Supporting Information

A luminescent 2D coordination polymer for selective sensing of nitrobenzene

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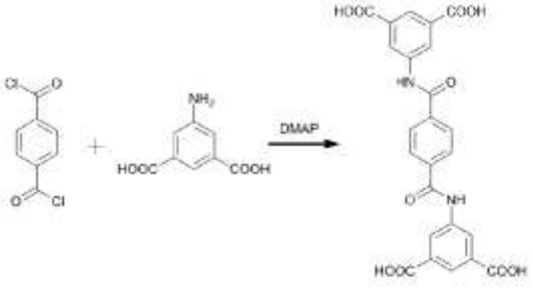
1. Materials and methods

All the chemicals were obtained from commercial sources and used as received. *Bis*-(3,5-dicarboxy-phenyl)terephthalamide (H_4L) was prepared according to the literature.[1] ^1H NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz in DMSO. The chemical shifts in the ^1H NMR spectra are reported in ppm relative to tetramethylsilane (TMS) as internal standard (0.0 ppm). Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. IR spectra were measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. The luminescence spectra for the powered solid samples immersed in different solvents were measured on a SHIMADZU RF-5301PC spectrofluorimeter, and the solid state photoluminescent spectra for the powdered solid samples were measured on a Hitachi F-4500 fluorescence spectrophotometer. All the measurements were carried out under the same experimental condition.

2. Synthesis and general characterizations



5-Aminoisophthalic acid (62 mmol, 11.23g) and 4-(dimethylamino)pyridine (DMAP, 6.2 mmol, 0.76g) were dissolved in 150 mL of anhydrous *N*,*N*'-dimethylacetamide under N_2. Terephthaloyl chloride (30 mmol, 6.09g) was dissolved with 50 mL of anhydrous *N*,*N*'-dimethylacetamide and added in drops. The mixture was stirred under nitrogen for 48h, and then 200 mL of 5% HCl was added to precipitate the product and dissolve the excess 5-aminoisophthalic acid and DMAP. The solid was washed by another 100 mL of 5% HCl followed by 50 mL of water and 50 mL ethanol. The damp product was kept in oven overnight to give a white powder. Yield 13.28 g (90%). Data for H_4L: Selected IR (KBr, cm^{-1}): 3376(b), 1716(s), 1678(m), 1558(vs), 1508(s), 1338(m), 1282(m), 1252(m), 1196(s), 759(m), 667(m). ^1H NMR (DMSO-d_6, δ ppm): 13.32 (4H, COOH), 10.77 (2H, CONH), 8.70 (4H, ArH), 8.24(2H, ArH), 8.17(4H, ArH). ^1H NMR spectrum and IR spectra of H_4L were shown in Fig. S1 and Fig. S2, respectively.

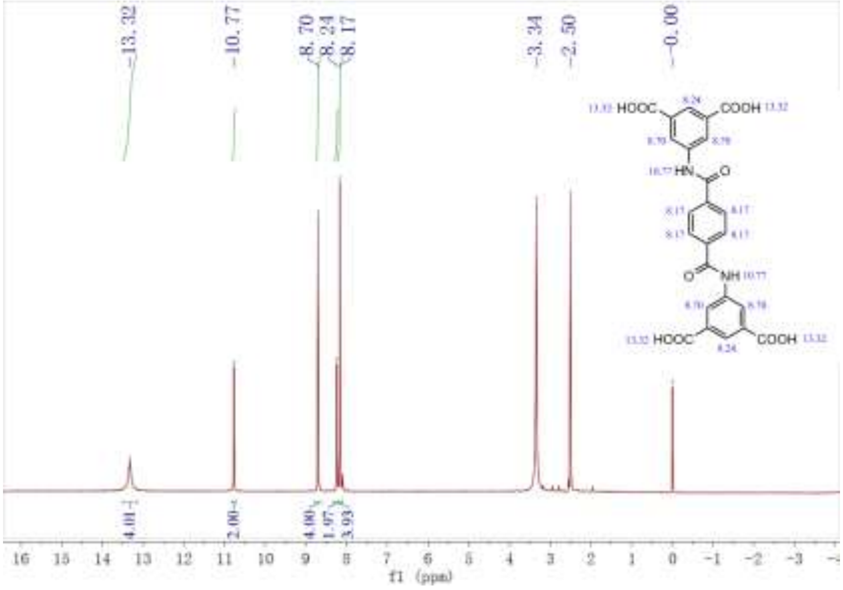


Fig. S1. ^{1}H NMR spectrum of H_4L.

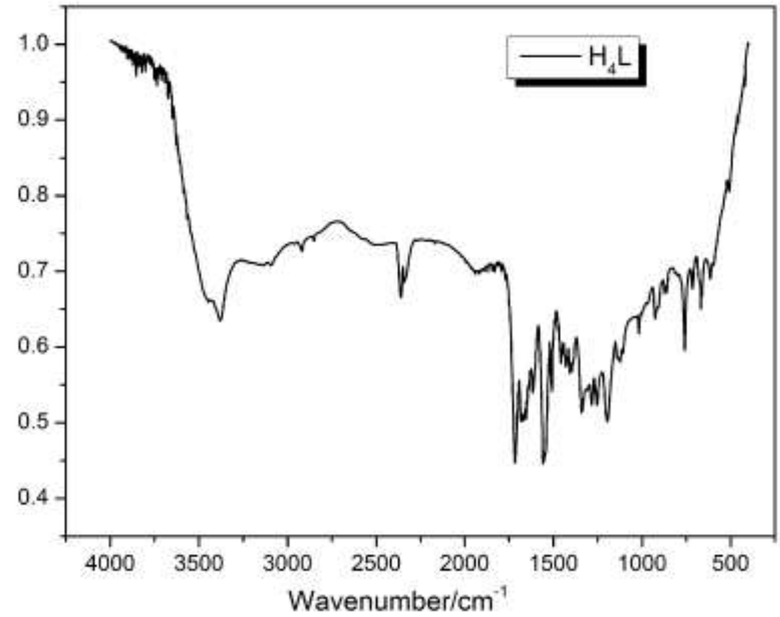


Fig. S2. IR spectrum of the ligand.

3. Synthesis of $[Zn_2(L)(bipy)(H_2O)_2]\cdot(H_2O)_3(DMF)_2$ (1)

H_4L (25 mg, 0.05 mmol) and 4,4'-bipyridine (7.8 mg, 0.05 mmol) were added to a mixture of 2 mL DMF/H_2O (3:1 in v/v) in a 10 mL vial. To this mixture, $Zn(NO_3)_2\cdot 6H_2O$ (45 mg, 0.15 mmol) was added. The vial was then sealed, heated to 75°C for 3 days, and the colorless block crystals of **1** were collected, washed with DMF, and dried in air. Yield: 42 mg, 83% based on H_4L. Anal. Calcd for $C_{40}H_{44}N_6O_{17}Zn_2$ (%): C, 47.49; H, 4.38; N, 8.31. Found: C, 47.79; H, 4.19; N, 8.19.

CCDC 937930 contains the supplementary crystallographic data for compound **1**. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

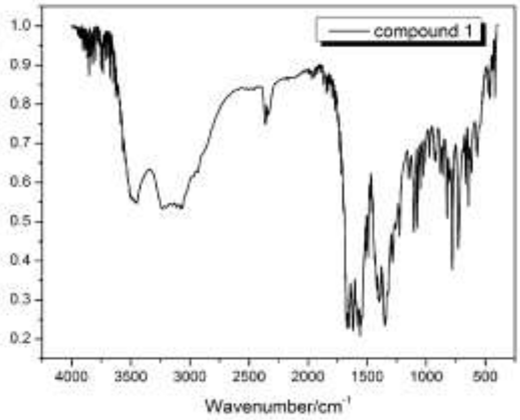


Fig. S3. IR spectrum of the compound **1**.

4. Power X-ray diffraction and thermogravimetric analysis

The powder X-ray diffraction spectra (PXRD) were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the PXRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury program version 3.0. Thermogravimetric (TG) analyses were carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10°C min^{-1} from ambient temperature to 700°C, an empty Al_2O_3 crucible was used as reference. The first weight loss observed from 110 to 226°C is attributed to the loss of guest molecules including three water molecules and two DMF molecules, with a weight loss of 19.42% (calculated 19.79%). Compound **1** is found to be stable up to about 376°C. The decomposition of the network began from 376 to 500°C.

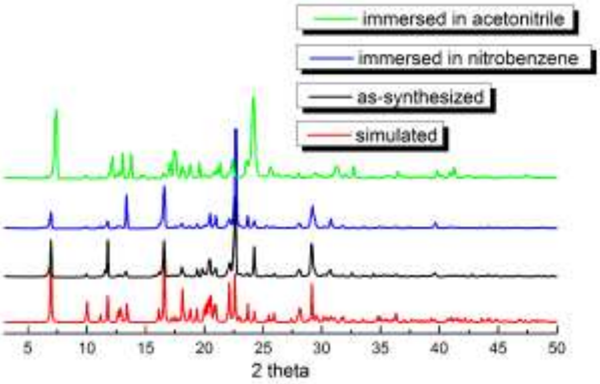


Fig. S4. PXRD patterns of compound **1**.

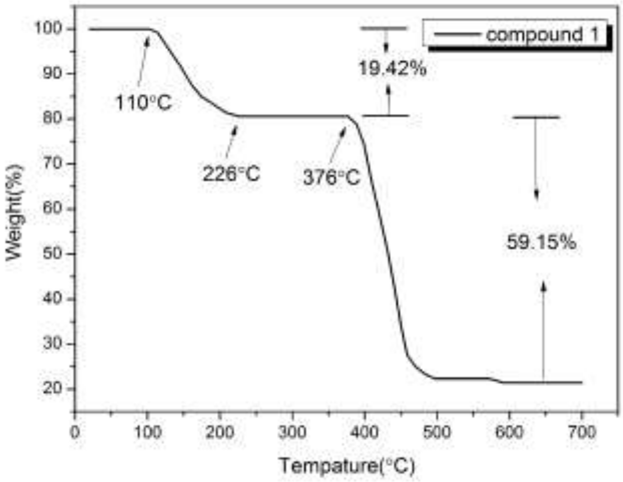


Fig. S5. Thermogravimetric analyses (TGA) curve for compound **1**.

5. Single crystal X-ray diffraction analysis

X-ray single-crystal diffraction data for compound **1** was collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo−Kα radiation (λ = 0.71073 Å) by ω scan mode. The program SAINT[2] was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semiempirical absorption corrections were applied using SADABS program).[3] Metal atoms in each complex were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. Hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. However, the hydrogen atoms of the water molecules were added by difference Fourier maps and refined with constrained. Guest solvent DMF molecules were highly disordered and were impossible to refine using conventional discrete-atom models. To resolve these issues, the contribution of DMF solvent electron density was removed by the SQUEEZE routine in PLATON.[4] Detailed crystallographic parameters are summarized in Table S1. The selected bond lengths and angles are given in Table S2, and hydrogen bonds are shown in Table S3.

Table S1. Crystal data and structure refinement for compound **1**.

	Compound **1**	
Empirical formula	$C_{17}H_{14}N_2O_7Zn$	
Formula weight	423.69	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, *P*-1	
Unit cell dimensions	a = 9.5010(19) Å	α = 95.85(3) deg.
	b = 9.6299(19) Å	β = 91.86(3) deg.
	c = 12.795(3) Å	γ = 111.73(3) deg.
Volume	1078.7(4) $Å^3$	
Z, Calculated density	2, 1.304 g/cm^3	
Absorption coefficient	1.174 mm^{-1}	
F(000)	432	
Crystal size	0.25 × 0.23 × 0.20 mm	
Theta range for data collection	3.09 to 27.48 deg	
Reflections collected / unique	9043 / 4954 [R(int) = 0.0281]	
Completeness to theta	98.40%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.791 and 0.753	
Goodness-of-fit	1.101	
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1143	
R indices (all data)	R1 = 0.0631, wR2 = 0.1235	

Table S2. Selected bond Lengths and angles for compound **1**.

Bond	Length (Å)	Angle	Deg. (°)
N(2)-Zn(1)	2.047(2)	O(4)#4-Zn(1)-O(1)	118.54(10)
O(6)-Zn(1)	2.000(3)	O(4)#4-Zn(1)-O(6)	109.30(12)
O(1)-Zn(1)	1.940(2)	O(1)-Zn(1)-O(6)	106.40(11)
O(4)-Zn(1)#3	1.925(2)	O(4)#4-Zn(1)-N(2)	125.05(10)
		O(1)-Zn(1)-N(2)	97.69(10)
		O(6)-Zn(1)-N(2)	96.68(11)

Table S3. Hydrogen bonds for compound **1** [Å and deg.].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(7W)-H(7WB)···O(5)#5	0.85	1.96	2.801(4)	170.4
O(7W)-H(7WA)···O(2)#6	0.85	2.09	2.928(4)	167.7
O(6)-H(6B)···O(3)#7	0.85	1.82	2.658(3)	167.7
O(6)-H(6A)···O(7W)#8	0.85	1.94	2.681(4)	144.2

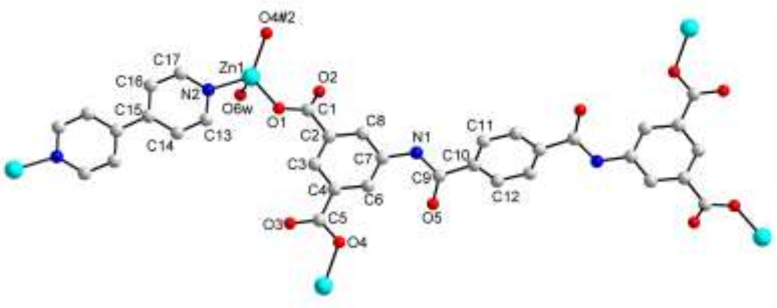


Fig. S6. The coordination environment of Zn(II) ions, bipy and L^{4-} ligand in **1**. Guest solvent molecules and H atoms are omitted for clarity.

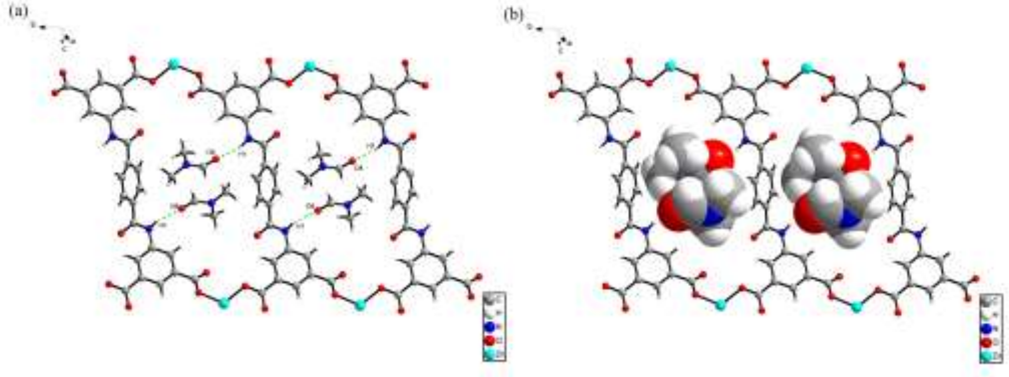


Fig. S7. (a) Hydrogen bonds between the imino groups and free DMF molecules inside the single layer. Hydrogen bonds are shown as green dashed line. (b) View of the free DMF molecules shown in space filling mode inside the single layer.

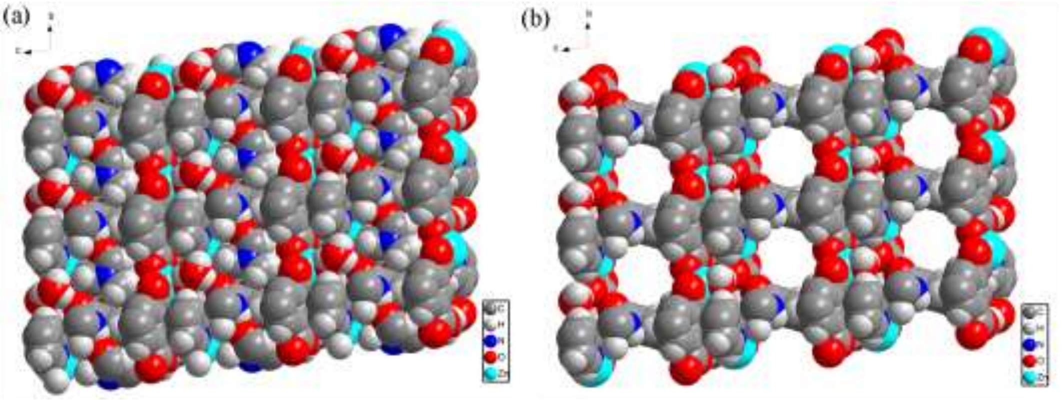


Fig. S8. Comparison of the space-filling representations of compound **1** between actual pore (a) and solvent-free channels (b) along the *a* axis.

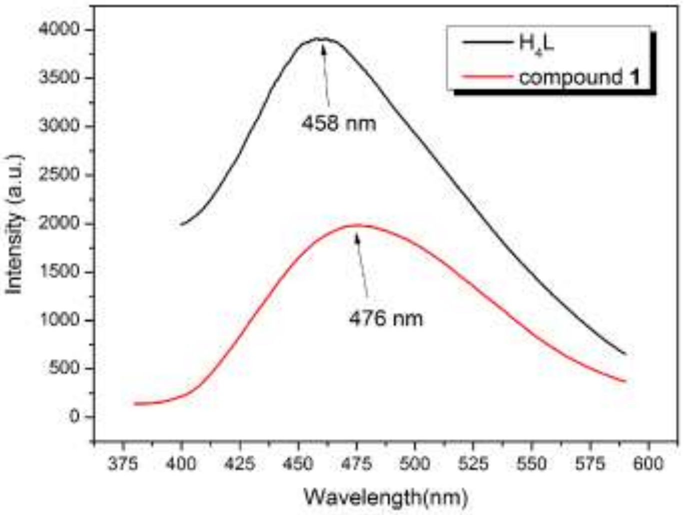


Fig. S9. Solid-state photoluminescent spectra of free H_4L ligand (black, λ_{ex} = 363 nm) and compound **1** (red, λ_{ex} = 350 nm) at room temperature.

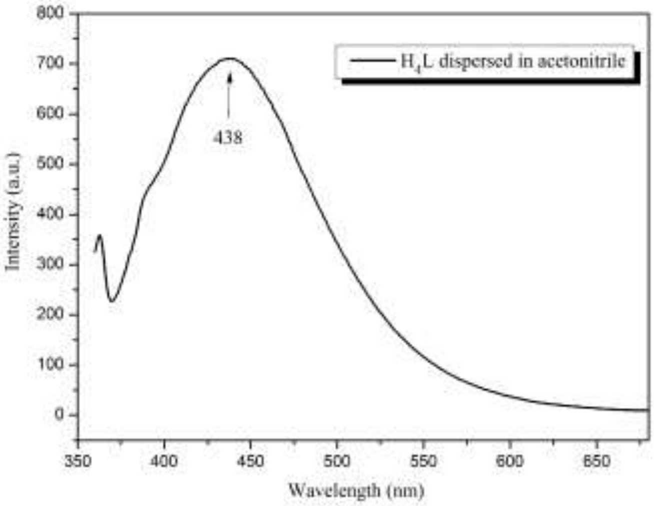


Fig. S10. Emission spectra of free H_4L ligand dispersed in acetonitrile when excited at 340 nm.

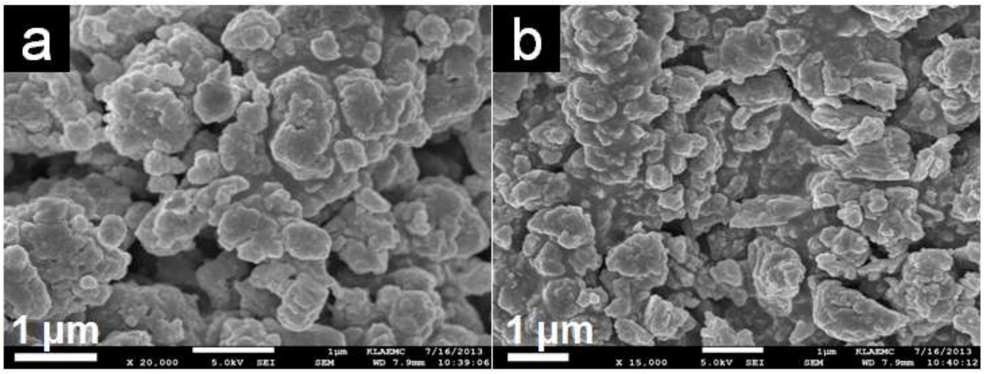


Fig. S11. Typical SEM image of the grinded sample of compound **1**.

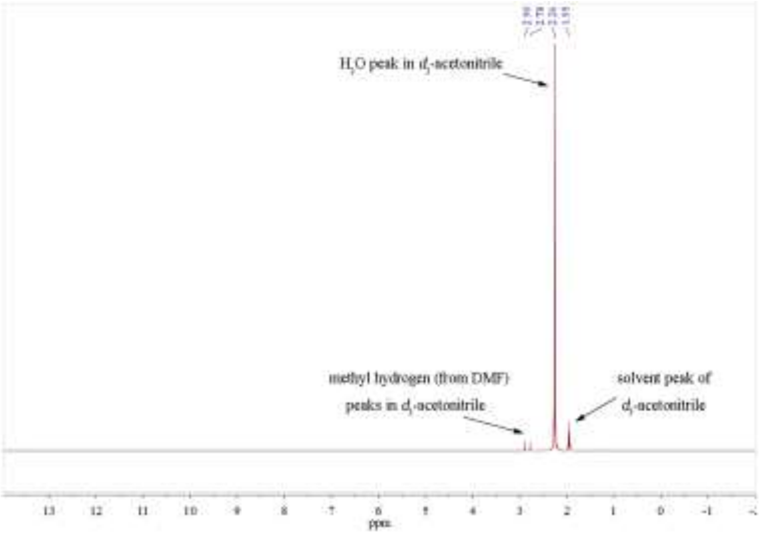


Fig. S12. ^{1}H NMR spectrum of the filtrate of compound **1** dispersed in d_3-acetonitrile after ultrasonication.

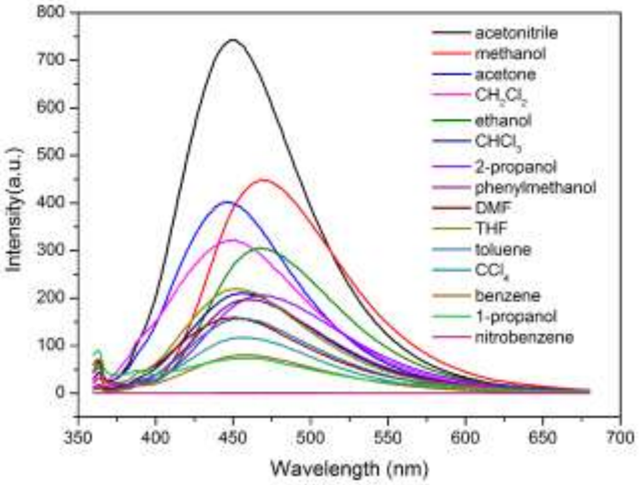


Fig. S13. Emission spectra of compound **1** in different solvents when excited at 350 nm.

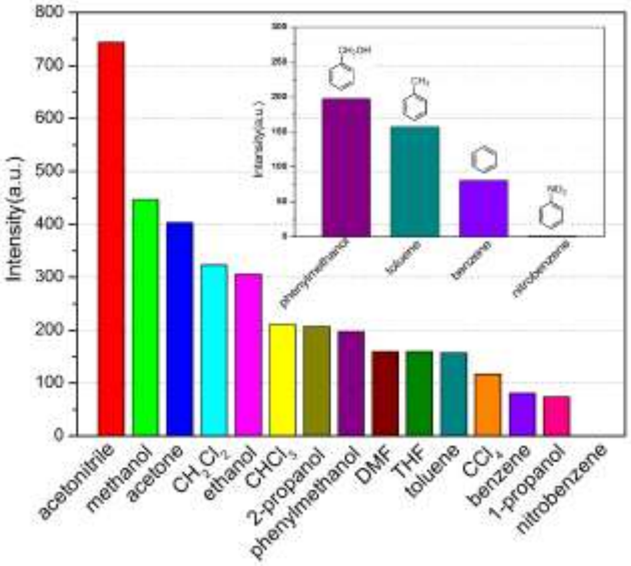


Fig. S14. Emission intensities of **1** in different solvents when excited at 350 nm. Inset: Emission intensities of **1** in aromatics with different substituents.

6. Fluorescence quenching titrations in dispersed medium

The fluorescence of compound **1** was measured by dispersing 3 mg of grounded sample in 3 mL acetonitrile and subsequently placed in a quartz cell of 1 cm width. All titrations were carried out by gradually adding nitrobenzene in an incremental fashion. Their corresponding fluorescence emission spectra were recorded at 298 K. Each titration was repeated several times to get concordant value. For all measurement, disperse solutions of **1** were excited at λ_{ex} = 350 nm and their corresponding emission wavelength was monitored from 360 to 680 nm. There was no change in shape of the emission spectra by gradual addition of nitrobenzene to disperse solution of **1** in acetonitrile, only quenching of the initial fluorescence emission intensity was observed. The fluorescence efficiency was calculated by $[(F_0\text{-}F)/F_0]\times100\%$ (F_0 is the initial fluorescence intensity).

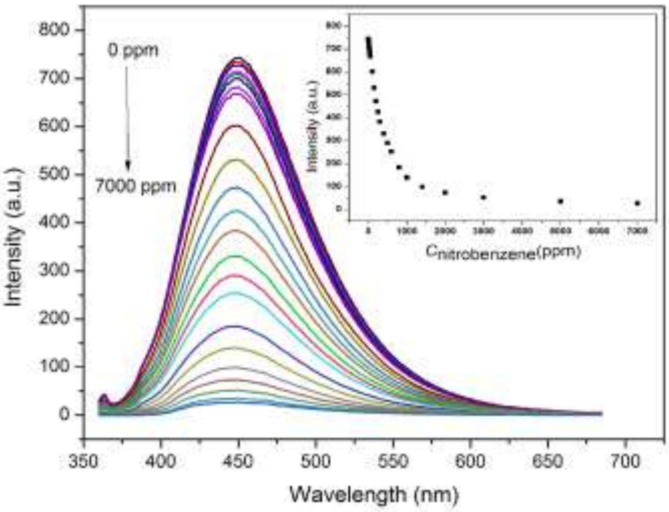


Fig. S15. Fluorescence titration of compound **1** dispersed in acetonitrile with the addition of different concentrations of nitrobenzene. Excitation wavelength was 350 nm and fluorescence emission was monitored from 360 nm to 680 nm. Inset: Plot of the maximum fluorescence emission of compound **1** dispersed in acetonitrile at different concentrations of nitrobenzene. Emission intensities at 450 nm were selected.

References

1 D. Hu and R. Kluger, *Biochemistry*, 2008, **47**, 12551.

2 *SAINT Software Reference Manual*; Bruker AXS: Madison, WI, 1998.

3 G. M. Sheldrick, *SHELXTL NT Version 5.1*. *Program for Solution and Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany: 1997.

4 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.