₃-AMT)₁₈]⁻ NCs were stored at 4 °C for further characterizations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Scheme S1, S2 and Figures S1-S17 as described in the text (PDF)

Video S1 as described in the text (MOV)

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Author Contributions

The project was designed and supervised by E. S. S. R. J. synthesized the chromophore and nanocluster. R. J. and E. S. S. conducted experiments. N. 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 interests.

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ABBREVIATIONS

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