Supporting Information

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

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Scheme 1 and 2

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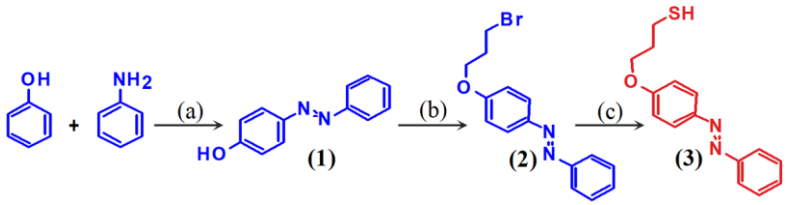


Scheme S1. Scheme for the synthesis of C_3-AMT (molecules 1-3). (a) HONO, 0 °C (b) 1,3-dibromopropane, K_2CO_3/KI, acetone, 80 ºC (c) HMDST/TBAF, Distilled THF, -10 ºC.

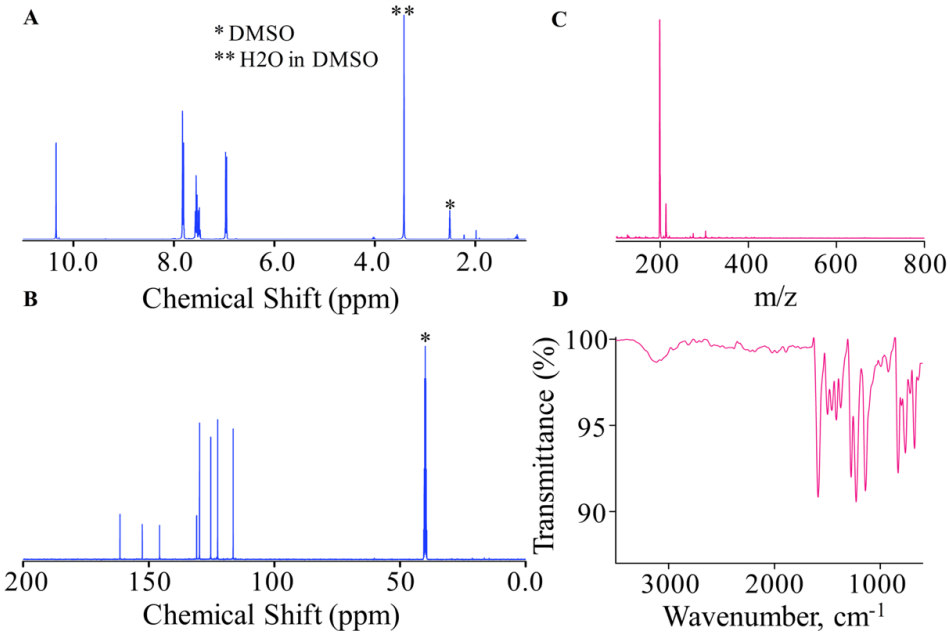


Figure S1. (A) ^{1}H and (B) ^{13}C NMR, (C) LC-MS, and (D) FT-IR spectra of *molecule **1***.

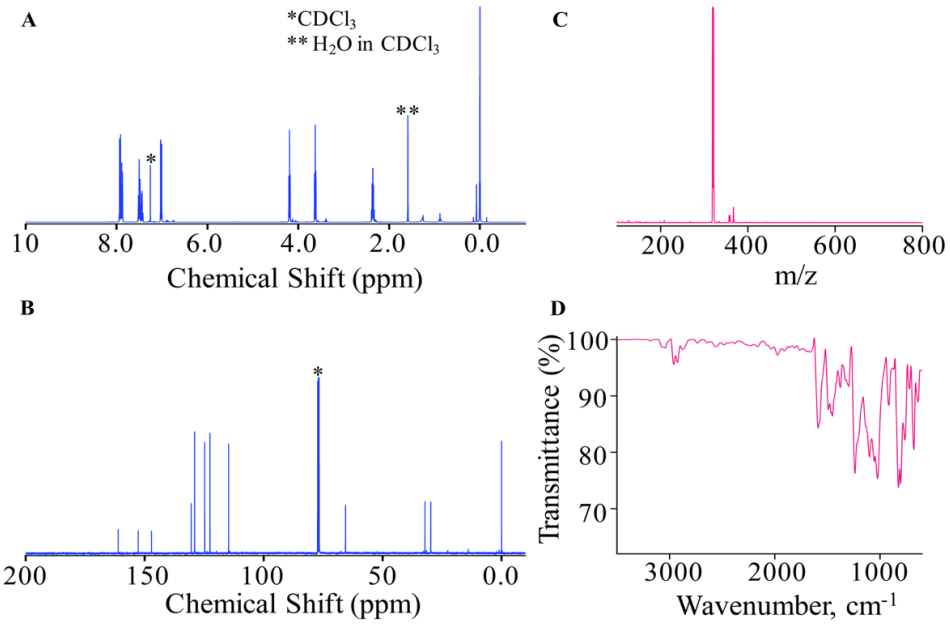


Figure S2. (A) ^{1}H and (B) ^{13}C NMR, (C) LC-MS, and (D) FT-IR spectra of *molecule **2***.

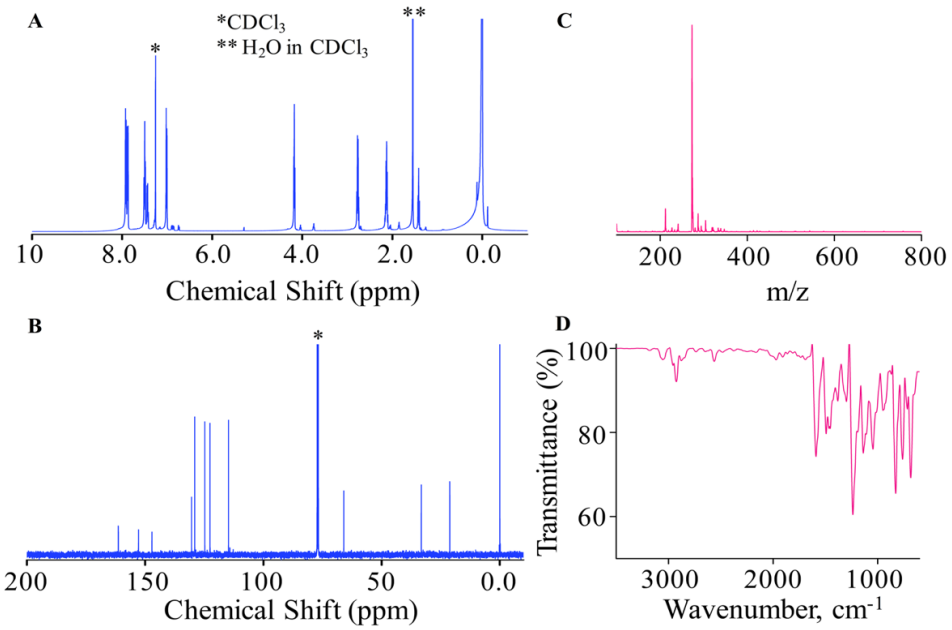


Figure S3. (A) ^{1}H and (B) ^{13}C NMR, (C) LC-MS, and (D) FT-IR spectra of *molecule **3***.

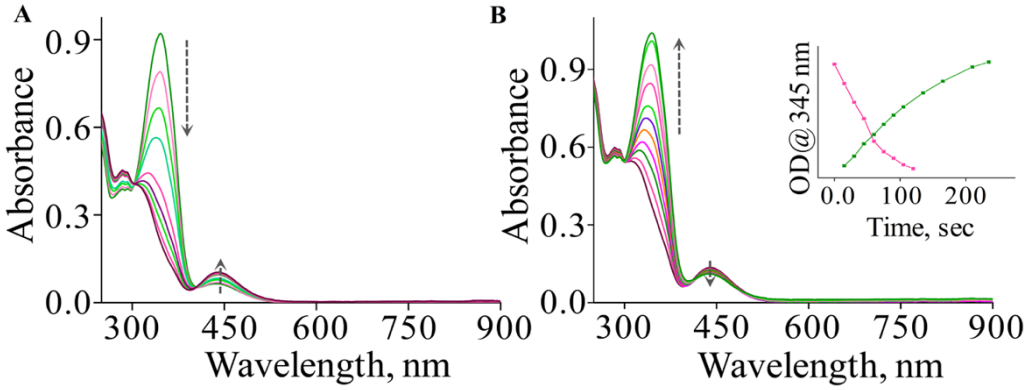


Figure S4. (A and B) Temporal absorption spectra of C_3-AMT illuminated under (A) 345 nm and (B) 435 nm light. A plot of OD at 345 nm *vs.* illumination time under 345 and 435 nm excitation shows reversible photo-switching (inset in Figure S4B).

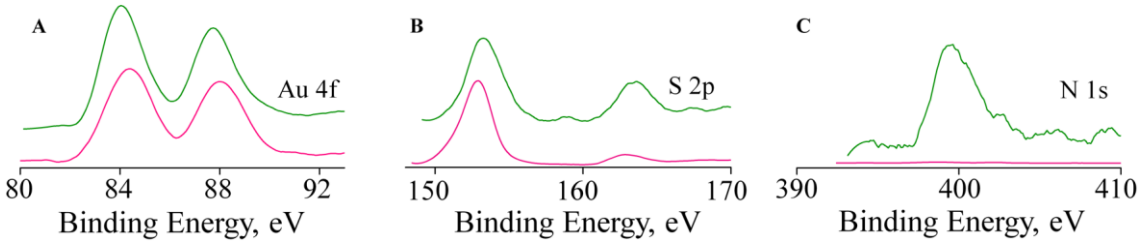


Figure S5. (A-C) XPS spectra of (A) Au 4f, (B) S 2p, and (C) N 1s levels of $[Au_{25}(PET)_{18}]^-$ (pink), and $[Au_{25}(C_3\text{-AMT})_{18}]^-$ (green).

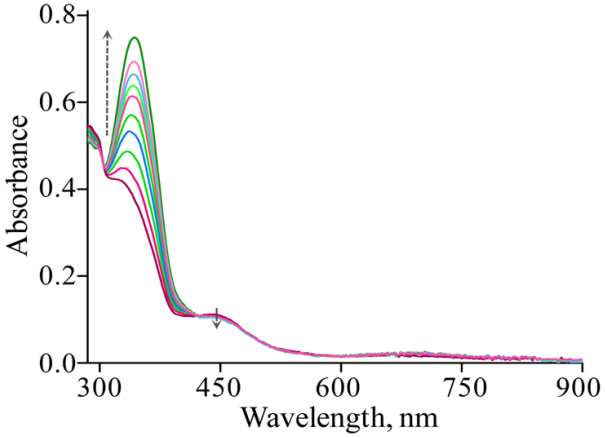


Figure S6. Temporal absorption spectra of $[Au_{25}(C_3\text{-AMT})_{18}]^-$ NC under 435 nm excitation.

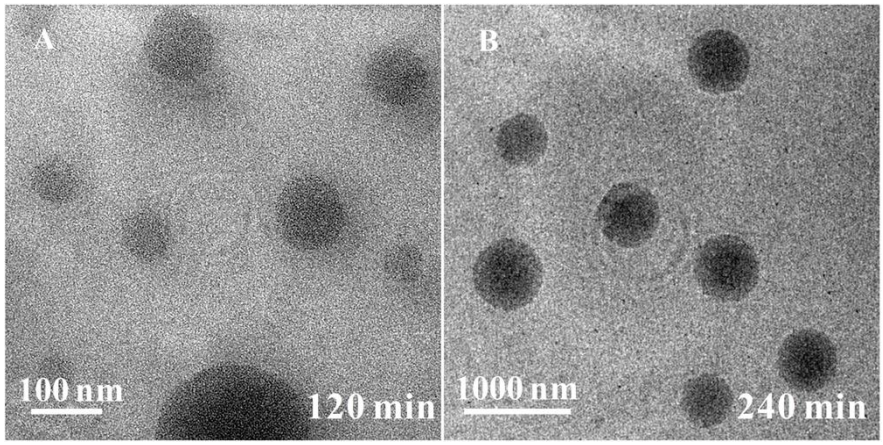
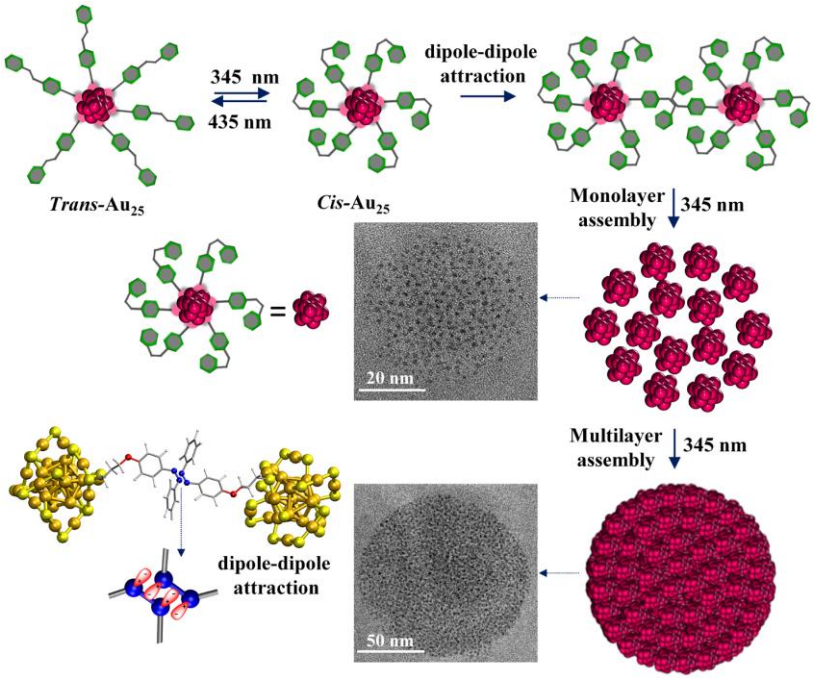


Figure S7. Larger area TEM images of $[Au_{25}(C_3\text{-AMT})_{18}]^-$ NC self-assembly illuminated under 345 nm light for (A) 120 min and (B) 240 min.



Scheme 2. The mechanism for the dipole-induced self-assembly of $[Au_{25}(C_3\text{-AMT})_{18}]^-$ NCs and their possible arrangements in the superstructure are represented. Corresponding TEM micrographs are shown.

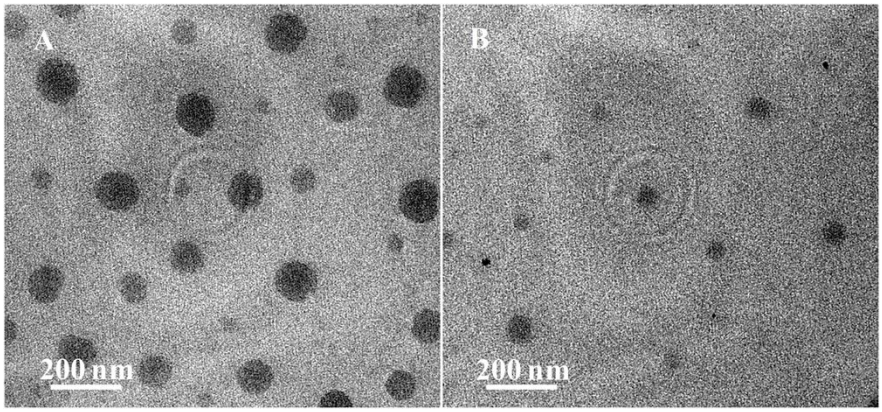


Figure S8. Larger area TEM images of $[Au_{25}(C_3\text{-AMT})_{18}]^-$ superstructures disassembly illuminated under 435 nm light for (A) 150 min and (B) 240 min.

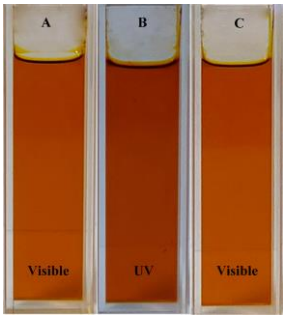


Figure S9. Photographs of $[Au_{25}(C_3\text{-AMT})_{18}]^-$ NC solution during switchable self-assembly under (A) visible light (B) UV light and (C) visible light. The color of NC solution changed from yellowish orange to reddish-orange under UV light and *vice versa* under visible light.

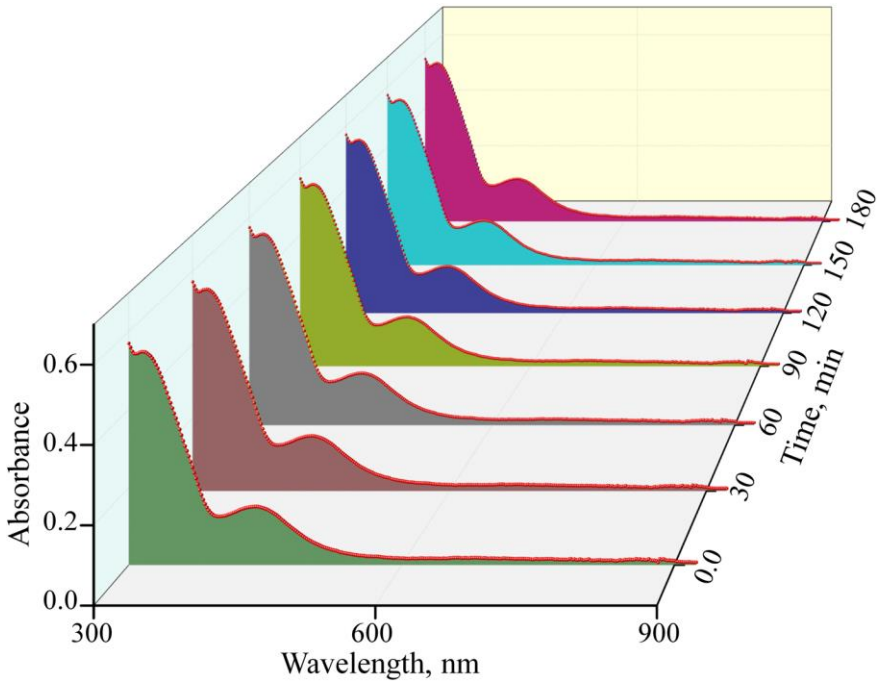


Figure S10. Temporal absorption spectra of self-assembled NCs recorded under dark conditions (30-180 min).

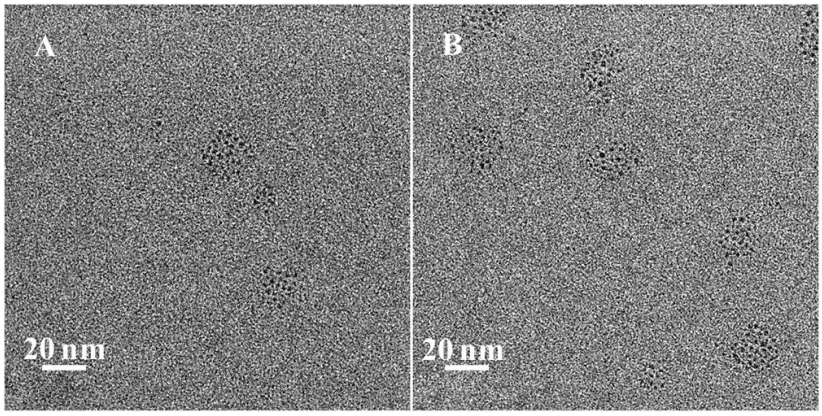


Figure S11. TEM images of $[Au_{25}(PET)_{18}]^-$ (A) before and (B) after 240 min light illumination (345 nm).

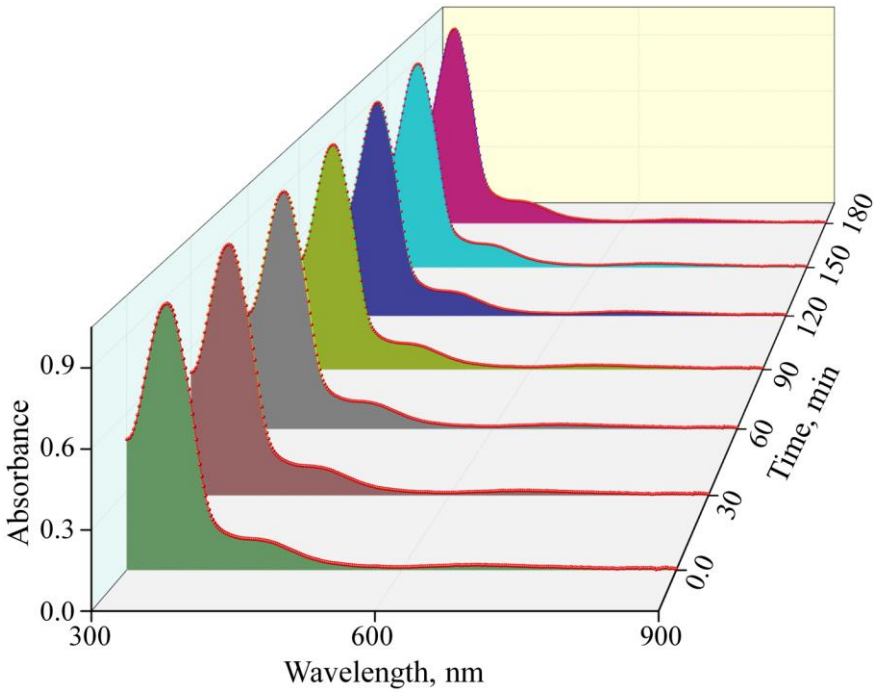


Figure S12. Temporal absorption spectra of *trans* NCs recorded under dark conditions (30-180 min).

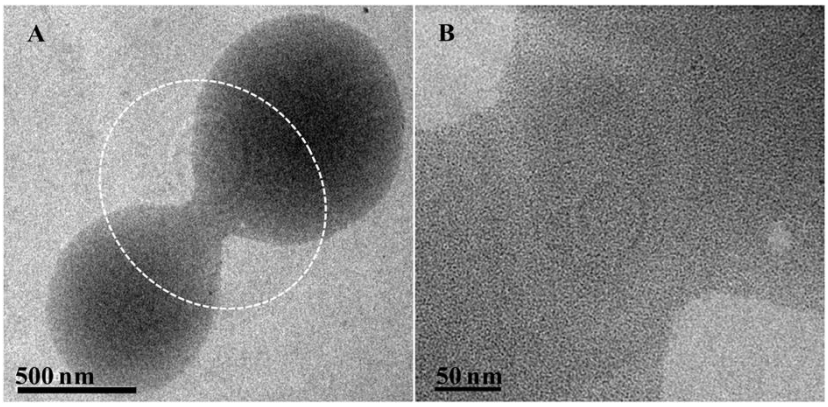


Figure S13. (A) TEM image of $[Au_{25}(C_3\text{-AMT})_{18}]^-$ self-assembled dimer. (B) Zoom-in and focused HRTEM image taken from the interface of dimer shows periodic self-assembly of NC.

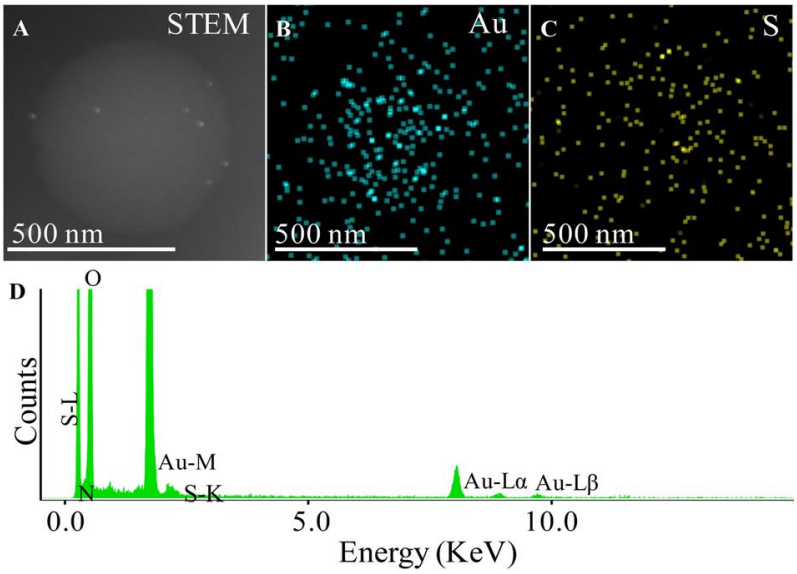


Figure S14. (B and C) Elemental maps (B-gold and C-sulfur), and (D) EDS spectrum of a single $[Au_{25}(C_3\text{-}AMT)_{18}]^-$ superstructure (A) using scanning transmission electron microscopy (STEM).

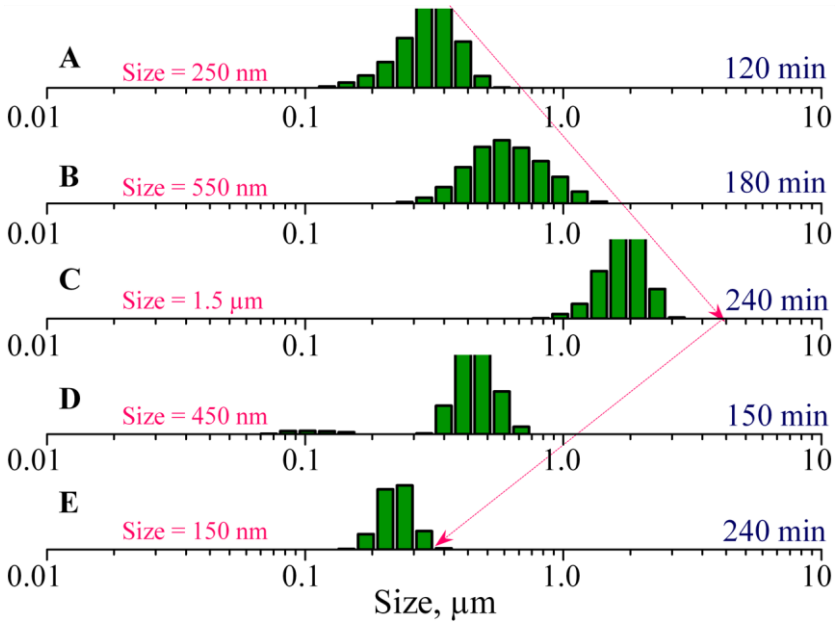


Figure S15. DLS spectra of $[Au_{25}(C_3\text{-}AMT)_{18}]^-$ NCs during the light-induced (A-C) self-assembly (under 345 nm), and (D and E) disassembly (under 435 nm) at different time intervals.

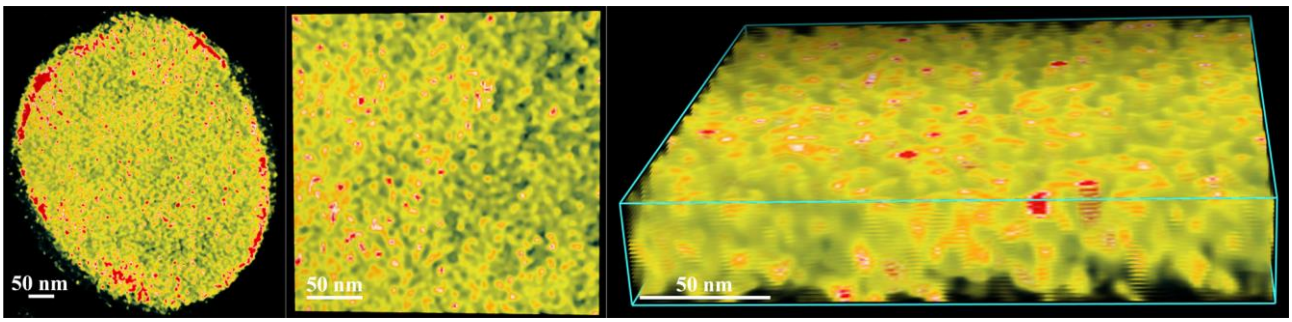


Figure S16. Cross-sectional views of the 3D reconstructed disc-like superstructure of NC.

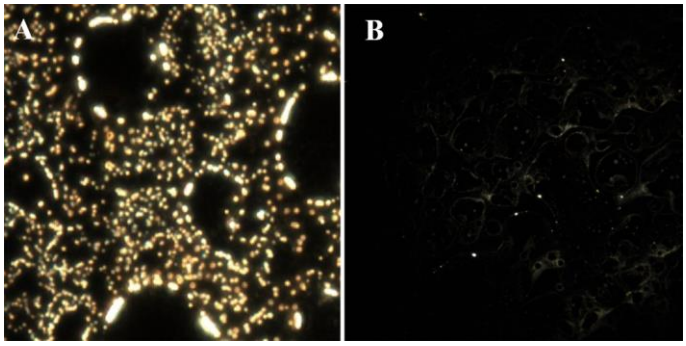


Figure S17. Dark-field scattering images collected from (A) $[Au_{25}(C_3\text{-AMT})_{18}]^-$ superstructures and (B) control sample (solvent alone).