

Supplementary Information

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

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Experimental Section

Reagents and Materials

Analytical-grade chemicals and solvents were used here without any additional purification. Phenol, aniline, potassium nitrite (KNO₂), 1,3-dibromopropane, 1,9-dibromononane, hexamethyldisilathiane (HMDST), tetrabutylammonium fluoride (TBAF), tetraoctylammonium bromide (TOAB), ammonium chloride (NH₄Cl), ammonia solution (25%), potassium carbonate (K₂CO₃), potassium iodide (KI), 2-phenylethanethiol (PET), gold(III) chloride trihydrate (HAuCl₄·3H₂O), and sodium borohydride (NaBH₄) were purchased from Sigma Aldrich.

Synthesis of molecule 1 (M1)

M1 was synthesized using the protocol used in our earlier work.¹ ¹H NMR (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).; ¹³C NMR (100 MHz, DMSO-*d*₆); δ = 161.01, 152.13, 145.26, 130.51, 129.36, 124.90, 122.14, 115.98.; LC-MS (C₁₂H₁₀N₂O), *m/z* +1 = 199.; FT-IR (ν_{max}) = 3117, 1587, 1500 – 1370, 1275, 1227, 1139, 831, and 762 cm⁻¹. ¹H and ¹³C NMR, LC-MS, and FT-IR spectra of **M1** are shown in **Figures S1-S3**.

Synthesis of molecule 2 (**M2**)

M2 was synthesized using the protocol used in our earlier work.¹ ¹H NMR (400 MHz, CDCl₃); 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).; ¹³C NMR (100 MHz, CDCl₃); δ = 161.27, 152.88, 147.27, 130.55, 129.18, 124.91, 122.71, 114.86, 65.75, 32.39, 29.95.; LC-MS (C₁₅H₁₅N₂OBr), *m/z*+1 = 319 and 321.; FT-IR (*v*_{max}) = 2960 – 2870, 1588, 1500 – 1370, 1237, 1100 – 1020, 916, 825-760, and 678 cm⁻¹. ¹H and ¹³C NMR, LC-MS, and FT-IR spectra of **M2** are shown in **Figures S4-S6**.

Synthesis of molecule 3 (**M3**)

M3 was synthesized using the protocol used in our earlier work.¹ ¹H NMR (400 MHz, CDCl₃); 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).; ¹³C NMR (100 MHz, CDCl₃); δ = 161.45, 152.89, 147.19, 130.53, 129.18, 124.91, 122.70, 114.84, 66.08, 33.37, 21.34.; LC-MS (C₁₅H₁₆N₂OS), *m/z*+1 = 273.; FT-IR (*v*_{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 **M3** are shown in **Figures S7-S9**.

Synthesis of molecule 4 (**M4**)

M4 was synthesized using a reported protocol with required modifications.¹ 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. ¹H NMR (500 MHz, CDCl₃); 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).; ¹³C NMR (125 MHz, CDCl₃); 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, 26.12.; LC-MS (C₂₁H₂₇N₂OBr), *m/z*+1 = 403 and 405.; FT-IR (*v*_{max}) = 2930 – 2850, 1591, 1500 – 1410, 1298, 1246, 1137, 1012, 839, 764,720, and 682 cm⁻¹. ¹H and ¹³C NMR, LC-MS, and FT-IR spectra of **M4** are shown in **Figures S10-S12**.

Synthesis of molecule 5 (**M5**)

M5 was synthesized using a reported protocol with required modifications.¹ 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 μL; 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 NH_4Cl solution. The crude product was chromatographed over silica gel and eluted with a 2% ethyl acetate/hexane mixture to yield the final product (**M5**). ^1H NMR (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).; ^{13}C NMR (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, 24.79.; LC-MS ($\text{C}_{21}\text{H}_{28}\text{N}_2\text{OS}$), $m/z+1$ = 357.; FT-IR (ν_{max}) = 2925 – 2850, 2560, 1591, 1500 – 1380, 1302, 1242, 1140 – 1100, 1010, and 840 – 770 cm^{-1} . ^1H and ^{13}C NMR, LC-MS, and FT-IR spectra of **M5** are shown in **Figures S13-S15**.

Synthesis of PET-NC

PET-NC was synthesized using a reported protocol.²

Synthesis of C₃-NC

Synthesis of C₃-NCs were performed using a reported method in the literature.^{3,4} Briefly, to a solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (20 mg/2 mL of acetonitrile), TOAB (33 mg/2 mL acetonitrile) 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 acetonitrile 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 methanol/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.

Synthesis of C₉-NC

Synthesis of C₃-NCs were performed using a reported method in the literature.^{3,4} Briefly, to a solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (20 mg/2 mL of acetonitrile), TOAB (33 mg/2 mL acetonitrile) 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 acetonitrile 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 NaBH_4 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 methanol/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.

Instrumentation

¹H and ¹³C NMR spectra were recorded in Bruker, AVANCE III HD 400/500 MHz spectrometers. VARIAN, Cary 500 Scan spectrometer was used to record UV-Vis absorbance spectra. Bruker, Tensor 27 spectrometer recorded FT-IR spectra (attenuated total reflectance mode; ATR). Waters, Xevo TQD Triple Quadrupole Mass Spectrometry was used for Liquid chromatography-mass spectrometry (LC-MS). TEM was performed in JEOL 3010 (300 kV) transmission electron microscope. Scanning transmission electron microscopy (STEM) images with EDS and elemental mapping were collected in FEI, Talos F200S (200 kV) transmission electron microscope. TEM images for transmission electron microscopy tomographic reconstruction were collected using Jeol F200 S/TEM operated at 200 keV. Carl-Zeiss SUPRA 55VP field emission scanning electron microscope was used to record FESEM images with EDS and elemental mapping. Thermo Scientific ESCALAB 250Xi instrument was used to collect X-ray photoelectron spectra. Agilent Technologies 5500 series AFM/SPM microscope was used for AFM measurements. High-resolution tapping mode (AC mode) AFM images were collected using Oxford Instruments, Asylum Cypher ES. Newport, Mercury-Xenon light source (500 W) equipped with a monochromator (Oriel) was used for the photoisomerization of chromophores and NCs. Cytoviva hyperspectral imaging system (HSI) equipped with CytovivaTM high-resolution dark-field condenser (oil immersion) was used to collect Dark-field scattering images. The optimized energy-minimized structures of NCs were accomplished by density functional theory (DFT) using a grid-based projector augmented waves (GPAW) software package.

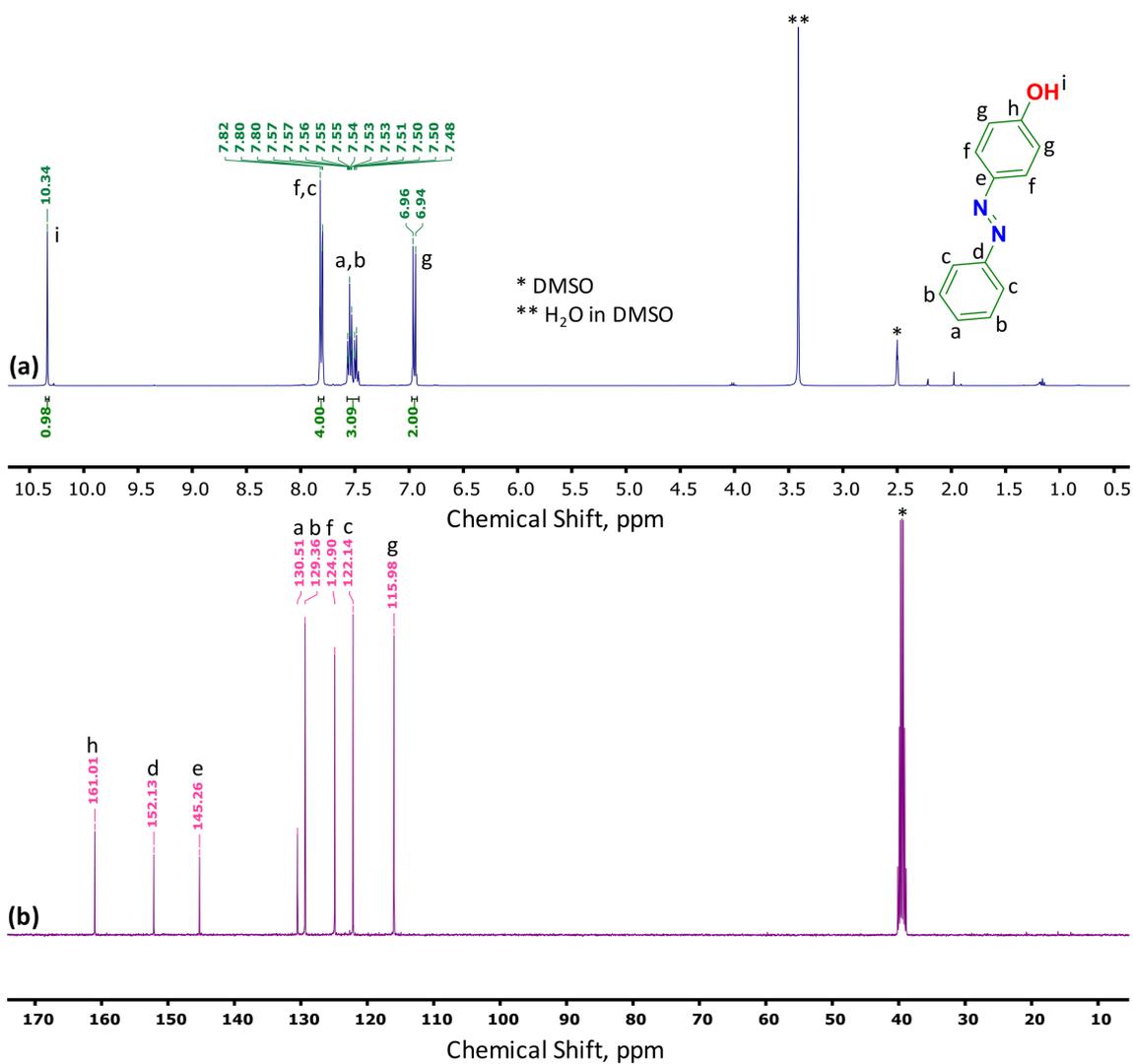


Figure S1. (a) ^1H and (b) ^{13}C NMR spectra of M1.

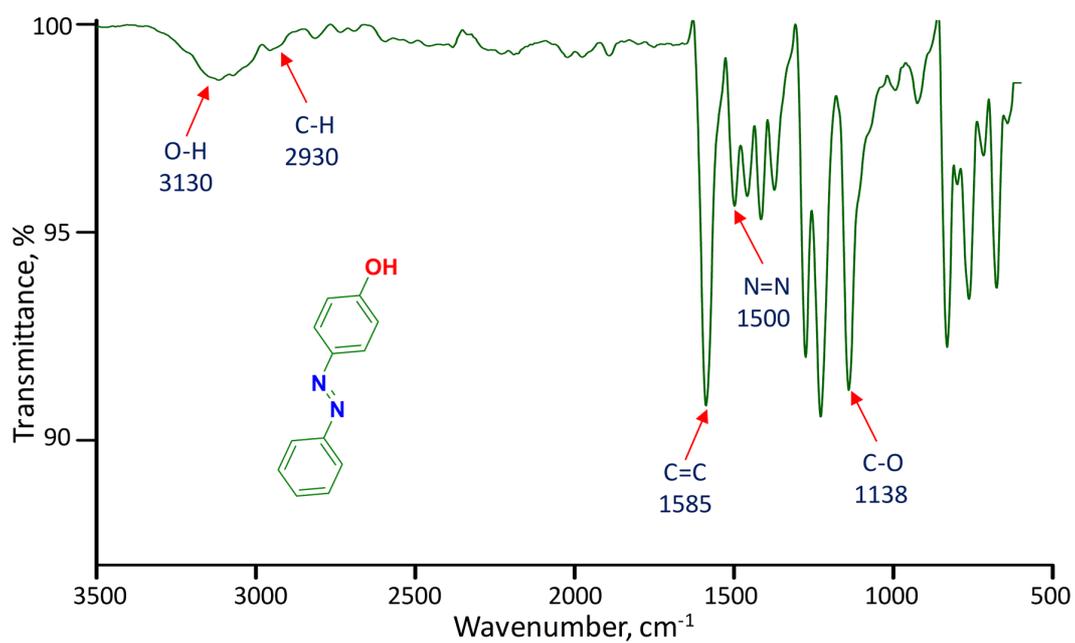


Figure S2. FT-IR spectrum of M1.

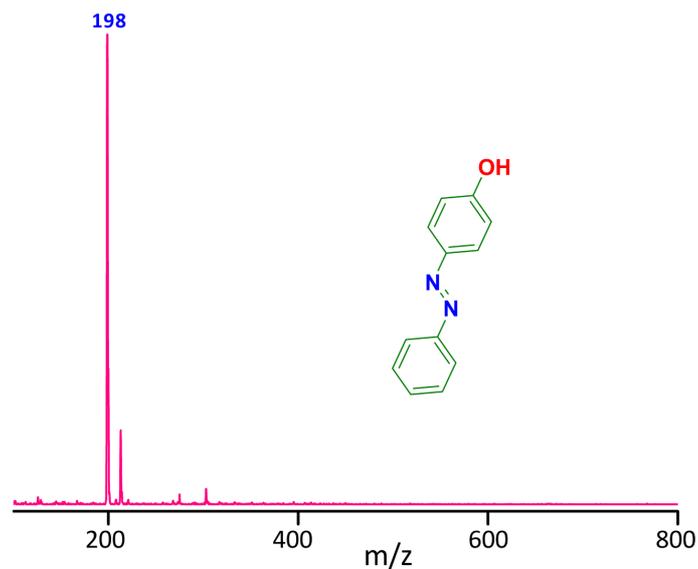


Figure S3. LC-MS spectrum of M1.

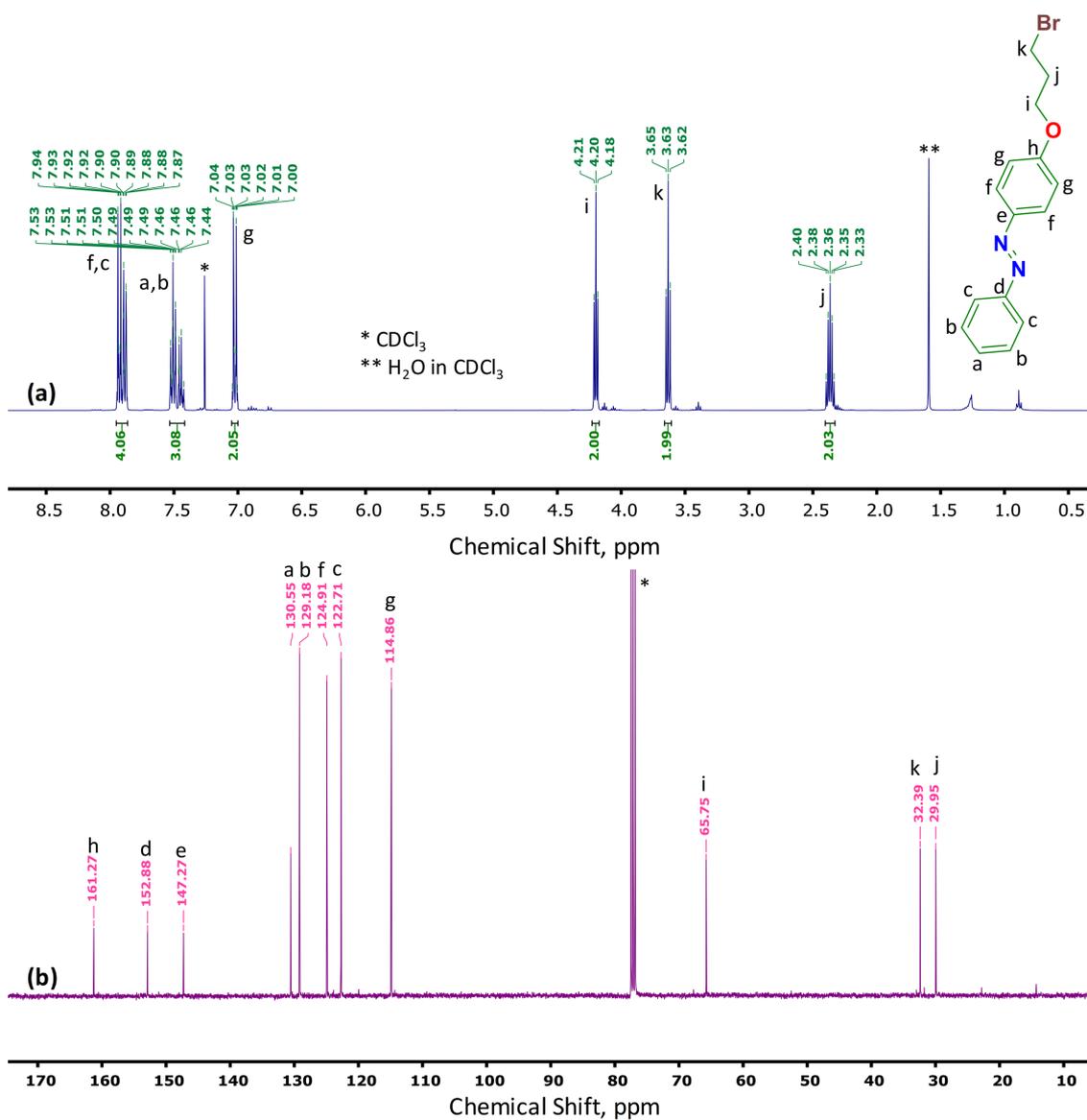


Figure S4. (a) ¹H and (b) ¹³C NMR spectra of M2.

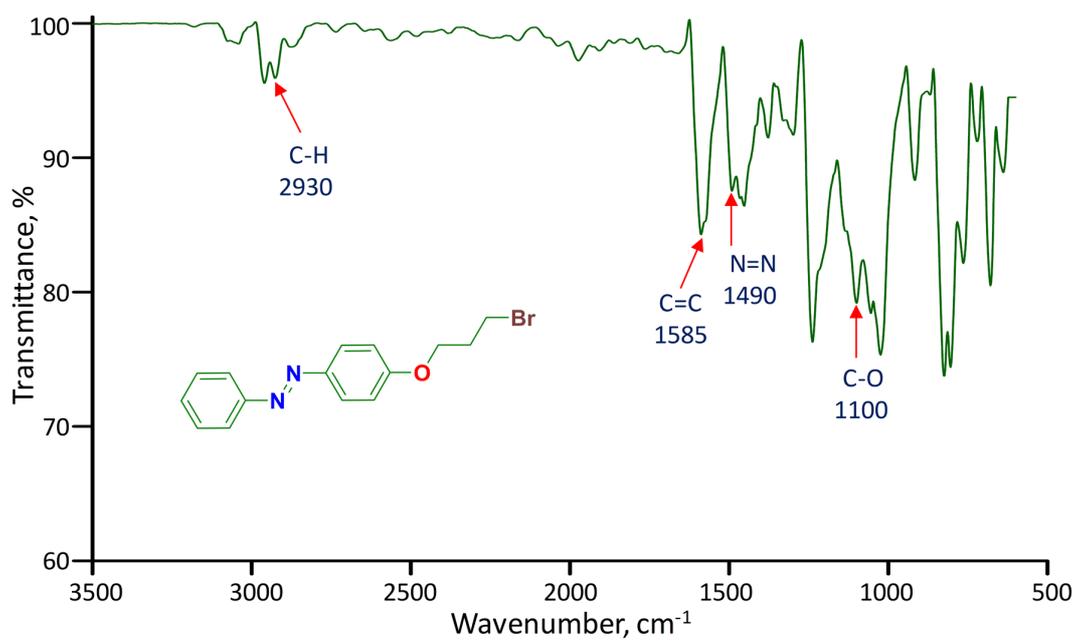


Figure S5. FT-IR spectrum of M2.

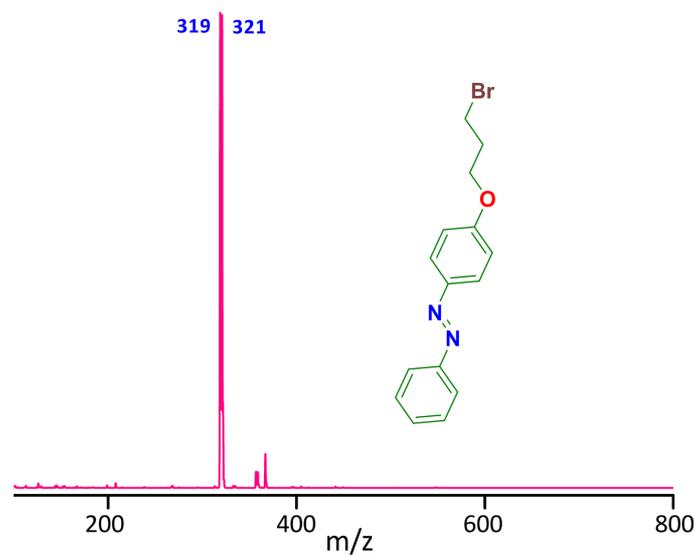


Figure S6. LC-MS spectrum of M2.

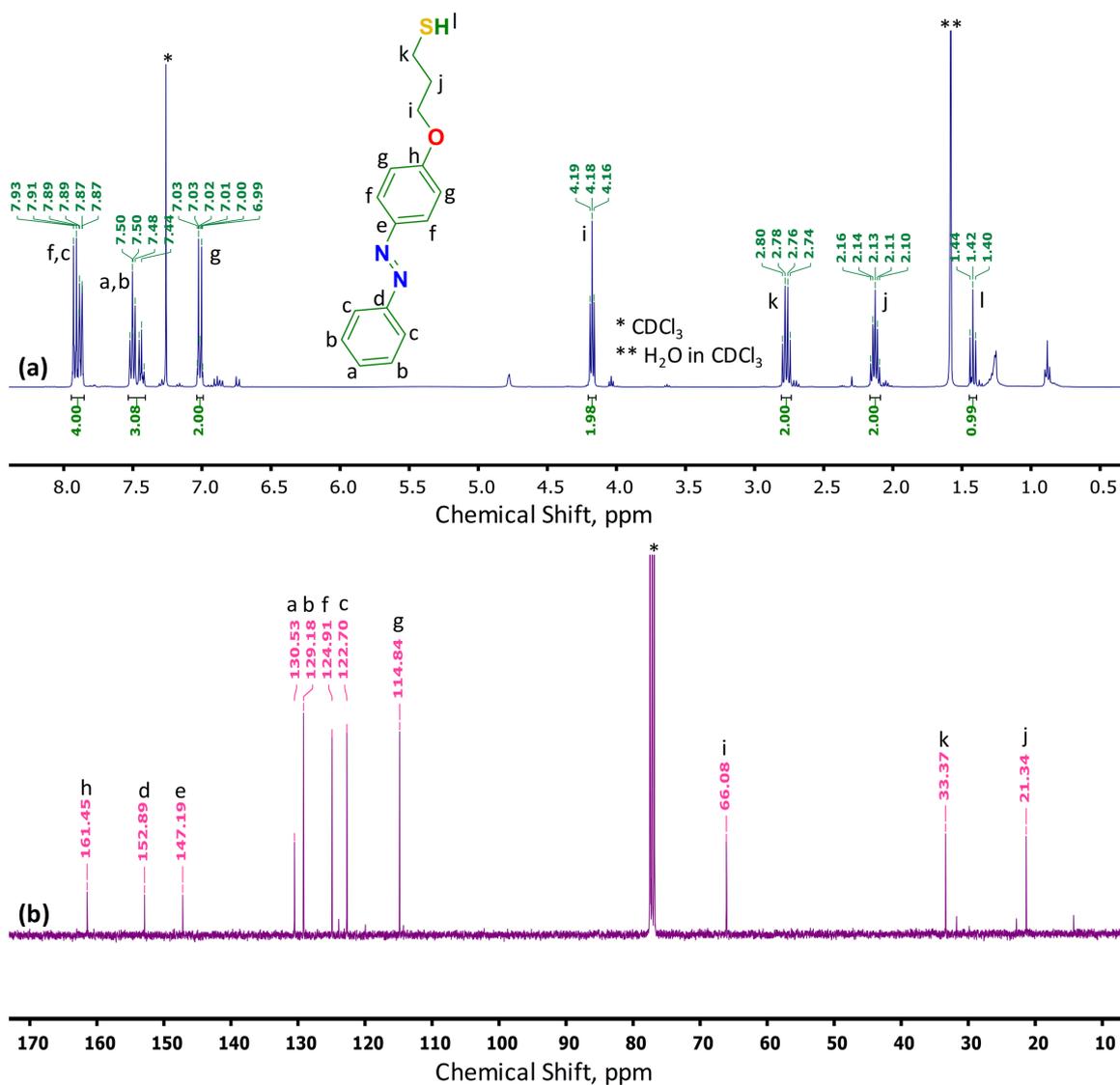


Figure S7. (a) ^1H and (b) ^{13}C NMR spectra of M3.

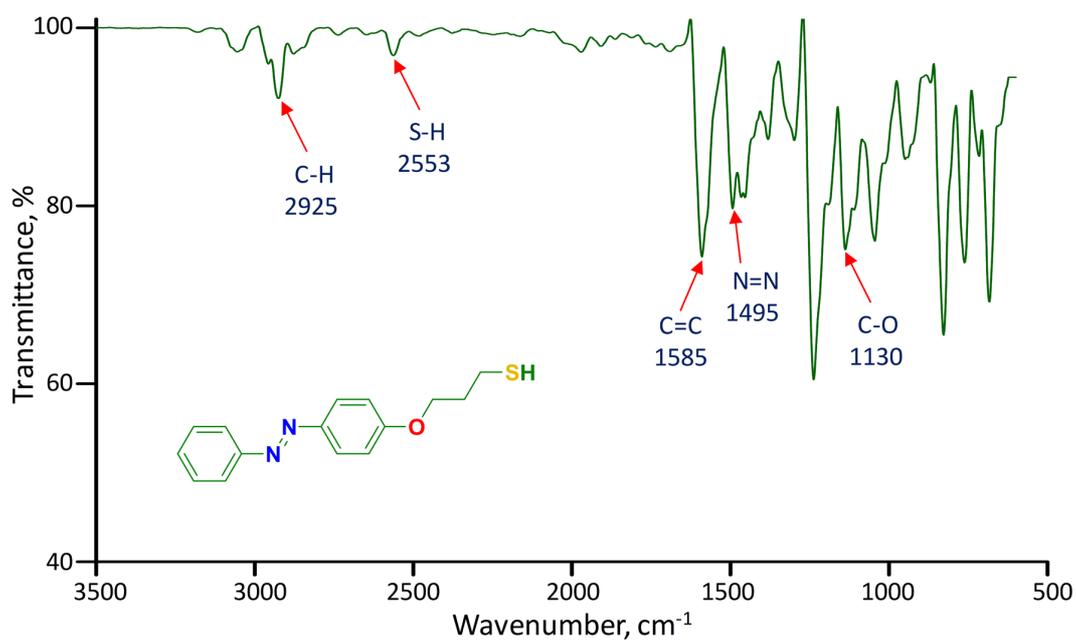


Figure S8. FT-IR spectrum of M3.

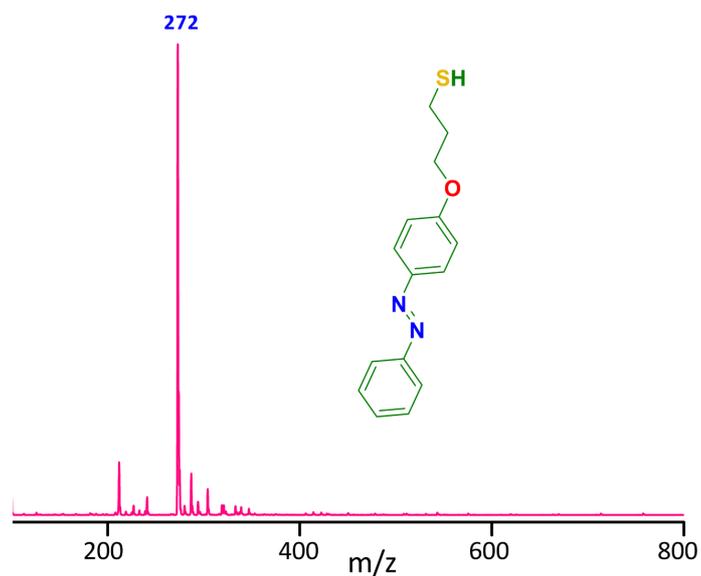


Figure S9. LC-MS spectrum of M3.

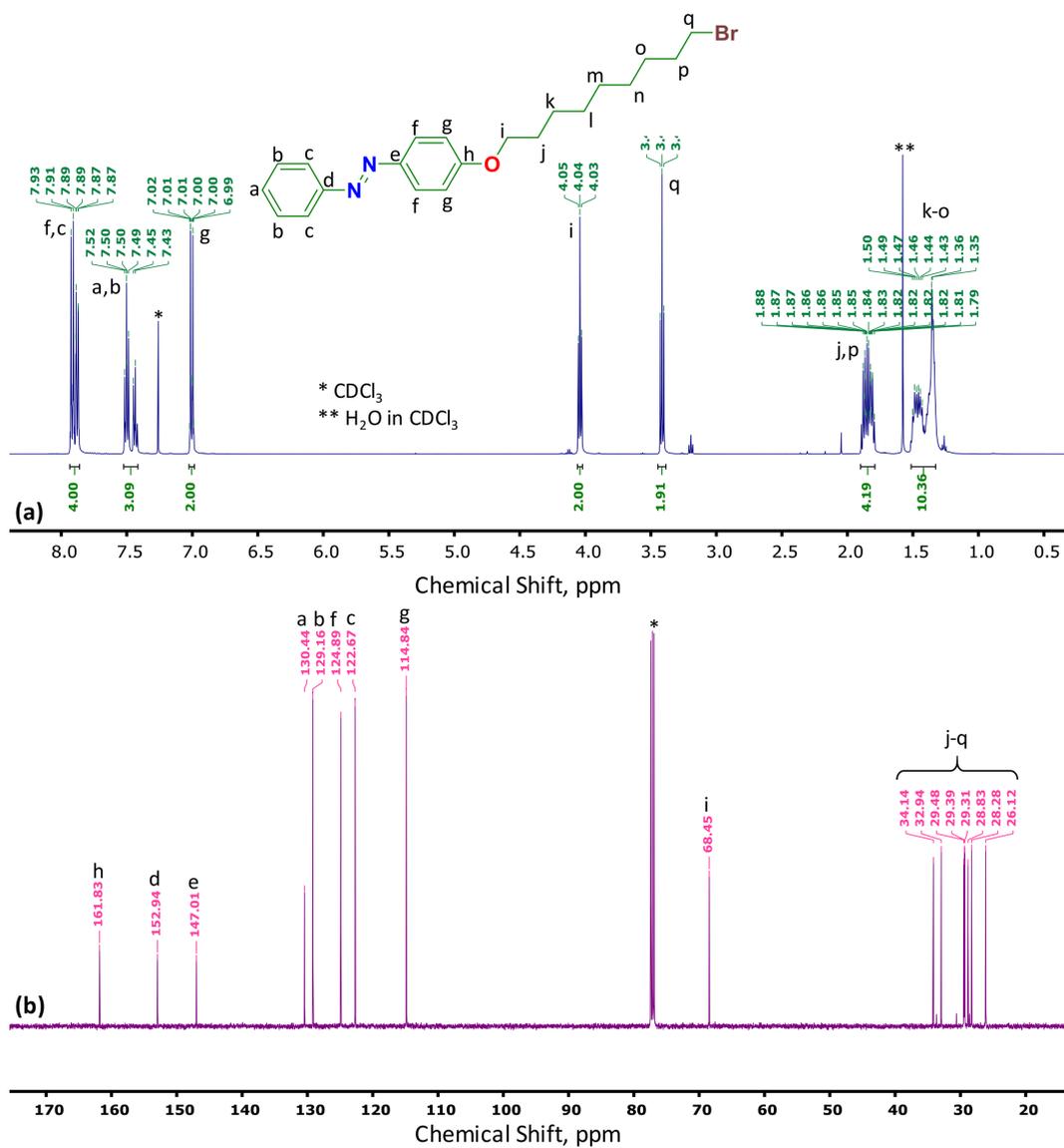


Figure S10. (a) ^1H and (b) ^{13}C NMR spectra of M4.

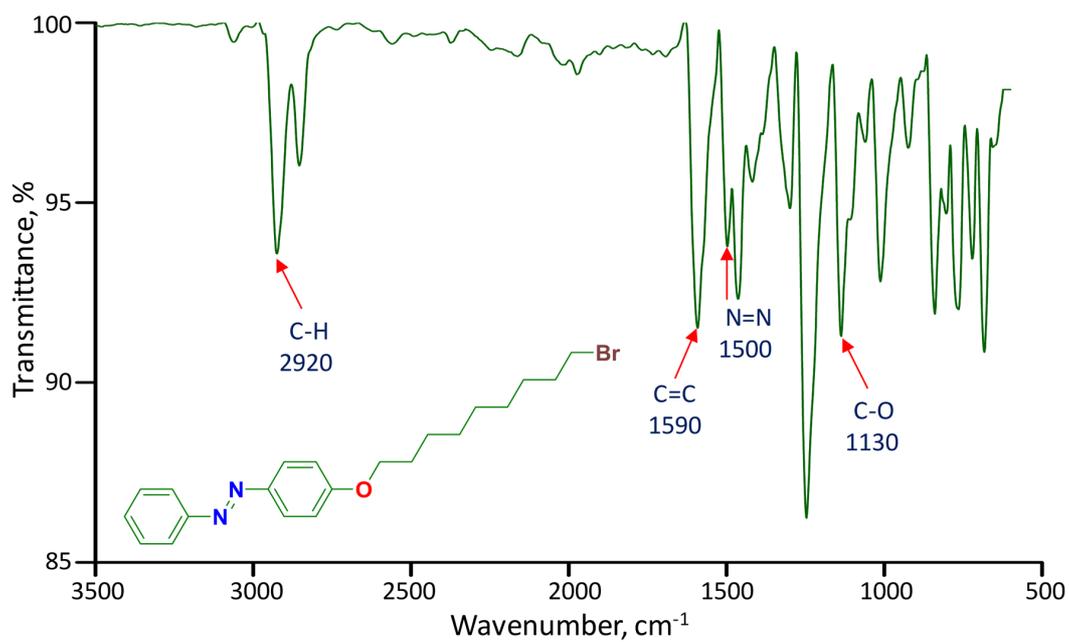


Figure S11. FT-IR spectrum of M4.

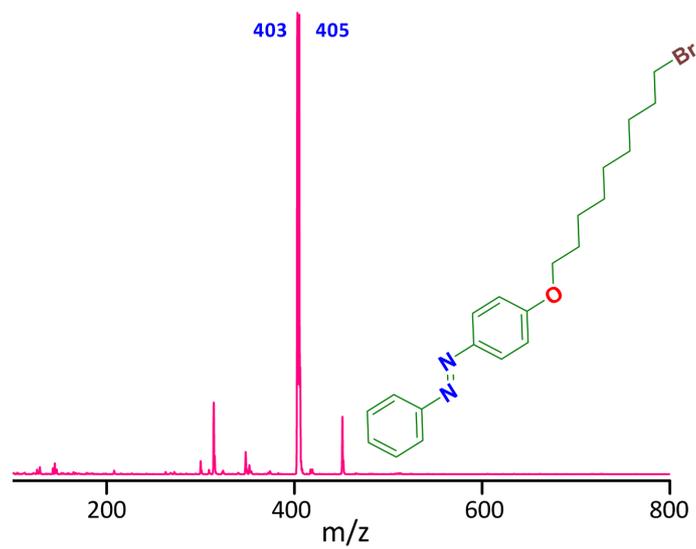


Figure S12. LC-MS spectrum of M4.

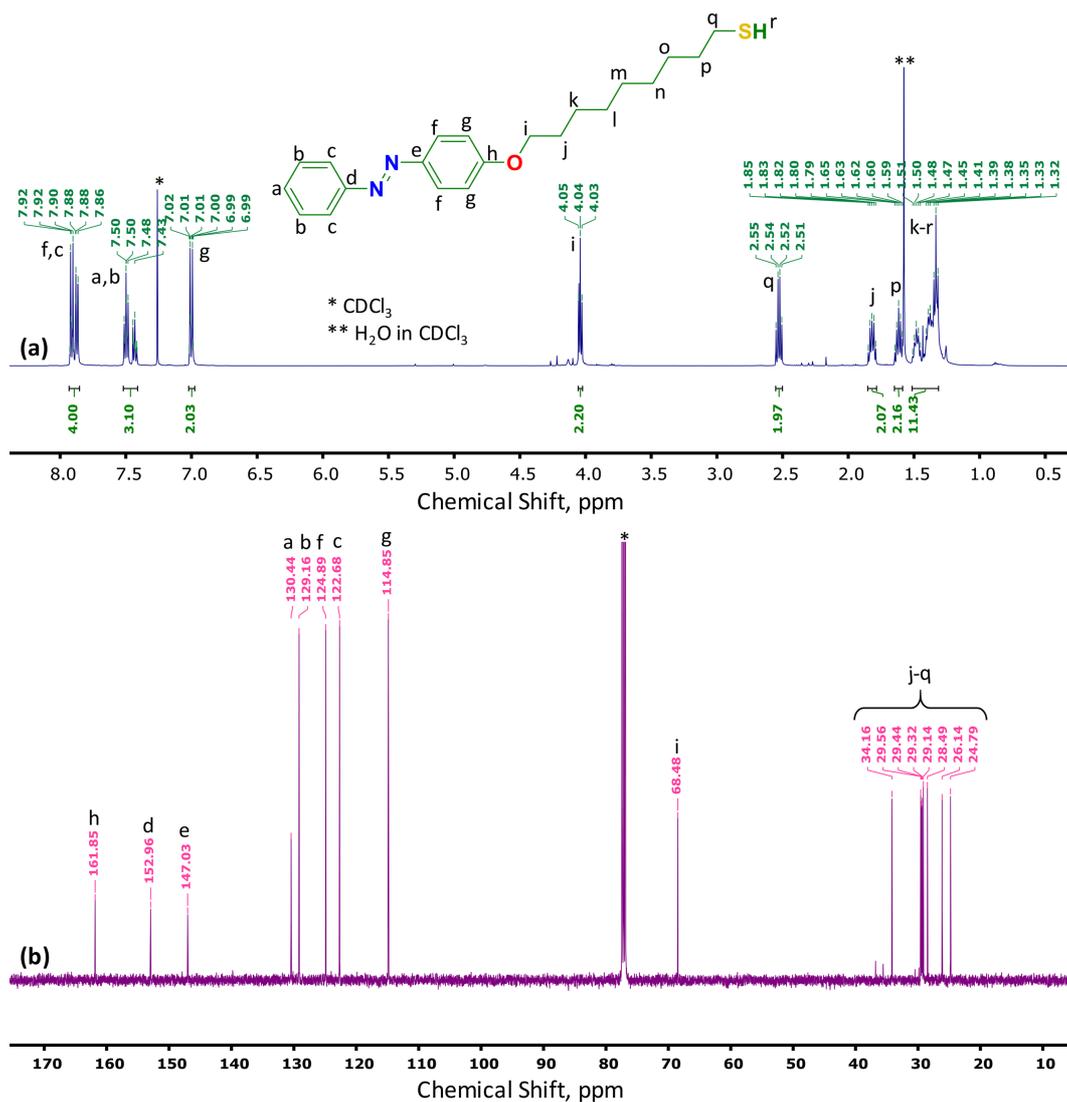


Figure S13. (a) ^1H and (b) ^{13}C NMR spectra of **M5**.

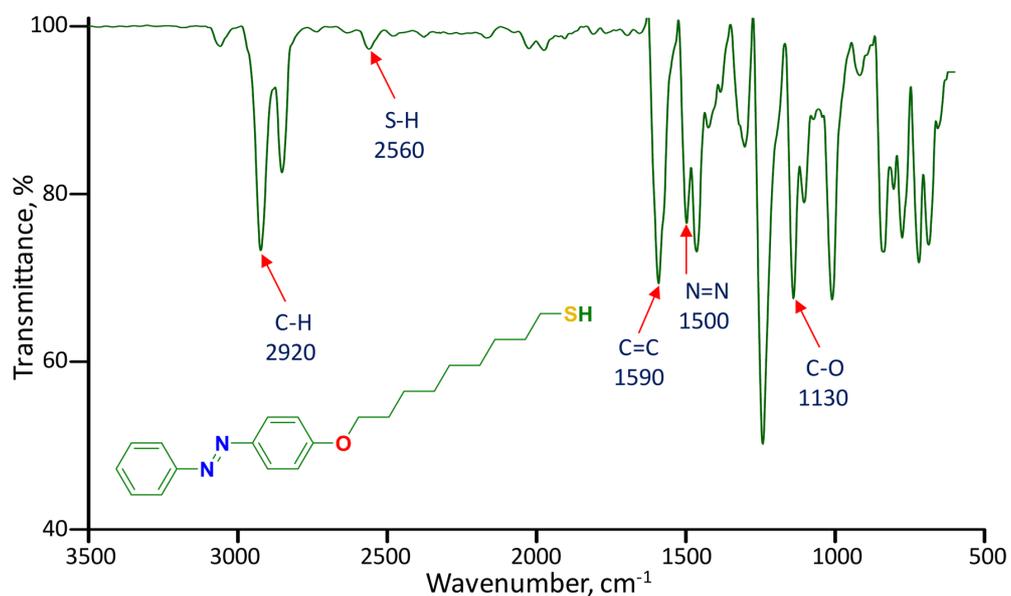


Figure S14. FT-IR spectrum of **M5**.

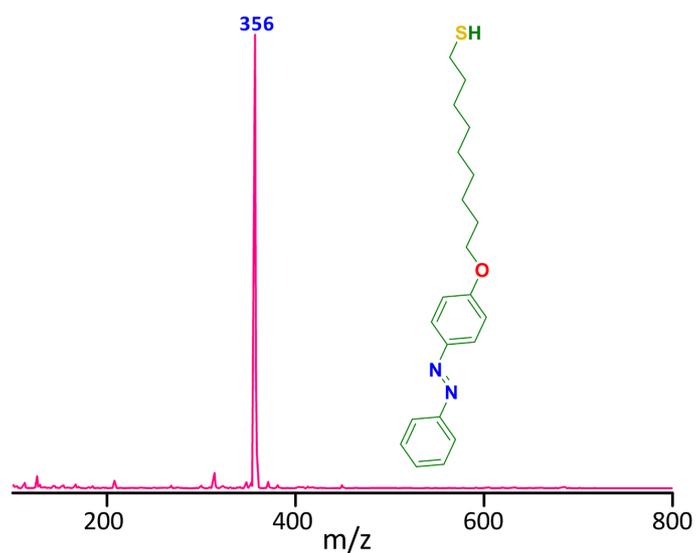


Figure S15. LC-MS spectrum of **M5**.

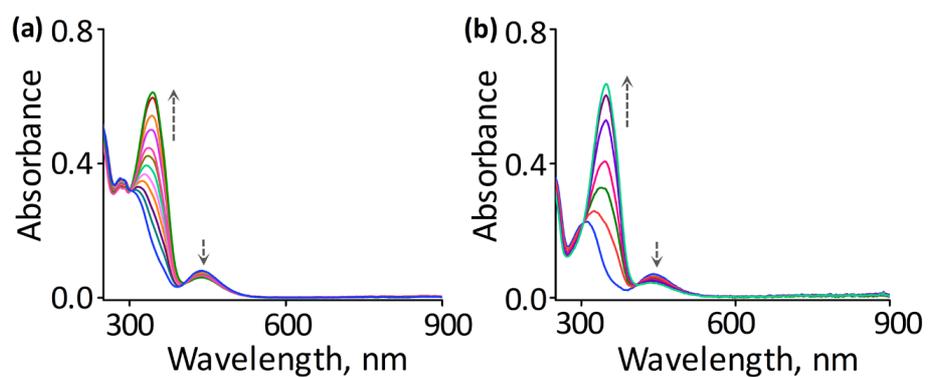


Figure S16. The temporal absorption spectra of (a) C_3 -AMT (M3) and (b) C_9 -AMT (M5) illuminated under 435 nm light.

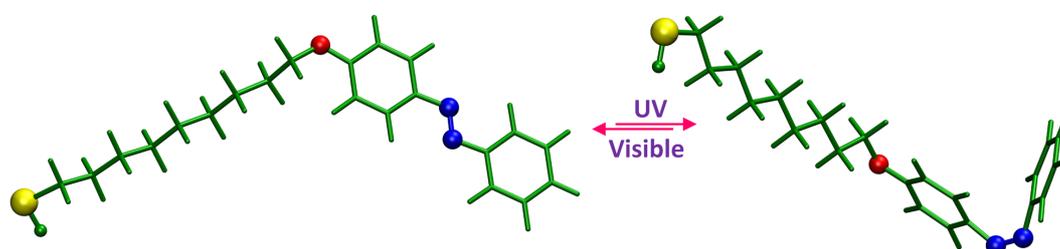


Figure S17. Energy-minimized structures of two geometrical isomers of C_9 -AMT (M5).

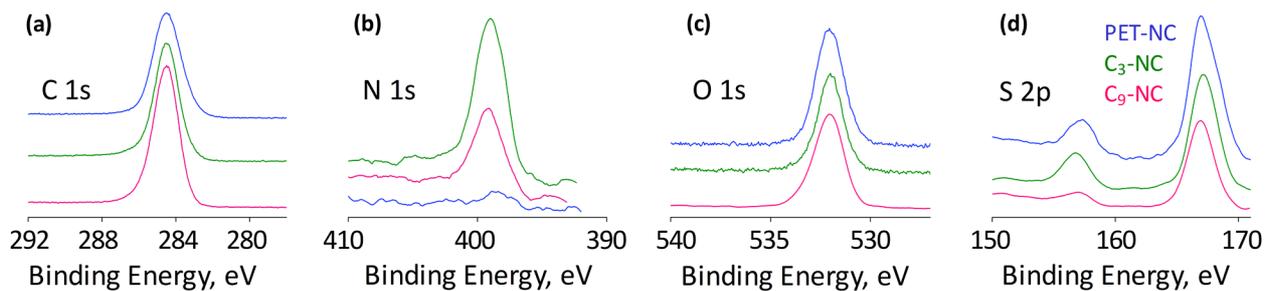


Figure S18. XPS spectra of (a) C 1s, (b) N 1s, (c) O 1s, and (d) S 2p levels of PET-NC (blue), C₃-NC (green), and C₉-NC (pink).

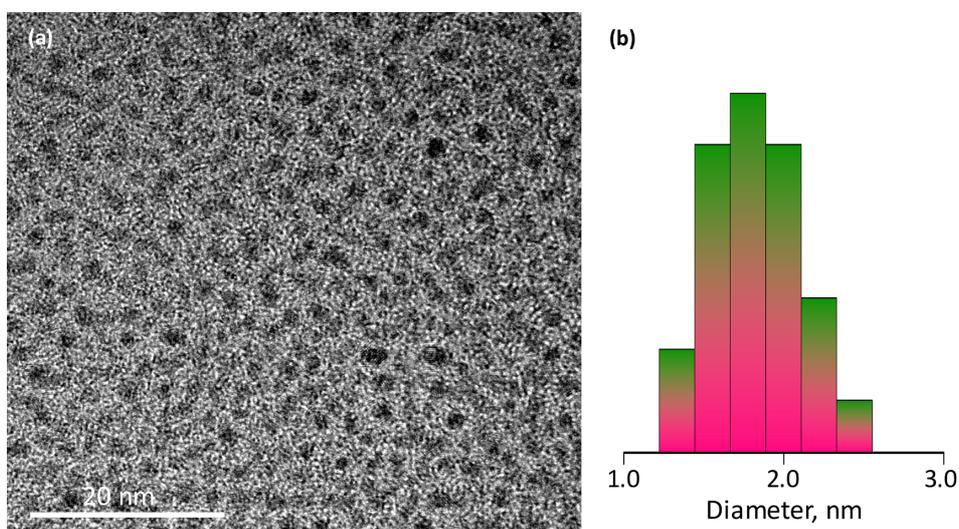


Figure S19. (a) HRTEM micrograph of C₉-NC and (b) corresponding size distribution.

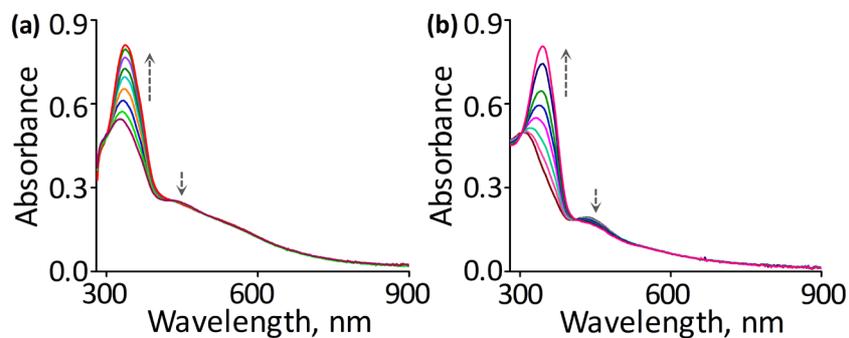


Figure S20. Temporal absorption spectra of (a) C₃-NC and (b) C₉-NC illuminated under 435 nm light.

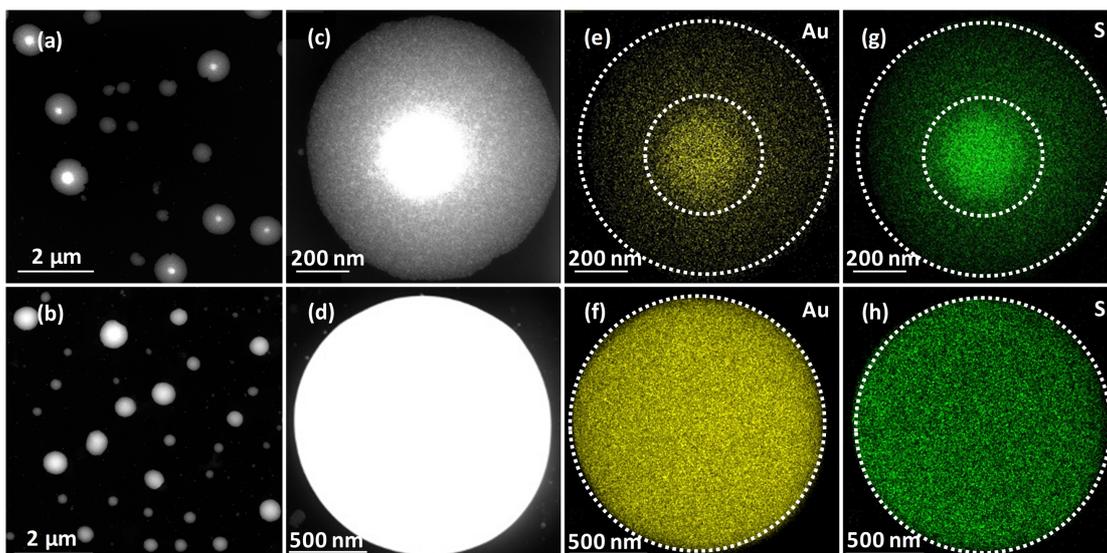


Figure S21. (a and b) Large area STEM images captured from (a) C₃-NC and (b) C₉-NC assembly. (c and d) A single STEM image from (c) C₃-NC and (d) C₉-NC assembly. The elemental maps of a single superstructure derived from (e and g) C₃-NC and (f and h) C₉-NC demonstrate the presence of (e and f) gold and (g and h) sulfur.

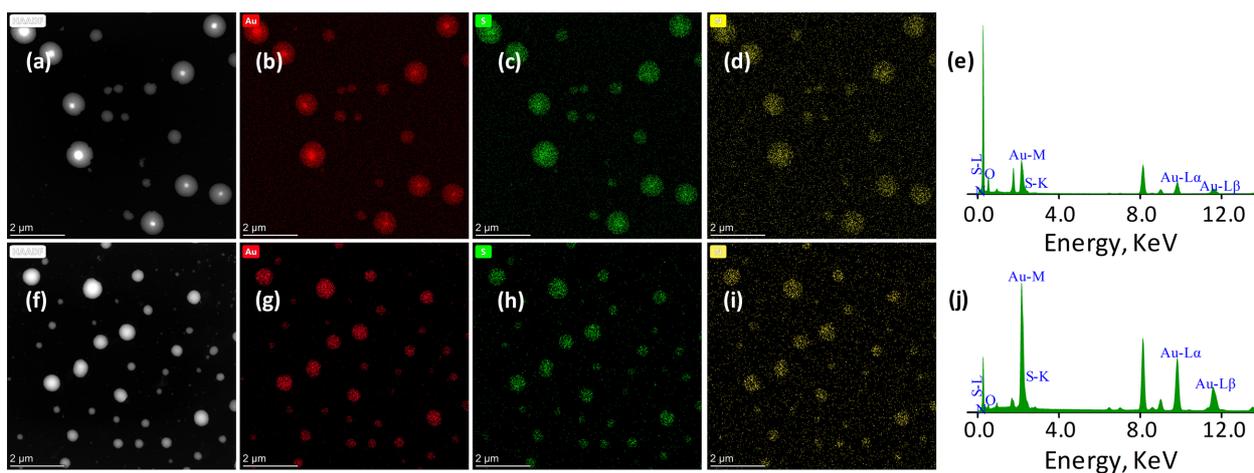


Figure S22. (a and f) STEM, (b-d and g-i) elemental maps (b and g-gold; c and h-sulfur; d and i-nitrogen), and (e and j) EDS spectra recorded from (e) C₃-NC and (j) C₉-NC assemblies.

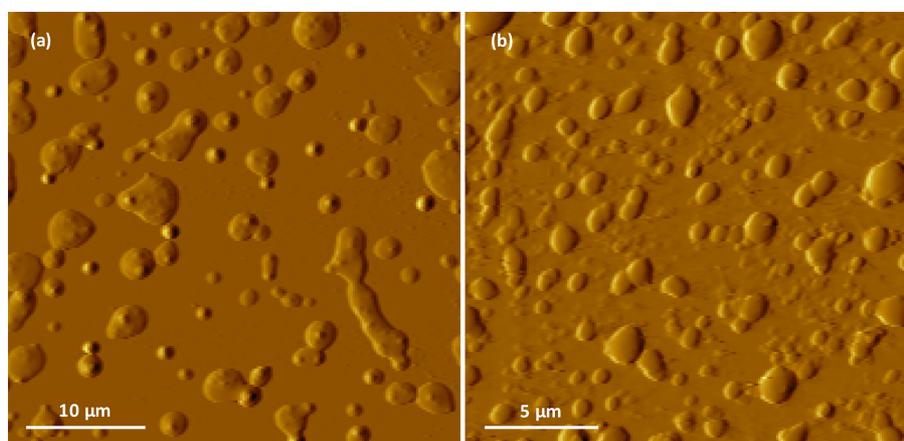


Figure S23. (a and b) Large area AFM images of (a) C₃-NC and (b) C₉-NC assemblies.

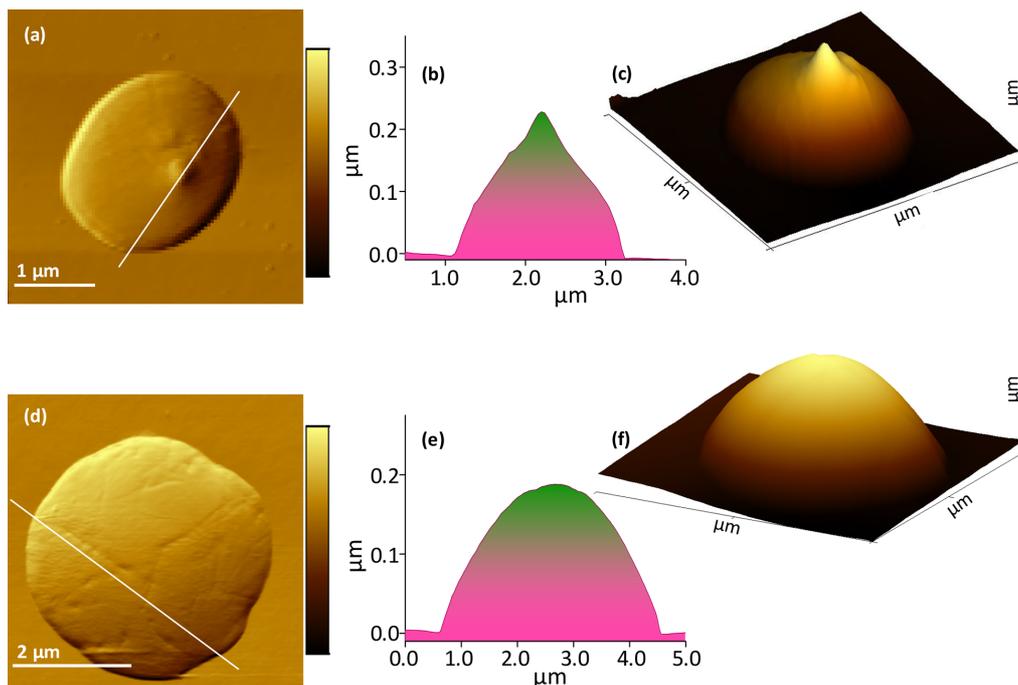


Figure S24. (a and d) AFM images of single superstructure derived from (a) C₃-NC and (d) C₉-NC. Corresponding (b and e) height profiles and (c and f) 3D images.

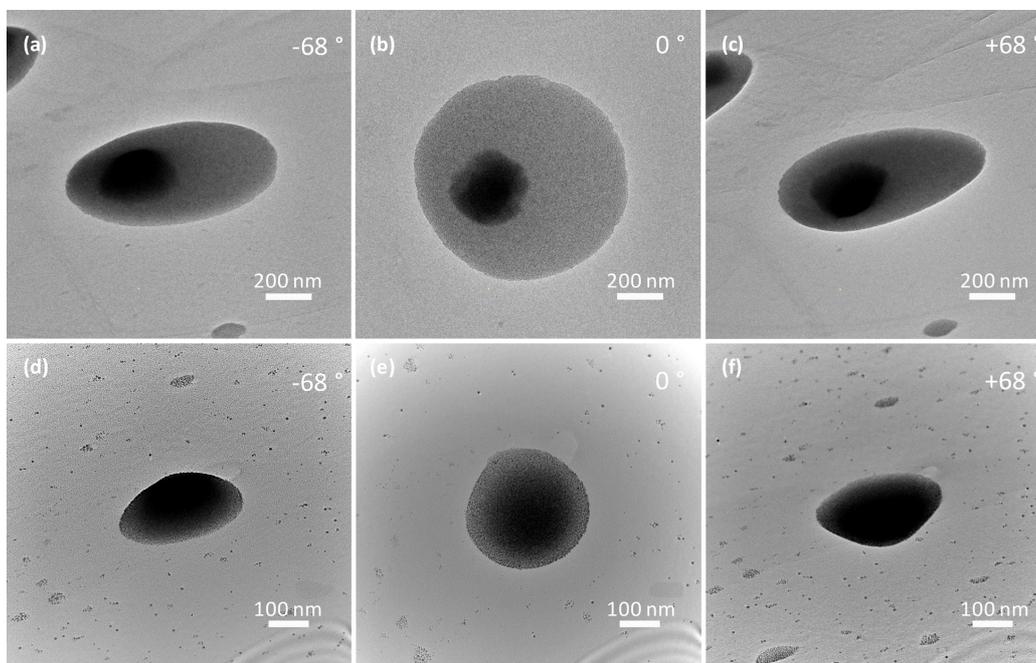


Figure S25. TEM images of (a-c) C₃- and (d-f) C₉- NC assembly at different tilt angles.

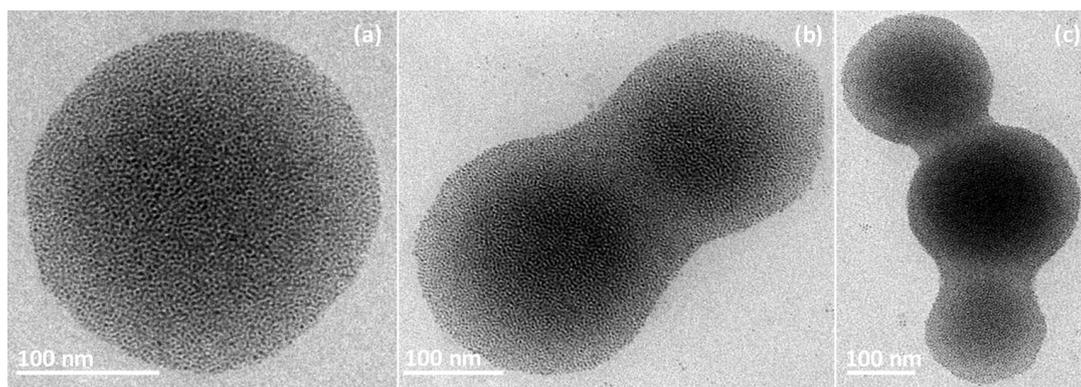


Figure S26. (a-c) TEM micrographs of (a) monomer, (b) dimer, and (c) trimer derived from C₉-NCs in early stages.

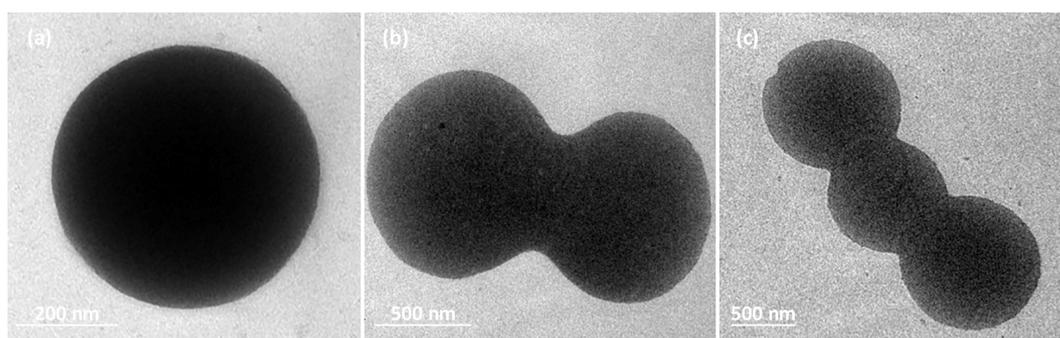


Figure S27. (a-c) TEM micrographs of (a) monomer, (b) dimer, and (c) trimer derived from C₉-NCs.

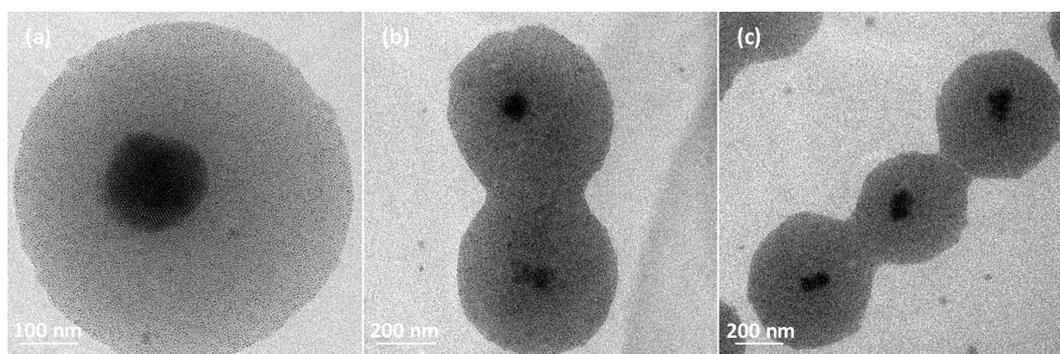


Figure S28. (a-c) TEM micrographs of (a) monomer, (b) dimer, and (c) trimer derived from C₃-NCs.

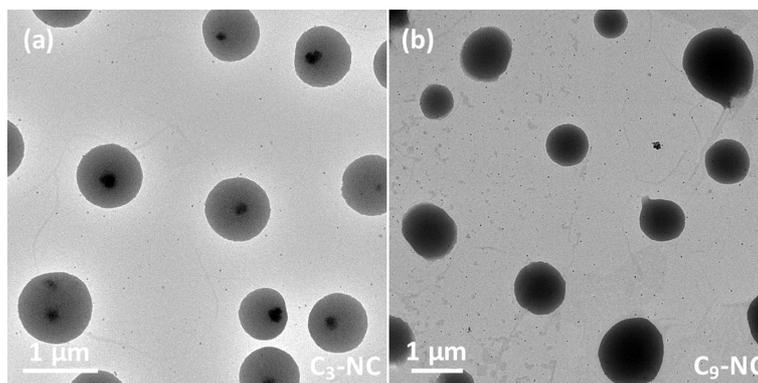


Figure S29. (a and b) TEM micrographs of (a) C₃-NC and (b) C₉-NC assembly recorded after one year.

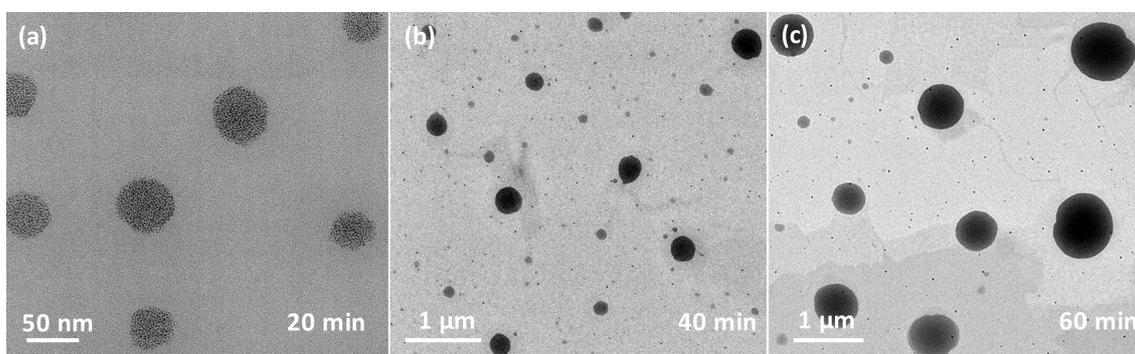


Figure S30. The mechanism for the formation of disc-like assembly. The temporal TEM micrographs of C₉-NC solution under 345 nm illumination for (a) 20 min, (b) 40 min, and (c) 60 min.

References

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