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Supporting information for

Photoresponsive reversible self-assembly of rod-coil amphiphiles containing spiropyran group

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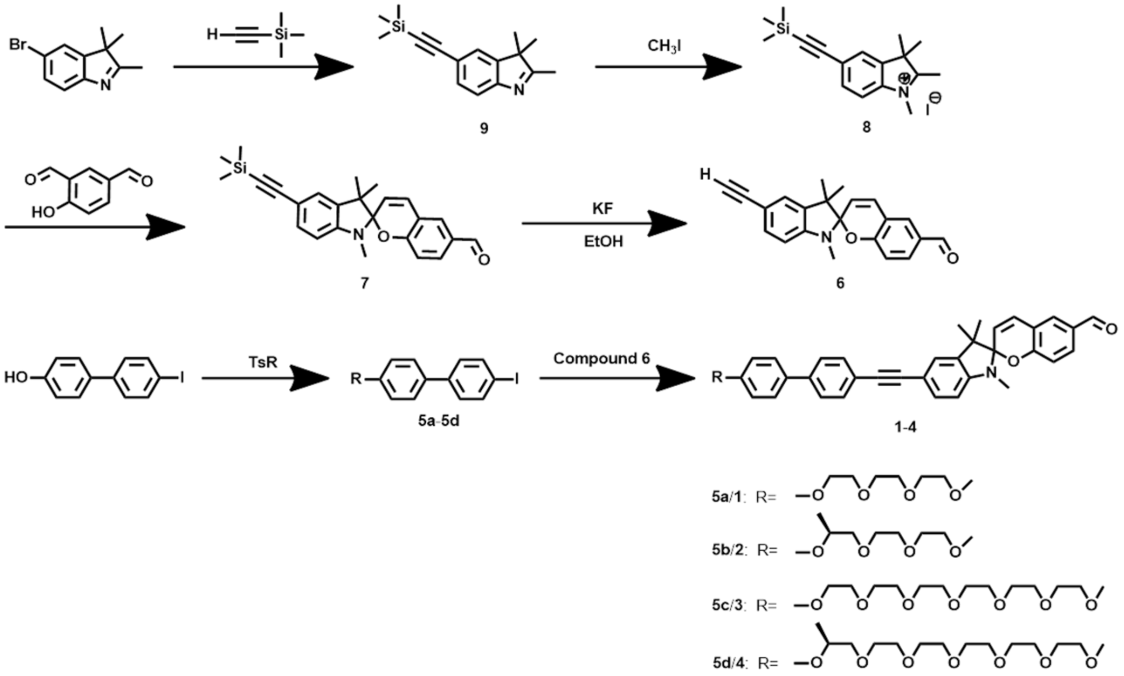
1. Techniques

Column chromatography filled silica gel (100-200 mesh) was used to achieve the separation of impurities. ^{1}H-NMR (300 MHz) spectra and ^{13}C-NMR (75 MHz) were recorded in $CDCl_3$ on a Bruker AM-300 instrument. UV-Vis and FL spectra were obtained from a Shimadzu UV-1650PC spectrometer and a Hitachi F-4500 fluorescence spectrometer, respectively. TEM images were collected with a JEOL 2100plus microscope. AFM images were produced by an Agilent 5500 Atomic Force Microscope. All TEM and AFM samples were prepared by freeze-drying at -85°C.

2. Experimental



Scheme S1. Synthesis route of compounds **1-4**.

Synthesis of compounds 1-4：

Synthesis of compound **9**: 5-Bromo-2,3,3-trimethyl-3H-indole (5.000 g, 20.998 mmol), trimethylsilylacetylene (4.527 g, 46.194 mmol), cuprous iodide (0.160 g, 0.840 mmol) and tetrakis(triphenylphosphine)palladium (0.485 g, 0.420 mmol) were dissolved in 150 mL dry THF, added 15 mL triethylamine and then refluxed for 24 h under nitrogen atmosphere and protected from light. After cooled to room temperature, the solvent was removed, put 50 mL water in the mixture, extracted the crude product by methylene chloride and ethyl acetate. Collected the organic phase and removed the solvent, purified the product through column chromatography, used petroleum ether, petroleum ether/ethyl acetate as mobile phase. Concentrated the solution and obtained brown solid (3.250 g, 12.724 mmol, yielded 60.6 %).

Synthesis of compound **8**: Weighted compound **9** (1.000 g, 3.915 mmol) and iodomethane (1.110 g, 7.820 mmol), dissolved in 60 mL acetonitrile, refluxed 8 h under nitrogen atmosphere. After cooled to room temperature, removed acetonitrile then washed the obtained solid by 20 mL ether three times, finally gained lilac solid (0.910 g, 3.365 mmol, yielded 85.8 %) after drying operation.

Synthesis of compound **7**: Dissolved compound **8** (0.500 g, 1.849 mmol) and 5-hydroxyisophthalaldehyde (0.333 g, 2.218 mmol) in 60 mL anhydrous ethanol. After dripped triethylamine (0.374 g, 3.696 mmol), the system was refluxed for 10 h under nitrogen atmosphere and protected from light. Then removed the solvent when the mixture cooled to room temperature, added 30 mL water, extracted the crude product by methylene chloride and ethyl acetate. Collected the organic phase and removed the solvent, purified the product through column chromatography, used petroleum ether, petroleum ether/methylene chloride as mobile phase. Concentrated the solution and obtained pale pink oily liquid (0.200 g, 0.498 mmol, yielded 27.0 %).

Synthesis of compound **6**: Compound **7** (0.200 g, 0.498 mmol) and potassium fluoride (0.289 g, 4.975 mmol) were dissolved in 60 mL anhydrous ethanol, refluxed for 18 h under nitrogen atmosphere and protected from light. After cooled to room temperature, the solvent was removed, put 30 mL water in the mixture, extracted the crude product by methylene chloride and ethyl acetate. Collected the organic phase and removed the solvent, purified the product through column chromatography, used petroleum ether/ethyl acetate as mobile phase. Concentrated the solution and obtained colorless oily liquid (0.050 g, 0.152 mmol, yielded 30.5 %).

Synthesis of compound **1**-**4**: Since the similarity of their synthetic methods, here take the synthetic route of molecule **1** as an example.

Synthesis of compound **5a**: Tri(ethylene glycol)monomethyl ether tosylate (2.000 g, 6.281 mmol) and 4-hydroxy-4'-iodobiphenyl (2.420 g, 8.176 mmol) were dissolved into 150 mL acetonitrile, added potassium carbonate (4.334 g, 31.377 mmol) and refluxed for 24 h. Then removed the solvent when cooled to room temperature, add 50 mL water in the mixture, extracted the crude product by methylene chloride and ethyl acetate. Collected the organic phase and removed the solvent, purified the product through column chromatography, used petroleum ether/methylene chloride as mobile phase. Concentrated the solution and obtained pale yellow solid (1.100 g, 2.487 mmol, yielded 39.6 %).

Synthesis of compound **1**: Compound **5a** (0.080 g, 0.181 mmol), cuprous iodide (0.001 g, 5.252 μmol) and tetrakis (triphenylphosphine) palladium (0.003 g, 2.596 μmol) were dissolved in 50 mL dry THF, added 15 mL triethylamine. After refluxed under nitrogen atmosphere and protected from light, 10 mL THF solution of compound **6** (0.050 g, 0.152 mmol) was added dropwise, then the mixture was continue refluxed for 24 h. After cooled to room temperature, the solvent was removed, put 10 mL water in the mixture, extracted the crude product by methylene chloride and ethyl acetate. Collected the organic phase and removed the solvent, purified the product through column chromatography, used petroleum ether/ethyl acetate as mobile phase. Concentrated the solution and obtained reddish brown solid (0.021 g, 0.033 mmol, yielded 21.4 %).

Compound **1**: Reddish brown solid, ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ ppm: 9.84 (s, 1H), 7.67 (s, 1H), 7.64 (d, *J* = 2.1 Hz, 2H), 7.54 – 7.52 (m, 6H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.94 (s, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 1H), 5.79 (d, *J* = 10.3 Hz, 1H), 4.21 – 4.16 (m, 2H), 3.92 – 3.87 (m, 2H), 3.79 – 3.74 (m, 2H), 3.72 – 3.65 (m, 4H), 3.58 – 3.53 (m, 2H), 3.39 (s, 3H), 2.77 (s, 3H), 1.32 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$) δ ppm: 190.53, 159.57, 158.58, 148.01, 139.94, 136.62, 133.13, 132.62, 132.04, 131.74, 129.68, 129.05, 128.42, 127.97, 126.47, 125.04, 122.17, 120.18, 118.95, 115.68, 115.01, 113.81, 106.85, 105.61, 91.02, 87.45, 71.96, 70.88, 70.69, 70.60, 69.77, 59.06, 51.97, 28.82, 19.93. MALDI-TOF-MS: Found $[M]^+$ 643.2945, molecular formula $C_{41}H_{41}NO_6$ requires $[M]^+$ 643.2934.

Compound **2**: Reddish brown solid (0.020 g, 0.030 mmol, yielded 19.8 %), ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ ppm: 9.84 (s, 1H), 7.68 (s, 1H), 7.64 (d, *J* = 2.6 Hz, 2H), 7.55 – 7.51 (m, 6H), 7.42 (d, *J* = 9.6 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.94 (s, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 1H), 5.79 (d, *J* = 10.3 Hz, 1H), 4.65 – 4.58 (q, 1H), 3.75 – 3.63 (m, 8H), 3.56 – 3.52 (m, 2H), 3.38 (s, 3H), 2.77 (s, 3H), 1.35 (d, *J* = 6.2 Hz, 3H), 1.32 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$) δ ppm: 190.55, 159.58, 157.75, 148.00, 139.97, 136.61, 132.62, 132.03, 131.74, 129.67, 129.12, 128.42, 128.00, 126.46, 125.04, 122.15, 120.18, 118.95, 116.36, 115.69, 113.81, 106.86, 105.61, 91.01, 87.45, 74.50, 73.30, 71.95, 71.01, 70.66, 70.58, 59.05,

51.97, 28.82, 19.93, 17.02. MALDI-TOF-MS: Found $[M]^+$ 657.7996, molecular formula $C_{42}H_{43}NO_6$ requires $[M]^+$ 657.7939.

Compound **3**: Yellow sticky solid (0.046 g, 0.059 mmol, yielded 23.2 %), ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ ppm: 9.84 (s, 1H), 7.67 (s, 1H), 7.64 (d, J = 2.7 Hz, 2H), 7.55 – 7.52 (m, 6H), 7.42 (d, J = 9.7 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 6.94 (s, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.52 (d, J = 8.1 Hz, 1H), 5.79 (d, J = 10.3 Hz, 1H), 4.21 – 4.16 (m, 2H), 3.91 – 3.86 (m, 2H), 3.79 – 3.59 (m, 18H), 3.56 – 3.52 (m, 2H), 3.38 (s, 3H), 2.77 (s, 3H), 1.32 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$) δ ppm: 190.52, 159.57, 158.58, 148.01, 139.93, 136.61, 133.12, 132.61, 132.03, 131.74, 129.67, 129.05, 128.41, 127.97, 126.46, 125.04, 122.17, 120.17, 118.95, 115.68, 115.00, 113.80, 106.85, 105.61, 91.03, 87.45, 71.94, 70.87, 70.65, 70.60, 70.52, 69.75, 67.54, 59.04, 51.96, 28.82, 19.92. MALDI-TOF-MS: Found $[M]^+$ 775.3704, $[M+H]^+$ 776.3803, molecular formula $C_{47}H_{53}NO_9$ requires $[M]^+$ 775.3720, $[M+H]^+$ 776.3793.

Compound **4**: Yellow sticky solid (0.033 g, 0.042 mmol, yielded 20.6 %), ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ ppm: 9.84 (s, 1H), 7.67 (s, 1H), 7.64 (d, J = 2.8 Hz, 2H), 7.54 – 7.51 (m, 6H), 7.42 (d, J = 9.5 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 6.94 (s, 1H), 6.83 (d, J = 8.3 Hz, 1H), 6.52 (d, J = 8.1 Hz, 1H), 5.79 (d, J = 10.3 Hz, 1H), 4.64 – 4.58 (q, 1H), 3.76 – 3.59 (m, 21H), 3.56 – 3.52 (m, 2H), 3.37 (s, 3H), 2.77 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H), 1.32 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$) δ ppm: 190.52, 159.56, 157.74, 148.00, 139.95, 136.61, 132.61, 132.03, 131.73, 129.67, 129.05, 128.42, 127.99, 126.45, 125.03, 122.14, 120.17, 118.94, 116.34, 115.68, 113.80, 106.85, 105.61, 91.02, 87.45, 74.47, 73.28, 71.93, 71.01, 70.62, 70.60, 70.58, 70.52, 59.04, 51.96, 28.81, 19.92, 17.02. MALDI-TOF-MS: Found $[M]^+$ 789.3965, $[M+H]^+$ 790.3922, molecular formula $C_{48}H_{55}NO_9$ requires $[M]^+$ 789.3877, $[M+H]^+$ 790.3950.

Substances and solvents mentioned in the synthesis method were used as received. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry nitrogen.

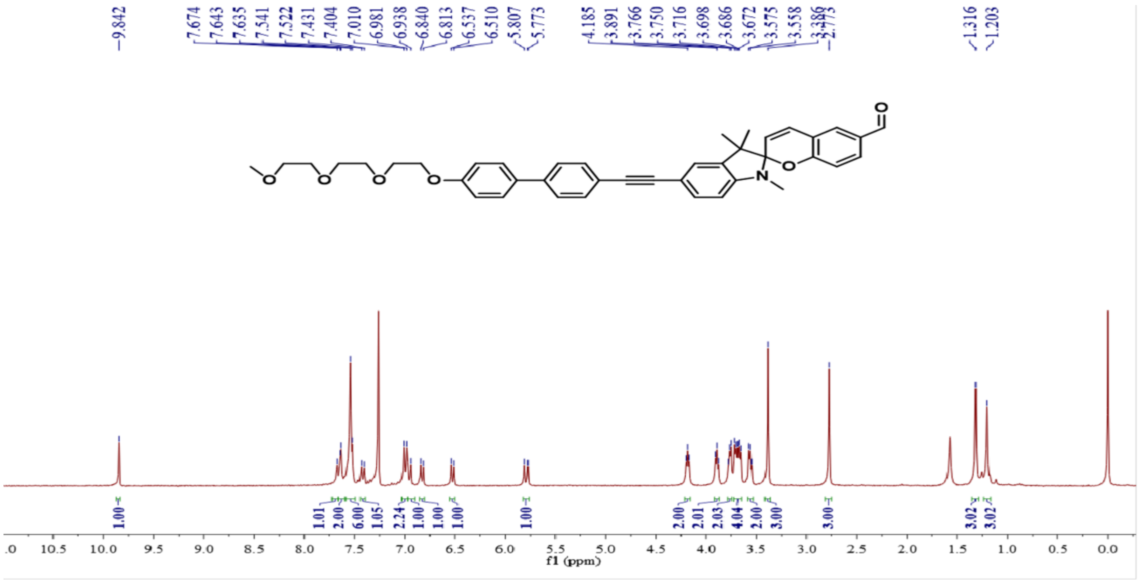


Figure S1. ^{1}H-NMR spectrum of molecule **1** in $CDCl_3$.

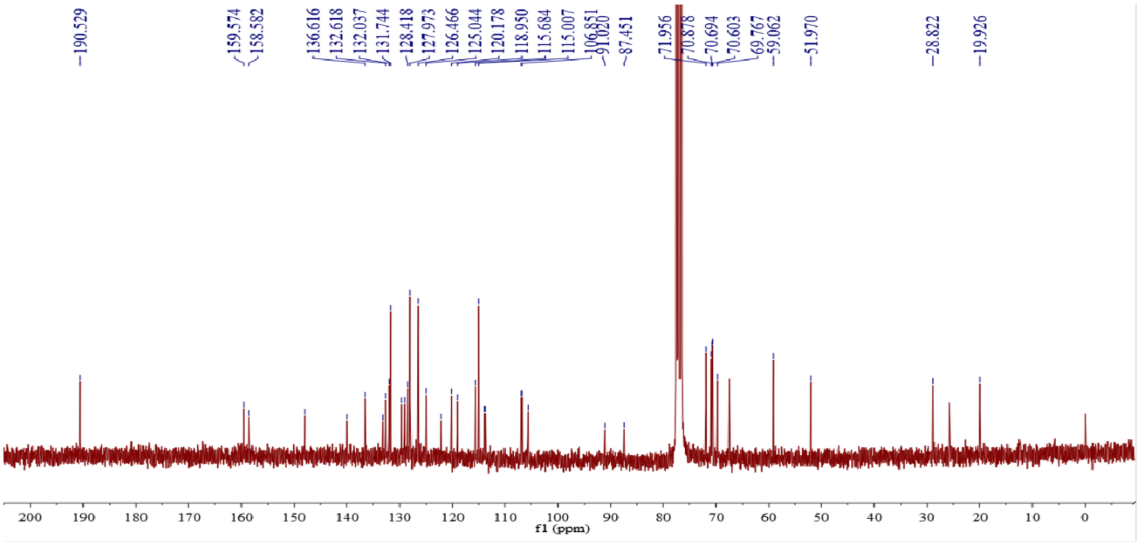


Figure S2. ^{13}C-NMR spectrum of molecule **1** in $CDCl_3$.

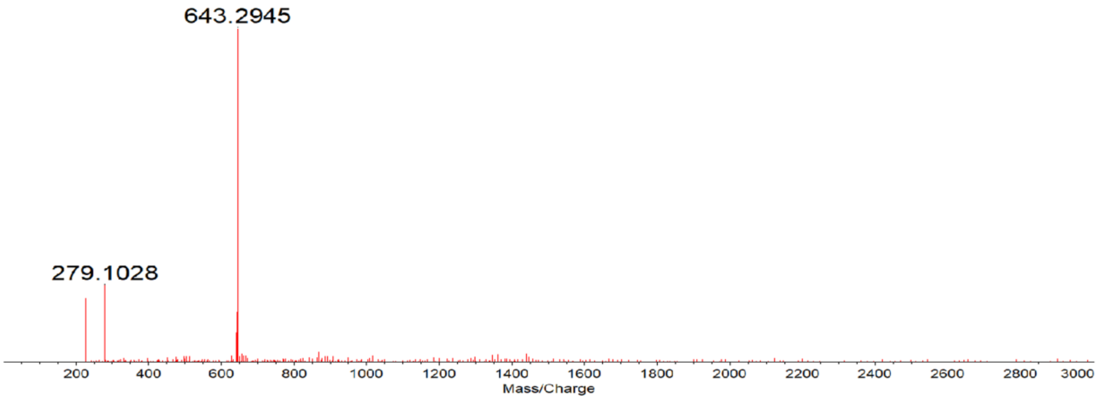


Figure S3. MALDI-TOF mass spectrum of molecule **1**.

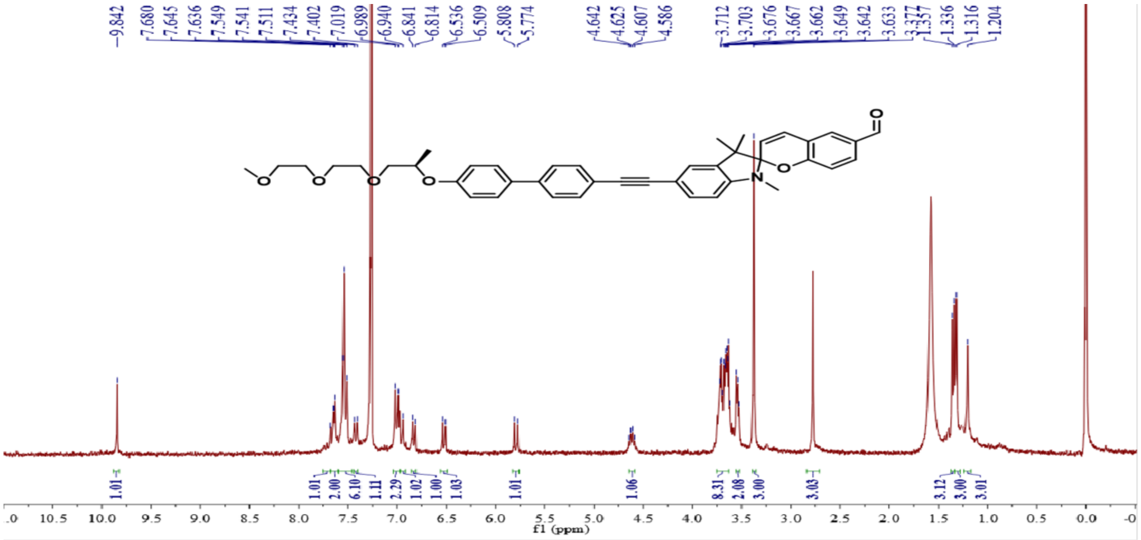


Figure S4. ^{1}H-NMR spectrum of molecule **2** in $CDCl_3$.

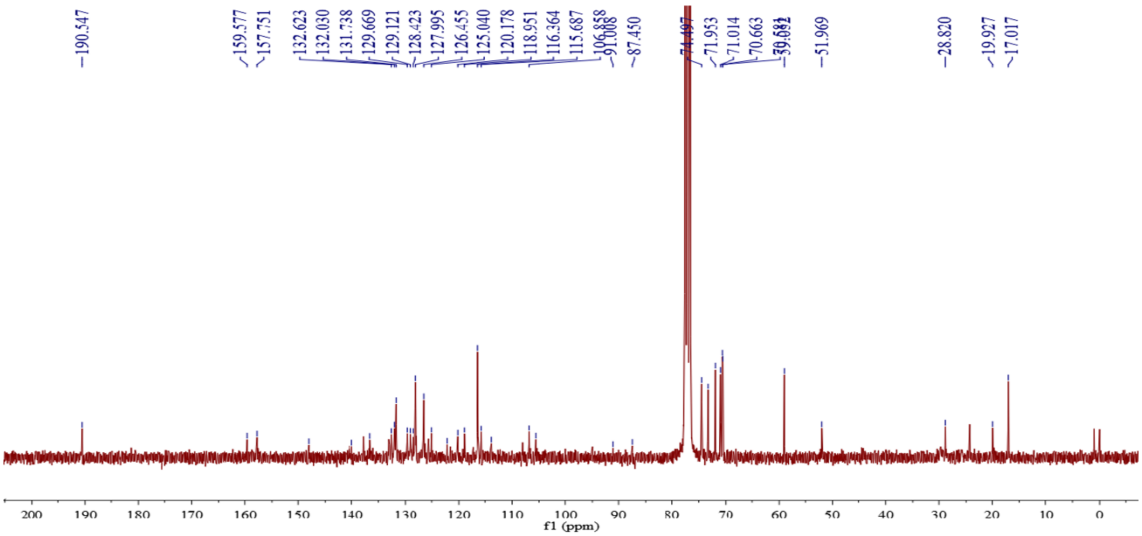


Figure S5. ^{13}C-NMR spectrum of molecule **2** in $CDCl_3$.

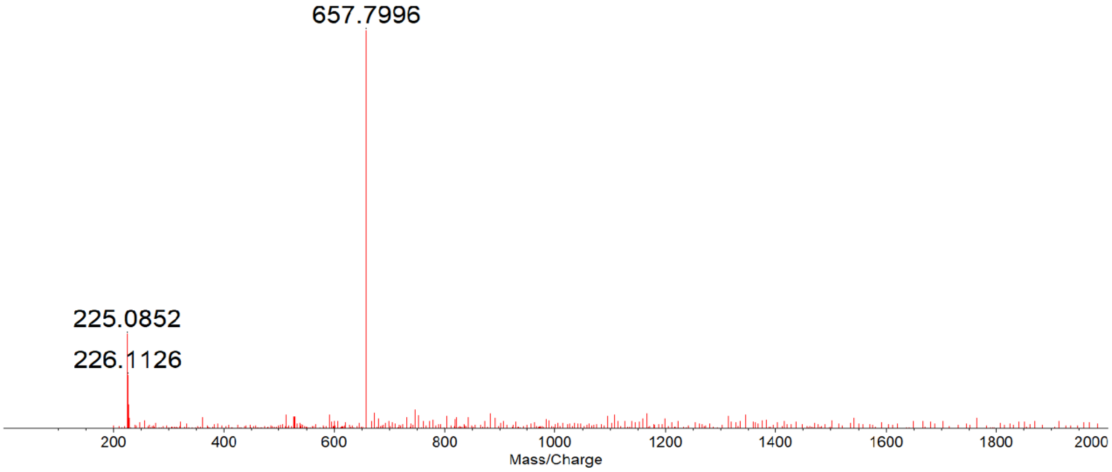


Figure S6. MALDI-TOF mass spectrum of molecule **2**.

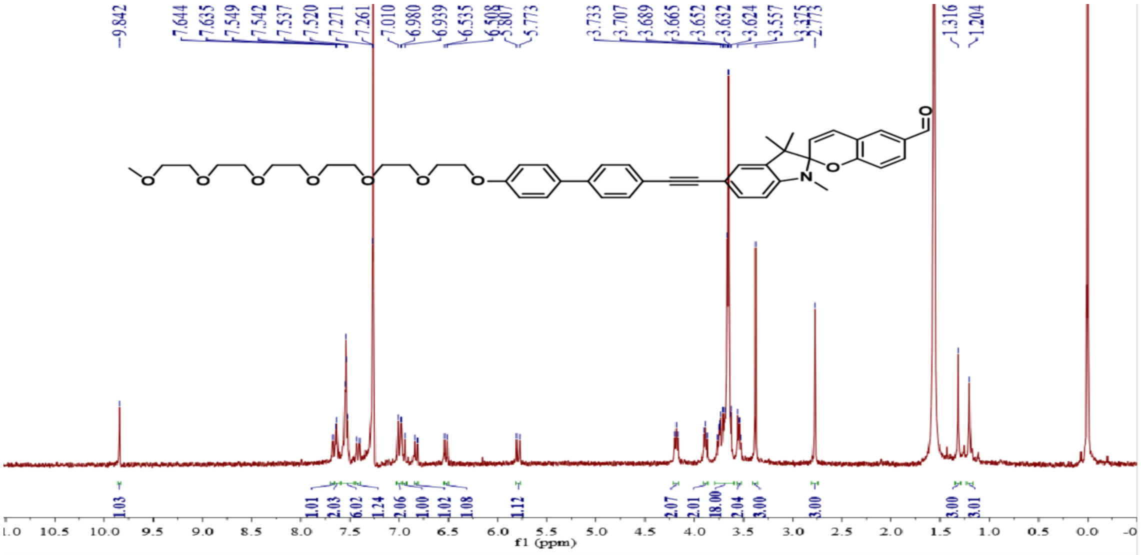


Figure S7. ^{1}H-NMR spectrum of molecule **3** in $CDCl_3$.

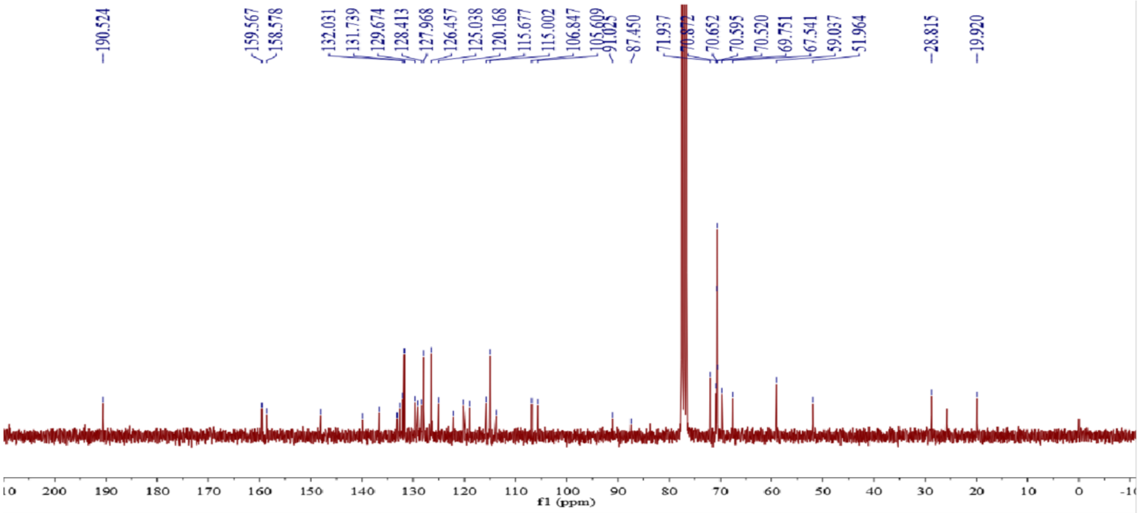


Figure S8. ^{13}C-NMR spectrum of molecule **3** in $CDCl_3$.

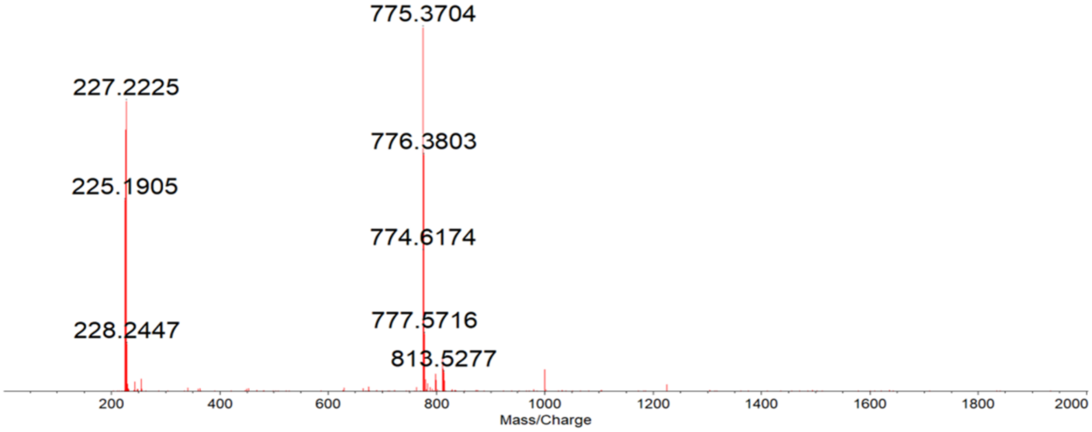


Figure S9. MALDI-TOF mass spectrum of molecule **3**.

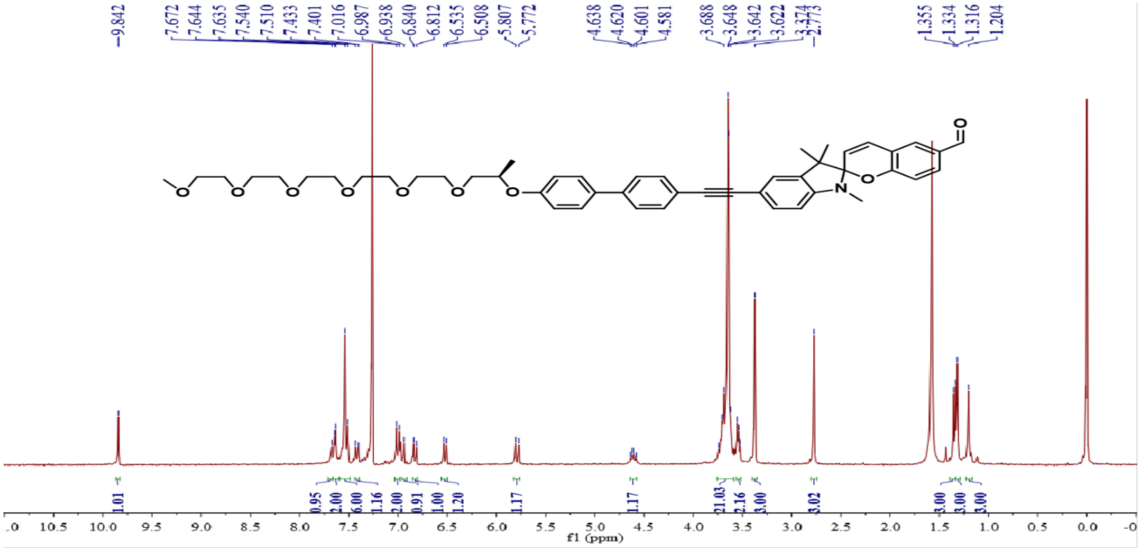


Figure S10. ^{1}H-NMR spectrum of molecule **4** in CDCl$_3$.

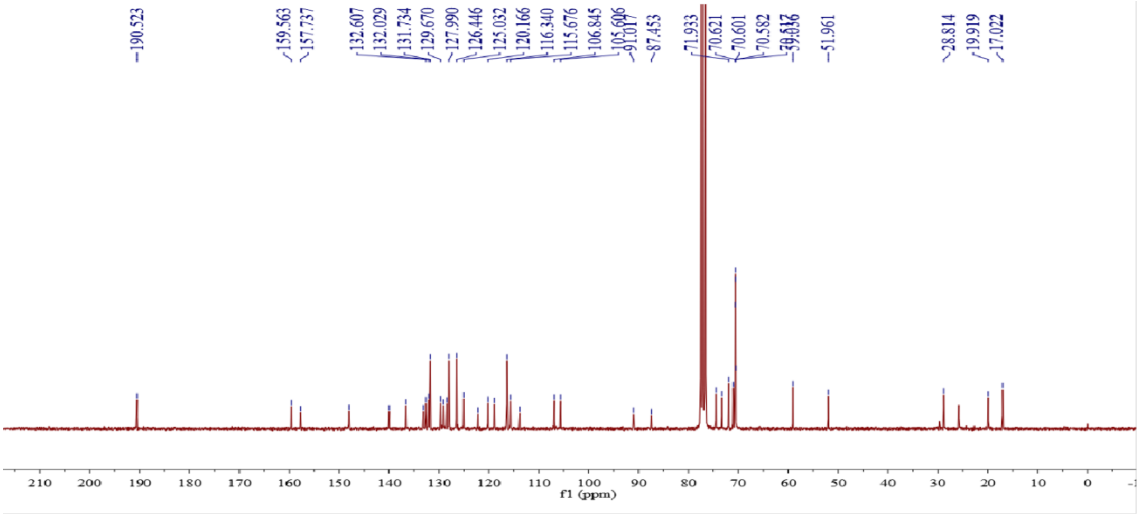


Figure S11. ^{13}C-NMR spectrum of molecule **4** in CDCl$_3$.

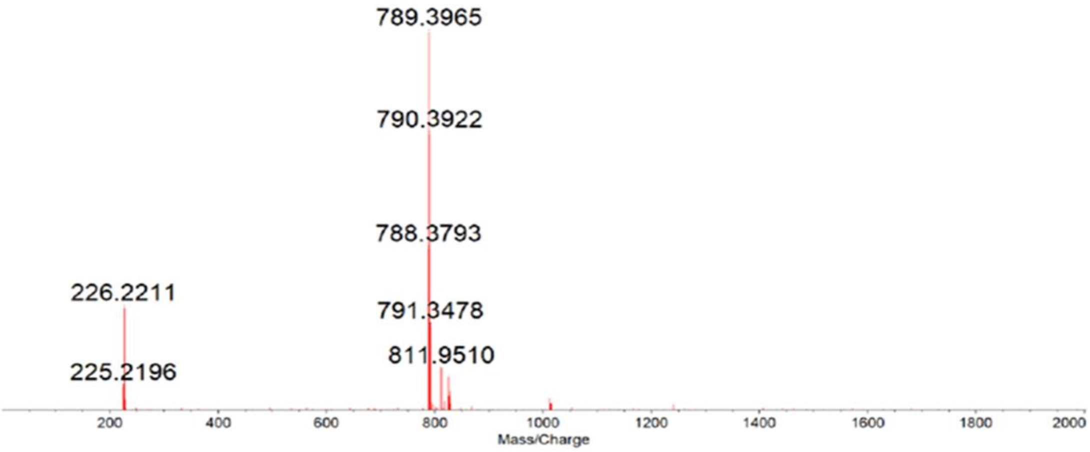


Figure S12. MALDI-TOF mass spectrum of molecule **4**.

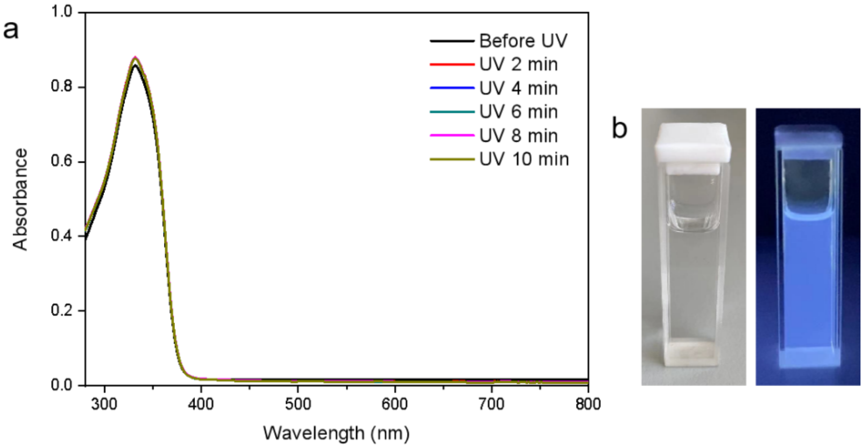


Figure S13. (a) The UV-Vis absorption spectrum of THF solution of **1** that exposed to UV light. (b) Photos of the THF solution of **1** after UV irradiation for 10 min, the left picture is under visible light, and the right one is under UV light. [c] = 20 μM, T = 25 ℃.

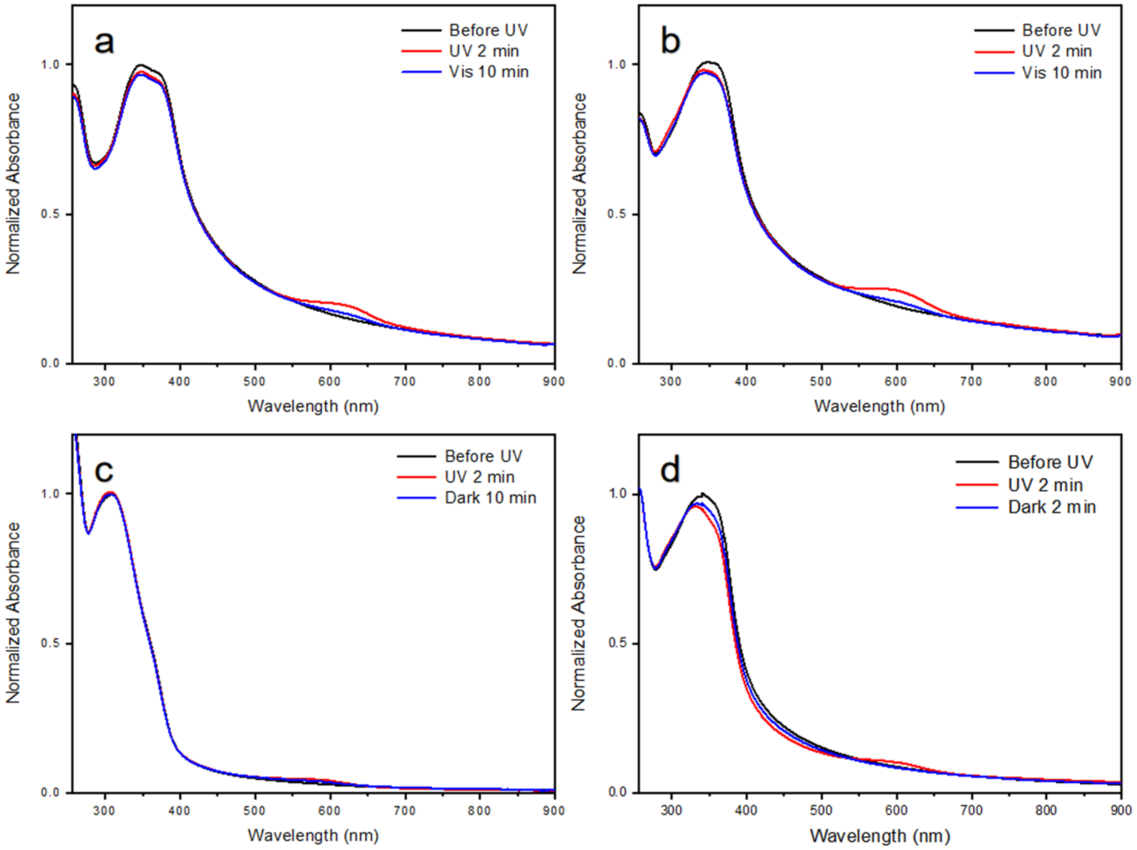


Figure S14. The UV-Vis absorption changes of (a) **1**, (b) **2**, (c) **3** and (d) **4** during the initial - irradiation - dark process. [c] = 20 μM, T = 25 ℃, THF:H_2O = 1:99 (v/v).

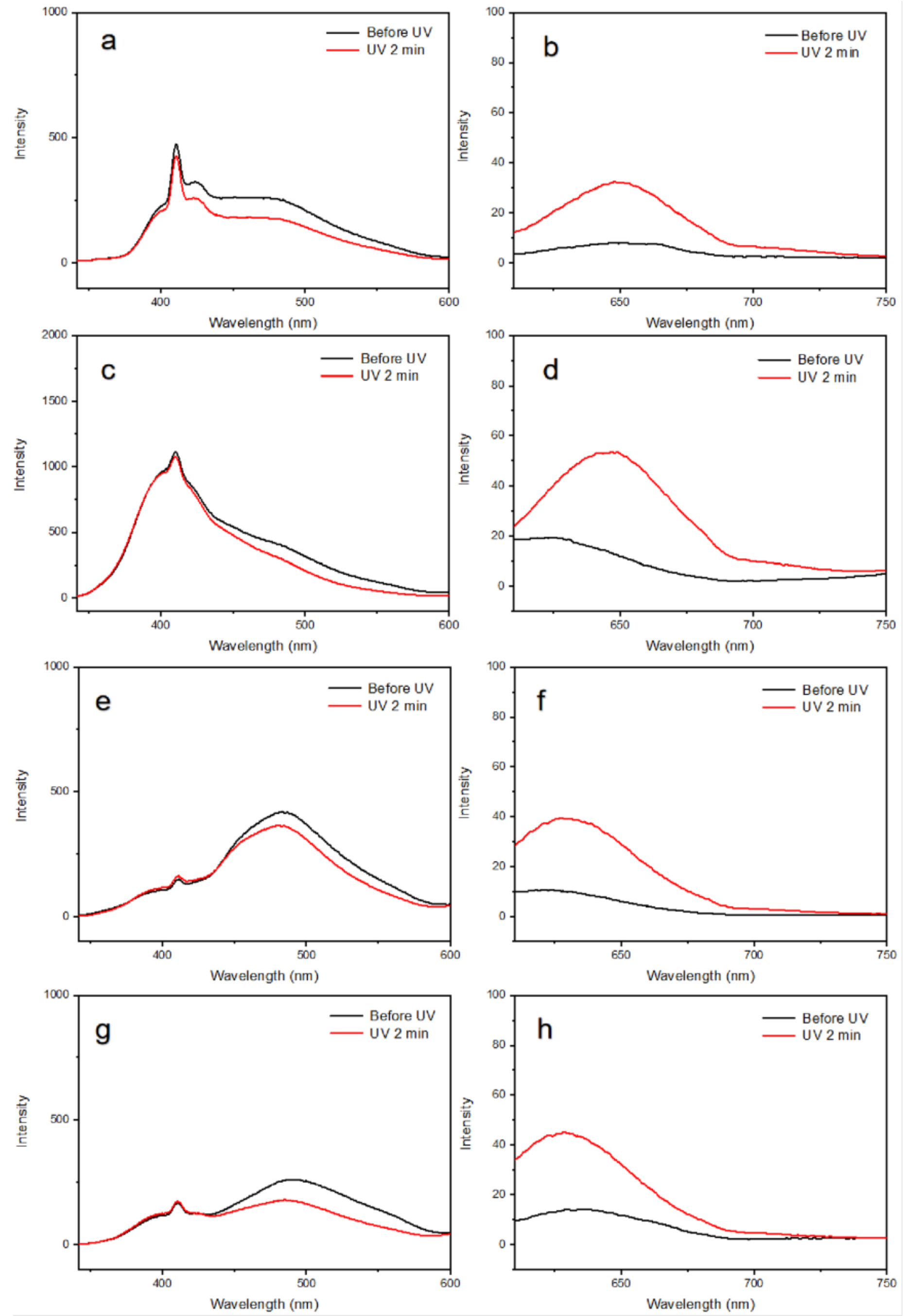


Figure S15. Fluorescence emission spectra of (a, b) **1**, (c, d) **2**, (e, f) **3** and (g, h) **4**. The excitation wavelength of (a, c, e, g) is 331 nm and (b, d, f, h) is 600 nm. [c] = 100 μM, T = 25 ℃, THF:H_2O = 1:99 (v/v).

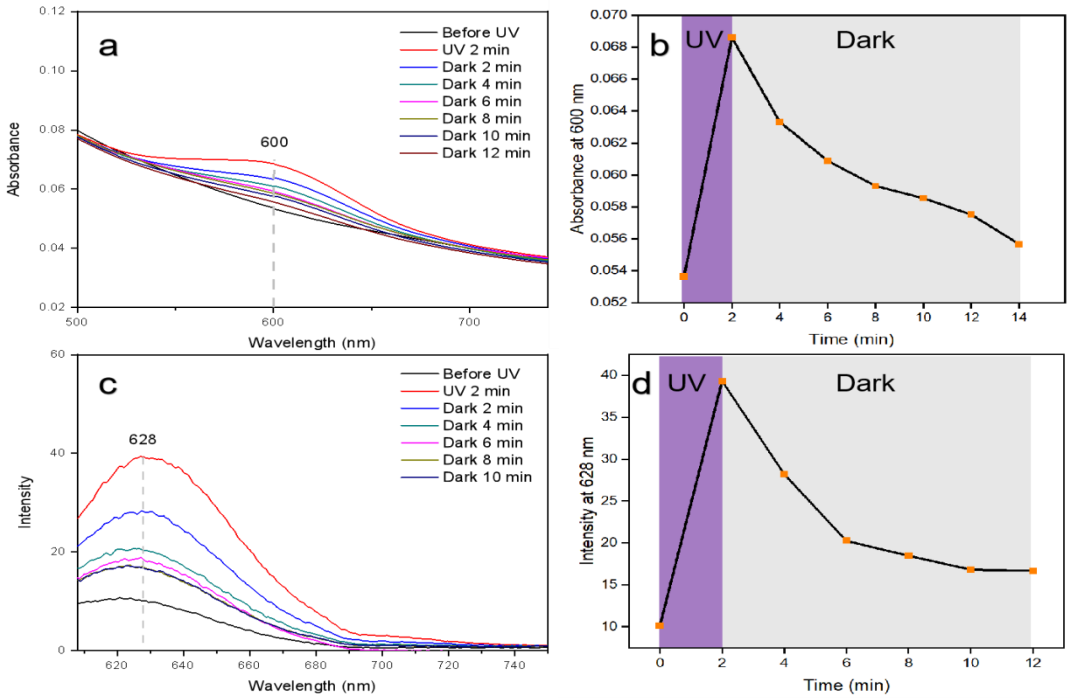


Figure S16. Spectrum changes of **3**'s solution during the initial - irradiation - dark process. (a) Change of UV-Vis absorption spectrum and (b) the variation trend of absorption at 600 nm in a. (c) Change of fluorescence emission spectrum (λ_{ex} = 600 nm) and (d) the variation trend of fluorescence emission at 628 nm in c. [c] = 100 μM, T = 25 ℃, THF:H_2O = 1:99 (v/v).

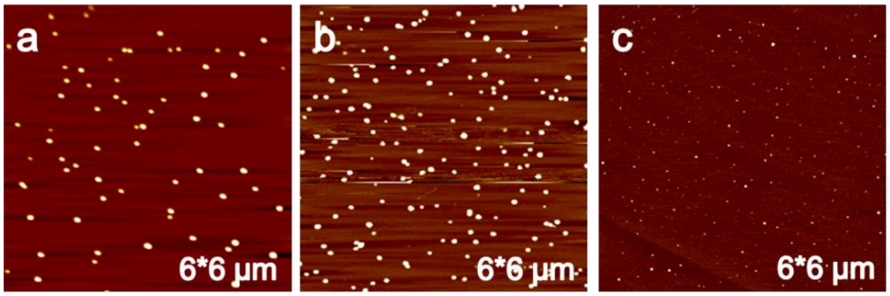


Figure S17. AFM images of the completely transformed assemblies after UV irradiation of compound (a) **1**, (b) **2**, and (c) **3**. [c] = 20 μM, THF:H_2O = 1:99 (v/v).

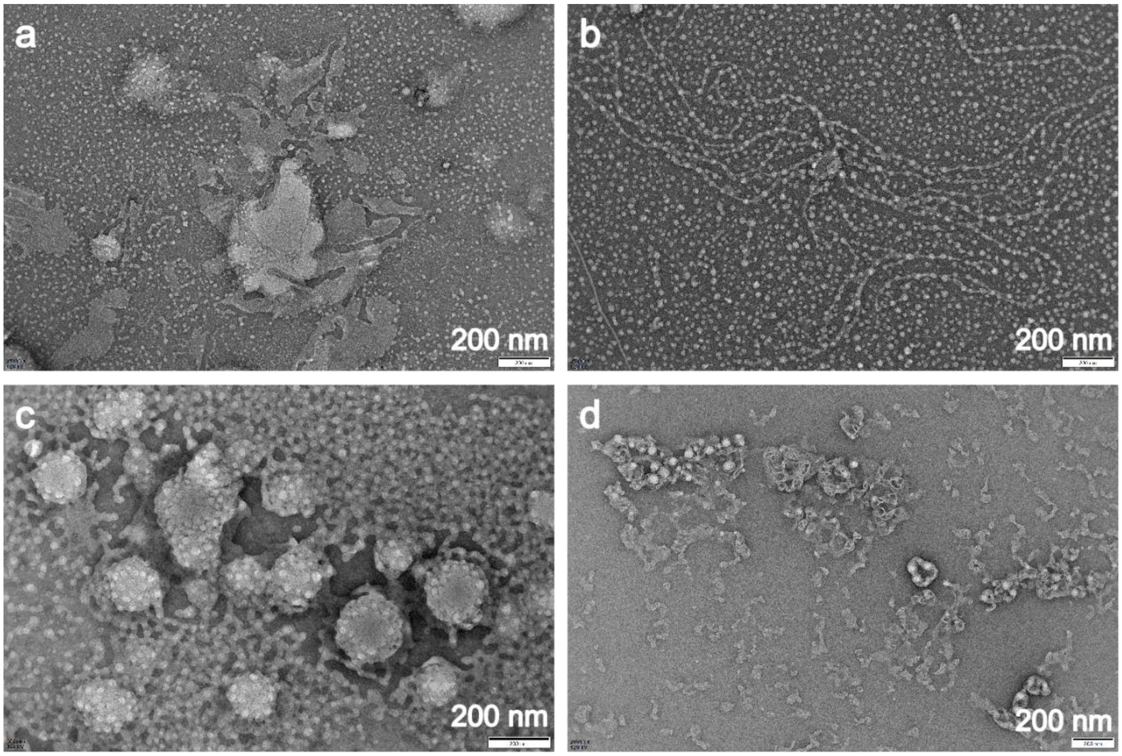


Figure S18. TEM images of UV irradiation for 5 min, shows the incomplete dissociation states of compounds (a) **1**, (b) **2**, (c) **3** and (d) **4**. [c] = 20 μM, THF:H_2O = 1:99 (v/v).

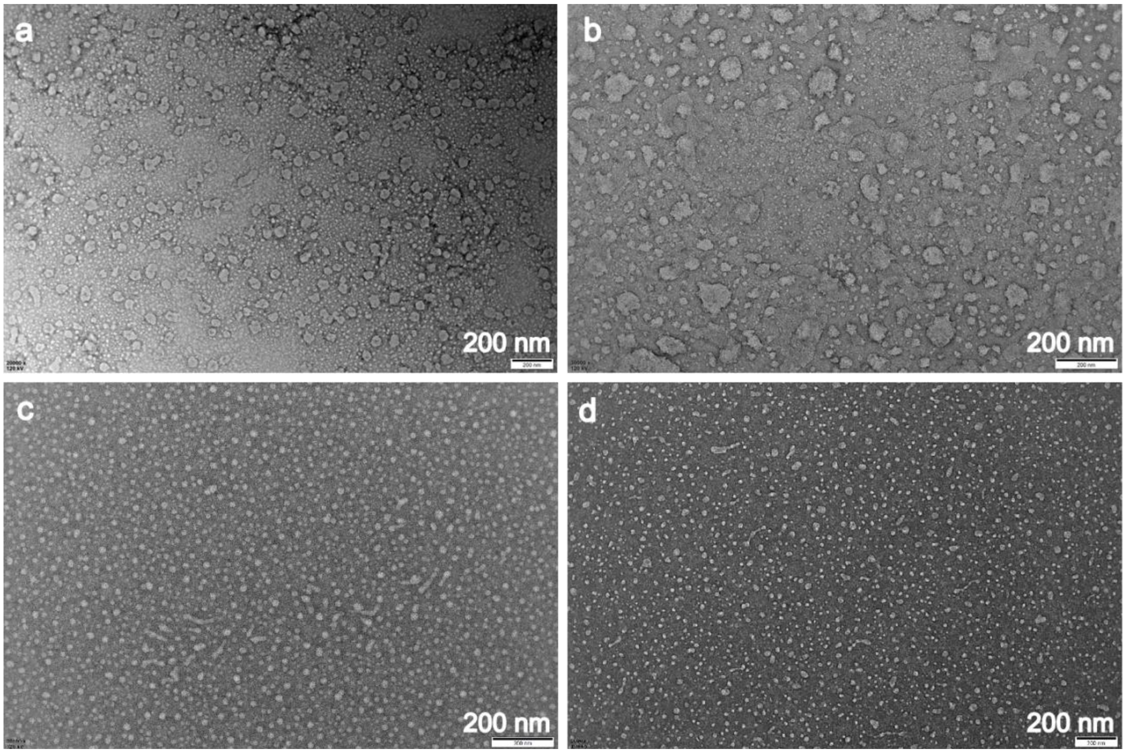


Figure S19. TEM images of compounds (a) **1**, (b) **2**, (c) **3** and (d) **4** at pH ≈ 2.0. [c] = 20 μM, THF:H_2O = 1:99 (v/v).

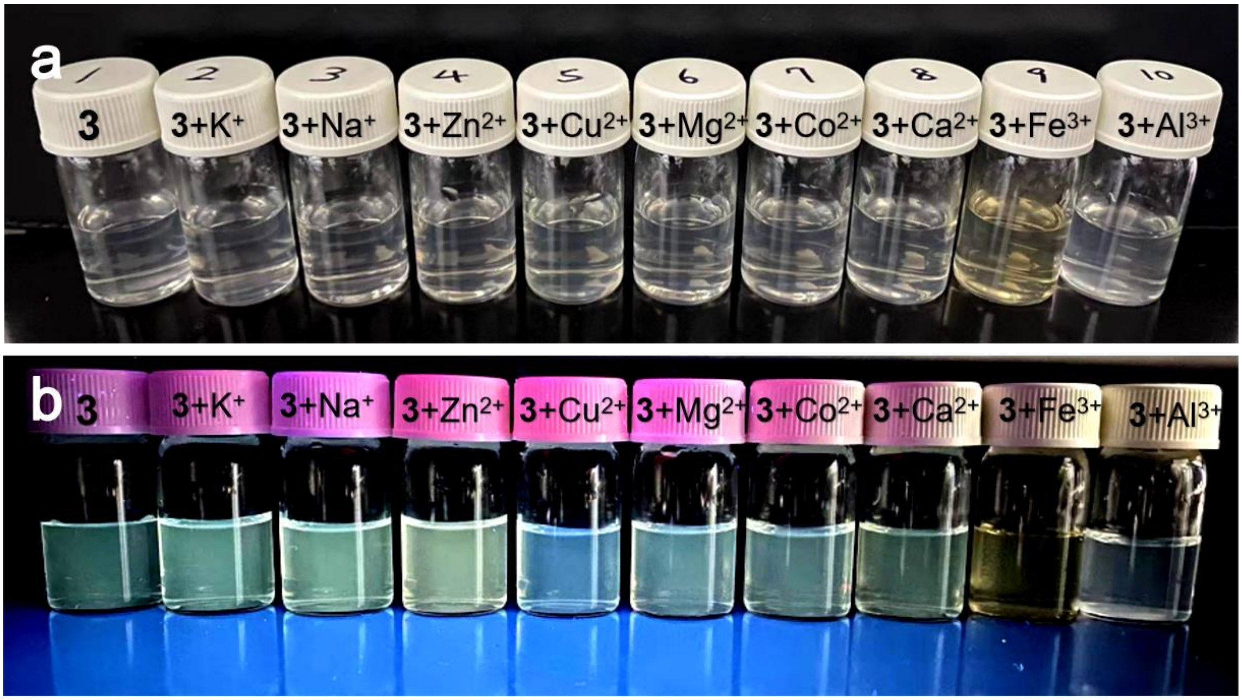


Figure S20. Comparison photos of THF/H_2O solution of **3** and its samples added different metal ions. (a) Under visible light and (b) under UV light. $[c]_{\mathbf{3}}$ = 50 μM, $[c]_{M}^{n+}$ = 500 μM, T = 25 ℃.

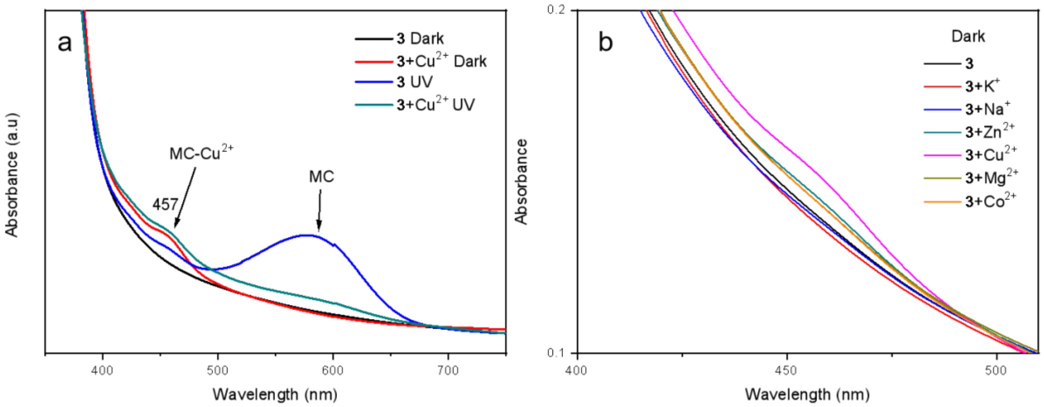


Figure S21. UV-Vis absorption of **3**'s solution. (a) Under different conditions and (b) added different metal ions. T = 25 ℃.

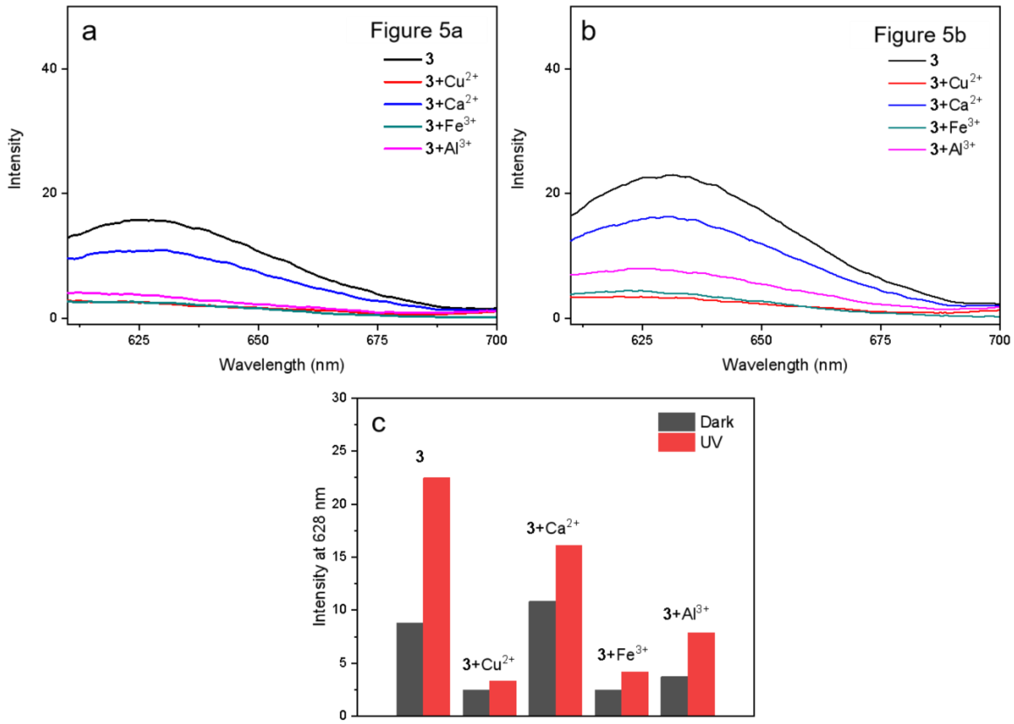


Figure S22. Fluorescence emission spectra of the five samples in Figure 5. (a) Figure 5a (dark condition), λ_{ex} = 600 nm, (b) Figure 5b (UV irradiation for 2 min), λ_{ex} = 600 nm. (c) Comparison of the fluorescence intensity of a and b at 628 nm.

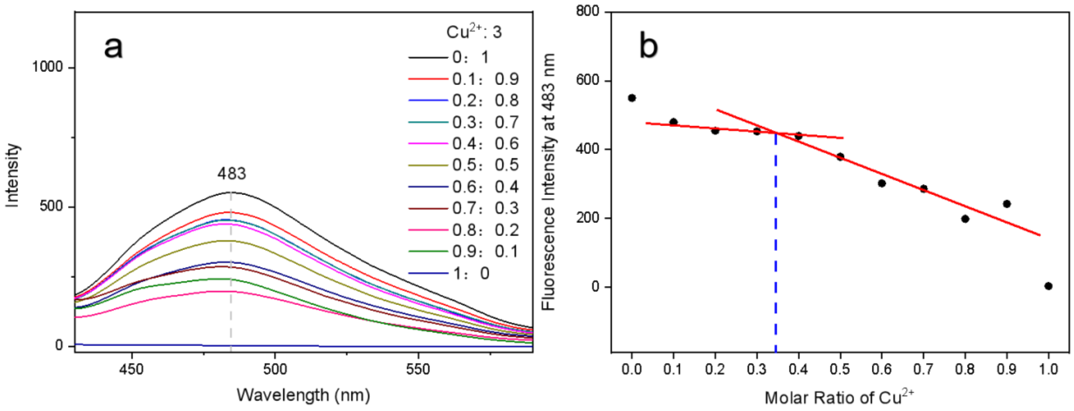
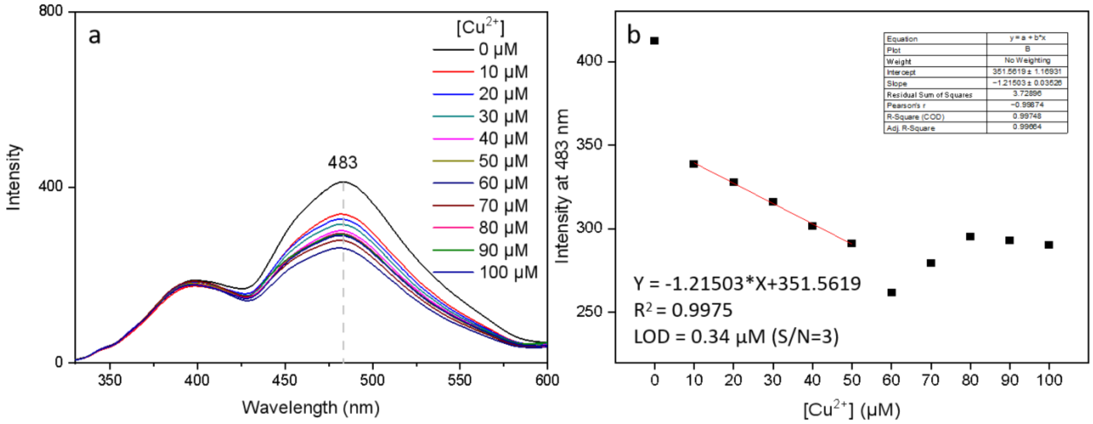


Figure S23. Gradient molar ratio spectroscopic measurement of copper ions to **3**. (a) The fluorescence emission spectrum (λ_{ex} = 331 nm) and (b) the variation trend of fluorescence intensity at 483 nm during the increase of the copper ion molar ratio. THF:H_2O = 1:99 (v/v), $[c]_{Cu^{2+}+\mathbf{3}}$ = 50 μM.



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	351.5619 ± 1.16931
Slope	−1.21503 ± 0.03526
Residual Sum of Squares	3.72896
Pearson's r	−0.99874
R-Square (COD)	0.99748
Adj. R-Square	0.99664

Figure S24. (a) Fluorescence spectra obtained by adding different concentrations of copper ions to a 50 μM solution of **3** and (b) the standard curve plot made from a. THF:H_2O = 1:99 (v/v).

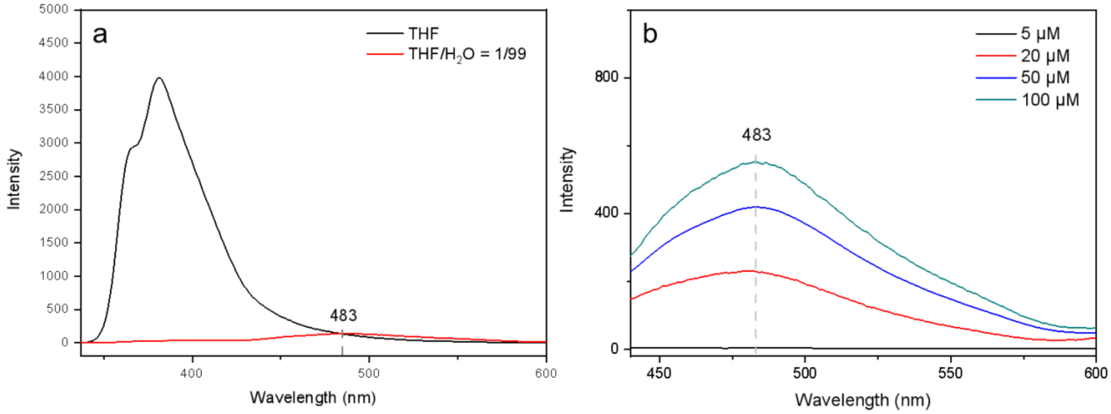


Figure S25. (a) Fluorescence emission spectrum of **3** in different solvents. [c] = 50 μM. (b) Fluorescence intensity at 483 nm of different concentrations of **3** in THF:H_2O = 1:99 (v/v) solution. λ_{ex} = 331 nm.

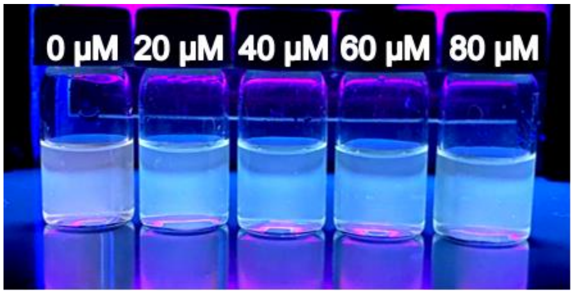


Figure S26. Comparison of fluorescence colors after adding different concentrations of copper ions into 50 μM solution of **3**. THF:H_2O = 1:99 (v/v).