

# Supporting Information

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

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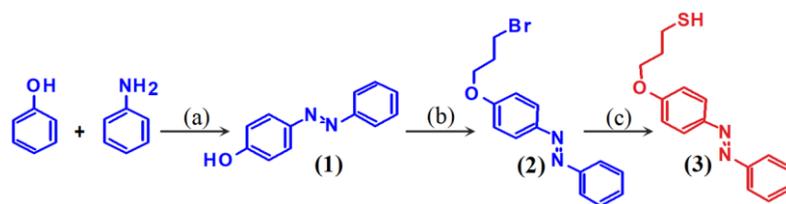
**This PDF file includes:**

**Figures S1-S17**

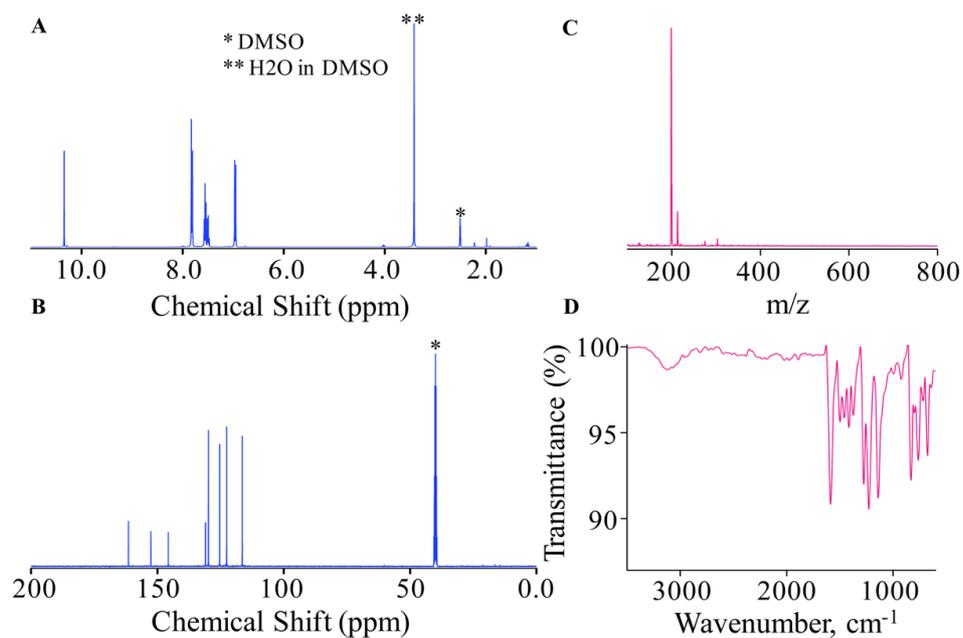
**Scheme 1 and 2**

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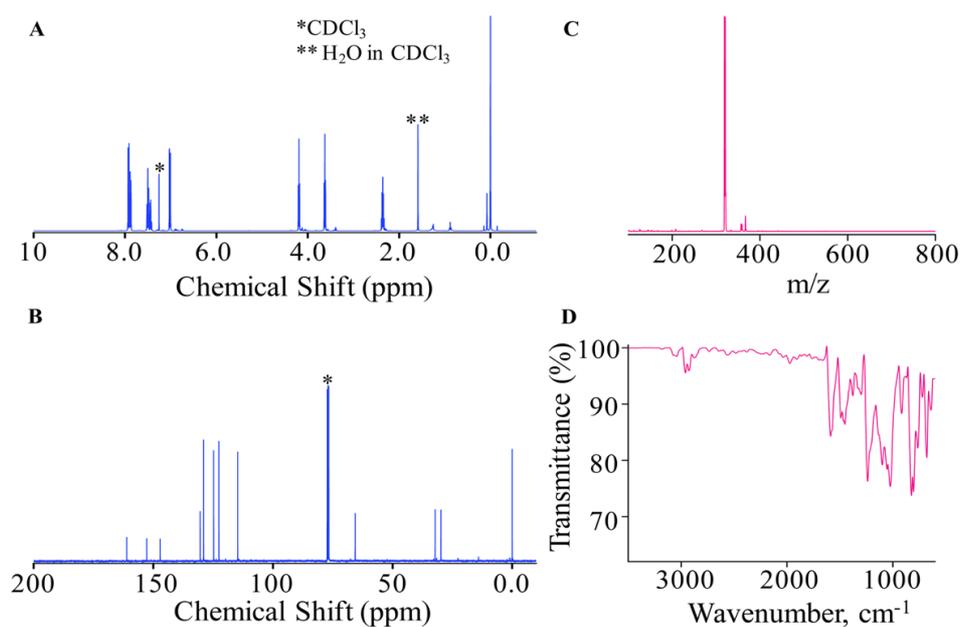
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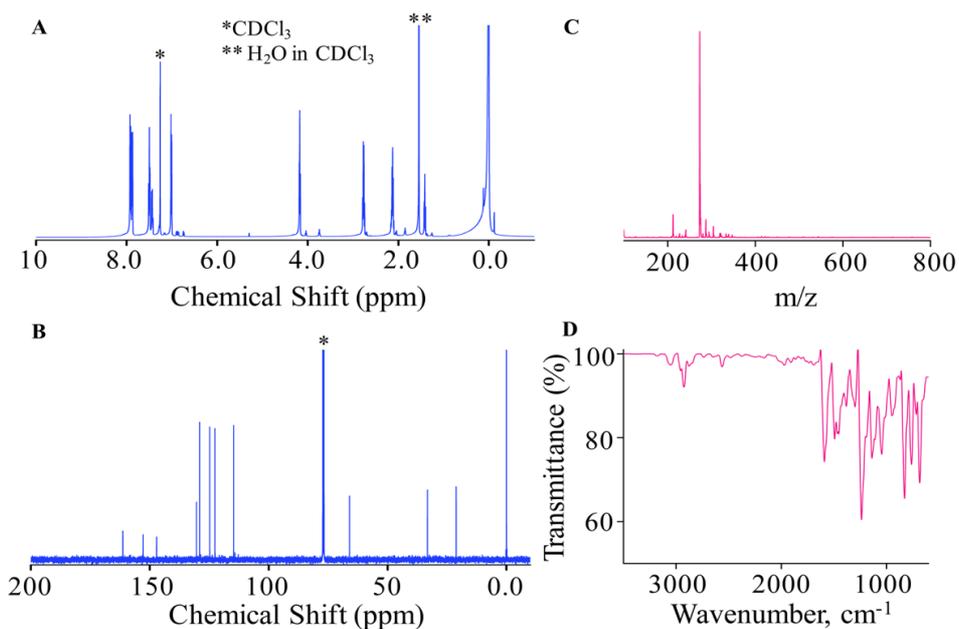
**Scheme S1.** Scheme for the synthesis of C<sub>3</sub>-AMT (molecules 1-3). (a) HONO, 0 °C (b) 1,3-dibromopropane, K<sub>2</sub>CO<sub>3</sub>/KI, acetone, 80 °C (c) HMDST/TBAF, Distilled THF, -10 °C.



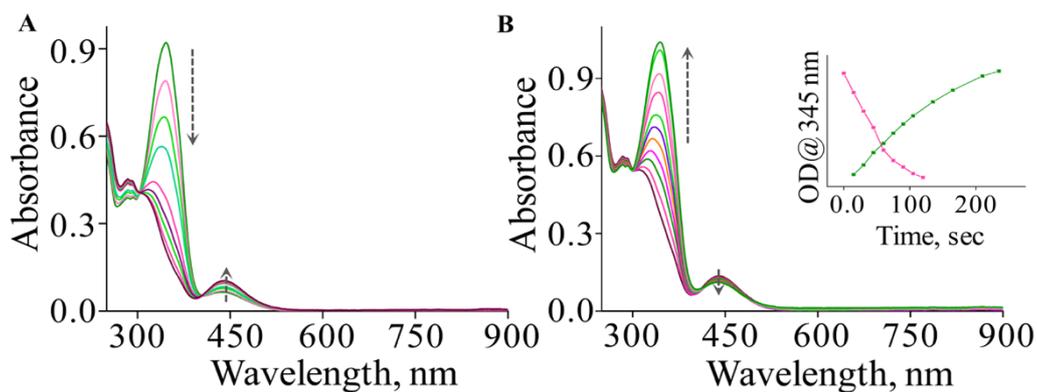
**Figure S1.** (A) <sup>1</sup>H and (B) <sup>13</sup>C NMR, (C) LC-MS, and (D) FT-IR spectra of *molecule 1*.



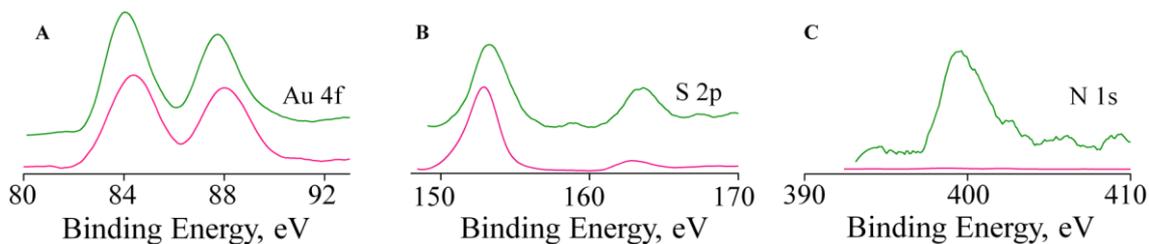
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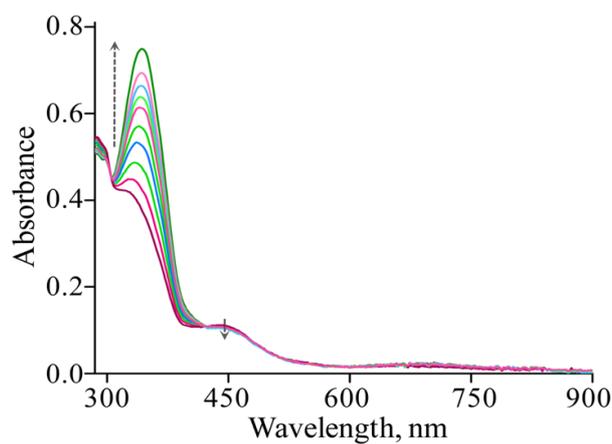
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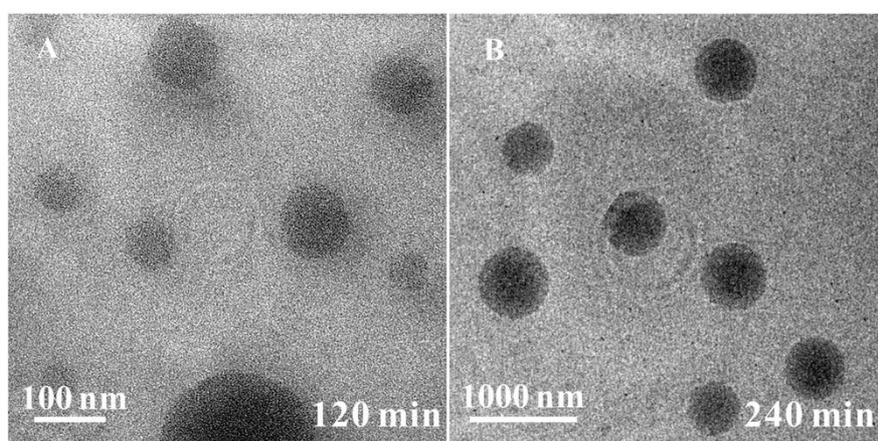
**Figure S4.** (A and B) Temporal absorption spectra of  $\text{C}_3\text{-AMT}$  illuminated under (A) 345 nm and (B) 435 nm light. A plot of OD at 345 nm vs. illumination time under 345 and 435 nm excitation shows reversible photo-switching (inset in Figure S4B).



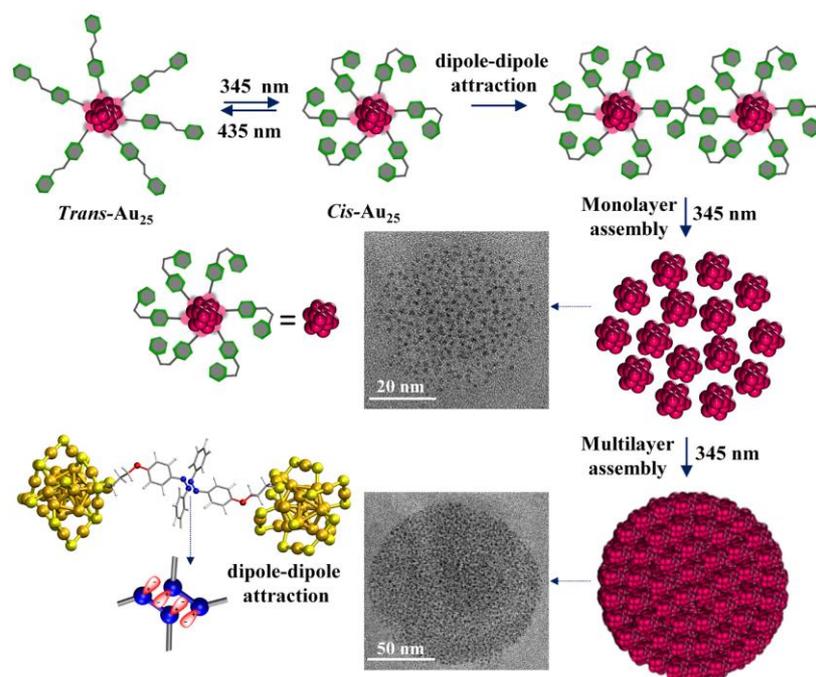
**Figure S5.** (A-C) XPS spectra of (A) Au 4f, (B) S 2p, and (C) N 1s levels of  $[\text{Au}_{25}(\text{PET})_{18}]^-$  (pink), and  $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$  (green).



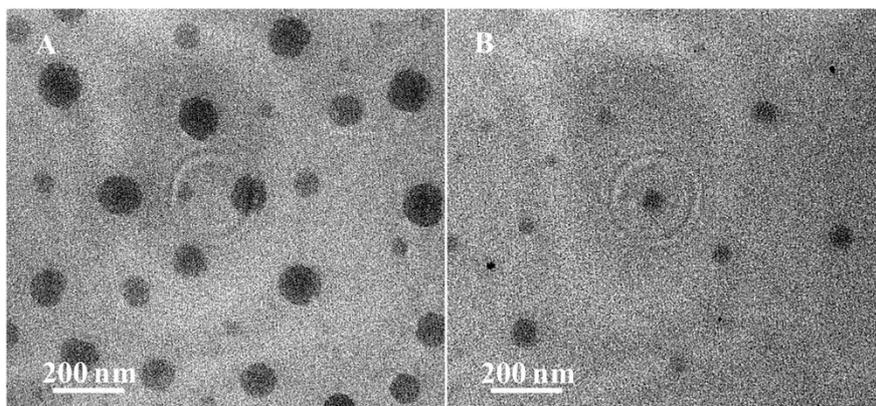
**Figure S6.** Temporal absorption spectra of  $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$  NC under 435 nm excitation.



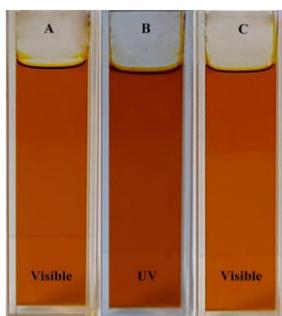
**Figure S7.** Larger area TEM images of  $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$  NC self-assembly illuminated under 345 nm light for (A) 120 min and (B) 240 min.



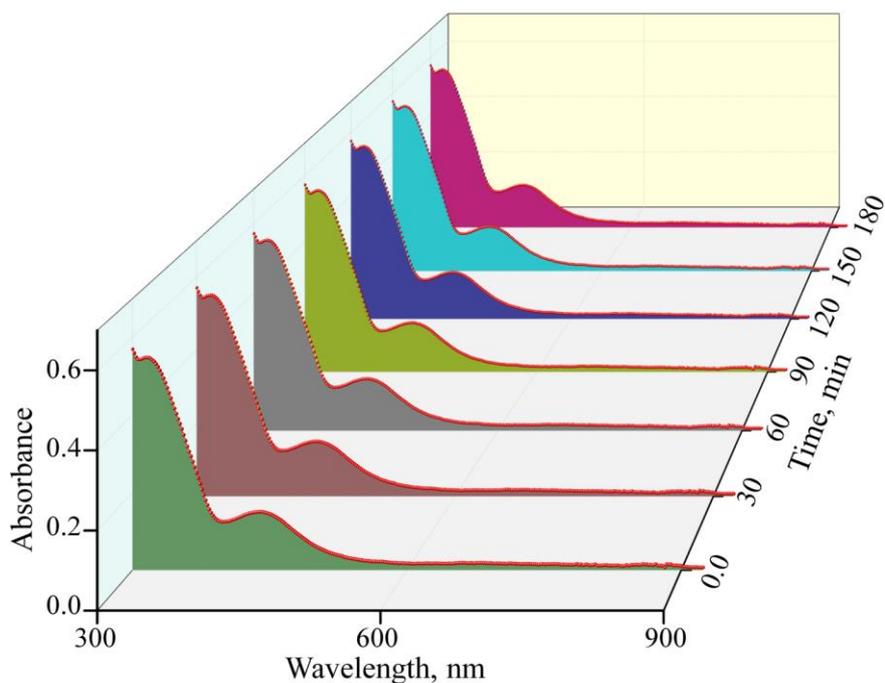
**Scheme 2.** The mechanism for the dipole-induced self-assembly of  $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$  NCs and their possible arrangements in the superstructure are represented. Corresponding TEM micrographs are shown.



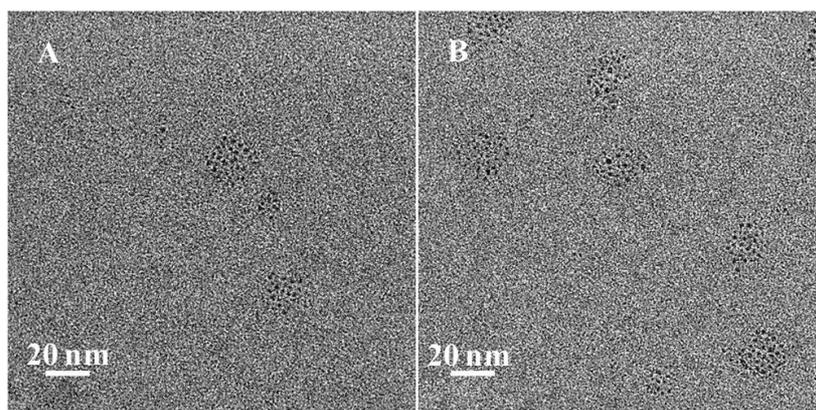
**Figure S8.** Larger area TEM images of  $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]$  superstructures disassembly illuminated under 435 nm light for (A) 150 min and (B) 240 min.



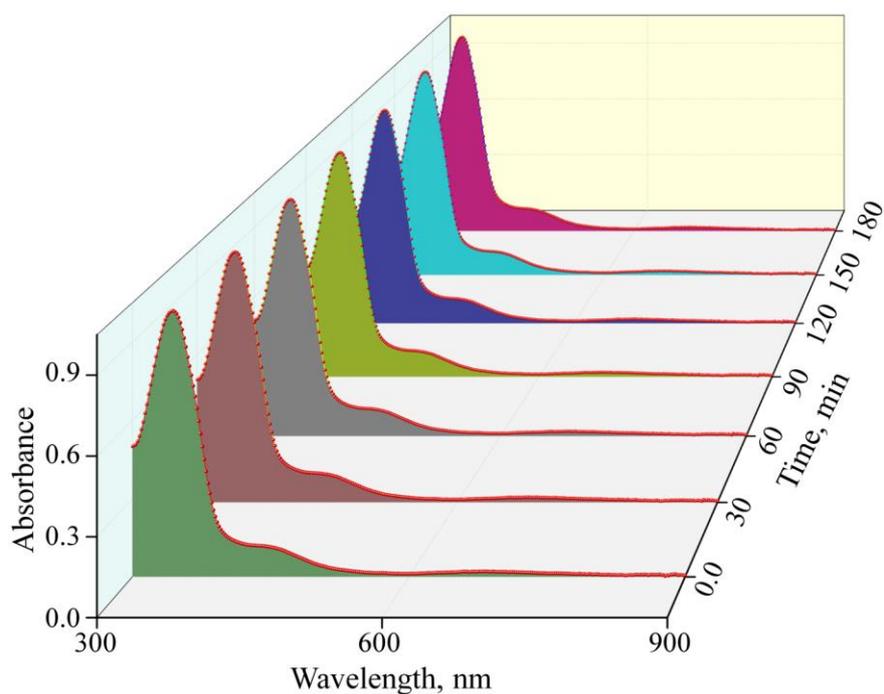
**Figure S9.** Photographs of  $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]$  NC solution during switchable self-assembly under (A) visible light (B) UV light and (C) visible light. The color of NC solution changed from yellowish orange to reddish-orange under UV light and *vice versa* under visible light.



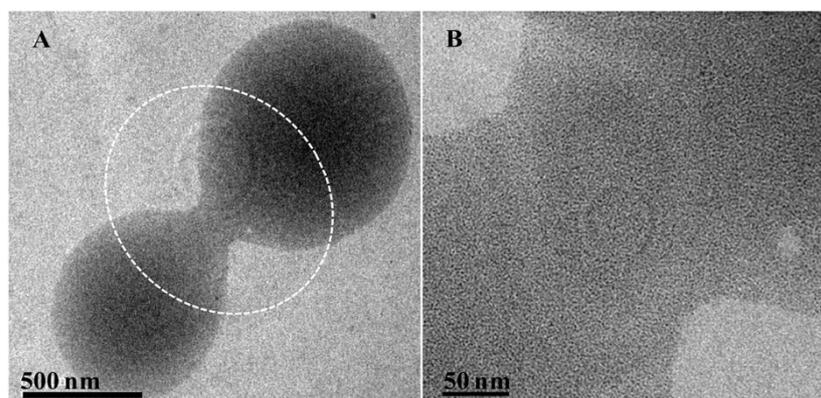
**Figure S10.** Temporal absorption spectra of self-assembled NCs recorded under dark conditions (30-180 min).



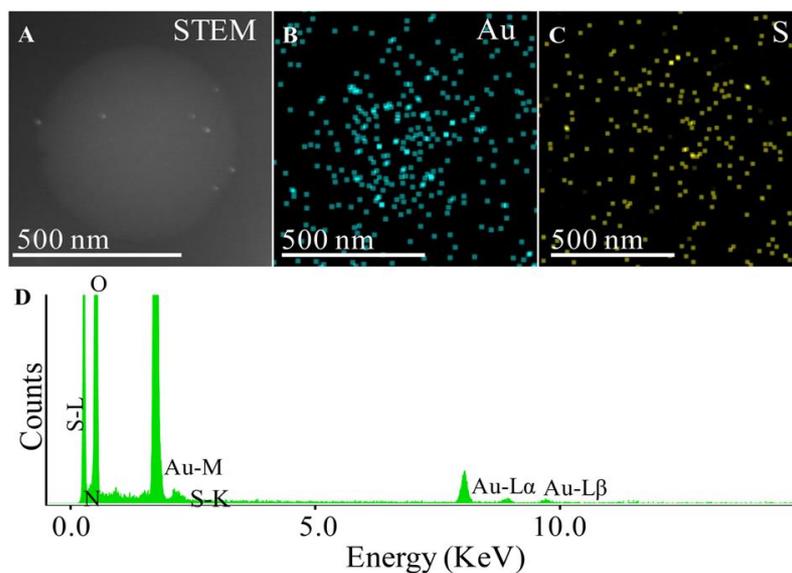
**Figure S11.** TEM images of  $[\text{Au}_{25}(\text{PET})_{18}]^-$  (A) before and (B) after 240 min light illumination (345 nm).



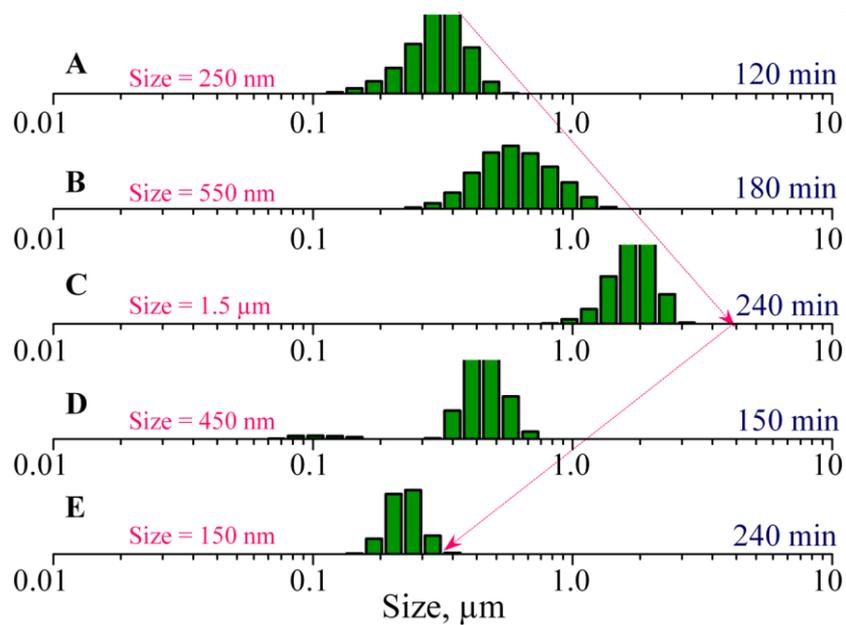
**Figure S12.** Temporal absorption spectra of *trans* NCs recorded under dark conditions (30-180 min).



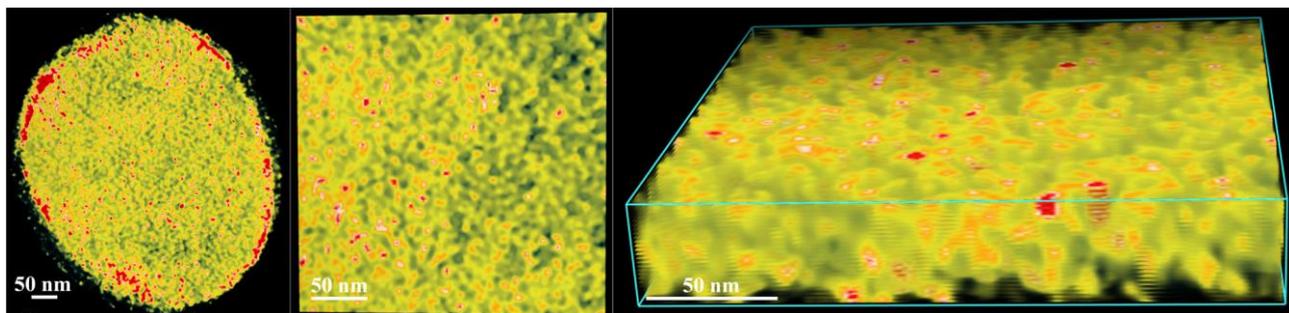
**Figure S13.** (A) TEM image of  $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$  self-assembled dimer. (B) Zoom-in and focused HRTEM image taken from the interface of dimer shows periodic self-assembly of NC.



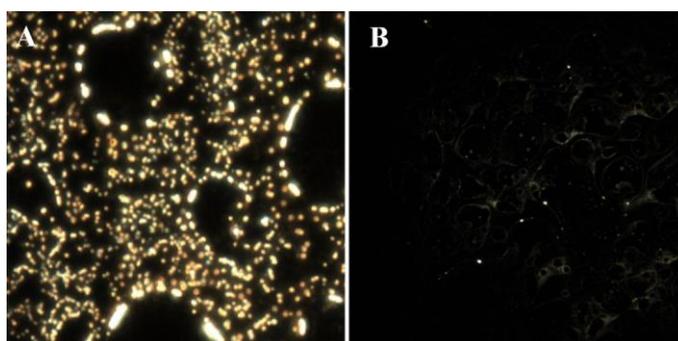
**Figure S14.** (B and C) Elemental maps (B-gold and C-sulfur), and (D) EDS spectrum of a single  $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$  superstructure (A) using scanning transmission electron microscopy (STEM).



**Figure S15.** 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.



**Figure S16.** Cross-sectional views of the 3D reconstructed disc-like superstructure of NC.



**Figure S17.** Dark-field scattering images collected from (A)  $[\text{Au}_{25}(\text{C}_3\text{-AMT})_{18}]^-$  superstructures and (B) control sample (solvent alone).