

Electronic Supplementary Information

Highly Efficient Light-Induced Self-Assembly of Gold Nanoparticles Promoted by Photoexcitation-Induced Aggregatable Ligands

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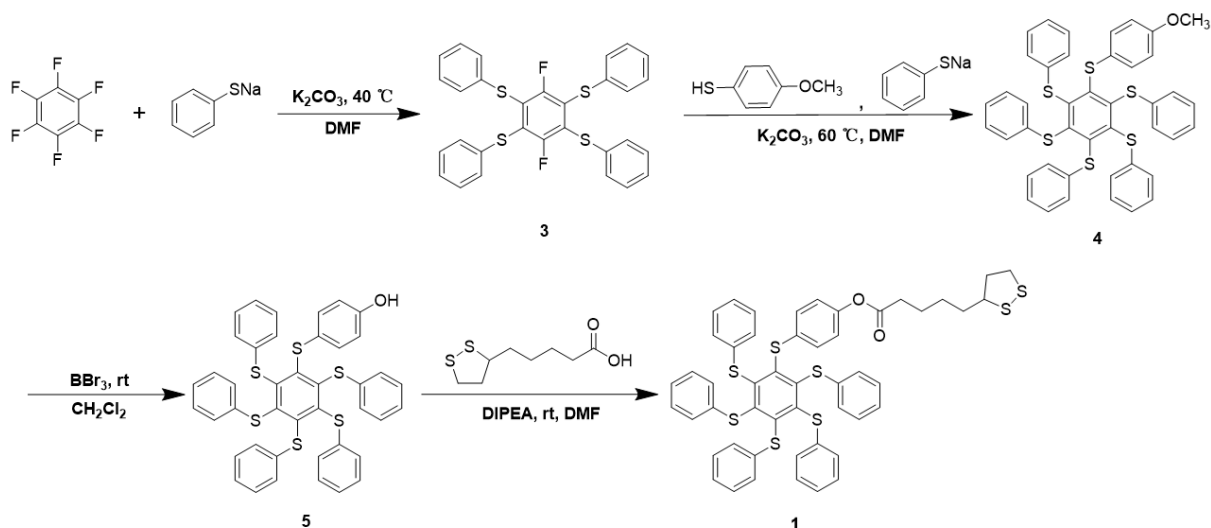
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1 General Information

All reagents were purchased from commercial sources and used directly without further purification. Lipoic acid was racemic. Reactions were monitored by TLC on silica gel GF 254 plates. Column chromatography was generally performed through silica gel (200–300 meshes). ^1H NMR, ^{13}C NMR, and 2D COSY ^1H NMR spectra were measured on a Bruker 400L spectrometer. High-resolution mass spectrometry (HRMS) data was measured by Matrix assisted laser desorption ionization-time of flight/time of flight mass spectrometer (5800). The UV-vis absorption spectra were recorded on a Shimadzu 1800 spectrophotometer. The photoirradiation experiments for the photoexcitation-induced molecular aggregation strategy were carried out using a hand-held UV lamp ($\sim 100 \mu\text{W cm}^{-2}$, 365 nm) in a sealed 10 mm quartz cell. High Contrast transmission electron microscopy (HCTEM) was performed on a HITACHI HT7800 with an accelerating voltage of 120 kV. Fourier transform infrared (FTIR) spectroscopy was carried out with a Thermofisher Nicolet 6700 spectrometer using KBr pellets as the sample matrix in the wavenumber range of 500–4000 cm^{-1} . Dynamic light scattering (DLS) experiments were carried out with Nano-Zeta Potential Analyzer ZS-90. Thermal gravimetric (TG) analyses were performed on a Mettler TG instrument under a dry nitrogen atmosphere at a heating rate of 10 K min^{-1} . The photos were taken with Canon EOS 800D.

2 Synthesis of Photoresponsive Persulfurated Benzene Ligand



Scheme S1. Synthesis route of ligand **1**.

Synthesis of compound 3: According to the literature method^[S1] with appropriate modification, perfluorobenzene (0.186 g, 1 mmol), sodium benzenethiolate (0.520 g, 4 mmol) were added into a round bottom flask capped with a septum under an argon atmosphere. DMF (20 mL) was injected *via* a syringe, and the mixture was stirred at 40 °C overnight. Water (20 mL) was poured into the flask while stirring, and a yellow precipitate was obtained. After collecting the solid by filtration, it was rinsed with ethanol and water. The crude powder was purified in a silica gel column with petroleum ether (PE) and dichloromethane (DCM) (20 : 1) and then dried under high vacuum.

Synthesis of compound 4: Compound 3 (3.276 g, 6 mmol), sodium benzenethiolate (1.188 g, 9 mmol), 4-methoxythiophenol (1.262 g, 9 mmol) and K₂CO₃ (1.656 g, 12 mmol) were added into a round bottom flask capped with a septum under an argon atmosphere. DMF (60 mL) was injected *via* a syringe, and the mixture was stirred at 80 °C for 24 h. Then, the resulting mixture was added to saturated brine and extracted with ethyl acetate (EtOAc). The volatiles were removed under vacuum to afford the crude product. The crude product was purified by column chromatography on silica gel with PE and DCM (10 : 1) and then dried under high vacuum. ¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.08 (m, 15H), 7.02 – 6.98 (d, J = 8.9 Hz, 2H), 6.96 – 6.92 (m, 10H), 6.72 – 6.68 (d, J = 9.01 Hz, 2H), 3.76 (s, 3H). ¹³C (100 MHz, CDCl₃) δ 158.7, 150.0, 148.1, 147.4, 147.3, 137.9, 137.8, 131.6, 129.0, 128.1, 128.1, 128.1, 126.1, 122.6, 114.6, 110.0, 55.4, 55.3, 31.6, 31.6, 30.4, 30.2. MS: MALDI-TOF MS, m/z [M]⁺: calcd. for C₄₃H₃₂OS₆, 756.08; found m/z [M + Na]⁺, 779.23.

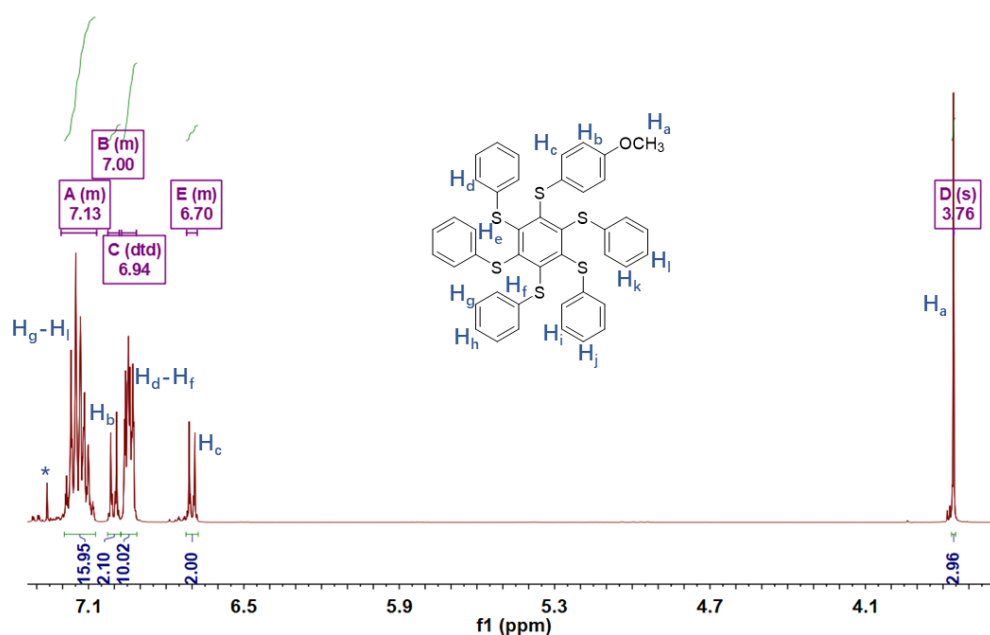


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 4.

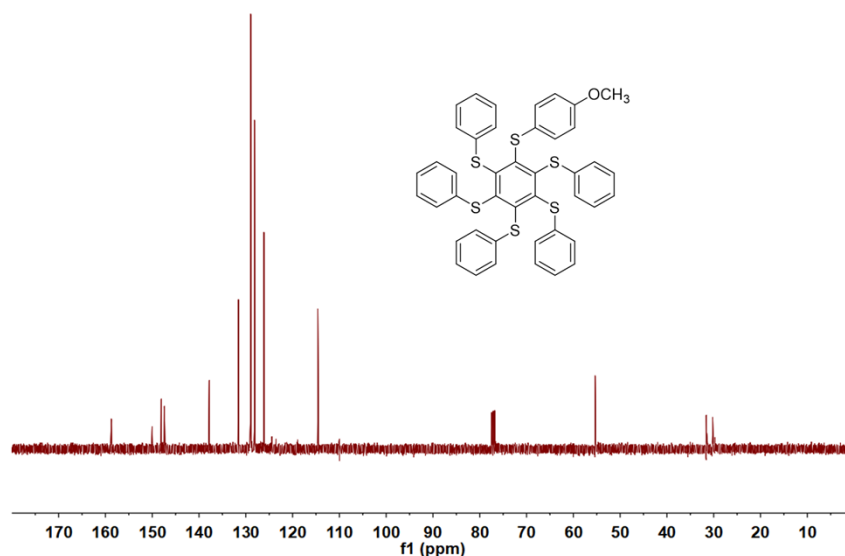


Figure S2. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of **4**.

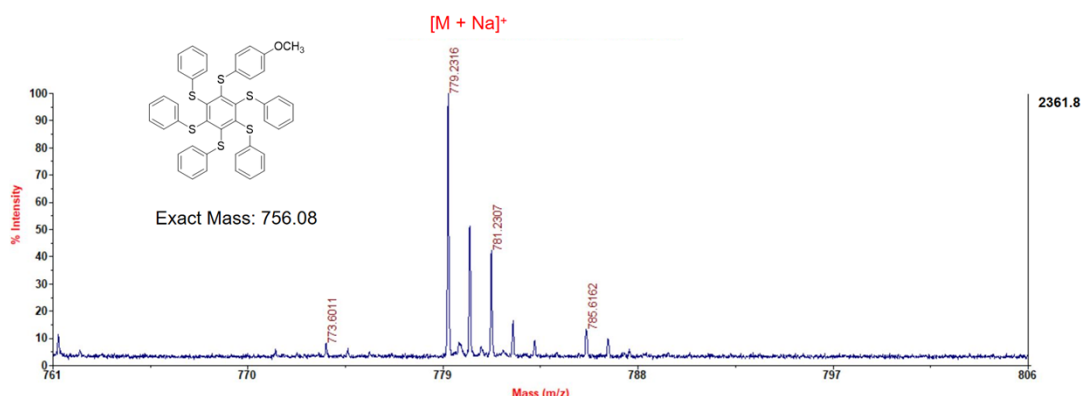


Figure S3. MALDI-TOF MS of **4**.

Synthesis of compound 5: Compound **4** (0.756 g, 1 mmol) was added into a round bottom flask capped with a septum under an argon atmosphere. Dry DCM (5 mL) and boron tribromide (1.93 mL, 20 mmol) was injected *via* a syringe, then the mixture was stirred at room temperature for 12 h. After that, the mixture was cooled in ice bath, and water was added dropwise. The resulting solution was extracted with EtOAc. The volatiles were removed under vacuum to afford the crude product. The crude product was purified by column chromatography on silica gel with PE and DCM (1 : 2) and then dried under high vacuum. ^1H NMR (400 MHz, CDCl_3) δ 7.18 – 7.06 (m, 15H), 6.97 – 6.87 (m, 12H), 6.65 – 6.60 (d, $J = 8.8$ Hz, 2H), 4.73 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.7, 149.8, 148.0, 147.5, 147.4, 137.8, 137.8, 137.7, 132.0, 131.8, 129.0, 129.0, 129.0, 129.0, 129.0, 128.4, 128.2, 128.1, 128.1, 128.1, 128.0, 126.2, 126.2, 116.1. MS: MALDI-TOF MS, m/z $[\text{M}]^+$: calcd. for $\text{C}_{42}\text{H}_{30}\text{OS}_6$,

742.06;

found

m/z

[m]⁺,

742.22.

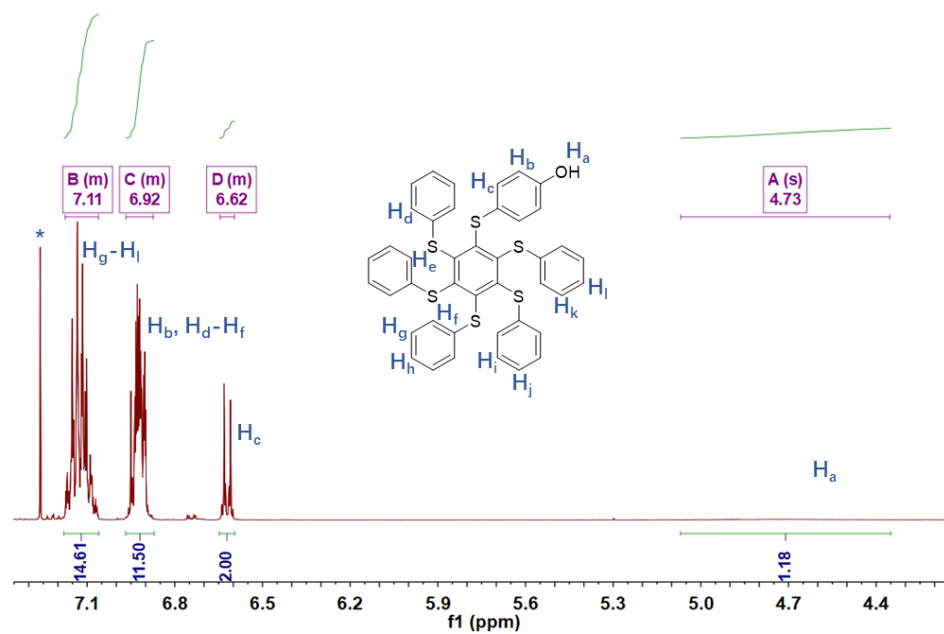


Figure S4. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 5.

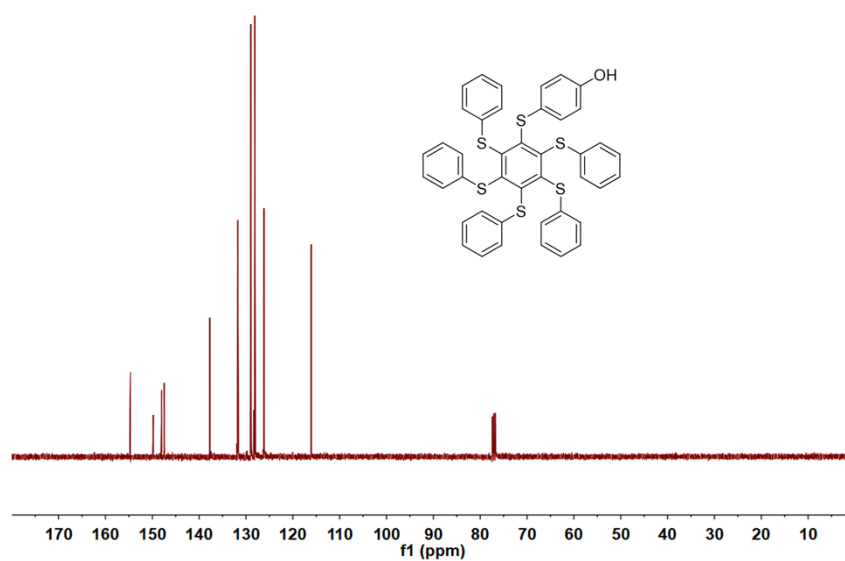


Figure S5. ¹³C NMR spectrum (100 MHz, CDCl₃, 298 K) of 5.

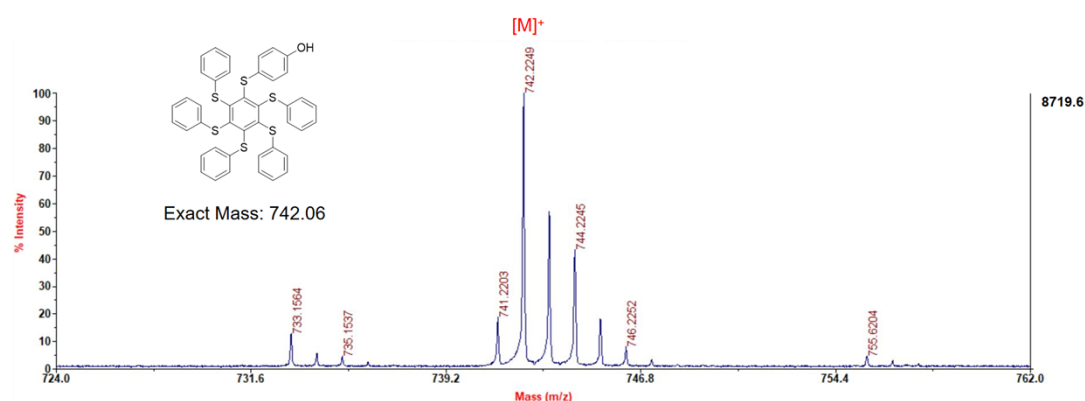


Figure S6. MALDI-TOF MS of **5**.

Synthesis of ligand 1: N,N'-Dicyclohexylcarbodiimide (DCC, 5.158 g, 25 mmol), lipoic acid (4.126 g, 20 mmol) and DMF (10 mL) were added into a round bottom flask. After stirring at room temperature for 15 min, compound **5** (0.742 g, 1mmol) and ethyldiisopropylamine (DIPEA, 1 mL, 6 mmol) was added, and the mixture was stirred at room temperature for 18 h. Then, the resulting mixture was added to saturated brine and extracted with EtOAc. The volatiles were removed under vacuum to afford the crude product. The crude product was purified by column chromatography on silica gel with PE and DCM (2 : 1) and then dried under high vacuum. ^1H NMR (400 MHz, CDCl_3) δ 7.19 – 7.07 (m, 15H), 6.98 – 6.86 (m, 14H), 3.61 (m, 1H), 3.25 – 3.08 (m, 2H), 2.56 (t, $J = 7.4$ Hz, 2H), 2.53 – 2.43 (m, 1H), 1.98 – 1.89 (m, 1H), 1.84 – 1.68 (m, 4H), 1.66 – 1.49 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 149.2, 148.2, 148.2, 148.0, 148.0, 137.6, 137.6, 134.6, 129.6, 129.0, 129.0, 129.0, 128.2, 128.2, 126.3, 126.2, 122.0, 56.3, 40.3, 38.6, 34.6, 34.2, 28.7, 24.6. MS: MALDI-TOF MS, m/z $[\text{M}]^+$: calcd. for $\text{C}_{50}\text{H}_{42}\text{O}_2\text{S}_8$, 930.10; found m/z $[\text{M} + \text{Na}]^+$, 953.35.

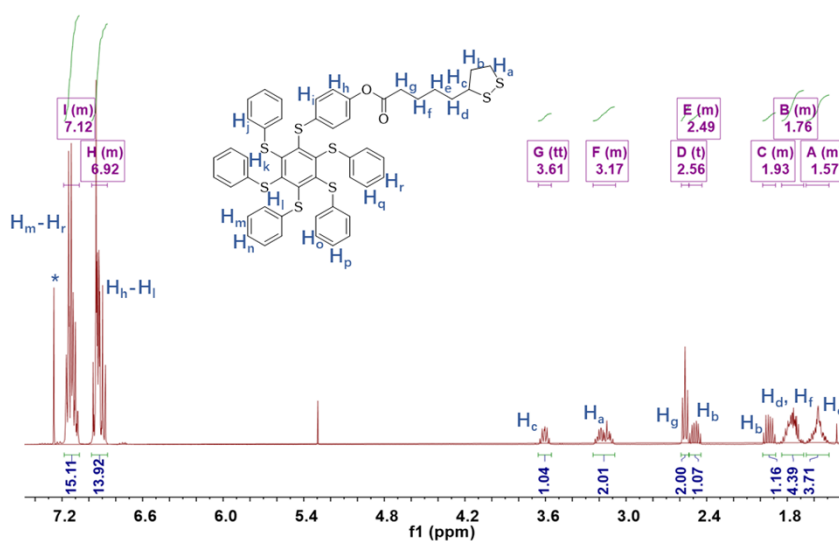


Figure S7. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **1**.

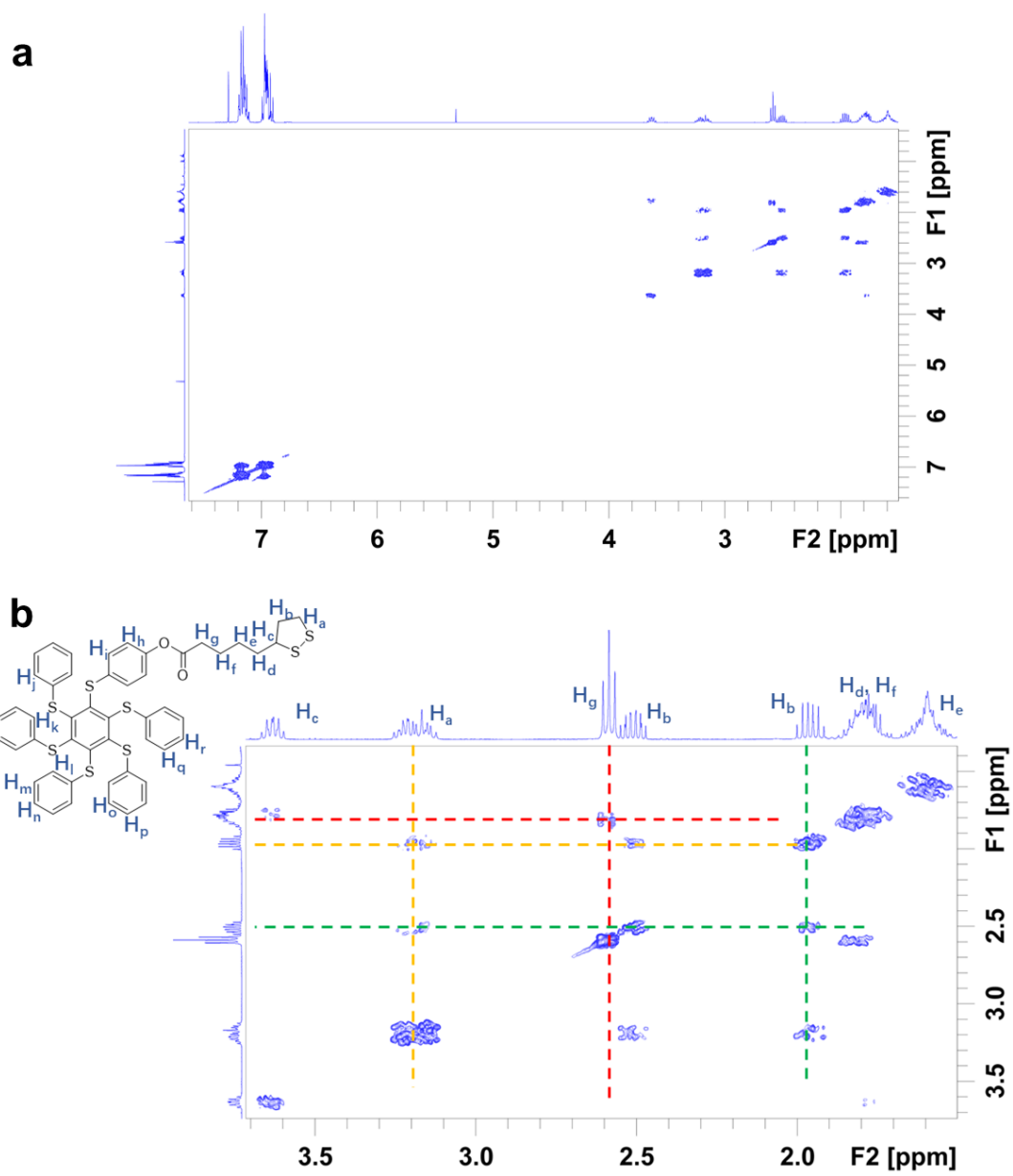


Figure S8. (a) 2D COSY ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **1**, (b) partial enlarged view of (a).

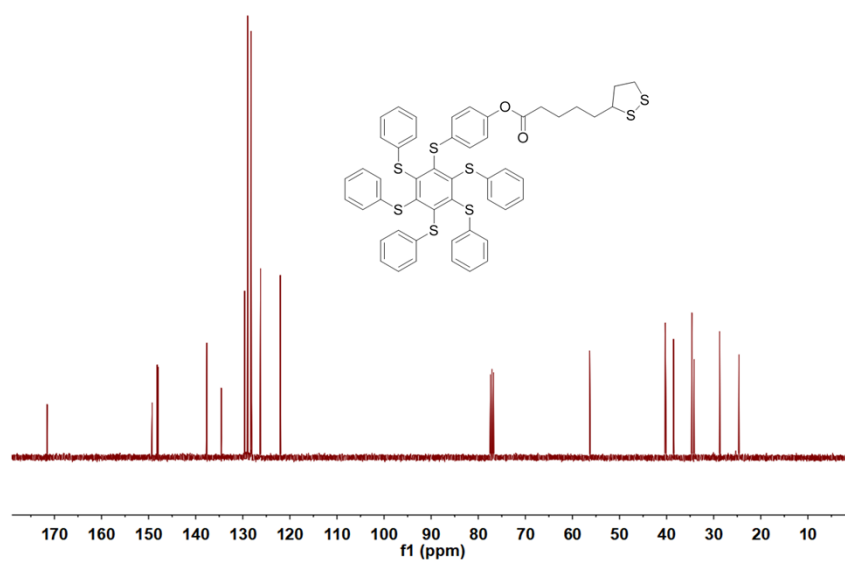


Figure S9. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of 1.

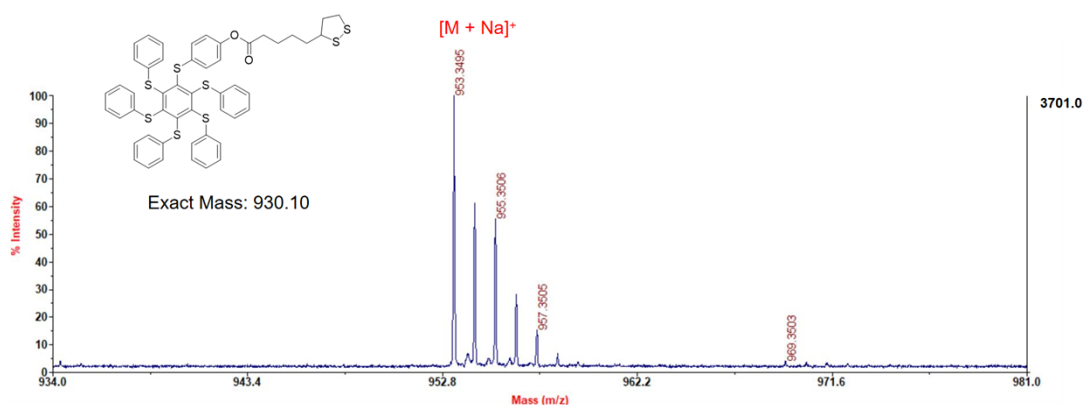
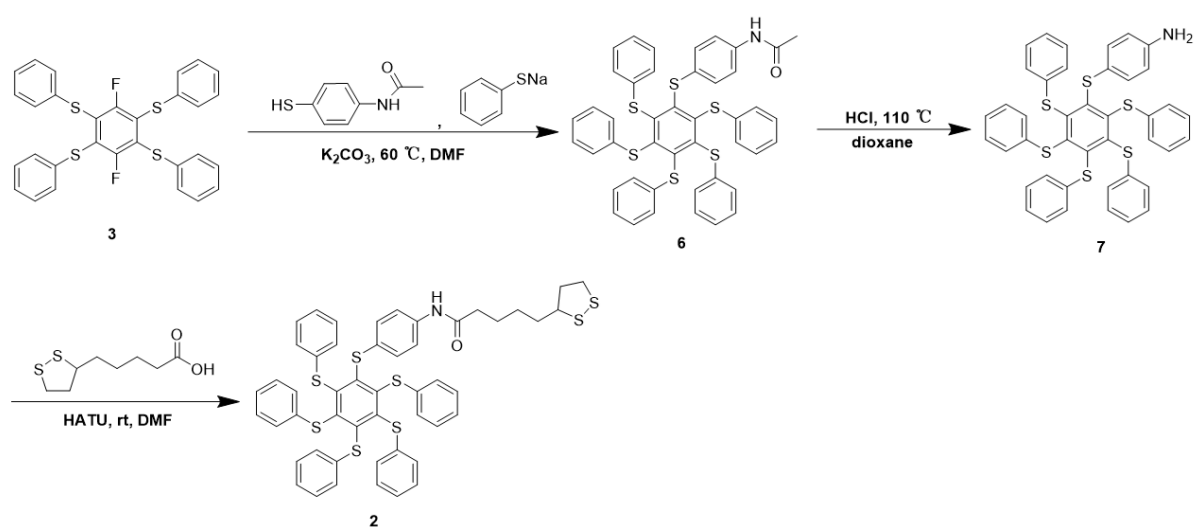


Figure S10. MALDI-TOF MS of 1.



Scheme S2. Synthesis route of ligand **2**.

Synthesis of compound 6: According to the literature method^[S1] with appropriate modification, compound **3** (3.276 g, 6 mmol), sodium benzenethiolate (2.376 g, 18 mmol), 4-Acetamidothiophenol (2.004 g, 12 mmol), K_2CO_3 (1.656 g, 12mmol) were added into a round bottom flask capped with a septum under an argon atmosphere. DMF (60 mL) was injected *via* a syringe and the mixture was stirred at 60 °C for 24 h. Then, the resulting mixture was added to saturated brine and extracted with EtOAc. The volatiles were removed under vacuum to afford the crude product. The crude product was purified by column chromatography on silica gel with PE and EtOAc (2:1) and then dried under high vacuum.

Synthesis of compound 7: According to the literature method^[S1] with appropriate modification, compound **6** (0.784 g, 1 mmol) was added into a three neck round bottom flask capped with a septum under an argon atmosphere. 1,4-dioxane (5 mL) and HCl (2 mL, 12 M) were injected *via* syringes and the mixture was stirred at 110 °C for 24 h. Upon completion, K_2CO_3 and saturated brine were added, and the resulting solution was extracted with EtOAc. The volatiles were removed under vacuum to afford the crude product. The crude product was purified by column chromatography on silica gel with PE and DCM (2:1) and then dried under high vacuum.

Synthesis of Ligand 2: 2-(7-Azabenzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HATU, 0.760 g, 2 mmol), lipoic acid (0.413 g, 2 mmol) and DMF (10 mL) were added into a round bottom flask. After stirring at room temperature for 15 min, compound **7** (0.741 g, 1mmol) and DIPEA (0.6 mL, 4 mmol) were added, and the mixture was stirred at room temperature for 18 h. Then, the resulting mixture was added to saturated brine and extracted with EtOAc. The volatiles were removed under vacuum to afford the

crude product. The crude product was purified by column chromatography on silica gel with DCM and then dried under high vacuum. ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 8.6$ Hz, 2H), 7.18 – 7.04 (m, 16H), 6.95 – 6.89 (m, 12H), 3.64 – 3.55 (m, 1H), 3.22 – 3.08 (m, 2H), 2.47 (dt, $J = 18.8, 6.5$ Hz, 1H), 2.35 (t, $J = 7.2$ Hz, 2H), 1.92 (m, 1H), 1.83 – 1.69 (m, 4H), 1.56 – 1.48 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 148.2, 147.9, 147.6, 137.7, 137.7, 136.5, 132.5, 129.7, 129.0, 129.0, 129.0, 128.2, 128.1, 128.1, 126.2, 126.2, 120.0, 110.0, 77.4, 77.1, 76.7, 56.4, 40.3, 38.5, 38.5, 37.5, 34.7, 28.9, 25.2. MS: MALDI-TOF MS, m/z $[\text{M}]^+$: calcd. for $\text{C}_{50}\text{H}_{43}\text{ONS}_8$, 929.11; found m/z $[\text{M} + \text{Na}]^+$, 952.34.

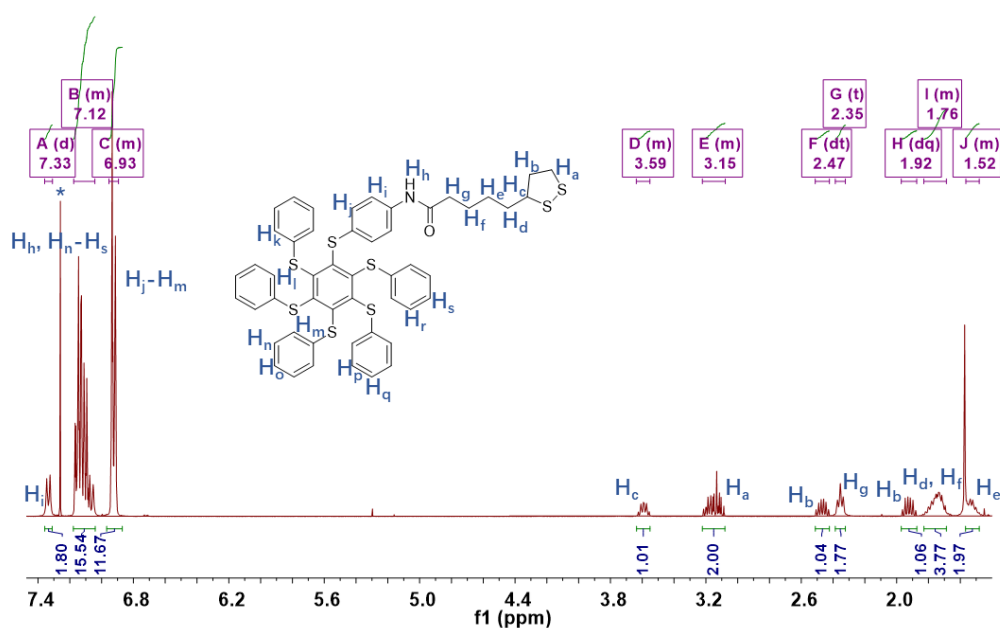
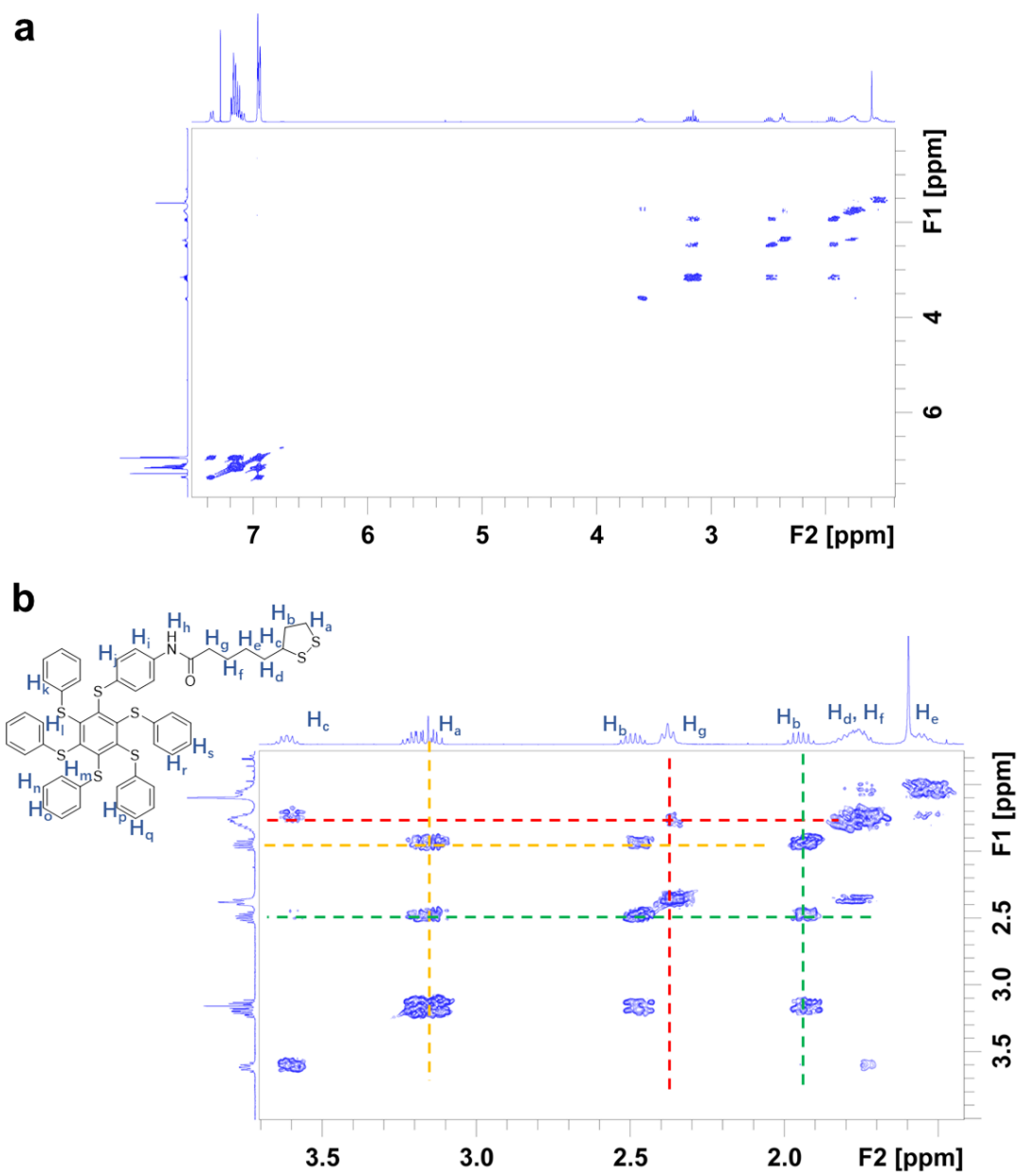


Figure S11. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of 2.



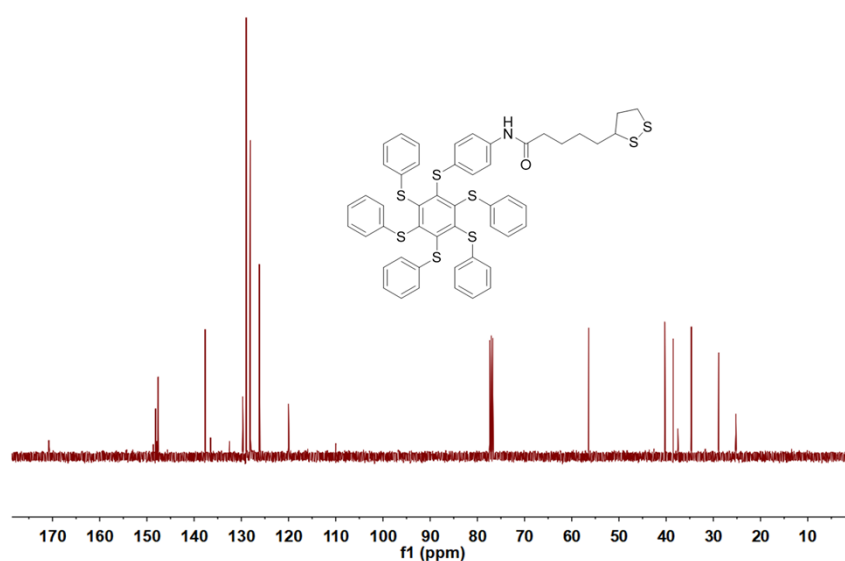


Figure S13. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of **2**.

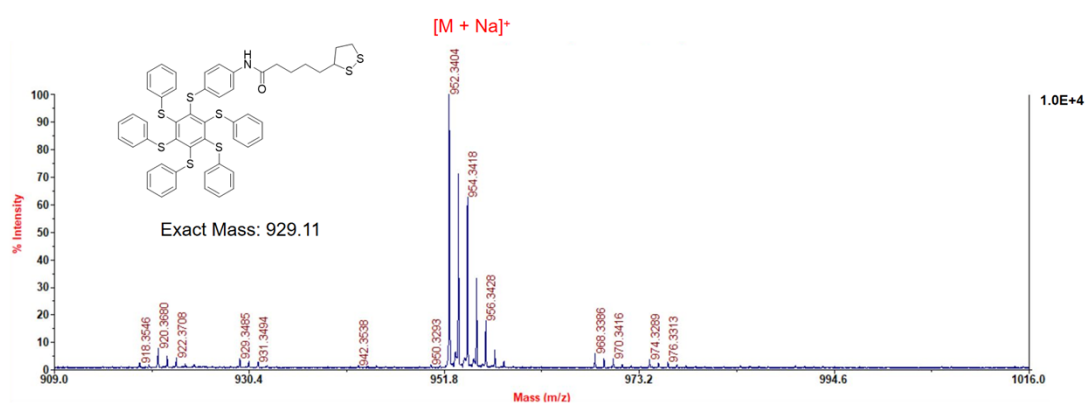


Figure S14. MALDI-TOF MS of **2**.

3 Study of Reversible Light-Induced Assembly-Disassembly of **1** and **2**

Toluene solutions of **1** and **2** were exposed to 365 nm irradiation for 10 s and placed in dark for 15 min for 5 cycles, and the sizes of **1** and **2** in the situations of $h\nu$ "ON" and $h\nu$ "OFF" were measured by DLS, respectively.

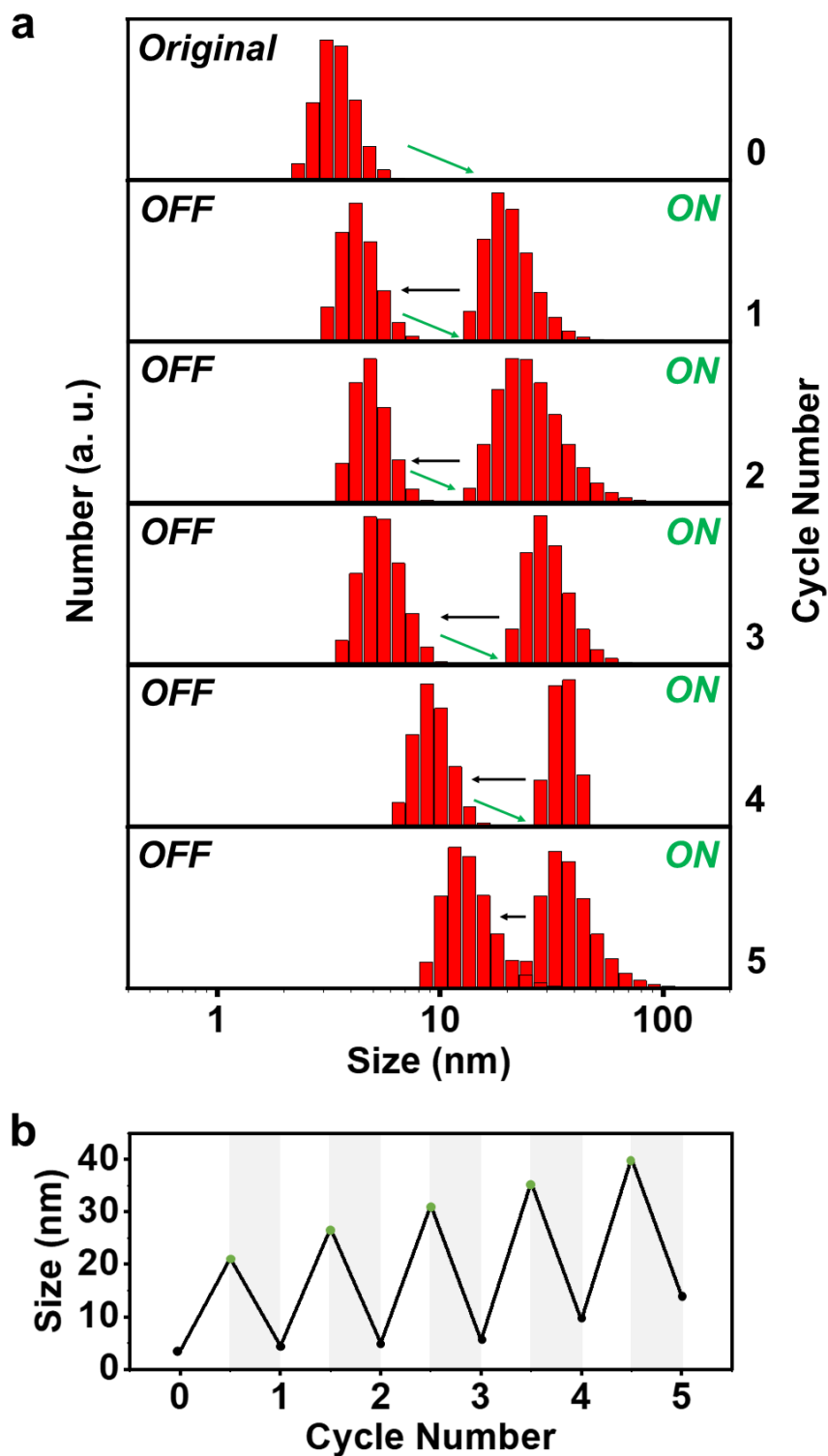


Figure S15. (a) Five assembly–disassembly cycles of **2** in toluene solution (1×10^{-3} M) as followed by DLS. Ligand **2** assembled under 365 nm irradiation for 10 s, and disassembled in dark for 15 min. (b) Average particle size calculated by (a).

4 Study of Optical Absorption of 1 and 2 in Toluene Solution under Irradiation

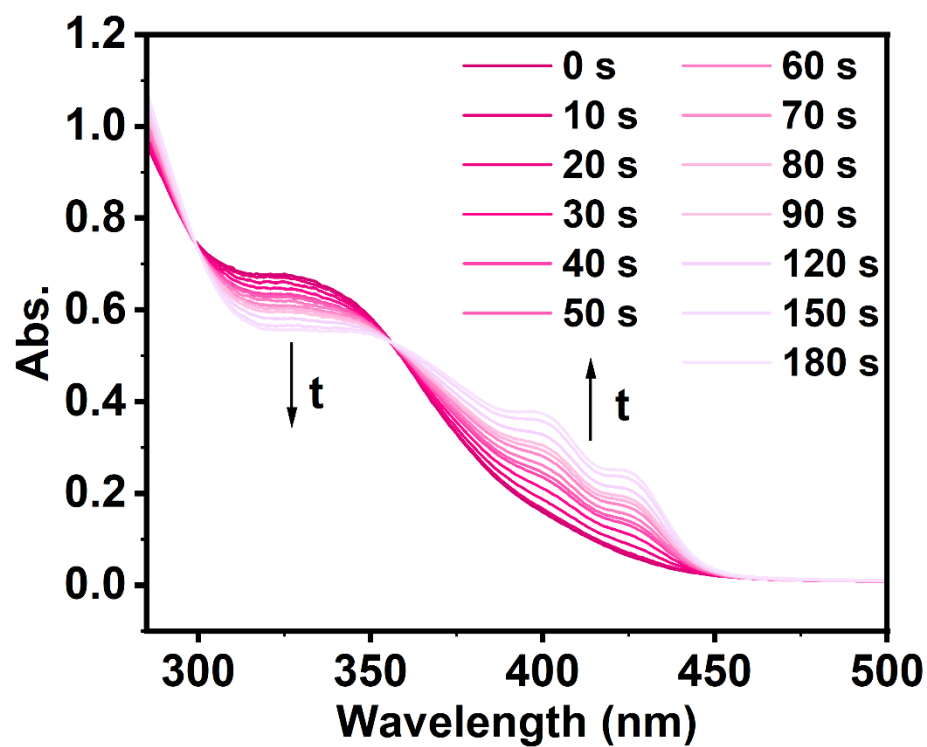


Figure S16. Continuous monitoring of the absorption spectra of **2** in toluene solution (1×10^{-5} M) under 365 nm light irradiation for a period of time.

5 Preparation of Gold Nanoparticles (Au NPs)

0.1 g of HAuCl_4 and 5 mL of oleylamine were added into a round bottom flask and stirred until the HAuCl_4 was dissolved completely, then 5 mL toluene was added and the mixture was stirred at 120 °C for one hour. The yellow solution turned colorless and finally red wine. After cooling to room temperature, 10 mL of ethanol (EtOH) was added. The AuNPs were collected by centrifugation (7000 rpm, 15 min) from the solution, dispersed in 5ml of toluene again, and washed with EtOH twice. Normally, the Au NPs were stored in 20 mL of toluene at 4 °C, and concentrated before use.

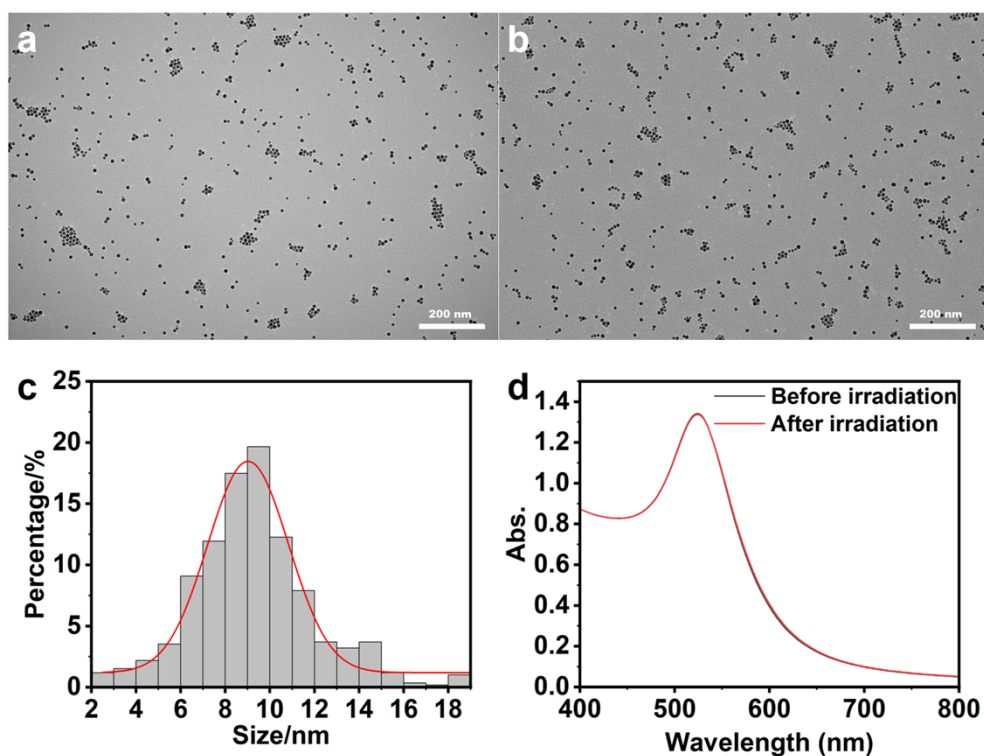


Figure S17. TEM images of non-functionalized Au NPs in toluene solution (a) before and (b) after 365 nm light irradiation for 3 min. (c) Size-distribution histograms of non-functionalized Au NPs in toluene solution. (d) Absorption spectra of non-functionalized Au NPs before and after 365 nm irradiation for 3 min, respectively.

6 Preparation of Persulfurated Benzene-Functionalized Au NPs (1/2-Au NPs)

The persulfurated benzene-functionalized Au NPs were prepared using a ligand-exchange reaction. Typically, concentrated solution of Au NPs ($V_{\text{Au NPs}}$) was diluted in toluene (V_{toluene}), and toluene solution of ligands **1** or **2** (0.04 M, V_L) was added, and the mixtures with concentration gradient (c_L) were stirred for 1 h. Excess ligands were removed by centrifugation (12000 rpm, 50 min). The functionalized AuNPs were collected and washed with toluene twice. The specific proportion of concentrated toluene solution of Au NPs and ligands is shown in the table S1.

Table S1. Preparation formula of persulfurated benzene-functionalized Au NPs

| Sample | Ligand | $V_{\text{Au NPs}} / \mu\text{L}$ | $V_{\text{toluene}} / \mu\text{L}$ | $V_L / \mu\text{L}$ | c_L / M |
|----------------|--------|-----------------------------------|------------------------------------|---------------------|------------------|
| 1-Au NPs-0.001 | 1 | 250 | 4625 | 125 | 0.001 |
| 1-Au NPs-0.003 | 1 | 250 | 4375 | 375 | 0.003 |
| 1-Au NPs-0.005 | 1 | 250 | 4125 | 625 | 0.005 |
| 1-Au NPs-0.008 | 1 | 250 | 3750 | 1000 | 0.008 |
| 1-Au NPs-0.010 | 1 | 250 | 3500 | 1250 | 0.010 |
| 1-Au NPs-0.015 | 1 | 250 | 2875 | 1875 | 0.015 |
| 1-Au NPs-0.020 | 1 | 250 | 2250 | 2500 | 0.020 |
| 2-Au NPs-0.008 | 2 | 250 | 3750 | 1000 | 0.008 |

7 Concentration Effect on the Light-Induced Self-Assembly of 1-Au NPs

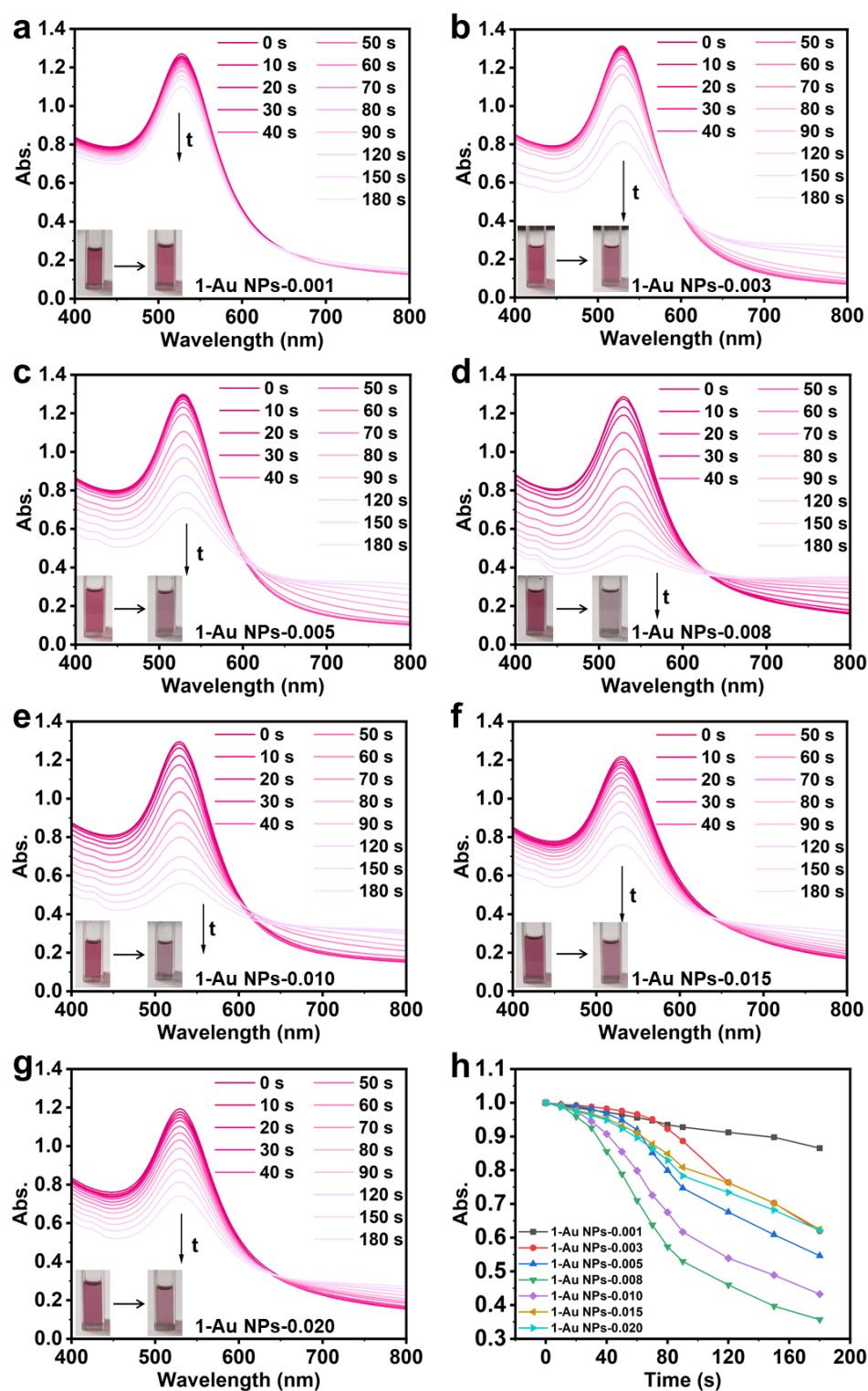


Figure S18. Continuous monitoring of the absorption spectral changes of (a) 1-Au NPs-0.001, (b) 1-Au NPs-0.003, (c) 1-Au NPs-0.005, (d) 1-Au NPs-0.008, (e) 1-Au NPs-0.010, (f) 1-Au NPs-0.015, and (g) 1-Au NPs-0.020 under 365 nm light irradiation for a period of time, respectively. (h) Normalized curves of the LSPR absorbance intensity change as a function of irradiation time.

8 Calculation of the Grafting Density of **1** on the Surface of **1-Au NPs-0.008**

1-Au NPs-0.008 for thermal gravimetric analysis (TGA) were collected from the solution by centrifugation and dried at 45 °C for 48 h under vacuum. TGA measurements were performed on a Mettler Toledo TGA instrument, and the measured temperature was ranged from 50 to 600 °C with a ramp rate of 10°C min⁻¹ under a nitrogen atmosphere. According to the TGA results, oleylamine evaporated completely around 270 °C, and **1** lost 75.46% of the weight above 250 °C. For **1-Au NPs-0.008**, the weight loss of 2.51% below 259 °C was attributed to the degradation of the oleylamine on Au NPs, weight loss of 5.68% above 259 °C was attributed to the degradation of **1**, and the remained 91.81% above 600 °C was attributed to the residual Au NPs.

The weight of each Au NP ($m_{\text{Au NP}}$) was calculated by the equation of $m_{\text{Au NP}} = \rho \pi D^3 / 6$, where $\rho = 19.3 \text{ g/cm}^3$ is the density of gold, and $D = 9.0 \text{ nm}$ is the average diameter of Au NPs. The mole number of Au NPs ($n_{\text{Au NP}}$) was calculated by the equation of $n_{\text{Au NP}} = 0.918 \times m_{\text{total}} / (m_{\text{Au NP}} \times N_A)$, where N_A represents the Avogadro constant. Similarly, the mole number of **1** (n_1) was calculated by the equation of $n_1 = 0.0568 \times m_{\text{total}} / M_1$, where $M_1 = 930.10 \text{ g mol}^{-1}$ is the mole mass of **1**. Therefore, the average number of **1** molecules on each Au NP (n) was $n_1 / n_{\text{Au NP}} = 0.0103 \times \rho \pi D^3 \times N_A / M_1$, and the calculated value is 295, and the grafting density (σ) of **1** molecules on the surface of **1-Au NPs-0.008** was $\sigma = n / (\pi D^2) = 1.16 / \text{nm}^2$.

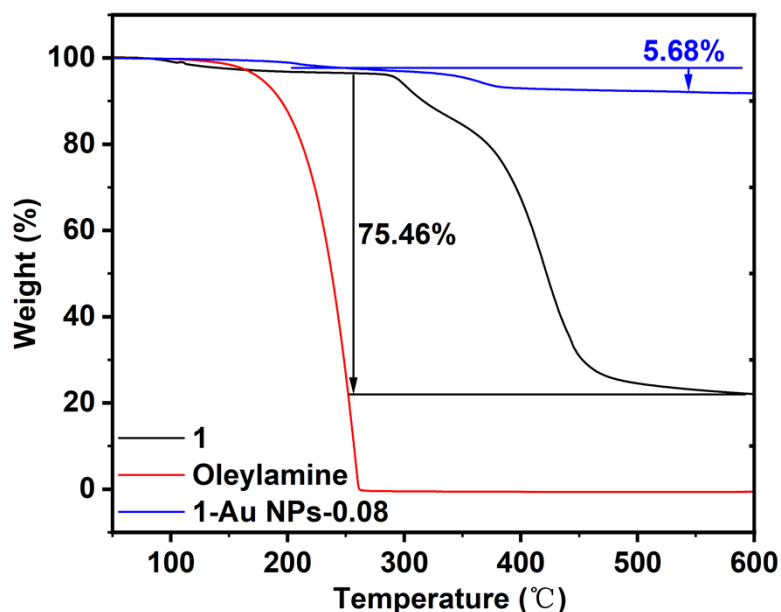


Figure S19. TGA thermograms of **1**, oleylamine, and **1-Au NPs-0.008**.

9 Study of Photochemical Stability of **1** and **1-Au NPs-0.008** under Irradiation

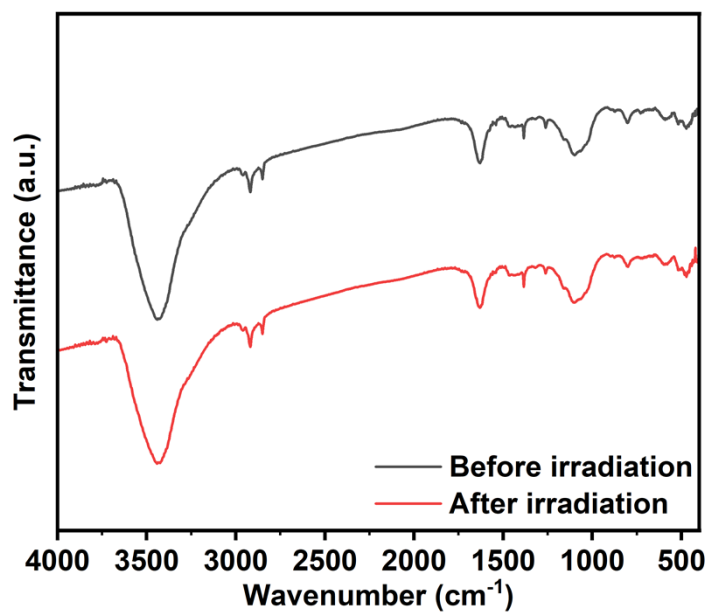


Figure S20. FTIR spectra of **1-Au NPs-0.008** before and after 365 nm irradiation for 3 min.

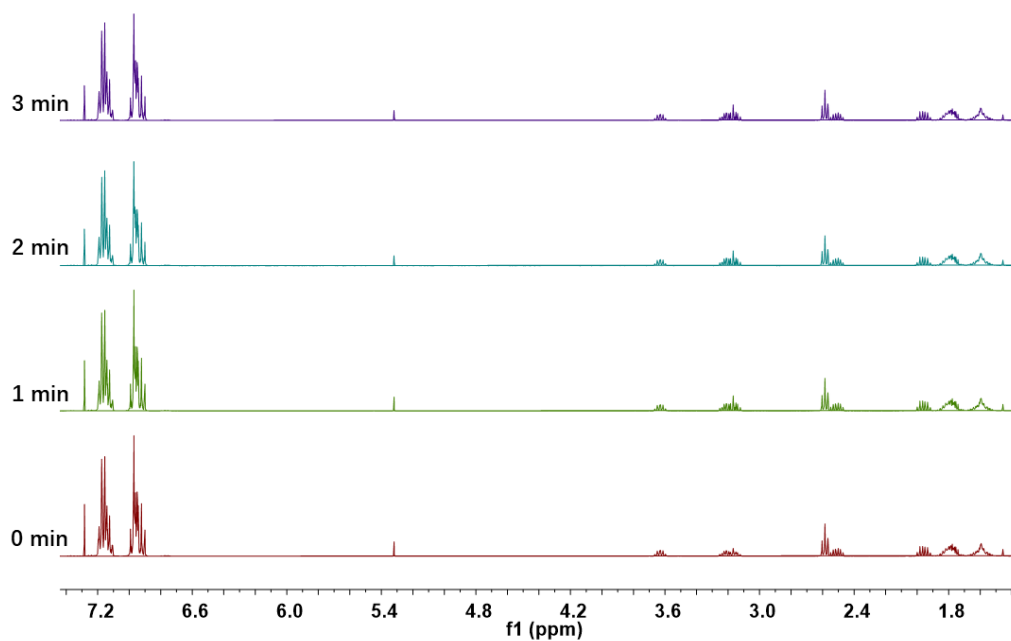


Figure S21. ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of **1** under 365 nm light irradiation for 0, 1, 2, 3 min, respectively.

10 Study of the LISA Property of 2-Au NPs-0.008

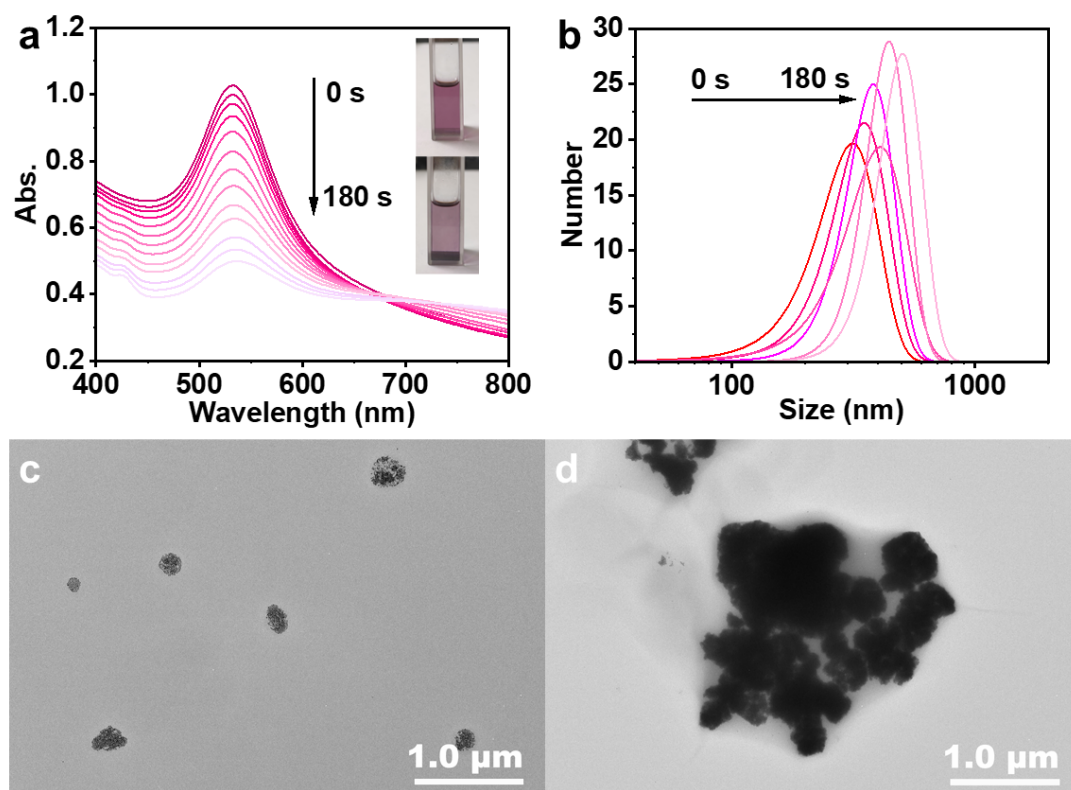


Figure S22. Continuous monitoring of (a) UV-vis spectra and (b) size of **2-Au NPs-0.008** under 365 nm irradiation for 3 min, respectively. The insets are the photographs of the sample before and after 365 nm irradiation for 3 min, respectively. TEM images of **2-Au NPs-0.008** (c) before and (d) after 365 nm irradiation for 3 min, respectively.

Reference

[S1] J. Gu, B. Yue, G. V. Baryshnikov, Z. Li, M. Zhang, S. Shen, H. Agren and L. Zhu, *Research*, 2021, 2021, 9862093.