Supporting Information

Perylene diimide-based supramolecular polymer with temperature-sensitive ratiometric fluorescence responsiveness in solution and gels

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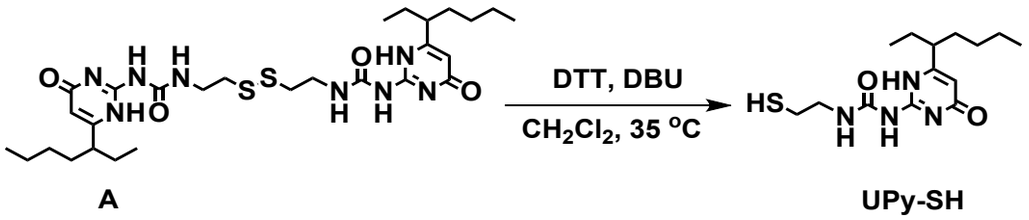
Experimental Section

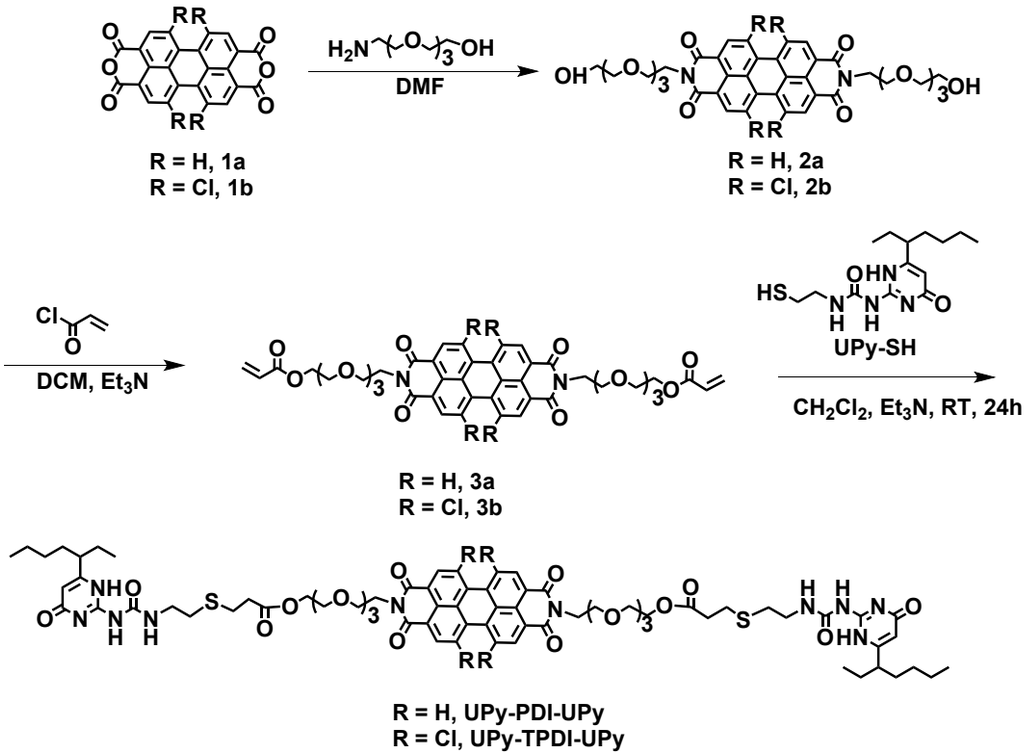
All reagents were bought from commercial sources, used as received unless otherwise stated.



Scheme S1. Synthesis route of UPy-SH.

Synthesis of UPy-SH

The preparation of **A** was achieved according to the previous literatures [1-3]. Then, **A** (800 mg, 1.28 mmol), DL-Dithiothreitol (DTT, 0.926 mg, 1.92 mmol) and four drops 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) were added to 100 mL CH_2Cl_2 and stirred at 35℃ for 15 min. The solution was washed with water to remove the excess DTT. The solvent was removed under reduced pressure to afford 772 mg of product UPy-SH, which was sufficiently pure for subsequent step. Yield: 96%.



Scheme S2. Synthesis route of UPy-PDI-UPy and UPy-TPDI-UPy.

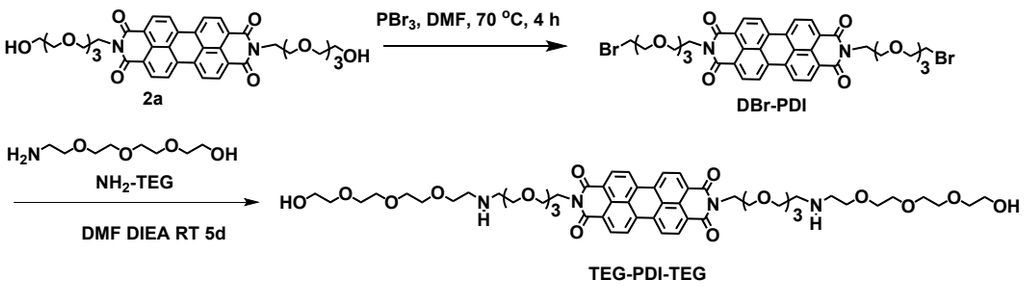
The preparation of 1a, 2a, 1b and 2b were achieved according to our previous report [4].

Synthesis of 3b

To a solution of **2b** (880 mg, 1 mmol) in 500 mL dry CH_2Cl_2 (DCM, 4 Å activated molecular sieves, 3 days) at 0 ºC, acryloyl chloride (109 mg, 1.2 mmol) and dry triethylamine (0.5 mL, 3.6 mmol) were added. The reaction mixture stirred for 2 h at 0 ºC, and kept overnight at room temperature (RT) under an argon atmosphere. After evaporation of the solvent, the product was purified via gel chromatography using CH_2Cl_2/CH_3OH (30:1, v/v). **3b**, a red solid, was obtained in 35% yield (346 mg). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.68 (s, 4H), 6.40 (d, 2H), 6.15 (q, 2H), 5.84 (d, 2H), 4.47 (t, 4H), 4.30 (t, 4H), 3.86 (t, 4H), 3.71-3.63(m, 20H).

Synthesis of UPy-TPDI-UPy

A mixture of **3b** (180 mg, 0.18 mmol), UPy-SH (170 mg, 0.54 mmol) and triethylamine (0.2 mL 1.44 mmol) in CH_2Cl_2 (30 mL) was stirred under N_2 at room temperature for 24 h. After evaporation of the solvent, the product was purified via gel chromatography using CH_2Cl_2/CH_3OH (100:1, v/v) as the eluent to afford **UPy-TPDI-UPy** (124 mg). Yield: 42%.^{1}H NMR (500 MHz, $CDCl_3$), δ: 13.12-13.07 (m, 2H), 11.95-11.86 (m, 2H), 10.45-10.33 (m, 2H), 8.65 (s, 4H), 5.80-5.76 (m, 2H), 4.47 (t, 4H), 4.22 (t, 4H), 3.84(t, 4H), 3.68-3.62 (m, 20H), 3.44-3.37 (m, 4H), 2.79-2.62 (m, 12H), 2.28 (m, 2H), 1.76-1.27 (m, 16H), 0.88-0.86 (m, 12H).



Scheme S3. Synthesis route of TEG-PDI-TEG.

Synthesis of DBr-PDI

To a solution of **2a** (742 mg, 1 mmol) in 20 mL dry DMF, PBr_3 (621 mg, 2.29 mmol) was added, The reaction mixture stirred for 4 h at 70 ºC, After cooling to room temperature, the reaction mixture was slowly poured into 5 % aq. $NaHCO_3$ (25 mL), then extracted respectively with 100 mL methylene dichloride three times. After evaporation of the solvent, the concentrate was poured into methanol to precipitate. After centrifugation, pouring out the supernatant and vacuum drying, the product **DBr-PDI** was achieved as red solid. (781 mg). Yield: 90 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.55 (d, 4H), 8.42 (d, 4H), 4.47 (t, 4H), 3.88 (t, 4H), 3.75-3.60 (m, 20H), 3.42 (t, 4H).

Synthesis of TEG-PDI-TEG

To a solution of **DBr-PDI** (174 mg, 0.2 mmol) in dry DMF (15 mL), N,N-diisopropylethylamine (DIEA, 400 μL, 2.28 mmol) and TEG-NH_2 (116 mg, 0.6 mmol) were added at room temperature under argon atmosphere, The reaction mixture was stirred for 5d. The solvent was evaporated, redissolved in 25 mL dichloromethane. Then, the solution was washed with 25 mL 2 M hydrogen chloride solution, dried over anhydrous sodium sulfate, filtered and evaporated. The product **TEG-PDI-TEG,** as a dark solid (42 mg), was purified by column chromatography via using CH_2Cl_2/CH_3OH (20:1, v/v) as the eluent. Yield: 19 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.52 (d, 4H), 8.44 (d, 4H), 4.46 (t, 4H), 3.86 (m, 8H), 3.67-3.31 (m, 40H), 2.03 (m, 12H).

Instruments

^{1}H-NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer in $CDCl_3$. Mass spectra (MS) was measured by electrospray ionization (ESI) at themicro TOF Focus from *Bruker* Daltonics. The nanoparticle diameters were determined by a Malvern Nano-ZS90 instrument, their morphologies were recorded on a Bruker Dimension Icon atomic force microscope (AFM) in the tapping mode. UV-visible spectra were recorded on a Shimadzu UV-2501 PC spectrophotometer at room temperature (298 K). Fluorescence spectra were recorded on an Edinburgh FLS920 (UK) fluorescence spectrophotometer at room temperature (298 K). Fluorescence lifetime (τ) measurements were carried out with a time-correlated single photon counting nanosecond fluorescence spectrometer (Edinburgh FLS920, UK) at ambient temperature (298 K). Fluorescence quantum yields were measured on an Edinburgh FLS920 (UK) fluorescence spectrometer equipped with an integrating sphere detector.

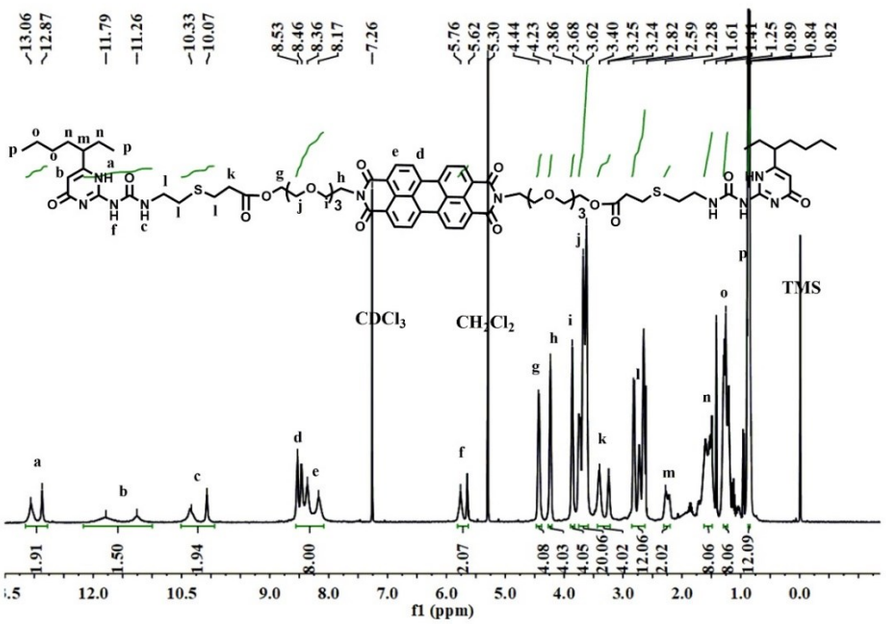


Figure S1. ^{1}H NMR spectrum of UPy-PDI-UPy (500 MHz, $CDCl_3$).

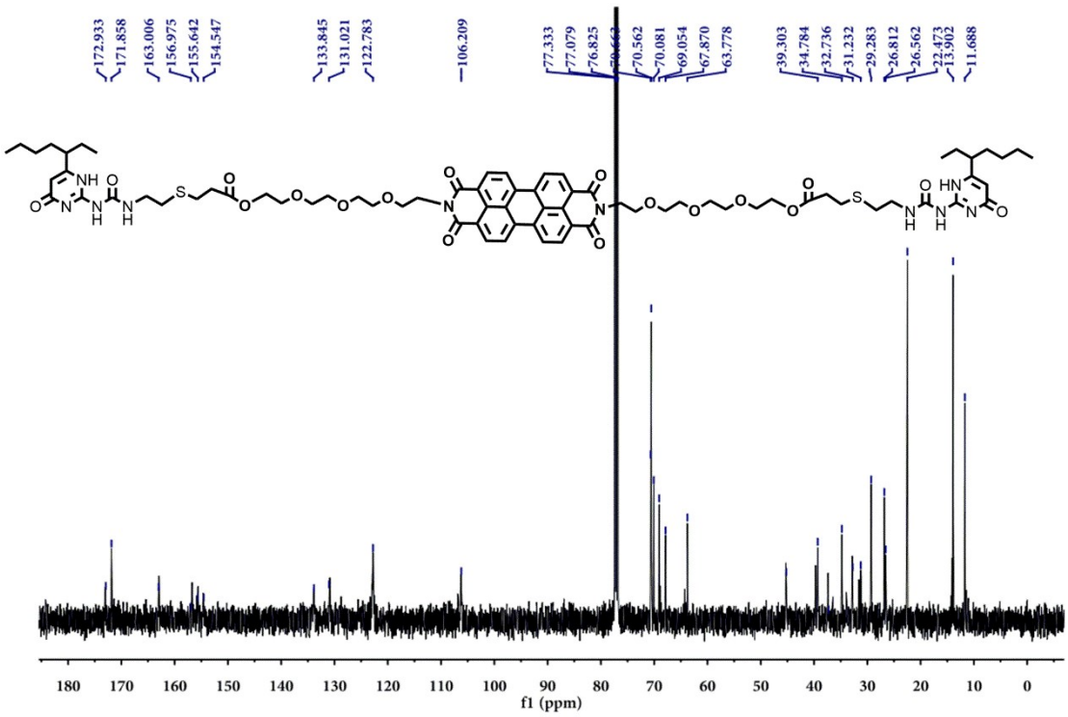


Figure S2. ^{13}C NMR spectrum of UPy-PDI-UPy (125 MHz, $CDCl_3$).

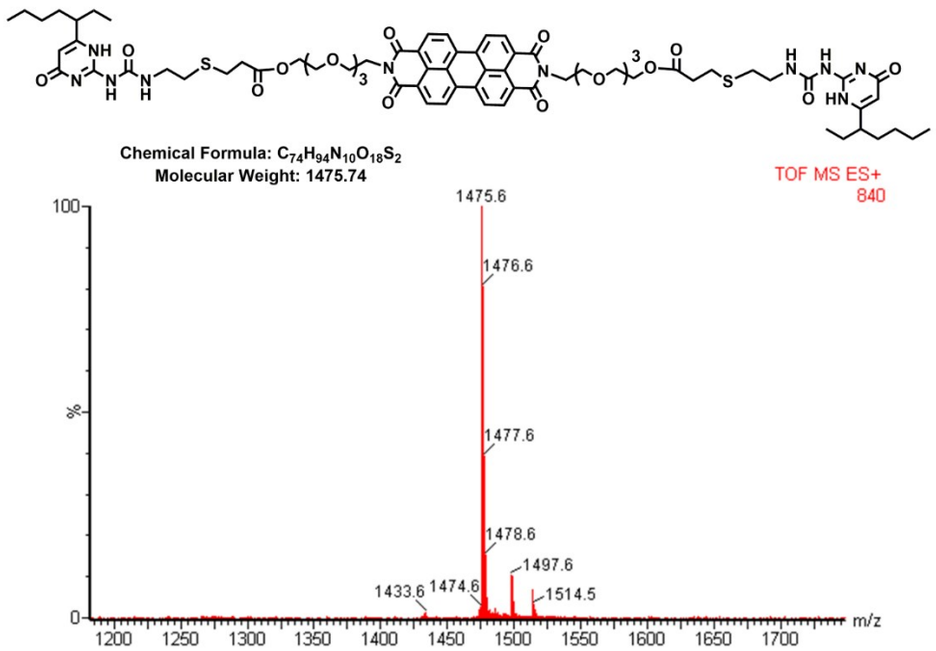


Figure S3. Mass spectrum of UPy-PDI-UPy.

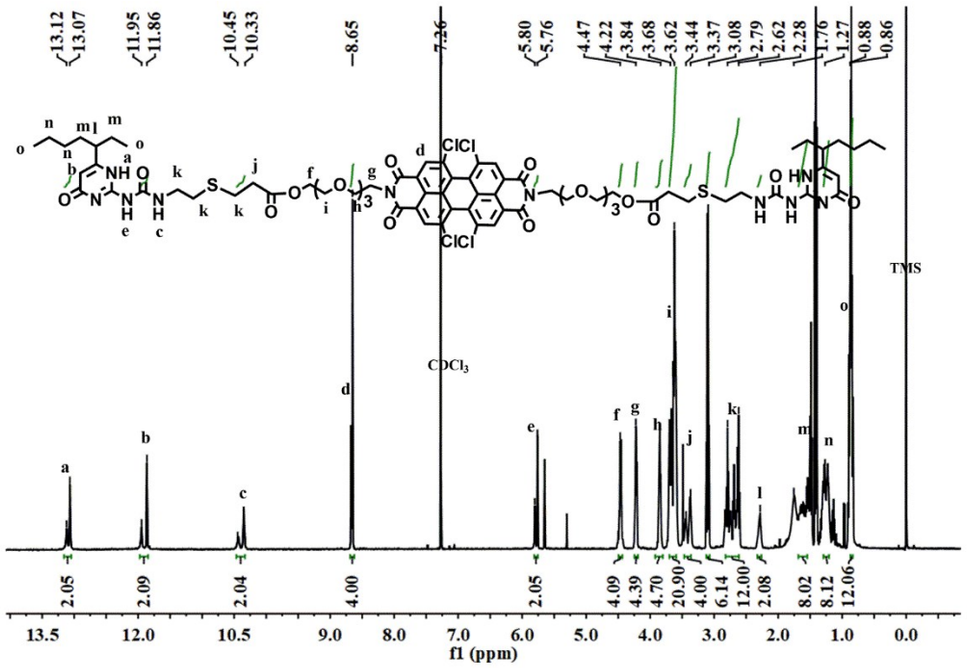


Figure S4. ^{1}H NMR spectrum of UPy-TPDI-UPy (500 MHz, $CDCl_3$).

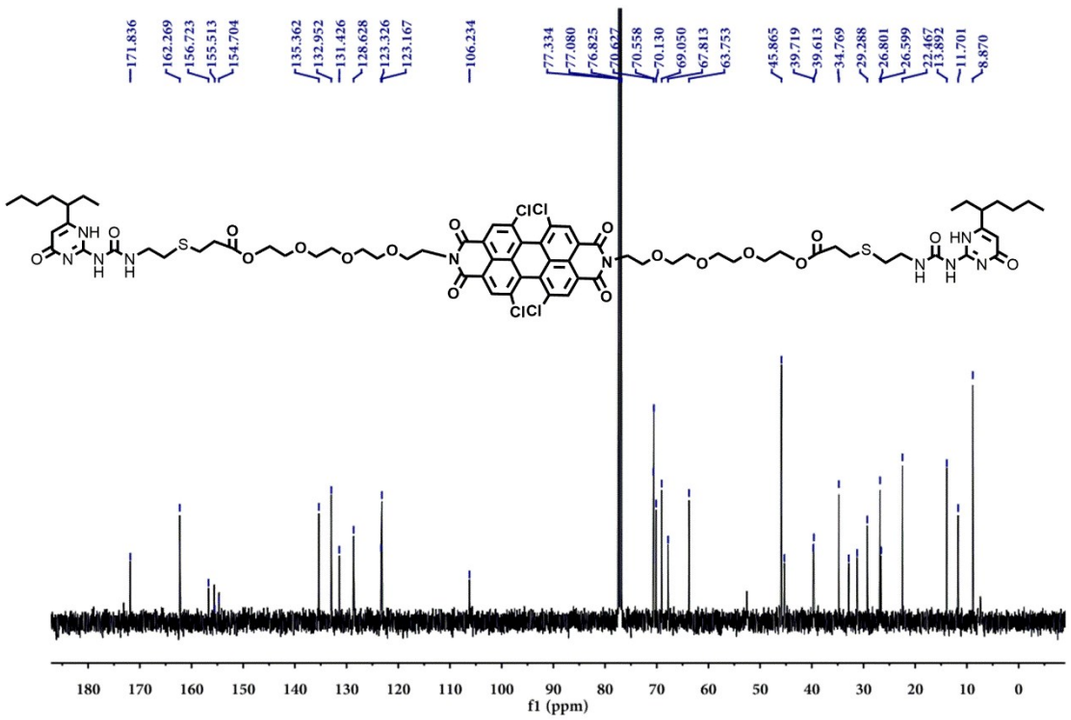


Figure S5. ^{13}C NMR spectrum of UPy-TPDI-UPy (125 MHz, $CDCl_3$).

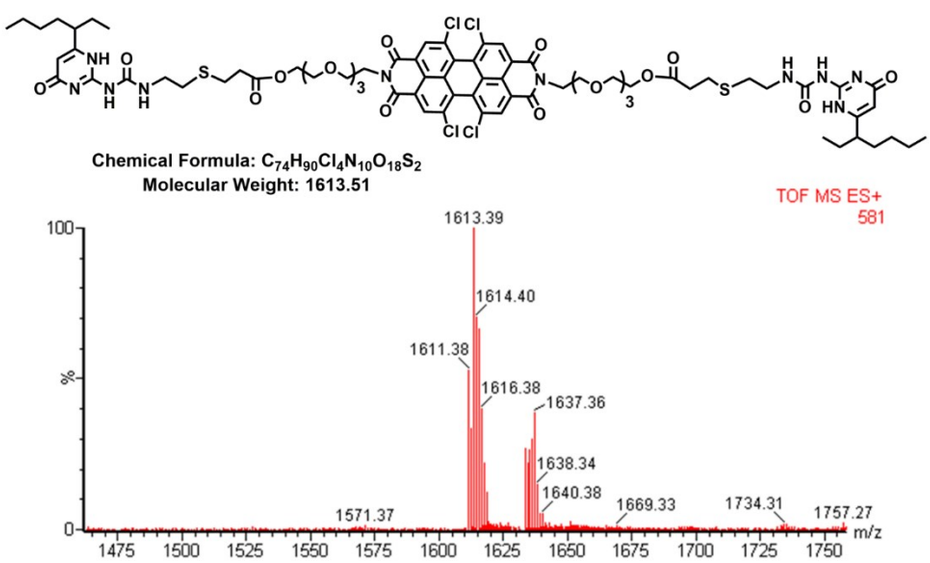


Figure S6. Mass spectrum of UPy-TPDI-UPy.

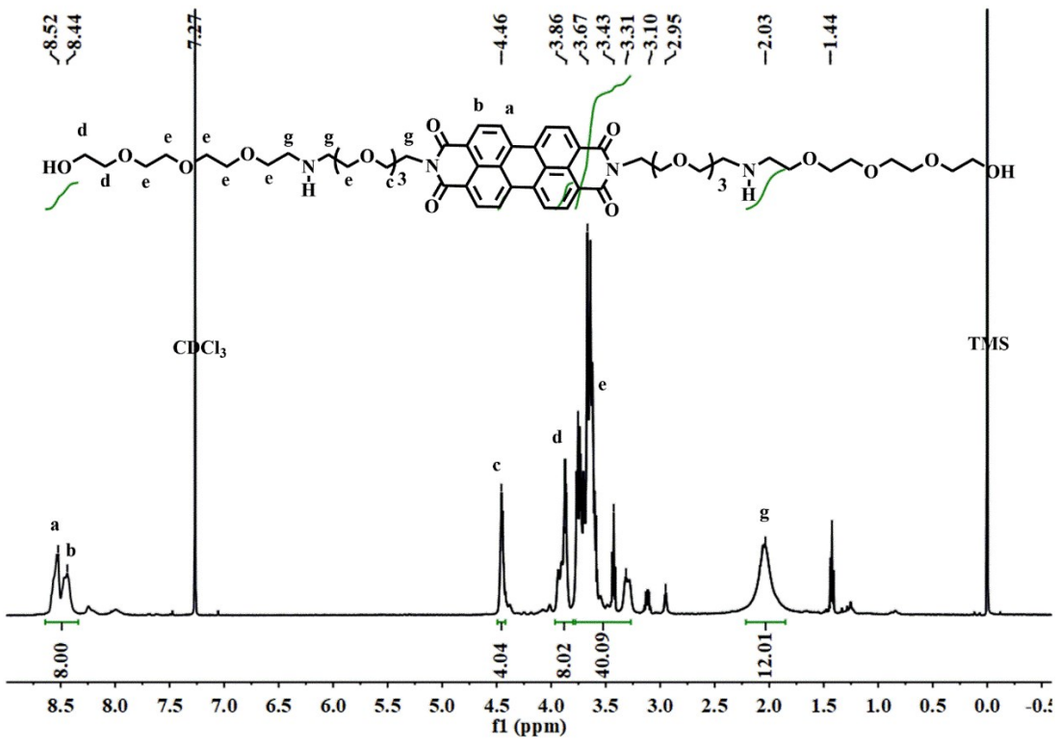


Figure S7. ^{1}H NMR spectrum of TEG-PDI-TEG (500 MHz, $CDCl_3$).

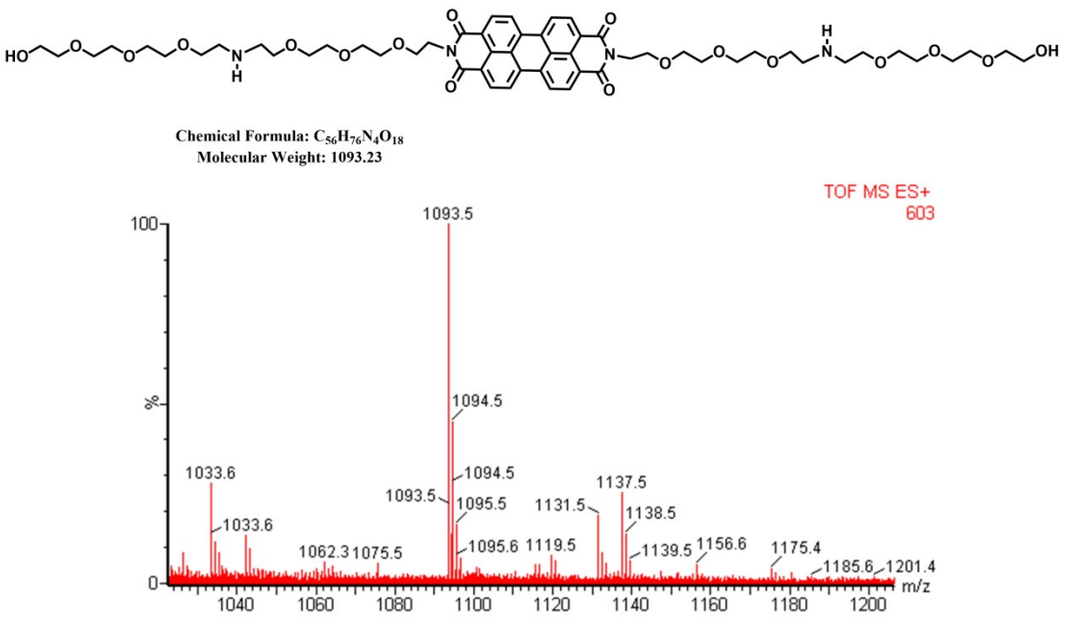


Figure S8. Mass spectrum of TEG-PDI-TEG.

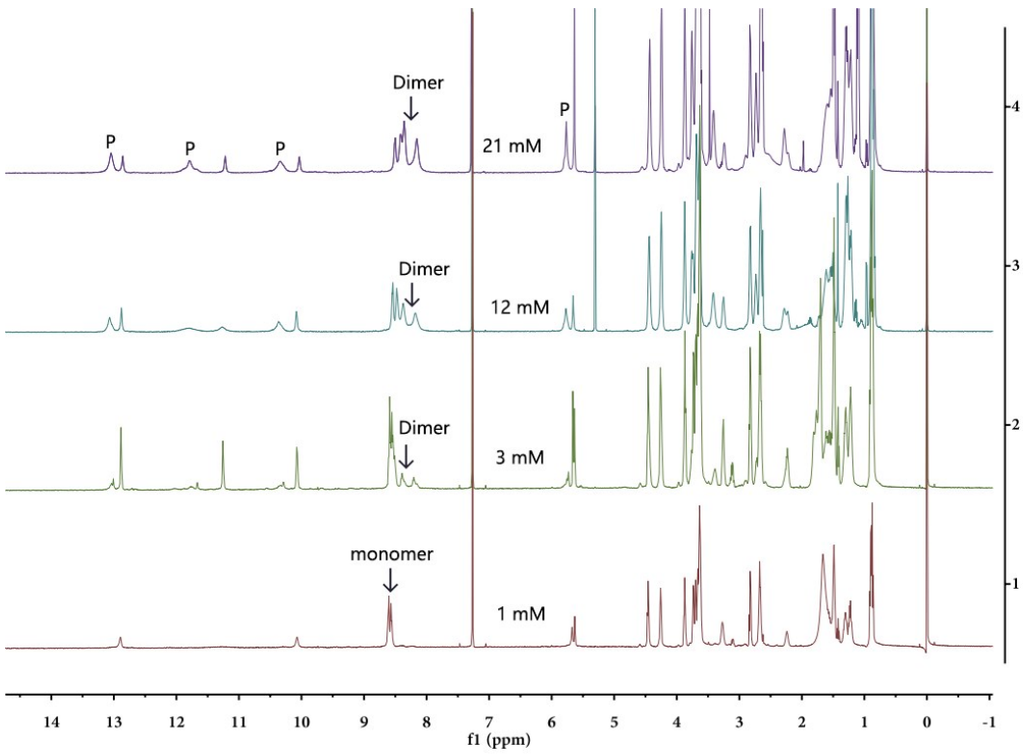


Figure S9. ^{1}H NMR spectrum of UPy-PDI-UPy at different concentrations (500 MHz, $CDCl_3$).

Note: Due to the limit of solubility, there are few insoluble substances in the $CDCl_3$ solution of UPy-PDI-UPy at 21 mM.

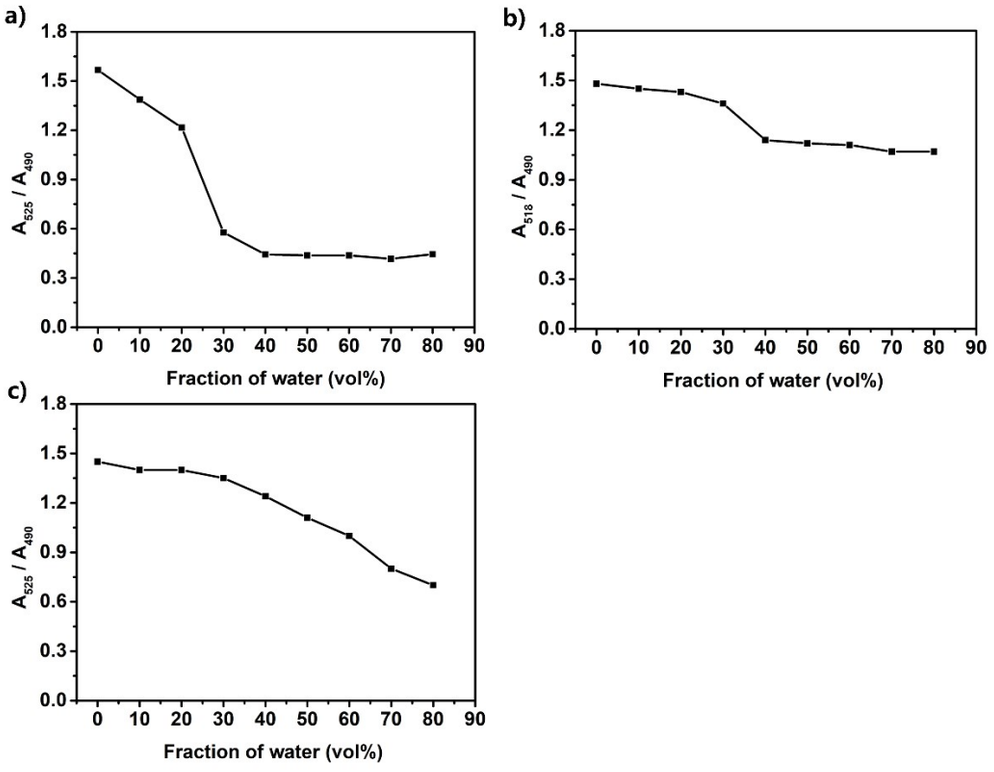


Figure S10. a) Absorbance ratio ($\mathbf{A_{525}/A_{490}}$) of UPy-PDI-UPy (50 μM) in DMF/H_2O solution with different water fraction. b) Absorbance ratio ($\mathbf{A_{518}/A_{490}}$) of UPy-TPDI-UPy (50 μM) in DMF/H_2O solution with different water fraction at 518 nm and 490 nm. c) Absorbance ratio ($\mathbf{A_{525}/A_{490}}$) of TEG-PDI-TEG (50 μM) in DMF/H_2O solution with different water fraction.

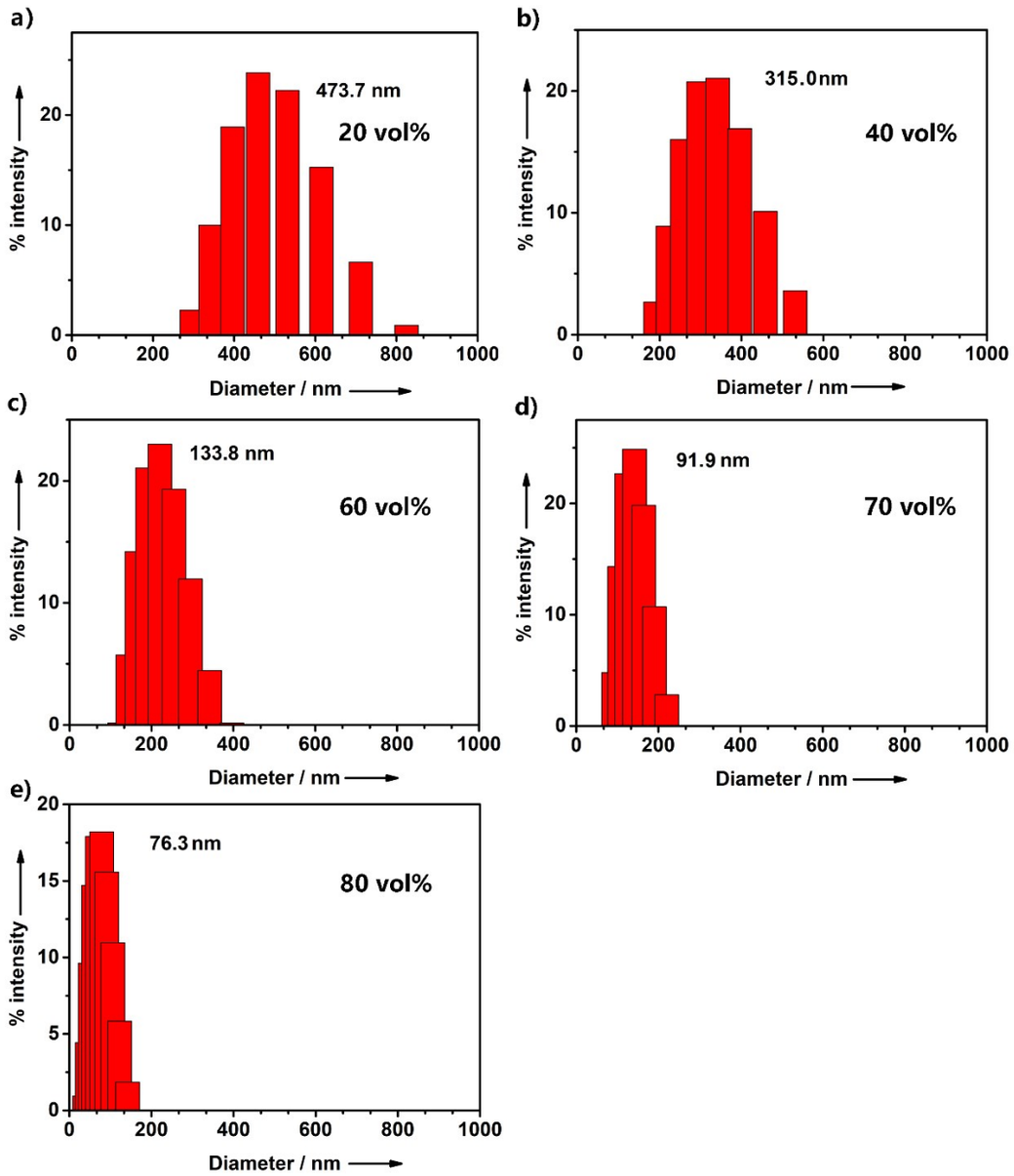


Figure S11. DLS distribution of UPy-PDI-UPy (50 μM) in DMF/H_2O solution with different water fraction.

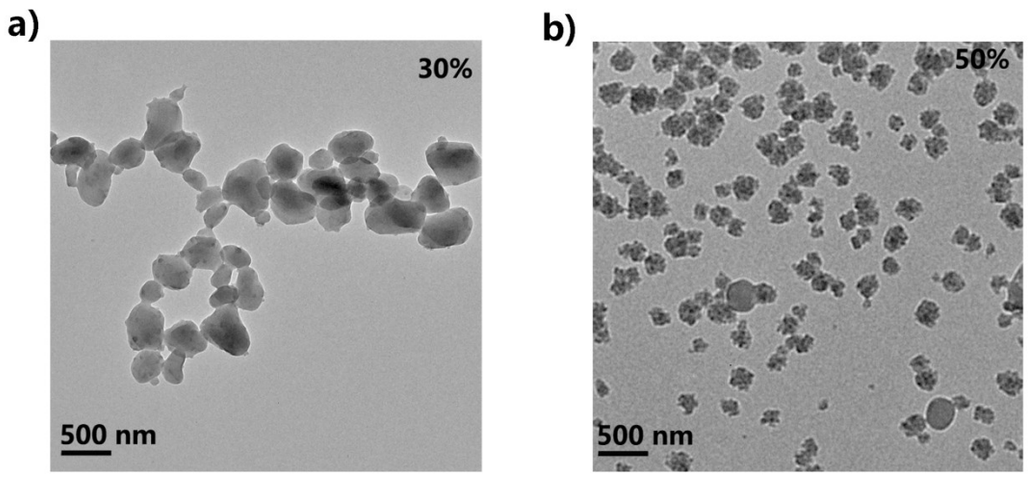


Figure S12. TEM image of UPy-PDI-UPy (50 μM) in DMF/H_2O solution with different (30 % and 50 %) water fraction.

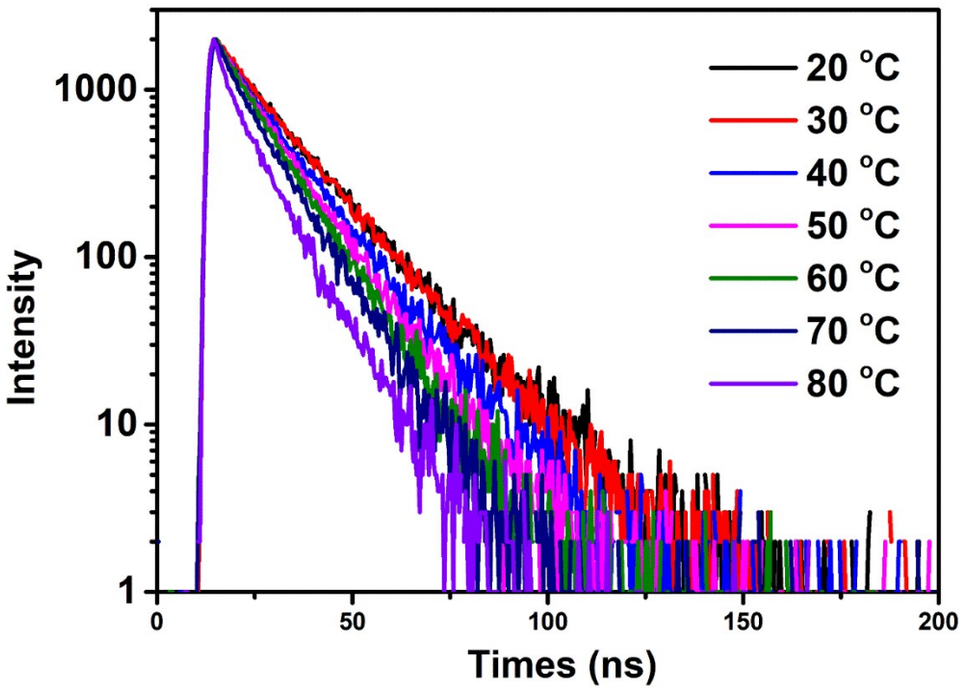


Figure S13. Fluorescence lifetime decay curves of UPy-PDI-UPy in DMF/H_2O: 50/50 (v/v) at various temperature, at 646 nm.

Average lifetimes data: 15.9 ns at 20 ℃, 15.4 ns at 30 ℃, 13.5 ns at 40 ℃, 12.3 ns at 50 ℃, 11.3 ns at 60 ℃, 10.5 ns at 70 ℃, 8.9 ns at 80 ℃.

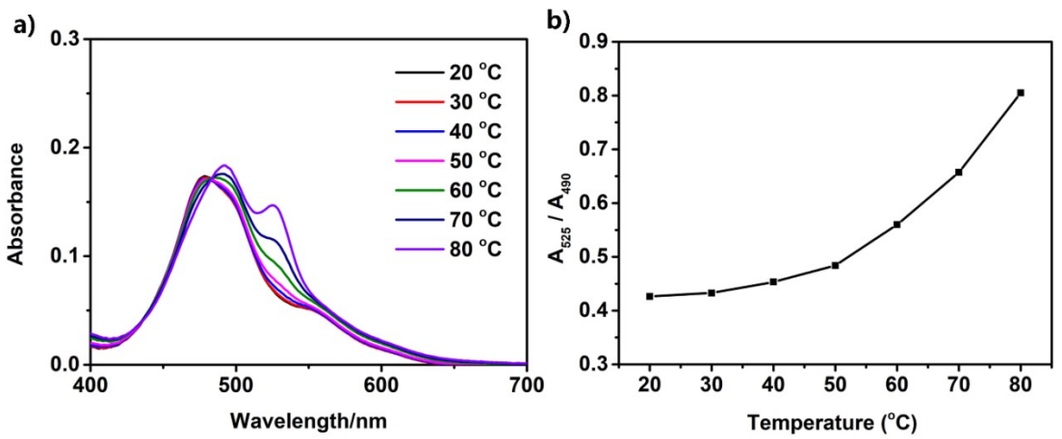


Figure S14. Absorption spectra of UPy-PDI-UPy (50 μM) in DMF/H_2O: 50/50 (v/v) at various temperature, and the absorbance intensity ratio at various temperature.

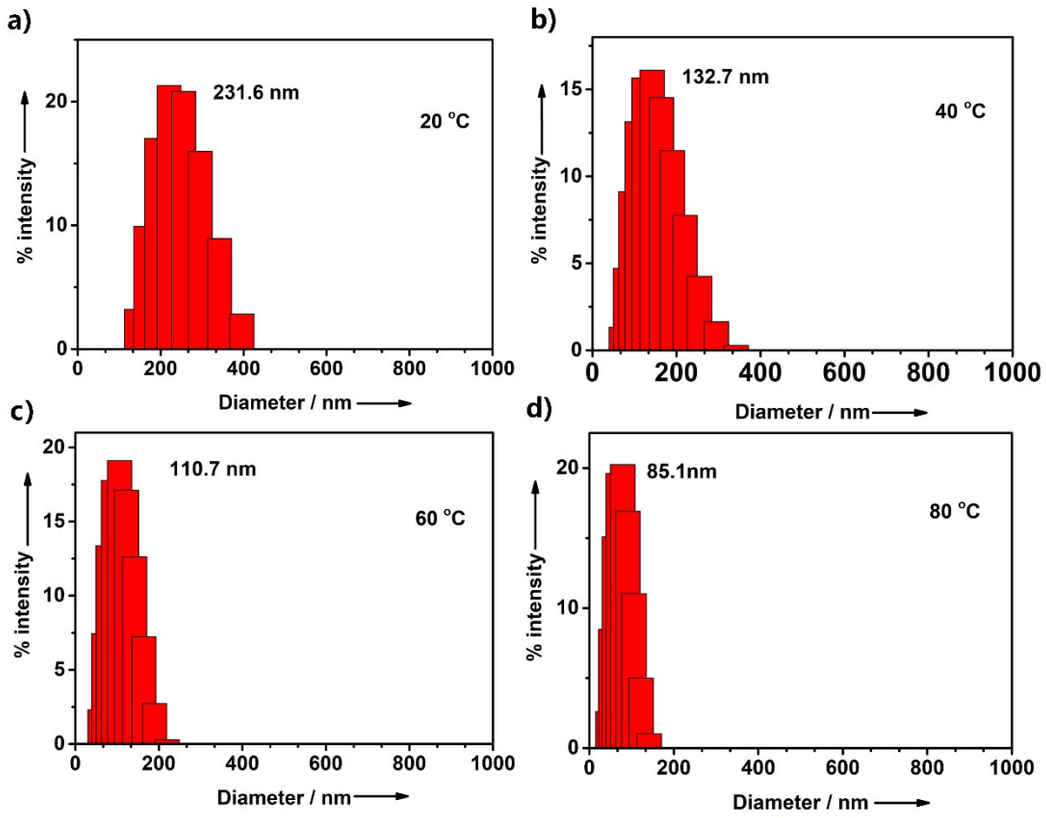


Figure S15. DLS distribution of UPy-PDI-UPy (50 μM) in DMF/H_2O: 50/50 (v/v) at various temperature.

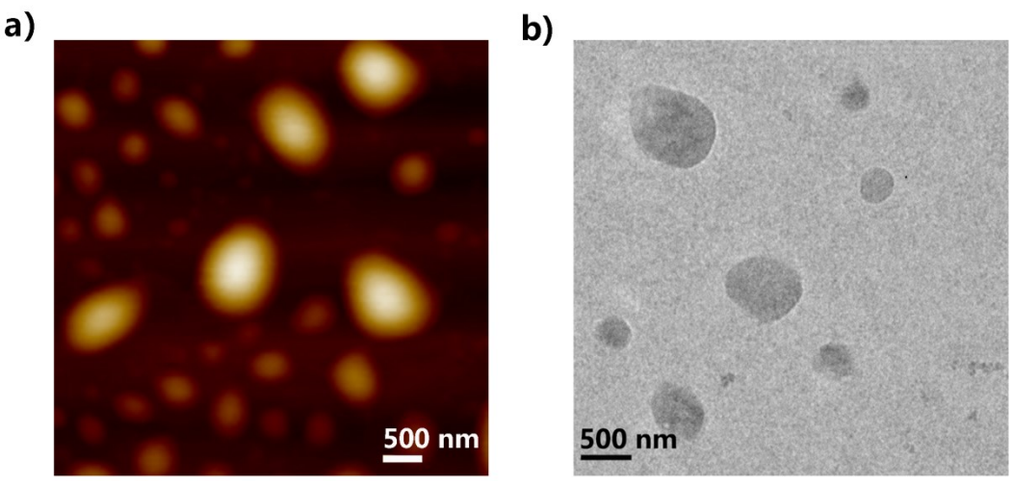


Figure S16. AFM (a) and TEM (b) images of the nanoparticles of UPy-PDI-UPy (50 μM) in DMF/H_2O: 50/50 (v/v) after the first heating then cooling to 20 °C.

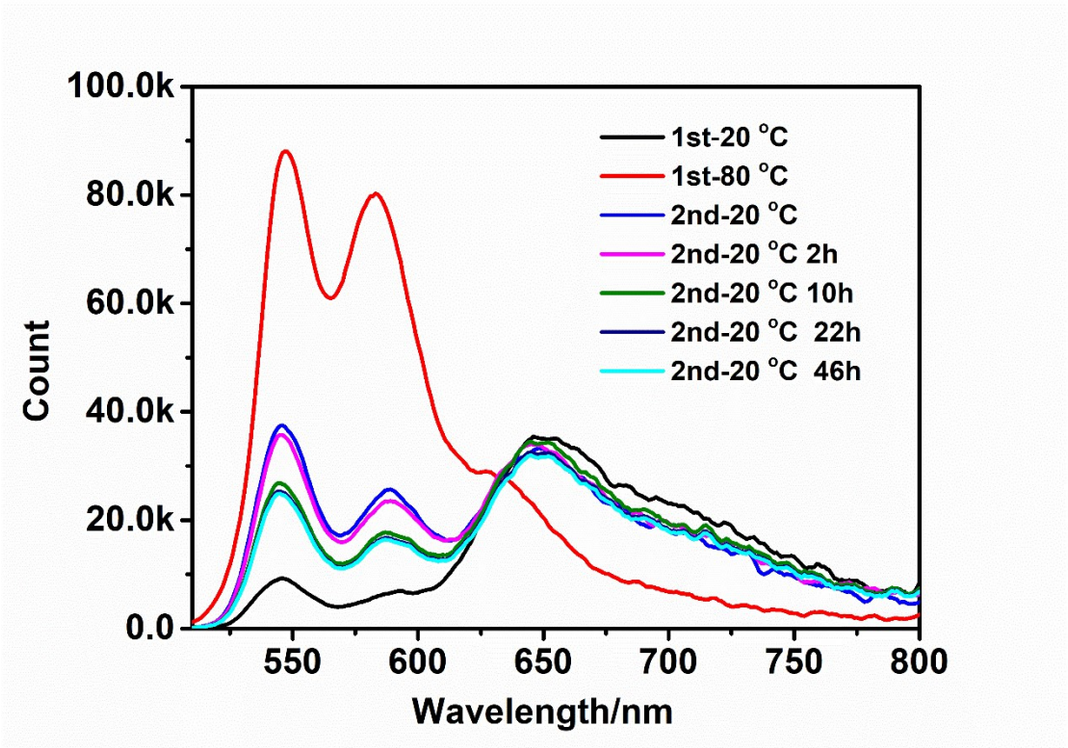


Figure S17. Fluorescence emission spectra of UPy-PDI-UPy in DMF/H_2O: 50/50 (v/v) at different temperature and time, λ_{ex}=490 nm.

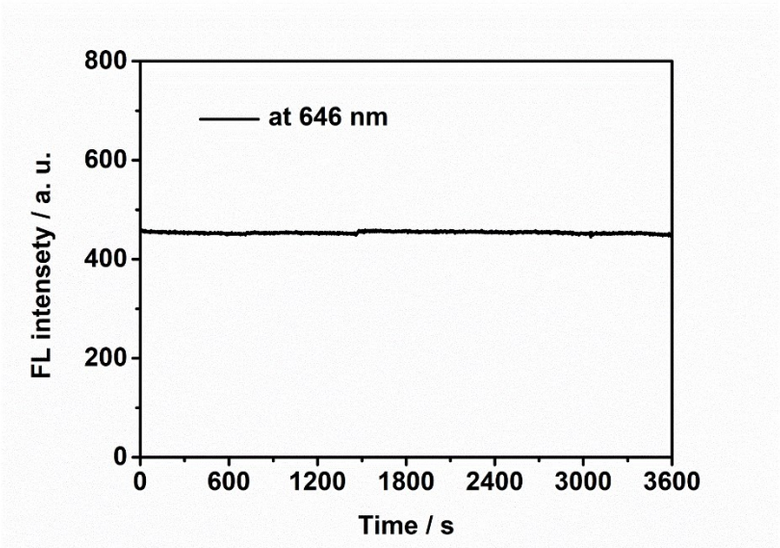


Figure S18. Photostability of UPy-PDI-UPy in DMF/H_2O: 50/50 (v/v), λ_{ex}=490 nm, λ_{em}=646 nm.

Table S1. The constitution of Gel1, Gel2, Gel3, Gel4.

No.	PDI derivatives	PEG amount (g)	PEG M_w
Gel1	UPy-PDI-UPy	0.7	10000
Gel2	UPy-PDI-UPy	1.0	10000
Gel3	UPy-PDI-UPy	1.0	2000
Gel4	TEG-PDI-TEG	1.0	10000

Note: The Gels was prepared by 0.5 mL of PDI derivative (50 μM) in DMF/H_2O: 50/50 (v/v) solution and some amount of PEG.

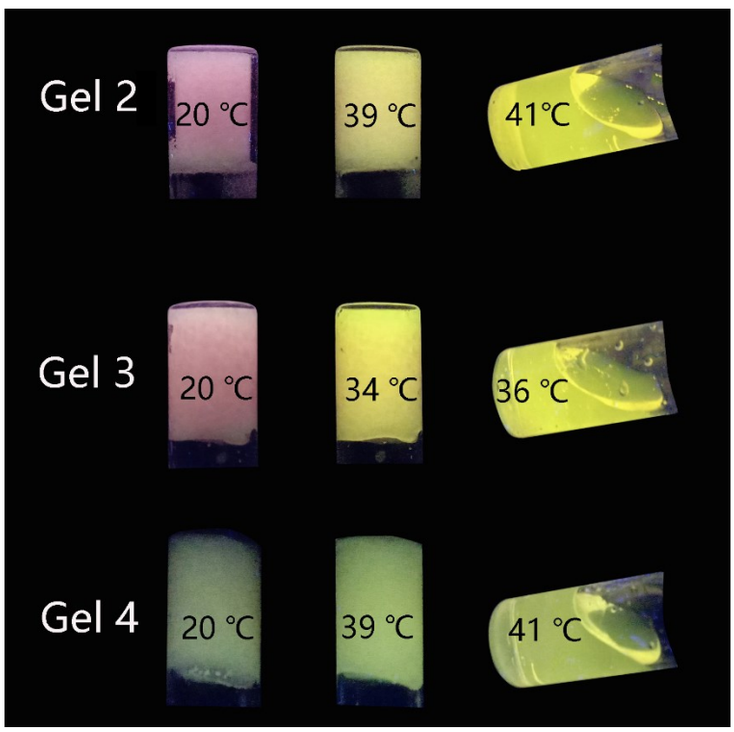


Figure S19. Fluorescence photographs of Gel2, Gel3, Gel4 at various temperature.

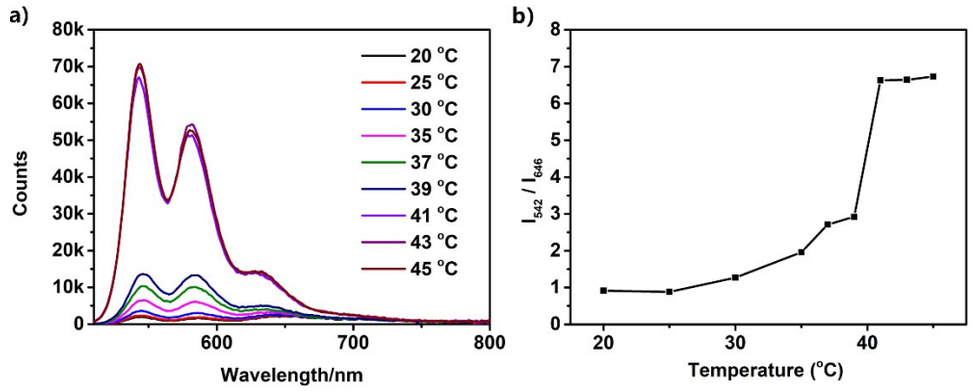


Figure S20. a) Temperature dependent fluorescence of the Gel2. λ_{ex}=490 nm, b) the fluorescence intensity ratio (I_{542}/I_{646}) of Gel2 at different temperature.

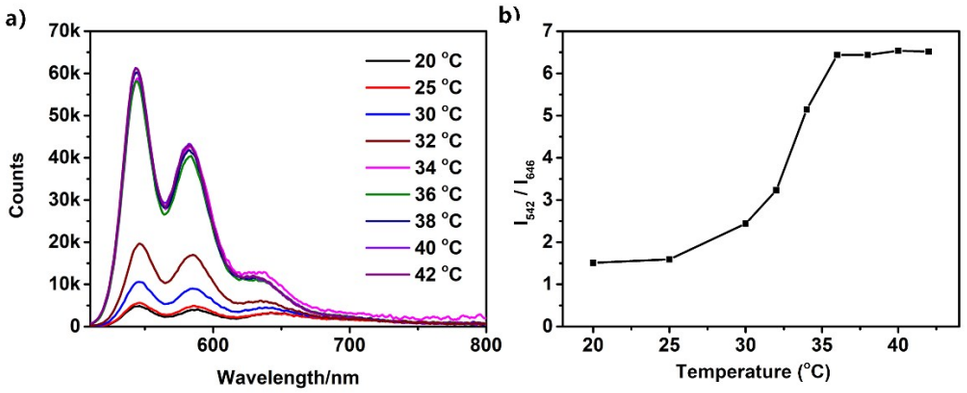


Figure S21. a) Temperature dependent fluorescence of the Gel3. λ_{ex}=490 nm, b) the fluorescence intensity ratio (I_{542}/I_{646}) of Gel3 at different temperature.

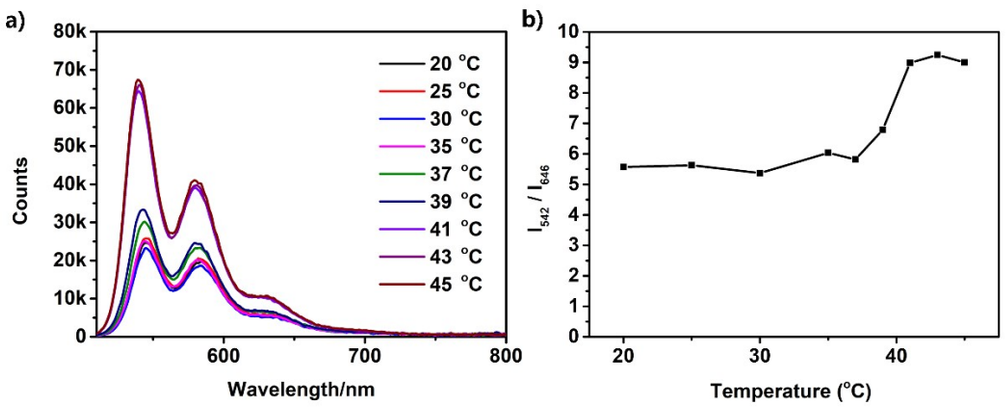


Figure S22. a) Temperature dependent fluorescence of the Gel4. λ_{ex}=490 nm, b) the fluorescence intensity ratio (I_{542}/I_{646}) of Gel4 at different temperature.

References

[1] Clay, R. J., Collom, T. A., Karrick, G. L., Wemple, J. A Safe, Economical Method for the Preparation of β-Oxo Esters. *Cheminform,* **1993***, 1993*(03), 290-292.

[2] Keizer, H. M., González, J. J., Margarita, S., Pilar, P., Sijbesma, R. P., Meijer, E. W., & Javier, D. M. Self-assembled pentamers and hexamers linked through quadruple-hydrogen-bonded 2-ureido-4[1H]-pyrimidinones. *Chemistry - A European Journal,* **2010***, 11*(16), 4602-4608.

[3] Peng, H. Q., Sun, C. L., Xu, J. F., Niu, L. Y., Chen, Y. Z., Wu, L. Z., Tung, C. H., Yang, Q. Z. Convenient synthesis of functionalized bis-ureidopyrimidinones based on thiol-yne reaction. *Chemistry - A European Journal,* **2014***, 20*(37), 11699-11702.

[4] Wang, W., Li, L.-S., Helms, G., Zhou, H.-H., Li, A. D. Q., To Fold or to Assemble? *Journal of the American Chemical Society* **2003,** *125* (5), 1120-1121.