

## 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 C<sub>3</sub>-NC and C<sub>9</sub>-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 C<sub>3</sub>-AMT and C<sub>9</sub>-AMT are identical in dichloromethane solution. When a similar experiment was performed using a solution of C<sub>3</sub>-NCs and C<sub>9</sub>-NCs, it resulted in self-assembled disc-like superstructures. Notably, the *trans*-*to*-*cis* photoswitching in C<sub>3</sub>-NC could accomplish only 65% even after 460 seconds of irradiation. On the other hand, C<sub>9</sub>-NC completed this process within 160 seconds of irradiation. The low photoswitching efficiency of the C<sub>3</sub>-NC analog is due to the short and rigid spacer length of C<sub>3</sub>-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 C<sub>3</sub>-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 C<sub>9</sub>-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.<sup>1–10</sup> Even minor modifications to a single metal atom can have a major influence on the behavior and functionality of NCs.<sup>11–16</sup> This characteristic makes NCs ideal building blocks for constructing two-dimensional and three-dimensional self-assembled superstructures with collective and enhanced properties.<sup>17–20</sup> 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.<sup>21–30</sup> Such assembled materials find applications in device fabrication,<sup>31–34</sup> green catalysis,<sup>35–39</sup> toxin/metal ion screening,<sup>40</sup> gas sensing,<sup>41,42</sup>

bioimaging, and therapeutics.<sup>43–47</sup> 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.<sup>48–51</sup> Recently, twenty-five atom gold (Au<sub>25</sub>) NCs functionalized with thiolated-spiropyran or -azobenzene ligands demonstrated the feasibility of light-induced reversible self-assembly for hierarchical structure formation across length scales.<sup>29,52,53</sup> 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 chemistry has been utilized in systems containing other metal clusters.<sup>54–56</sup> 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

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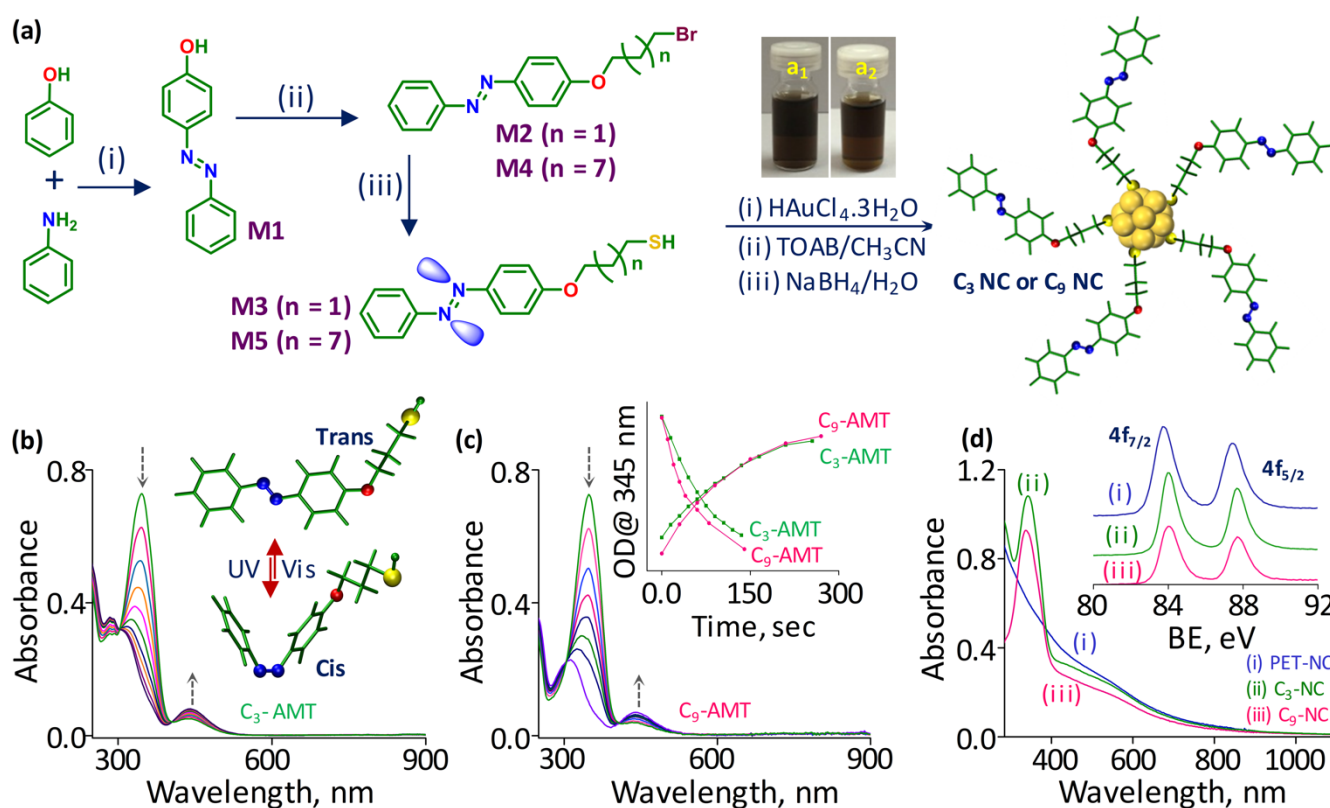
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of azobenzene alkyl monothiol (AMT) capped Au NCs. We used, azobenzene alkyl monothiol (AMT) protected NCs ( $C_3$ -NCs and  $C_9$ -NCs) with two different spacer lengths ( $C_3$ -AMT and  $C_9$ -AMT). The synthesis and characterization of ligands are presented in the supplementary information (Fig. S1-S15<sup>†</sup>). The time-dependent absorption spectra obtained from  $C_3$ -AMT and  $C_9$ -AMT dispersed in dichloromethane (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<sup>†</sup>). 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<sup>†</sup>, 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). Here, *cis* to *trans* conversion was not complete due to the overlap of  $n$ - $\pi^*$  transition of *cis* and *trans* isomers.<sup>57</sup> 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

of 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<sup>†</sup>). The time-dependent absorption spectra obtained from  $C_3$ -AMT and  $C_9$ -AMT dispersed in dichloromethane (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<sup>†</sup>). 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<sup>†</sup>, 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). Here, *cis* to *trans* conversion was not complete due to the overlap of  $n$ - $\pi^*$  transition of *cis* and *trans* isomers.<sup>57</sup> 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

## Result and Discussion

To investigate the role of chromophore-spacer length in the light-induced assembly of NCs, we first covalently linked the

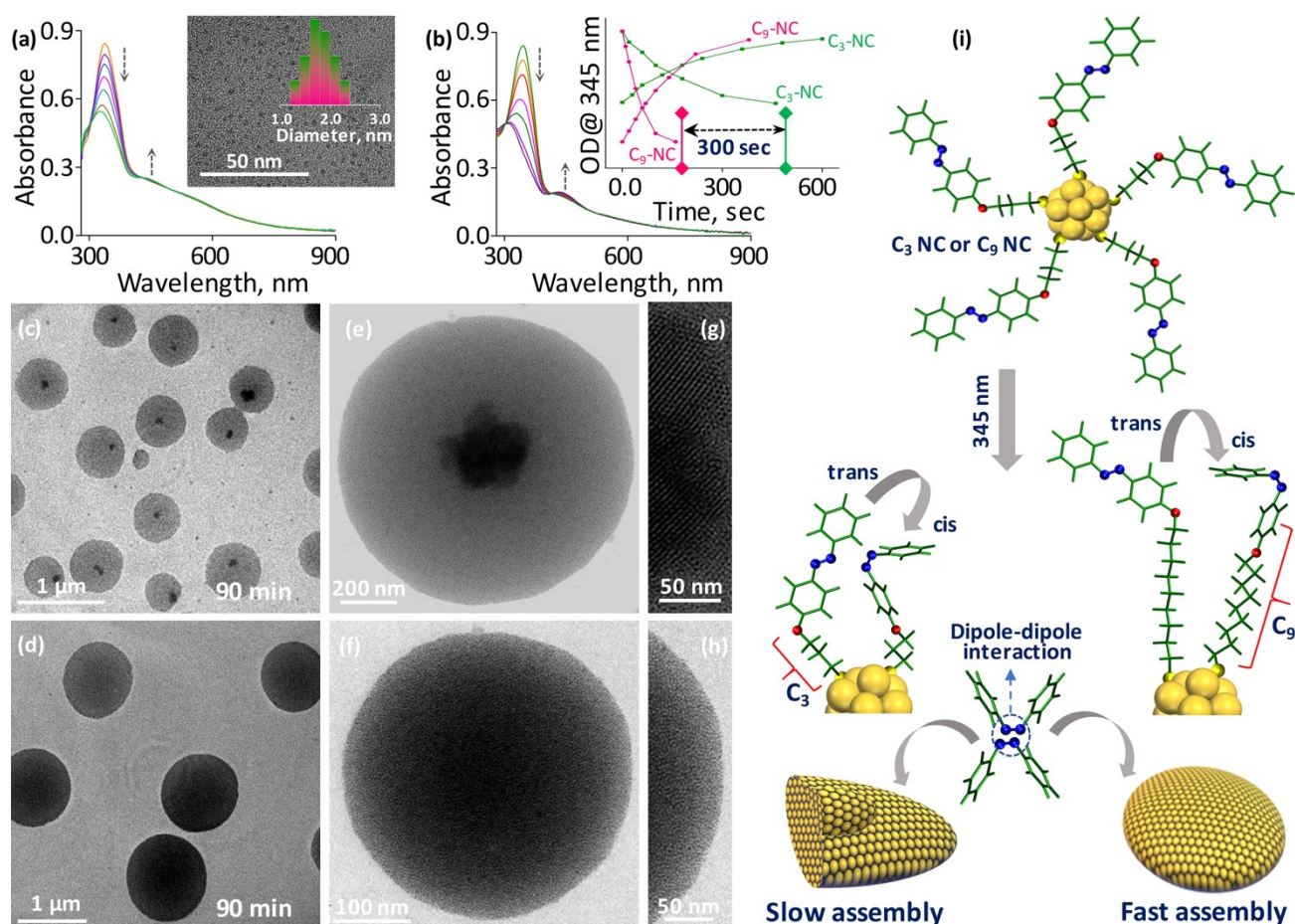


**Fig. 1** (a) Synthesis scheme of  $C_3$ -AMT and  $C_9$ -AMT (M1-M5),  $C_3$ -NC, and  $C_9$ -NC; (i) Conc. HCl, NaNO<sub>2</sub>, 0 °C (ii) 1,3-dibromopropane or 1,9-dibromononane, K<sub>2</sub>CO<sub>3</sub>, KI, acetone, 80 °C (iii) HMDST and TBAF, distilled THF, -10 °C. The photographs of  $C_3$  and  $C_9$  NC solutions are shown in a<sub>1</sub> and a<sub>2</sub>. (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<sub>3</sub>-AMT and C<sub>9</sub>-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<sub>3</sub>-NC and (iii) C<sub>9</sub>-NC recorded in DCM. The XPS spectra (Au 4f levels) of all three NCs are shown in the inset of Fig. 1d.

using the procedure reported for [Au<sub>144</sub>(PET)<sub>60</sub>] NCs (abbreviated as PET-NC; Fig. 1a, see SI for details; here PET represents 2-phenylethanthiol). The optical absorption features of C<sub>3</sub> and C<sub>9</sub> 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<sub>3</sub> and C<sub>9</sub> 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<sub>3</sub>-NC and C<sub>9</sub>-NC with that of PET-NC. The well-matching binding energy (BE) values of gold 4f electron orbitals in C<sub>3</sub>-NC and C<sub>9</sub>-NC compared to the reported values of PET-NC (inset in Fig. 1d) suggest similar metal core for all the three NCs (C<sub>3</sub>-NC, C<sub>9</sub>-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<sup>†</sup>. The core size of C<sub>3</sub>-NC and C<sub>9</sub>-NC was examined using TEM (transmission electron microscopy) analysis. TEM images from C<sub>3</sub>- and C<sub>9</sub>-NCs (inset in Fig. 2a and

Fig. S19<sup>†</sup>, respectively) show nearly uniform size distributions ( $1.9 \pm 0.14$  nm and  $1.87 \pm 0.12$  nm). The core sizes of C<sub>3</sub>- and C<sub>9</sub>-NCs are in agreement with that of the PET-NC.<sup>58</sup> Next, we evaluated the photoisomerization efficiency of C<sub>3</sub> and C<sub>9</sub> NC solutions in DCM under two different wavelengths of light. The absorption spectra of C<sub>3</sub> and C<sub>9</sub> NCs illuminated under 345 nm are shown in Fig. 2a and b, respectively. The time-dependent absorption spectra of C<sub>3</sub> and C<sub>9</sub> NCs recorded separately during the reverse (*cis-to-trans*) photoswitching (435 nm) are shown in Fig. S20a and b<sup>†</sup>. The combined plots of OD@345 nm vs. irradiation time recorded during the photoisomerization (*trans-to-cis* and *cis-to-trans*) of C<sub>3</sub> and C<sub>9</sub> NCs are shown in the inset of Fig. 2b. Notably, the time required for *trans-to-cis* photoswitching in C<sub>3</sub> and C<sub>9</sub> NCs (same concentration) under a similar intensity of light (0.2 mW/cm<sup>2</sup>) was found to be different. More precisely, the *trans-to-cis* photoswitching in C<sub>3</sub>-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, C<sub>9</sub>-NC completed the isomerization process within 160 seconds of illumination. Importantly, the *trans-to-cis* isomerization in C<sub>9</sub>-NC is comparable to free AMT molecules (inset in Fig. 1c; 140 sec).

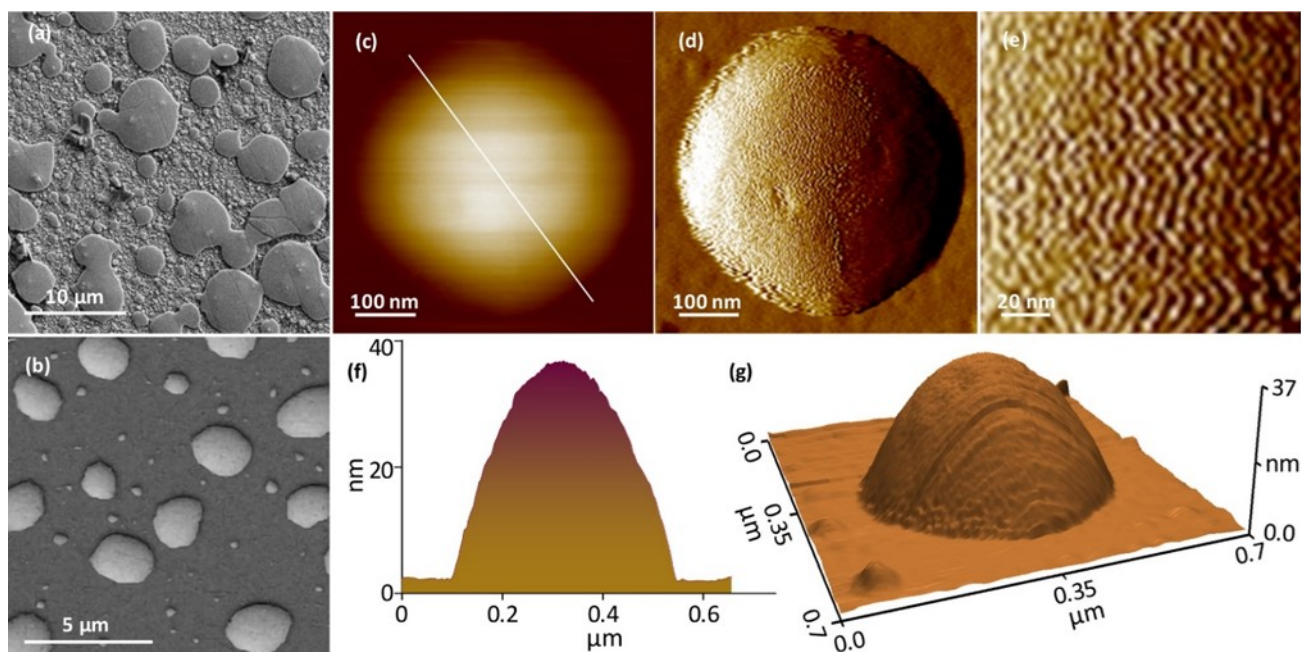


**Fig. 2** (a and b) Temporal optical absorption spectra recorded from (a) C<sub>3</sub>-NC and (b) C<sub>9</sub>-NC under 345 nm illumination. The TEM micrograph of C<sub>3</sub>-NC is shown in the inset of Fig. 2a. The combined plots of OD (*ca.* 345 nm) vs. irradiation time, using 345 nm and 435 nm lights recorded from C<sub>3</sub>-NC and C<sub>9</sub>-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.

While the isomerization is three times slower in the case of  $C_3$ -NCs. This suggests the effect of chromophore proximity on photoswitching. In  $C_9$ -NCs (longer spacer length;  $C_9$ -NC) the chromophore is located far from the metal surface. Furthermore, the spacer is flexible, allowing less steric crowding. However, in  $C_3$ -NCs (shorter spacer length;  $C_3$ -NC) 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,  $\sim 100 \mu\text{M}$  solutions of  $C_3$  and  $C_9$  NCs in DCM 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  $C_3$  and  $C_9$  NCs are shown in Fig. 2c and d, respectively. Though  $C_3$  and  $C_9$  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  $C_3$  and  $C_9$  NCs are shown in Fig. 2e and f, respectively. The  $C_3$ -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,  $C_9$ -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  $C_9$ -NC compared to the  $C_3$  analog is attributed to the negligible steric hindrance experienced at the NC-chromophore interface. The schematic shows the distant-dependent self-assembly in  $C_3$  and  $C_9$  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  $C_3$ - and  $C_9$ -NC assemblies are shown in Fig. S21a and b†, respectively. A contrast difference in the STEM image for  $C_3$ -NC assembly shows the existence of crystallized aggregates encapsulated within the disc-like structures (Fig. S21c†). The STEM micrograph recorded from the  $C_9$ -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  $C_3$ - and  $C_9$ -NCs are shown in Fig. S21e-h†. The large area STEM images, elemental maps (gold, sulfur, and nitrogen), and EDS spectra recorded from  $C_3$ - and  $C_9$ -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. 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.



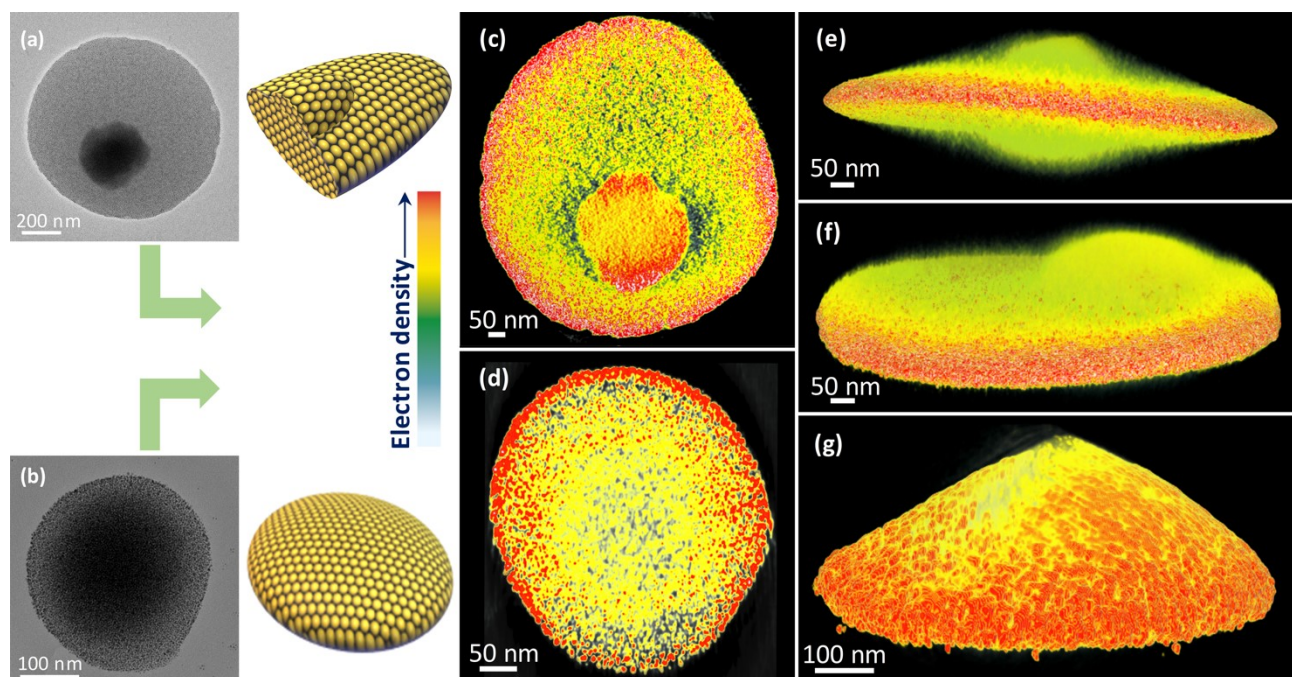
**Fig. 3** (a and b) FESEM images of (a)  $C_3$ -NC and (b)  $C_9$ -NC assemblies. (c and d) High-resolution tapping mode AFM (c-topography and d-amplitude) images of single superstructure derived from  $C_3$ -NC. (e) A zoomed and focused AFM image captured from the top surface of the  $C_3$ -NC assembly showed the NC direction in the assembly. (f and g) The height profile and three-dimensional (3D) AFM image of the same assembly.

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 TEM tomography<sup>59</sup> (detailed information in the SI). Accordingly, the 2D projections were collected between  $\pm 70^\circ$  with an increment angle of  $2^\circ$  (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 S<sub>1</sub> and S<sub>2</sub>†) 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

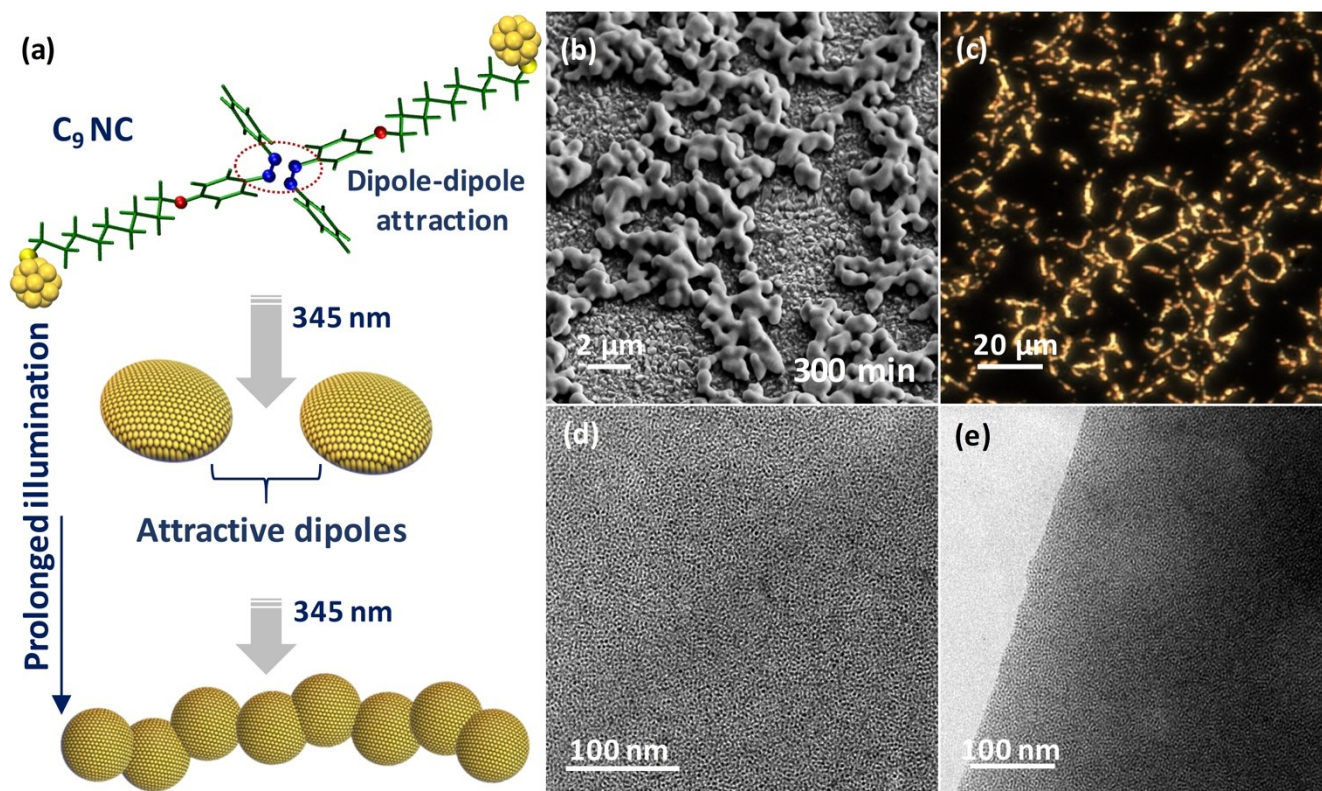
to non-uniform thickness between the center and the periphery.

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†).

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.



**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 (scale bar). (d and e) TEM micrographs from the surface and edge of the chain-like assembly.

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 spherical 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 nanoclusters 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 nanoclusters. However, the magnitude of assembly in chromophore-tethered nanoclusters 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<sub>3</sub>-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, <sup>1</sup>H, <sup>13</sup>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<sub>3</sub>-NC, and C<sub>9</sub>-NC; HR-TEM images and temporal absorption spectra of C<sub>3</sub>-NC, and C<sub>9</sub>-NC; STEM micrographs and elemental maps of C<sub>3</sub>-NC and C<sub>9</sub>-NC assemblies; AFM images of C<sub>3</sub>-NC and C<sub>9</sub>-NC assemblies; TEM images of C<sub>3</sub>-NC and C<sub>9</sub>-NC self-assembled monomer, dimer, and trimer; 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.

## Acknowledgements

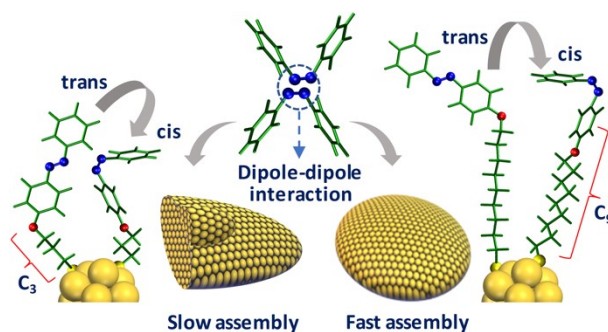
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## Table of Contents (ToC)



The light-induced reversible self-assembly of azobenzene chromophore-tethered gold nanoclusters with two different spacer lengths is being practiced. A faster assembly occurs when the chromophore is away from nanocluster surface due to negligible steric hindrance experienced at the NC-chromophore interface.