Supporting Information for

A Novel Pyrene-containing Fluorescent Organogel Derived From Quinoline-based Fluorescent Porbe: Synthesis, Sensing Properties, and Its Aggregation Behavior

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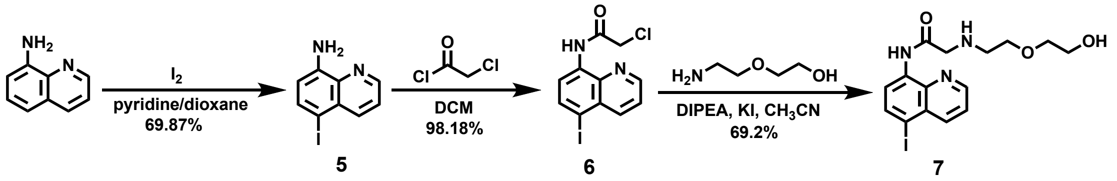
1. Synthesis of intermediates 7, 9, 14, 15

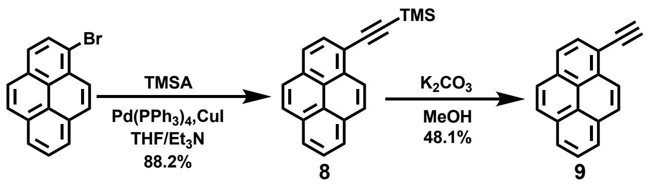


Scheme S1 Synthesis of intermediate **7**.

Compound **5**. Compound **5** was prepared according to previously reported methods. The 8-aminoquinoline (4.0 g, 27.74 mmol) was dissolved in dioxane (150 mL) and pyridine (150 mL) and the solution was cooled to 0 °C. Iodine (10.0 g, 39.40 mmol) was added in one portion. The solution progressively took a dark brown color. After 1 h, the ice bath was removed and a supplementary portion of iodine (4.1 g, 16.10 mmol) was added. The solution was further stirred for one hour at room temperature. A saturated solution of sodium thiosulfate was then added until the brown color disappeared. The mixture was extracted with dichloromethane and washed with water. After evaporation, the product was filtered through a short plug of silica, eluted with the dichloromethane/petroleum ether (3:1, v/v) to afford **5**. Yield: 5.23 g (69.9%). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 8.70 (dd, *J* = 1.6, 4.0 Hz, 1H), 8.26 (dd, *J* = 1.2, 8.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.43 (q, *J* = 4.4 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.08 (s, 2H).

Compound **6**. 2-chloroacetyl chloride (0.70 mL, 8.8 mmol) was dissolved in chloroform (100 mL), then added dropwise to a cooled, stirred solution of compound **5** (300 mg, 1.1 mmol) and triethylamine (464 mg, 3.3 mmol) in chloroform (100 mL) within 1 h, after stirred 2 h at room temperature, the mixture was removed under reduced pressure to obtain a yellow solid, which was used directly in the next reaction without further purification. Yield: 377.7 mg (98.2%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 10.73 (s, 1H), 8.97 (d, *J* = 4.0Hz, 1H), 8.42 (dd, *J* = 8.0, 16.0 Hz, 2H), 8.21 (d, *J* = 8.0Hz, 1H), 7.79 (dd, *J* = 4.0, 8.0 Hz, 1H), 4.62 (s, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 165.2, 149.9, 140.3, 138.7, 137.8, 134.6, 129.2, 124.2, 118.1, 91.2, 43.6. EI-MS m/z: M$^+$ calcd for $C_{11}H_8ClIN_2O$, 345.9; found, 346.

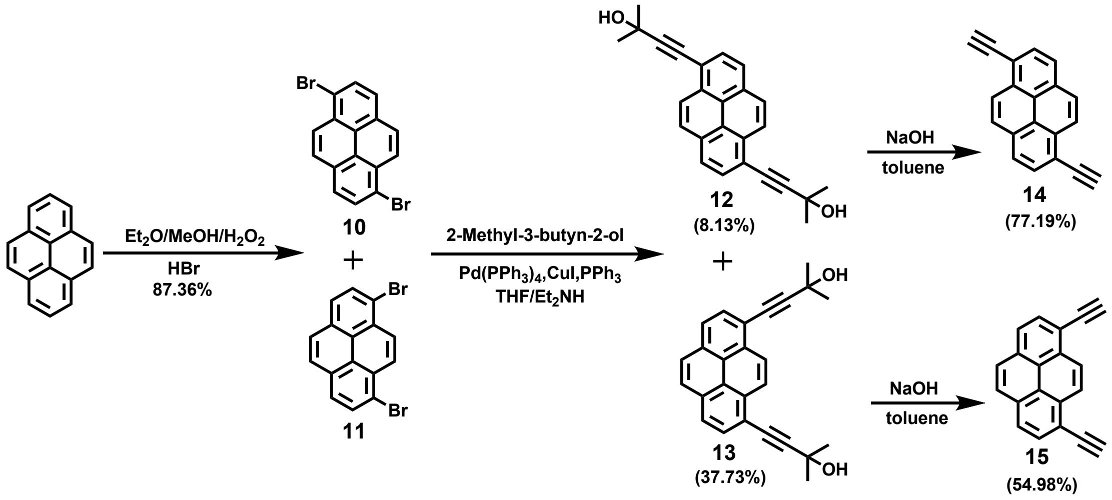
Compound **7**. Compound **6** (200 mg, 0.58 mmol), 2-(2-aminoethoxy)ethanol (0.58 mL, 5.77 mmol), N, N-diisopropylethylamine (1.01 mL, 5.77 mmol) and potassium iodide (60 mg, 0.36 mmol) were added to acetonitrile (90 mL), after stirred and refluxed for 10 h under nitrogen atmosphere, the mixture was cooled to room temperature and the mixture was removed under reduced pressure to obtain a brown solid, which was purified by silica gel column chromatography using dichloromethane /methanol (5:1, v/v) as eluent to afford **7**. Yield: 165.8 mg (69.2%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.25 (s, 1H), 8.81 (dd, *J* = 1.2, 4.0 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.36 (dd, *J* = 1.2, 8.4 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.53 (q, *J* = 4.4 Hz, 1H), 3.74 (dd, *J* = 6.0, 8.8 Hz, 4H), 3.64 (s, 2H), 3.60–3.57 (m, 2H), 3.01–2.99 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 171.0, 149.1, 140.6, 139.5, 138.2, 135.2, 129.7, 123.1, 117.9, 89.6, 72.4, 70.7, 61.8, 53.8, 49.5. HRMS : m/z: M$^+$ calcd for $C_{15}H_{18}N_3O_3I$: 415.0393; found: 415.0401.



Scheme S2 Synthesis of intermediate **9**.

Compound **8**. Compound **8** was prepared according to previously reported methods. A mixture of 1-bromopyrene (200 mg, 0.71 mmol), $Pd(PPh_3)_4$ (41 mg, 0.03 mmol), CuI (6.8 mg, 0.03 mmol) and triethylamine (20mL) in tetrahydrofuran (10mL) was bubbled with N_2 for 30 min., and then trimethylsilylacetylene (0.2 mL, 1.42 mmol) was added. The resulting solution was heated at 70 °C overnight in an inert atmosphere. The volatile was evaporated by rotavapor and the residue was subjected to column chromatography on silica gel, eluting with petroleum ether/dichloromethane (10:1, v/v) to yield a pale yellow crystalline product **8**. Yield: 187 mg (88.2%). It was characterized by 1H NMR giving the same analytical data as reported in the literature.

Compound **9**. Compound **9** was prepared according to previously reported methods. Compound **8** (1.59 g, 5.34 mmol), K_2CO_3 (2.21 g, 16.02mmol), and methanol (150 mL) were mixed together. The mixture was stirred at room temperature for 3h to afford **9**. Yield: 581 mg (48.1 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60 (d, *J* = 8.8 Hz, 1H), 8.24–8.17 (m, 4H), 8.11 (d, *J* = 8.4 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 3.63 (s, 1H).



Scheme S3 Synthesis of intermediate **14** and **15**.

Compounds **14** and **15**. Compounds **14** and **15** were prepared according to previously reported methods (X.-D. Xu, J. Zhang, X. Yu, L.-J. Chen, D.-X. Wang, T. Yi, F. Li, H.-B. Yang, *Chem. Eur. J.* **2012**, *18*, 16000–16013).

2. The ¹H NMR and ¹³C NMR spectra of compound 2–4

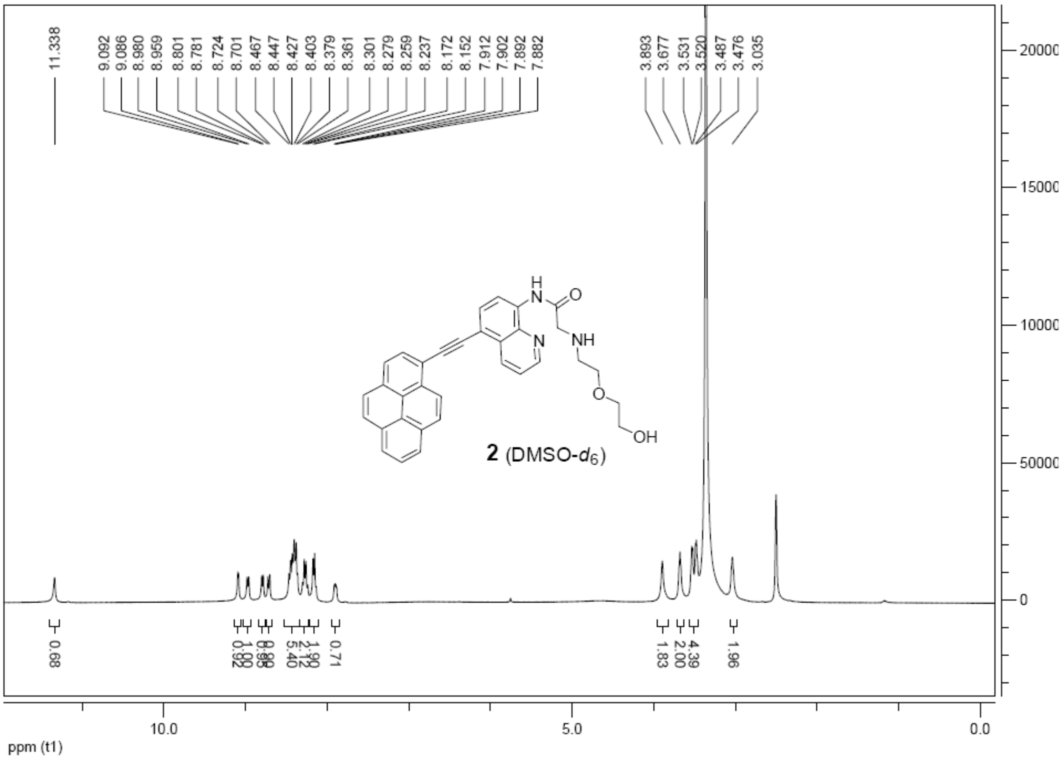


Fig. S1 The ¹H NMR spectra of compound **2**.

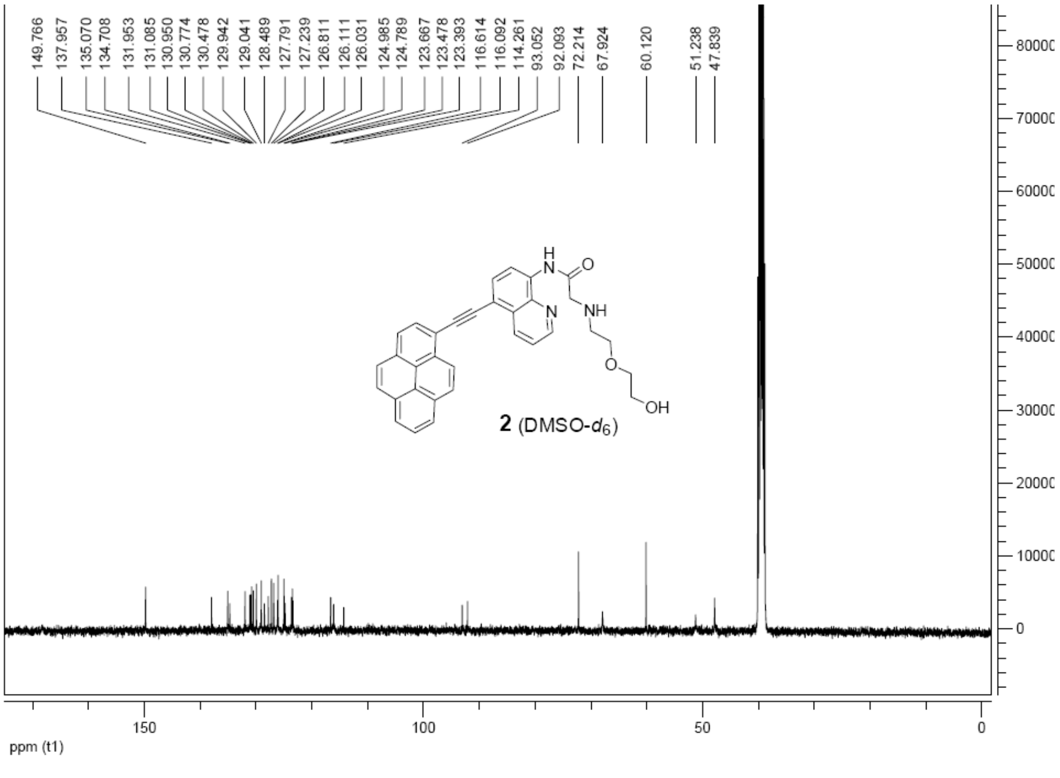


Fig. S2 The ¹³C NMR spectra of compound **2**.

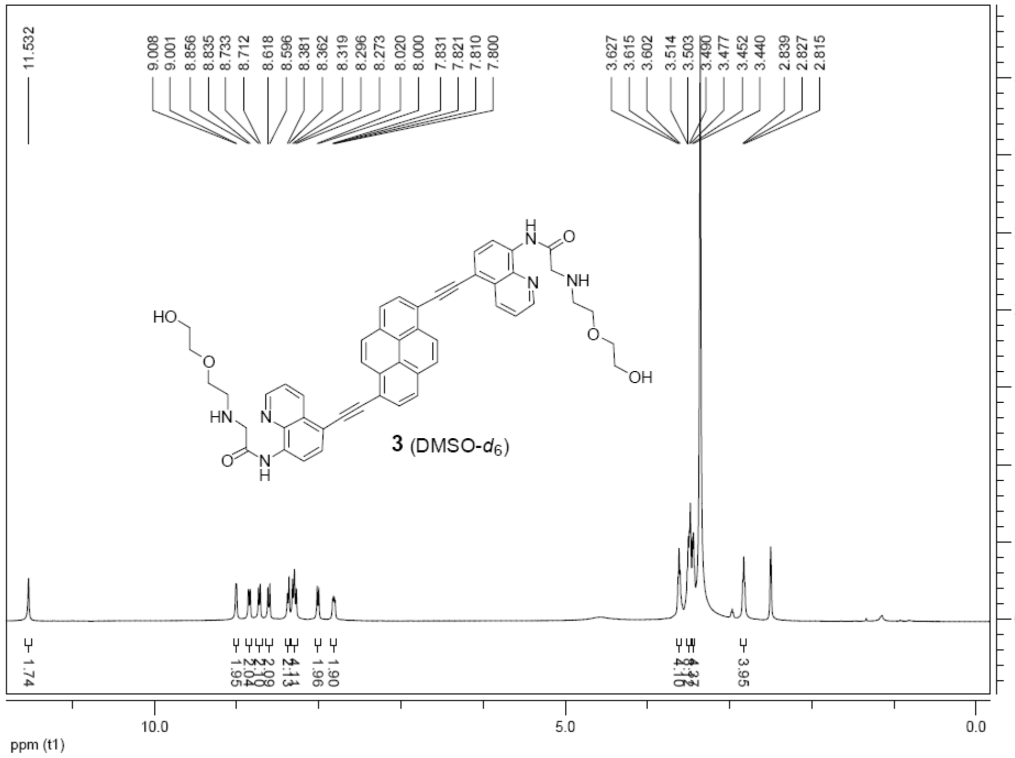


Fig. S3 The ^{1}H NMR spectra of compound **3**.

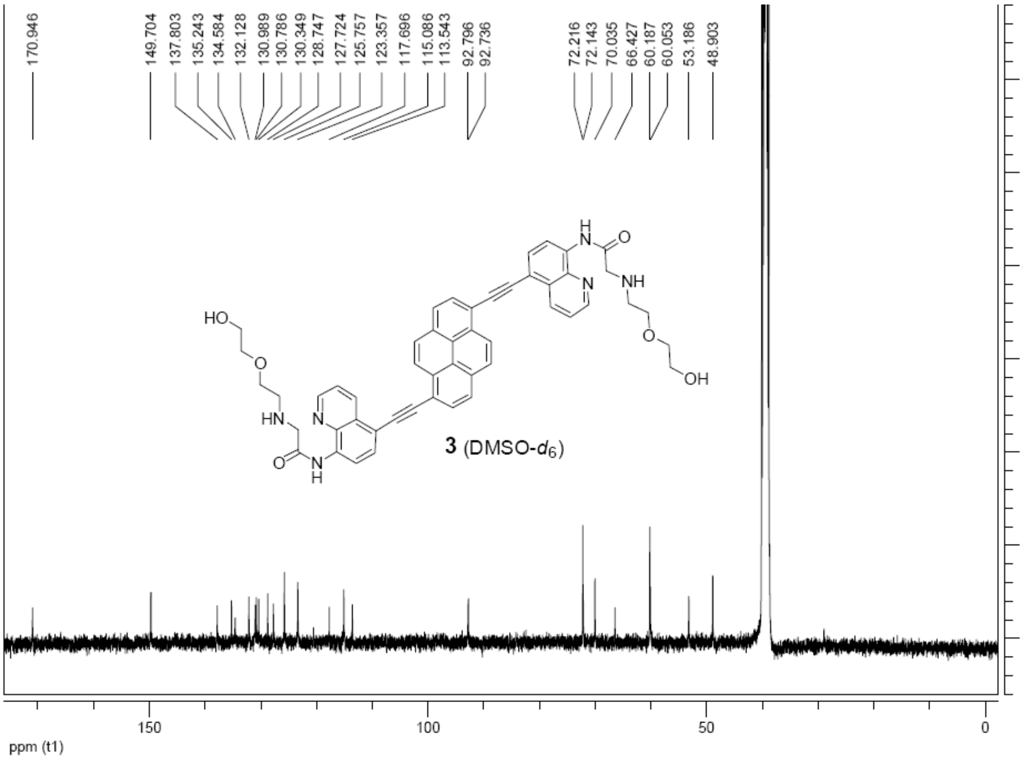


Fig. S4 The ^{13}C NMR spectra of compound **3**.

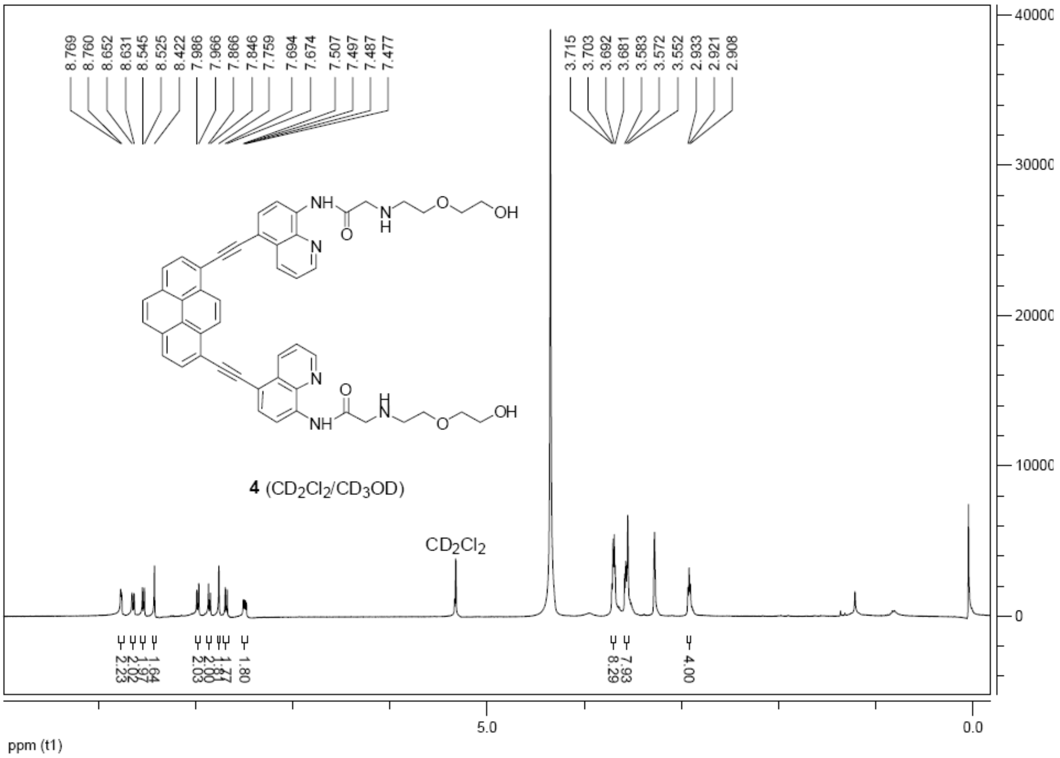


Fig. S5 The ^{1}H NMR spectra of compound **4**.

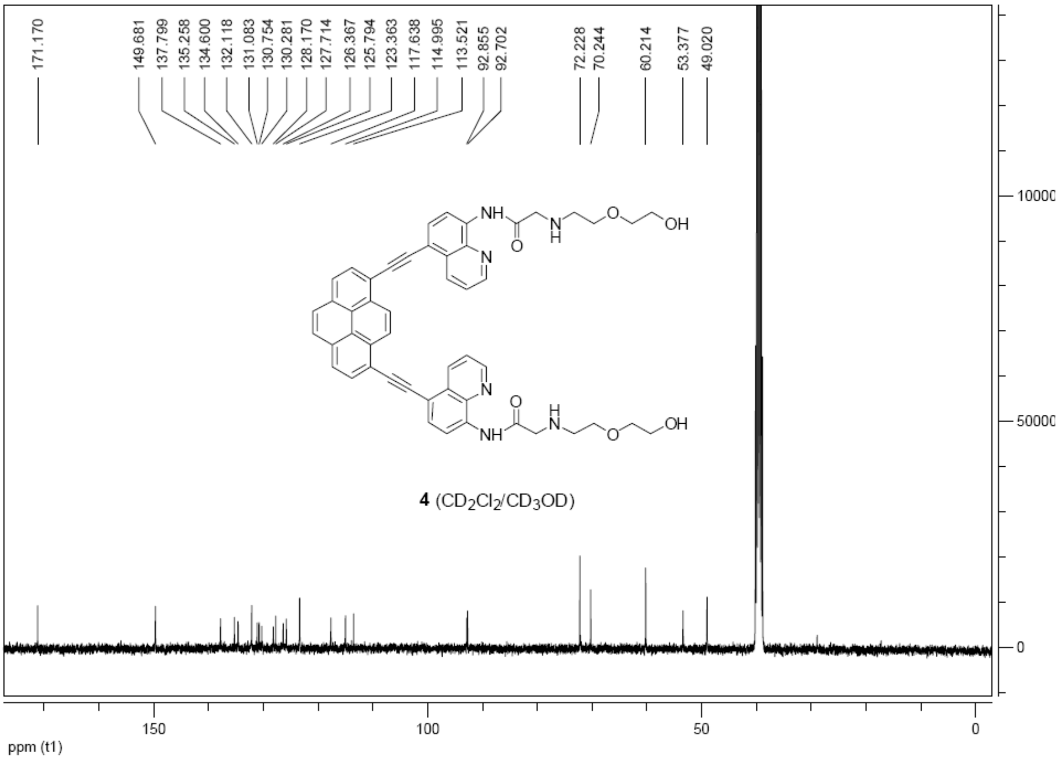


Fig. S6 The ^{13}C NMR spectra of compound **4**.

3. Photophysical properties of compounds 2–4 in various solvents

Table S1. Photophysical properties of compound **2** (1.0×10^{-5} M) in various solvents.

Solvent	λ_{abs} (nm)	ε ($M^{-1}\cdot cm^{-1}$)	λ_F (nm)	IF[a]
acetone	415	31800	453	422
	390	33800		
acetone/water	414	31500	475	164
(v/v, 1:1)	390	32500		
1,4-dioxane	418	27300	453	422
	396	30600	436	478
1,4-dioxane/water	414	27400	476	42
(v/v, 1:1)	389	29500		
tetrahydrofuran	418	30600	457	405
	395	34200	438	417
tetrahydrofuran/water	417	31000	465	288
(v/v, 1:1)	395	32700		
ethyl acetate	415	27500	452	410
	392	30600	433	429
methylbenzene	420	23700	461	303
	397	27900	438	370
dimethylbenzene	420	24100	460	325
	397	28400	438	400
n-propanol	415	26100	458	237
	390	29800		
n-propanol/water	412	25900	466	89
(v/v, 1:1)	389	29700		
chloroform	418	26400	458	324
	397	30200		
dichloromethane	418	31700	460	434
	397	34600		

a: slits: 2.5, 2.5 nm

Table S2. Photophysical properties of compound **3** (1.0×10^{-5} M) in various solvents.

Solvent	λ_{abs} (nm)	ε ($M^{-1}\cdot cm^{-1}$)	λ_F (nm)	IF[a]
acetone	448	72000	492	644
	430	79900	468	861
acetone/water	426	45500	492	338
(v/v, 1:1)			466	436
1,4-dioxane	433	70500	497	626
			468	>1000
1,4-dioxane/water	429	70200	493	471
(v/v, 1:1)			468	577
tetrahydrofuran	433	74100	498	571
			470	851
tetrahydrofuran/water	451	67200	495	587
(v/v, 1:1)	431	75000	468	707
ethyl acetate	430	73000	495	637
			466	988
methylbenzene	435	63200	501	497
			471	876
dimethylbenzene	435	63100	501	496
			471	879
n-propanol	429	70800	491	600
			465	879
n-propanol/water	428	70200	490	500
(v/v, 1:1)			465	653
chloroform	433	71100	498	559
			470	905
dichloromethane	432	80500	500	586
			471	868

a: slits: 2.5, 2.5 nm

Table S3. Photophysical properties of compound **4** (1.0×10^{-5} M) in various solvents.

Solvent	λ_{abs} (nm)	ε ($M^{-1} \cdot cm^{-1}$)	λ_F (nm)	IF[a]
acetone	432	49800	495	491
	370	46500	468	701
acetone/water	429	34000	494	222
(v/v, 1:1)	366	34900	466	285
1,4-dioxane	434	45700	498	474
	374	43800	468	847
1,4-dioxane/water	429	43700	493	306
(v/v, 1:1)	363	39100	468	391
tetrahydrofuran	434	48800	498	447
	376	48800	470	710
tetrahydrofuran/water	432	48900	498	464
(v/v, 1:1)	370	46100	468	640
ethyl acetate	431	45300	495	485
	370	43300	466	808
methylbenzene	437	40000	501	377
	379	39400	471	705
dimethylbenzene	436	40600	501	382
	379	40800	471	709
n-propanol	431	43100	491	453
	368	39400	465	720
n-propanol/water	428	40900	492	349
(v/v, 1:1)	365	37700	466	488
chloroform	434	45200	500	424
	377	41900	470	745
dichloromethane	434	49600	498	464
	376	46600	471	742

a: slits: 2.5, 2.5 nm

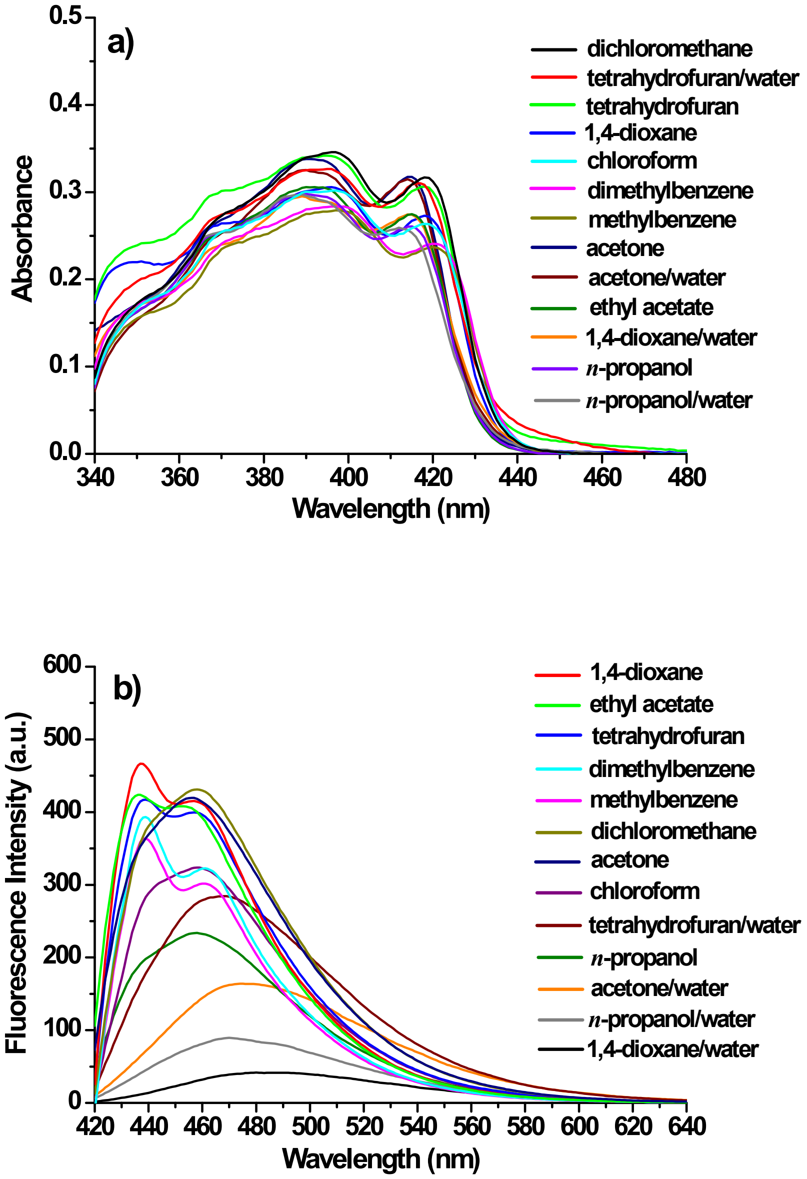


Fig. S7. UV-Vis (a) and fluorescence emission (b) spectra of compound **2** (10 μM) in various solvents. Slits: 2.5, 2.5 nm.

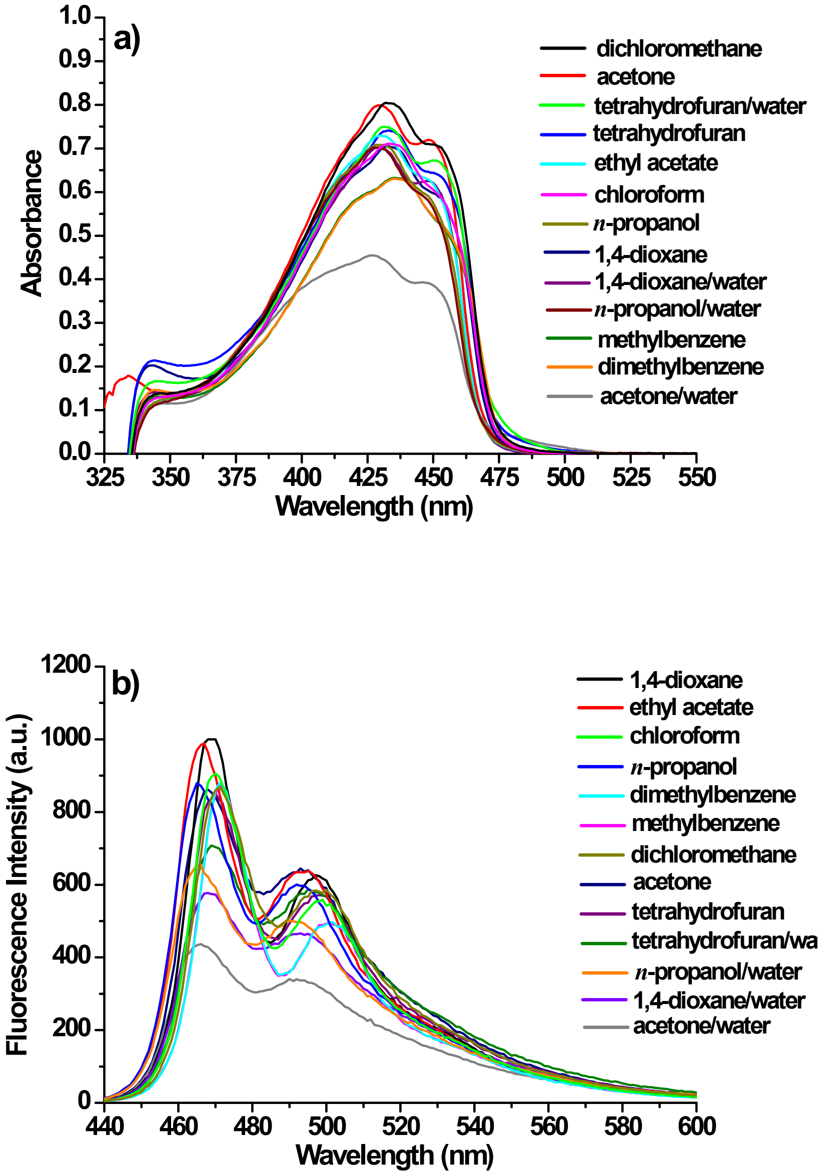


Fig. S8. UV-Vis (a) and fluorescence emission (b) spectra of compound **3** (10 μM) in various solvents. Slits: 2.5, 2.5 nm.

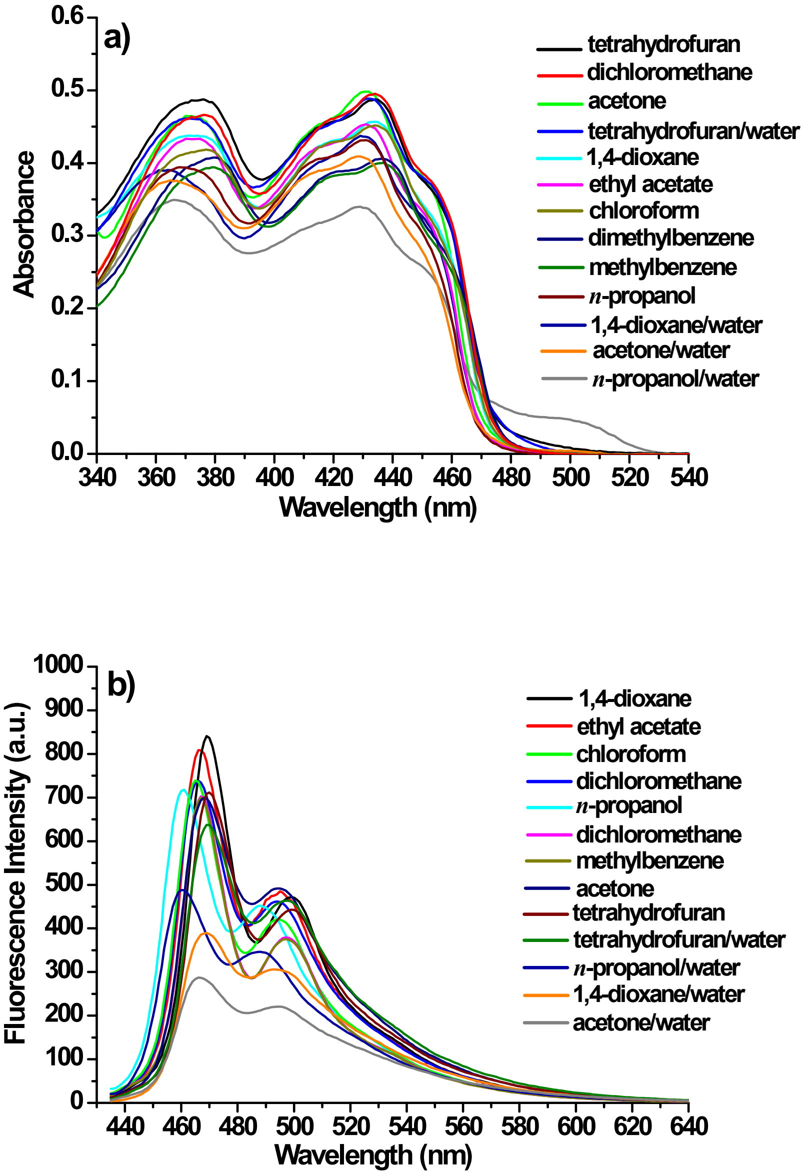


Fig. S9. UV-Vis (a) and fluorescence emission (b) spectra of compound **4** (10 μM) in various solvents. Slits: 2.5, 2.5 nm.

4. Fluorescence response of compounds 2–4 to various metal ions

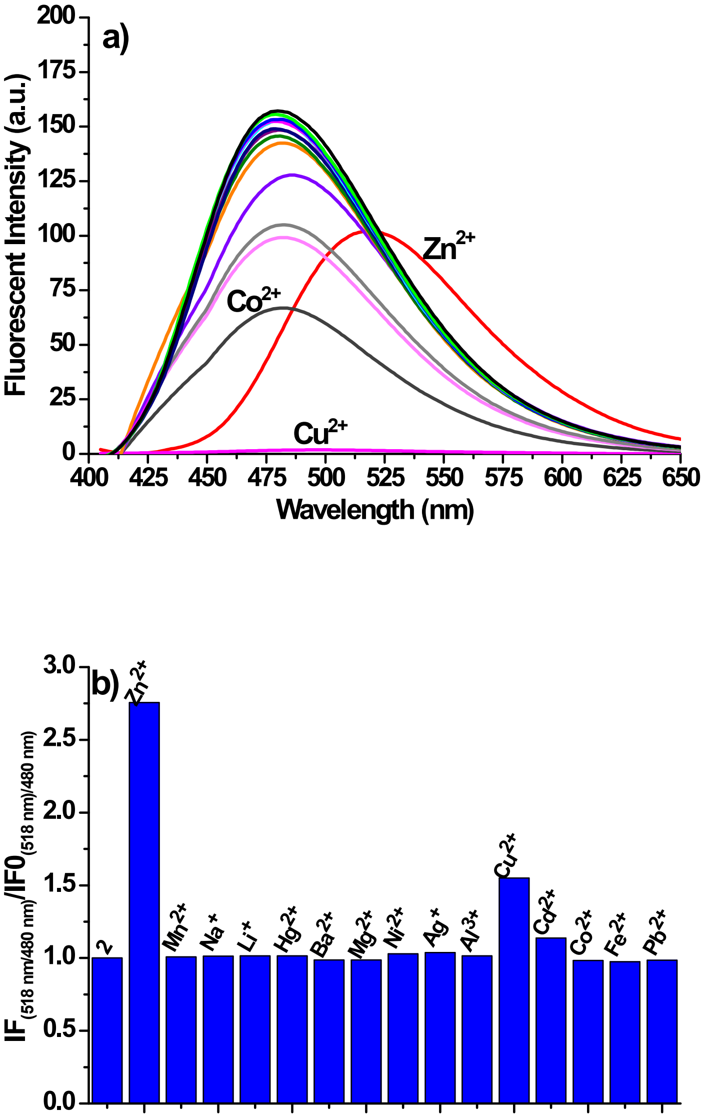


Fig. S10. (a) Fluorescence emission spectra of **2** (10 μM) in the presence of various metal ions (40 μM) in acetone/water (1:1, v/v, 10 mM Tris-HCl, pH 7.2). (b) Fluorescence intensity ratio of **2** (10 μM) at 518 and 480 nm (I_{518nm}/I_{480nm}) in the presence of 4 equiv. various metal ions to free **2** (10 μM) at 518 and 480 nm (I_{518nm}/I_{480nm}) in acetone/water (1:1, v/v, 10 mM Tris-HCl, pH 7.2).

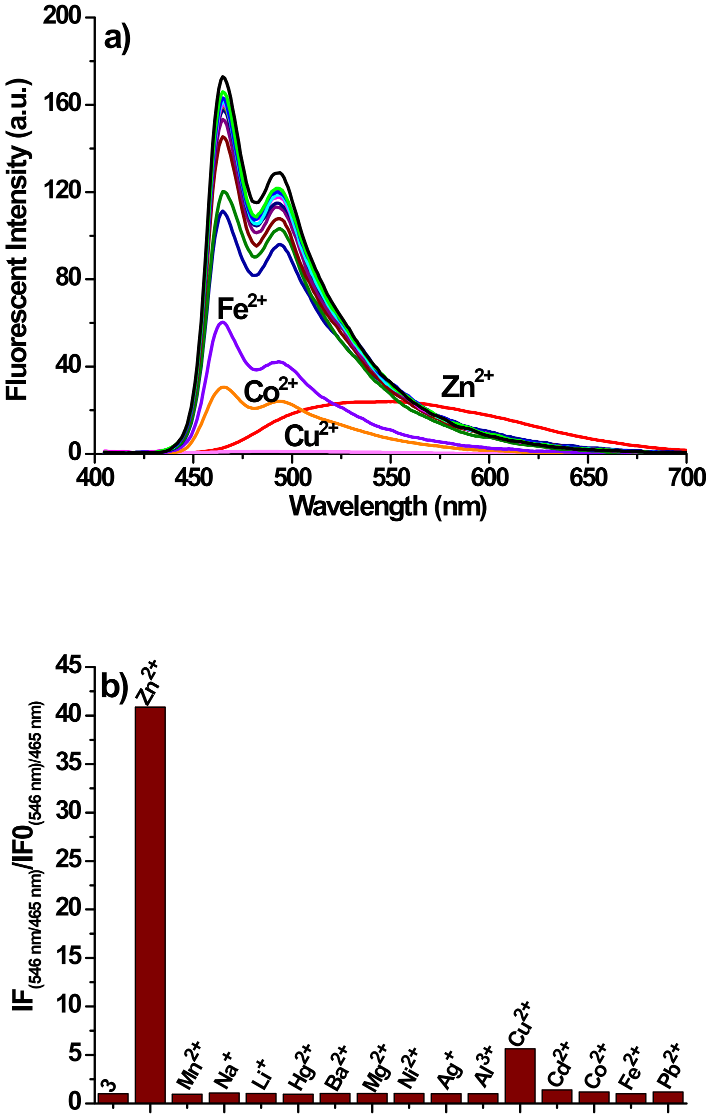


Fig. S11. (a) Fluorescence emission spectra of **3** (10 μM) in the presence of various metal ions (40 μM) in acetone/water (1:1, v/v, 10 mM Tris-HCl, pH 7.2). (b) Fluorescence intensity ratio of **3** (10 μM) at 546 and 465 nm ($I_{546\mathrm{nm}}/I_{465\mathrm{nm}}$) in the presence of 4 equiv. various metal ions to free **3** (10 μM) at 546 and 465 nm ($I_{546\mathrm{nm}}/I_{465\mathrm{nm}}$) in acetone/water (1:1, v/v, 10 mM Tris-HCl, pH 7.2).

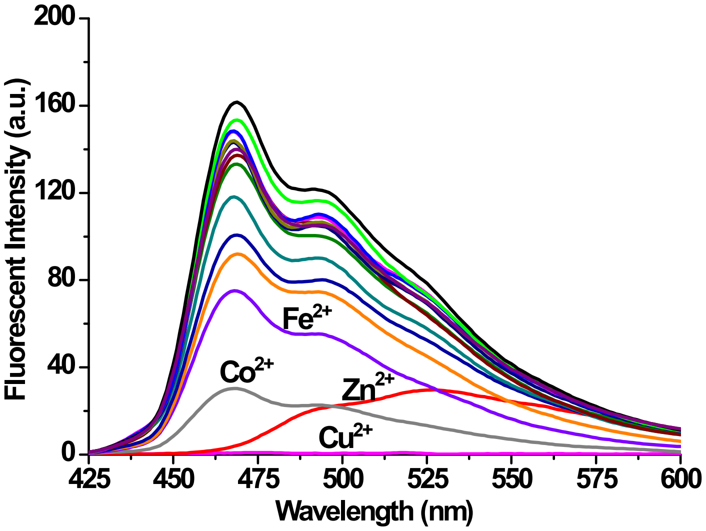


Fig. S12. Fluorescence emission spectra of **4** (10 μM) in the presence of various metal ions (40 μM) in acetone/water (1:1, v/v, 10 mM Tris-HCl, pH 7.2).

5. SEM images of the xerogels of 4 in various solvents

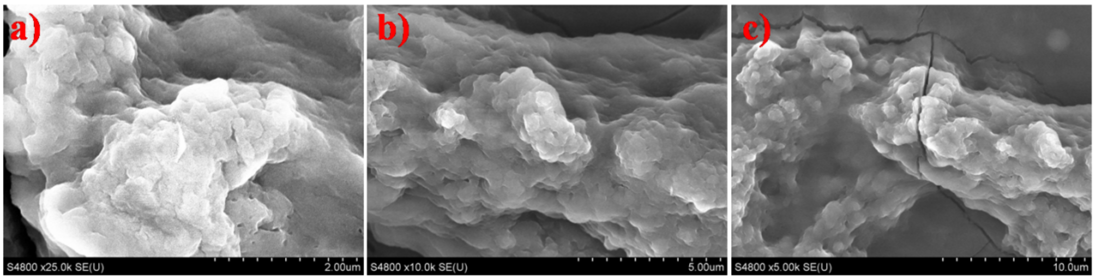


Fig. S13 SEM images of the xerogels of **4** in acetone. Scale bars: (a) 2.0 μm; (b) 5.0 μm; (c) 10.0 μm.

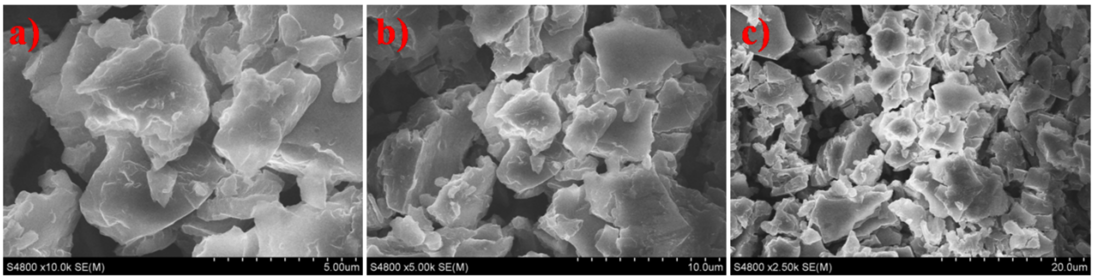


Fig. S14 SEM images of the xerogels of **4** in dioxane. Scale bars: (a) 5.0 μm; (b) 10.0 μm; (c) 20.0 μm.

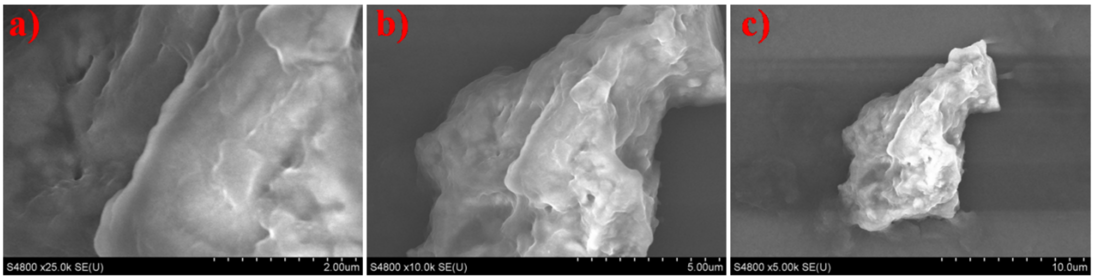


Fig. S15 SEM images of the xerogels of **4** in tetrahydrofuran. Scale bars: (a) 2.0 μm; (b) 5.0 μm; (c) 10.0 μm.

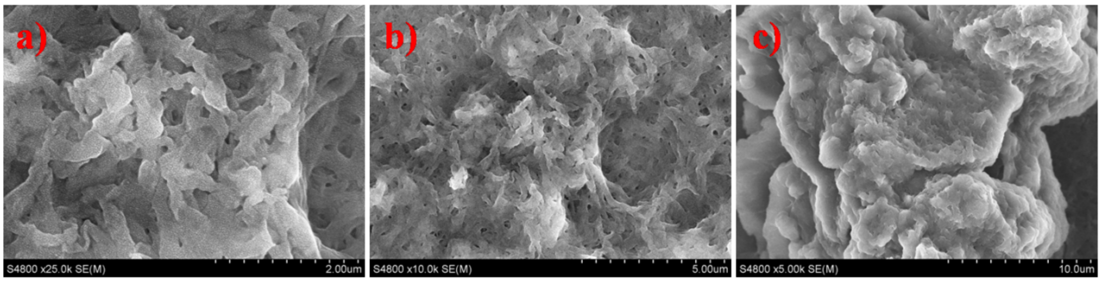


Fig. S16 SEM images of the xerogels of **4** in ethyl acetate. Scale bars: (a) 2.0 μm; (b) 5.0 μm; (c) 10.0 μm.

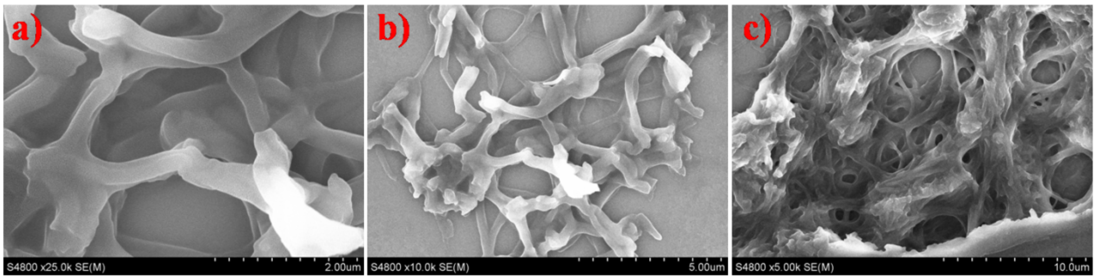


Fig. S17 SEM images of the xerogels of **4** in dichloromethane. Scale bars: (a) 2.0 μm; (b) 5.0 μm; (c) 10.0 μm.

6. The responsive behavior of organogel 4 to Zn^{2+}

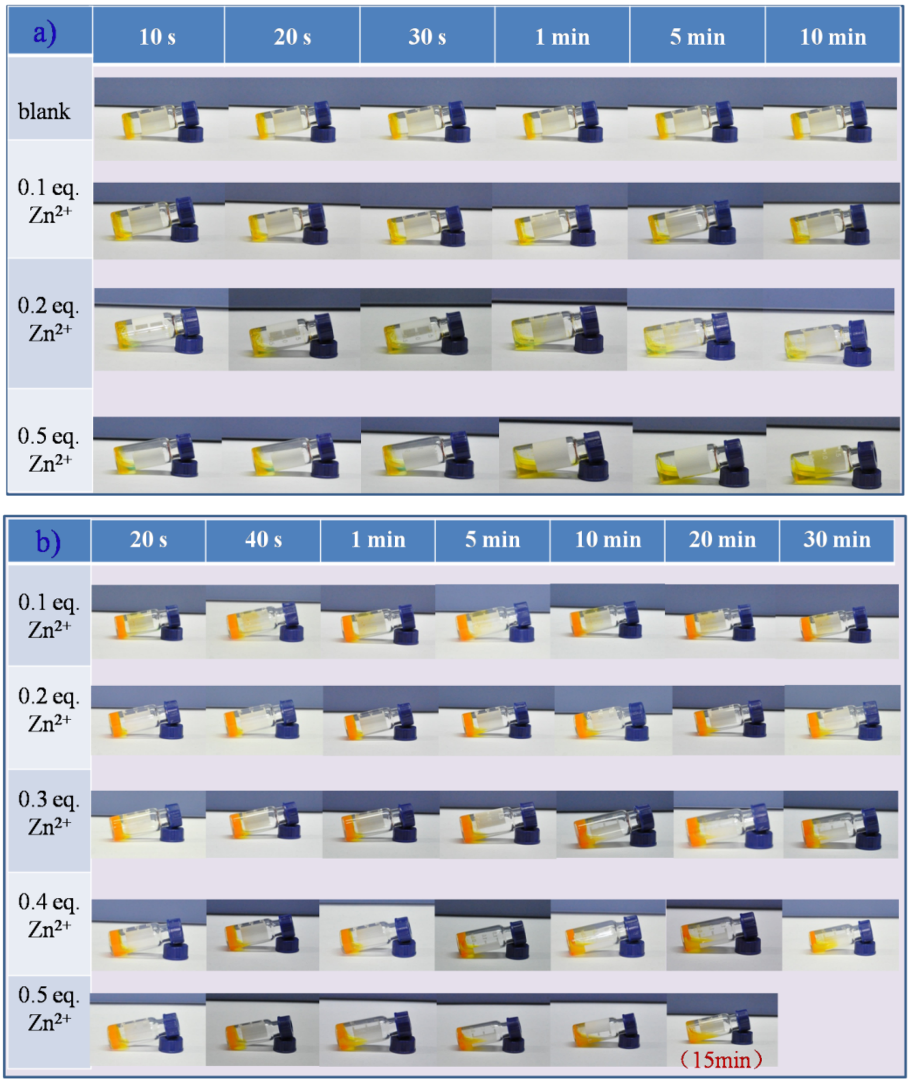


Fig. S18 Photographs demonstrating of the gel–sol transition of **4** in acetone (a) and dioxane (b) by addition of Zn^{2+} with different concentrations and different time. (10 s, 40 s and so on means the time after adding Zn^{2+} to the gel of **4**, 0.1 eq. Zn^{2+}, 0.2 eq. Zn^{2+} and so on means the concentration of Zn^{2+} added to the gel of **4**)