

Supporting Information

Two coordination polymers with enhanced ligand-centered luminescence and assembly imparted sensing ability for acetone

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Experimental details

1. Materials and Methods

All the chemicals were obtained from commercial sources and used without further purification. 2,4,6-tris[4-(1H-imidazole-1-yl)]-benzene (Tipb) was prepared according to the literature.¹ IR spectra were measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. All the photoluminescent spectra for powered solid samples or liquid suspensions were recorded on a Varian Cary Eclipse spectrofluorimeter.

2. Synthesis of [Cd(tipb)(pta)_{0.5}(NO₃)(H₂O)]·(DMF)_x(H₂O)_y (**1**) and [Cd(tipb)(mta)] (DMF)_x(H₂O)_y (**2**)

Tipb (0.05 mmol), Cd(NO₃)₂·6H₂O (0.05 mmol) and H₂pta (0.05 mmol) were dissolved in a mixture solvent of DMF (2.0 mL), ethanol (0.5 mL) and distilled water (0.5 mL), to which 3 drops of pyridine was then added. Colorless block crystals of **1** were obtained by the solvothermal reaction at 85 °C for three days in a vial (10 mL). The samples of **1** were washed with DMF and dried in air. Yield: 21 mg, 54.05% based on Tipb. The colorless block crystals of **2** were synthesized in the same condition except that H₂mta was added instead of H₂pta as auxiliary ligand. Yield: 26 mg, 67.10% based on Tipb.

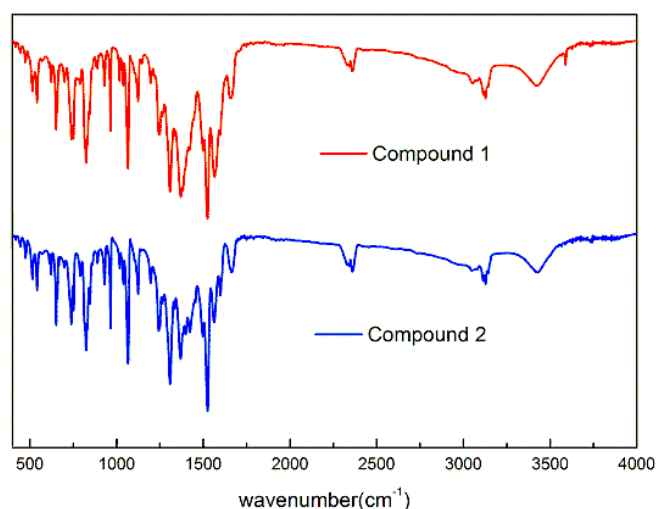


Fig. S1 IR spectra of compounds **1** and **2**.

3. Single crystal X-ray diffraction analysis

X-ray single-crystal diffraction data for compounds **1** and **2** were collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) by ω scan mode. The program SAINT² was used for the integration of diffraction profiles. All the structures were solved by direct method using the SHELXS program of 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 compound 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 . The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The hydrogen atoms of water molecules were added by difference Fourier maps and refined with constrained. Guest solvent H₂O and DMF molecules in compounds **1** and **2** are highly disordered and impossible to be refined using conventional discrete-atom models. The contribution of DMF solvent electron density was removed by the SQUEEZE routine in PLATON in order to resolve the problems⁴.

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 Al₂O₃ crucible was used as reference.

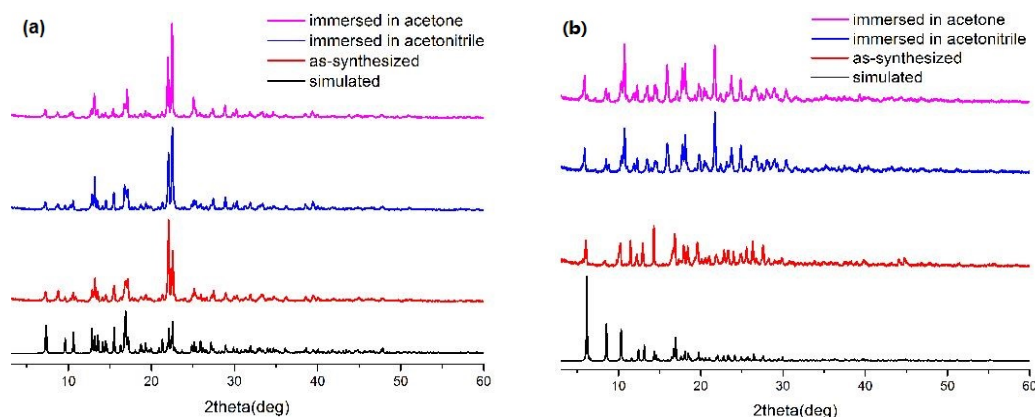


Fig. S2 PXRD patterns of compounds (a) **1** and (b) **2**.

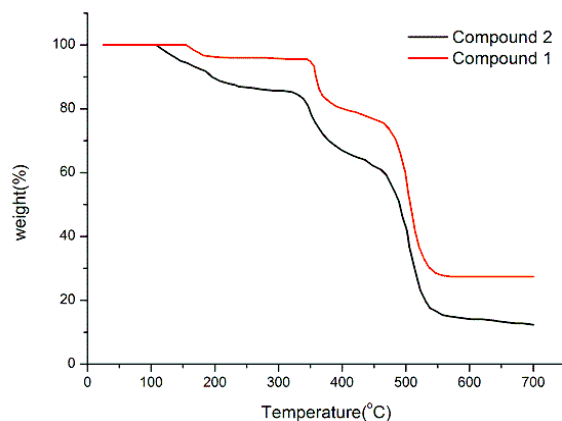


Fig. S3 Thermogravimetric analysis (TGA) curves for compounds **1** and **2**.

5. Fluorescence titrations

The fluorescence spectra of compounds **1** and **2** were measured with 3 mL of their suspensions in acetonitrile (1 mg/mL) at 298 K. All titrations were carried out by the gradual addition of acetone in an incremental fashion. Each titration was repeated several times to get concordant values. No shape change but only intensity decrease was observed in the emission spectra during the titration process. The fluorescence quenching efficiency was calculated with $(1 - I/I_0) \times 100\%$, I_0 and I are respectively the fluorescence intensities before and after the addition of acetone.

6. Detection of gas phase acetone

These experiments were carried out with a CP loaded plate, which was prepared by daubing the slurry of ~50 mg power CP sample and 0.2 mL ethanol on a quartz plate. After the evaporation of ethanol, the CP powder produced a coating on the substrate. This CP loaded plate was placed diagonally in an optical quartz cuvette. After placing an acetone containing capillary (providing acetone vapor) within and sealing, this home-made setup was immediately subject to fluorescence measurement with the excitation at 280 nm.

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

Empirical formula	C ₃₇ H ₂₆ N ₇ O ₆ Cd
Formula weight	775.05
Temperature	293(2) K
Crystal system	Triclinic
space group	P-1
Unit cell dimensions	
a(Å)	11.010(2)
b(Å)	12.821(3)
c(Å)	12.932(3)
α(deg)	91.21(3)
β(deg)	110.33(3)
γ(deg)	106.46(3)
Volume(Å ³)	1627.0(6)
Z	2
Calculated density (mg/m ³)	1.582
Absorption coefficient	0.731 mm ⁻¹
F(000)	784
Limiting indices	-14<=h<=14, -16<=k<=16, -16<=l<=16
Reflections collected / unique	17448 / 7458 [R(int) = 0.0452]
Completeness to theta = 27.48	99.8 %
Goodness-of-fit on F ²	1.099
Final R indices [I>2σ(I)]	R1 = 0.0510, wR2 = 0.0869
R indices (all data)	R1 = 0.0729, wR2 = 0.0936

Table S2 Bond lengths [Å] and angles [°] for compound **1**

Cd(1)-N(3)#1	2.291(3)	N(3)#1-Cd(1)-N(1)	91.50(11)
Cd(1)-N(1)	2.324(3)	N(3)#1-Cd(1)-N(5)#2	167.48(11)
Cd(1)-N(5)#2	2.330(3)	N(1)-Cd(1)-N(5)#2	86.44(11)
Cd(1)-O(1)	2.345(3)	N(3)#1-Cd(1)-O(1)	84.36(11)
Cd(1)-O(6)	2.349(3)	N(1)-Cd(1)-O(1)	95.26(11)
Cd(1)-O(3)	2.436(3)	N(5)#2-Cd(1)-O(1)	83.54(10)
		N(3)#1-Cd(1)-O(6)	86.70(10)
		N(1)-Cd(1)-O(6)	177.57(10)
		N(5)#2-Cd(1)-O(6)	95.67(10)
		O(1)-Cd(1)-O(6)	86.20(10)
		N(3)#1-Cd(1)-O(3)	105.83(12)
		N(1)-Cd(1)-O(3)	101.92(11)
		N(5)#2-Cd(1)-O(3)	86.67(11)
		O(1)-Cd(1)-O(3)	159.63(10)
		O(6)-Cd(1)-O(3)	77.03(10)

Table S3 Crystal data and structure refinement for compound **2**

Empirical formula	C ₄₁ H ₂₈ N ₆ O ₄ Cd
Formula weight	781.10
Temperature	293(2) K
Crystal system	Monoclinic
space group	P21/c
Unit cell dimensions	
a (Å)	10.390(2)
b (Å)	15.238(3)
c (Å)	28.827(6)
α(deg)	90
β(deg)	95.33(3)
γ(deg)	90
Volume(Å ³)	4544.2(16)
Z	4
Calculated density (mg/m ³)	1.060
Absorption coefficient	0.521 mm ⁻¹
F(000)	1584.0
Limiting indices	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected / unique	40880 / 10423 [R(int) = 0.1338]
Completeness to theta = 27.48	99.8 %
Goodness-of-fit on F ²	1.000
Final R indices [I > 2σ(I)]	R1 = 0.0846, wR2 = 0.2020
R indices (all data)	R1 = 0.1942, wR2 = 0.2437

Table S4 Bond lengths [Å] and angles [°] for compound **2**

Cd(2)-O(3)#1	2.279(5)	O(3)#1-Cd(2)-N(5)#2	129.6(2)
Cd(2)-N(5)#2	2.301(6)	O(3)#1-Cd(2)-N(1)#3	92.4(2)
Cd(2)-N(1)#3	2.318(6)	N(5)#2-Cd(2)-N(1)#3	94.5(2)
Cd(2)-N(3)	2.350(6)	O(3)#1-Cd(2)-N(3)	89.8(2)
Cd(2)-O(1)	2.371(5)	N(5)#2-Cd(2)-N(3)	87.2(2)
Cd(2)-O(2)	2.527(5)	N(1)#3-Cd(2)-N(3)	175.4(2)
N(1)-Cd(2)#4	2.318(6)	O(3)#1-Cd(2)-O(1)	89.98(18)
N(5)-Cd(2)#5	2.301(6)	N(5)#2-Cd(2)-O(1)	140.17(19)
O(3)-Cd(2)#6	2.279(5)	N(1)#3-Cd(2)-O(1)	86.8(2)

Table S5 A literature survey about the performance of the reported CP-based acetone sensors

CP	quenching efficiency with other organics	Detected minimal amount of acetone	Ref.
Eu(BTC)(H ₂ O)·1.5H ₂ O	-70–36%	0.3 vol. %	5
Yb(BPT)(H ₂ O)·(DMF) _{1.5} (H ₂ O) _{1.25}	-133–86%	0.5 vol. %	6
Eu ₂ (pzdc)(pzdc)(ox)(H ₂ O) ₄ ·8H ₂ O	1–46%	0.5 vol. %	7
Tb(BTC)(H ₂ O) ₆	-56–21%	0.3 vol. %	8
Cd ₃ (L)(H ₂ O) ₂ (DMF) ₂ ·5DMF	-71–52%	0.1 vol. %	9
Cd ₃ (L)(dib)·3H ₂ O·5DMA	-52–35%	0.1 vol. %	9

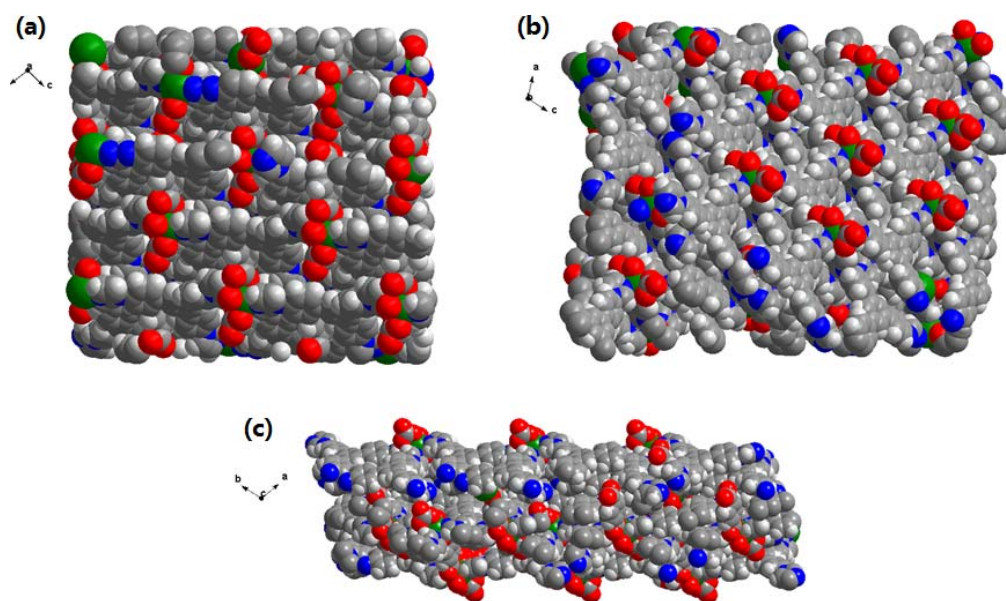


Fig. S4 The space-filling representations of compound **1** viewed along (a) *a*, (b) *b*, (c) *c* axes. Guest solvent molecules and H atoms are omitted for clarity.

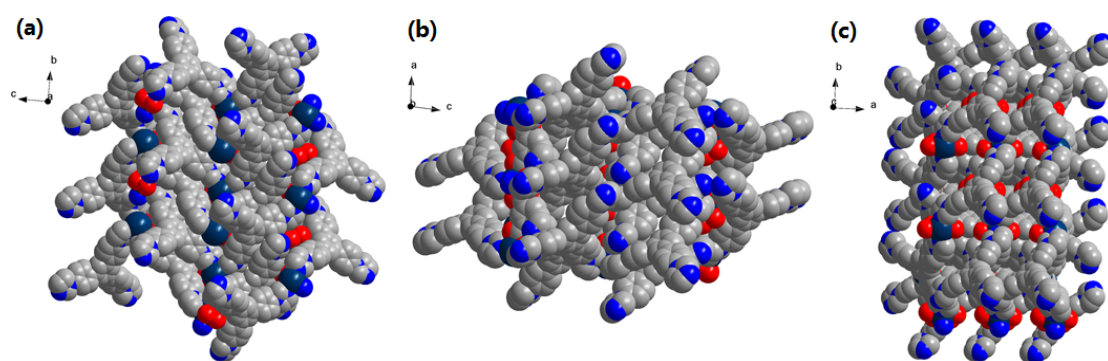


Fig. S5 The space-filling representations of compound **2** viewed along (a) *a*, (b) *b*, (c) *c* axes. Guest solvent molecules and H atoms are omitted for clarity.

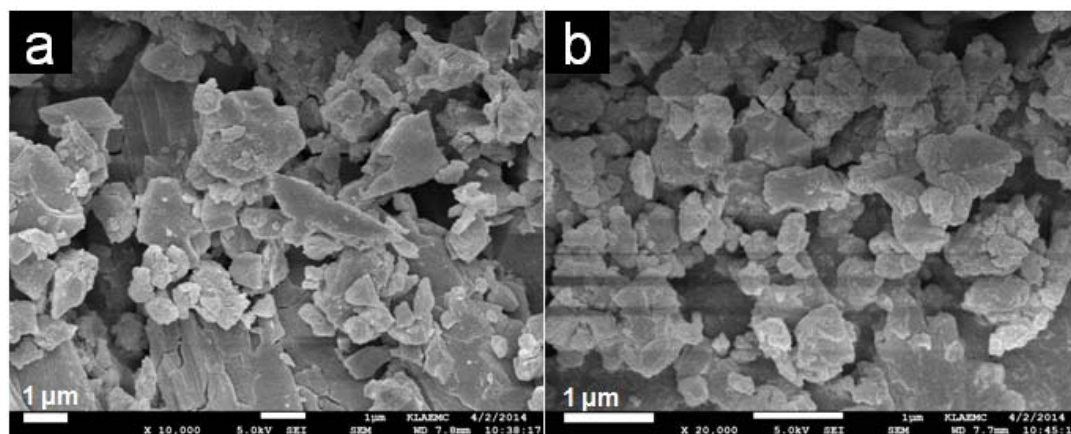


Fig. S6 SEM photographs of the ground samples of (a) **1** and (b) **2**.

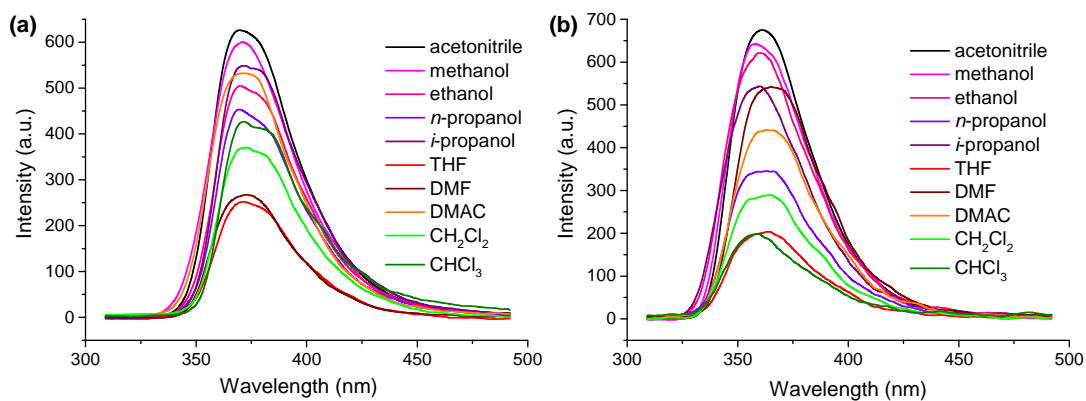


Fig. S7 Emission spectra of compounds (a) **1** and (b) **2** dispersed in different organic solvents, $\lambda_{\text{ex}} = 280$ nm.

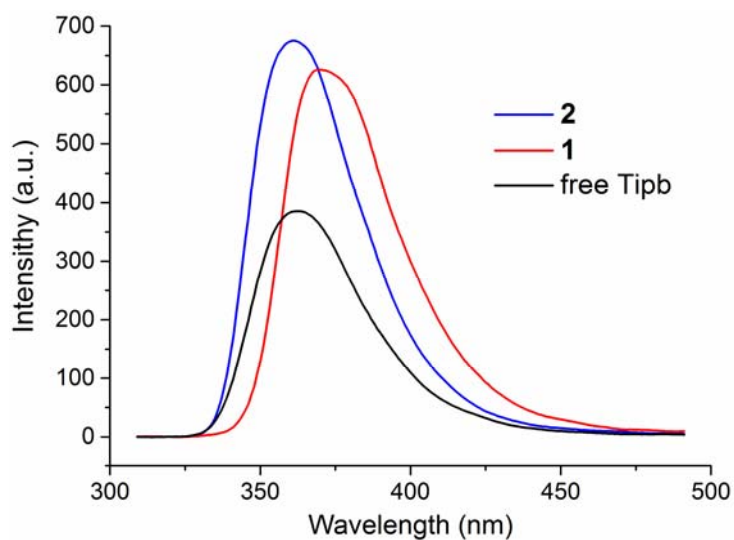


Fig. S8 Emission spectra of compounds **1**, **2** and Ttipb ligand dispersed in acetonitrile, $\lambda_{\text{ex}} = 280$ nm.

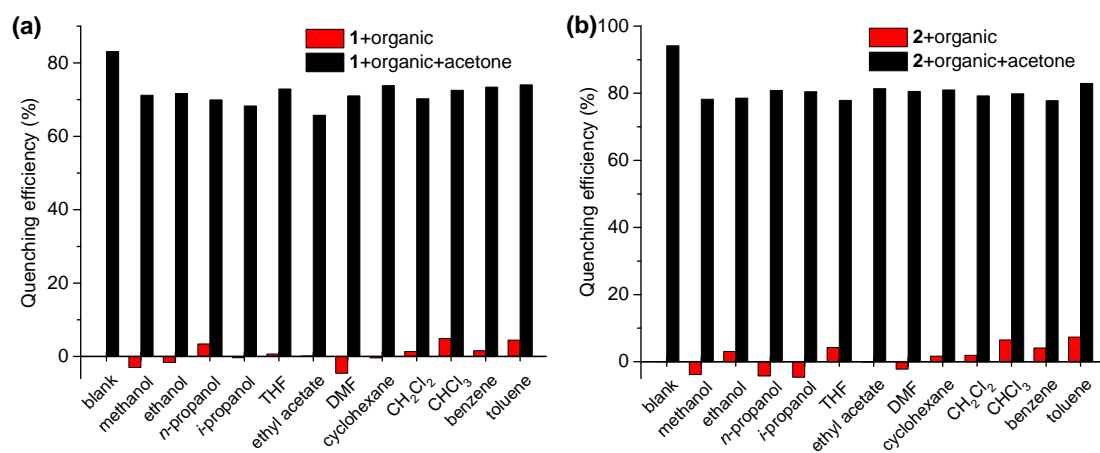


Fig. S9 Quenching efficiency of (a) **1** and (b) **2** upon the addition of different organics (red) and subsequent addition of acetone (black), $\lambda_{\text{ex}} = 280$ nm.

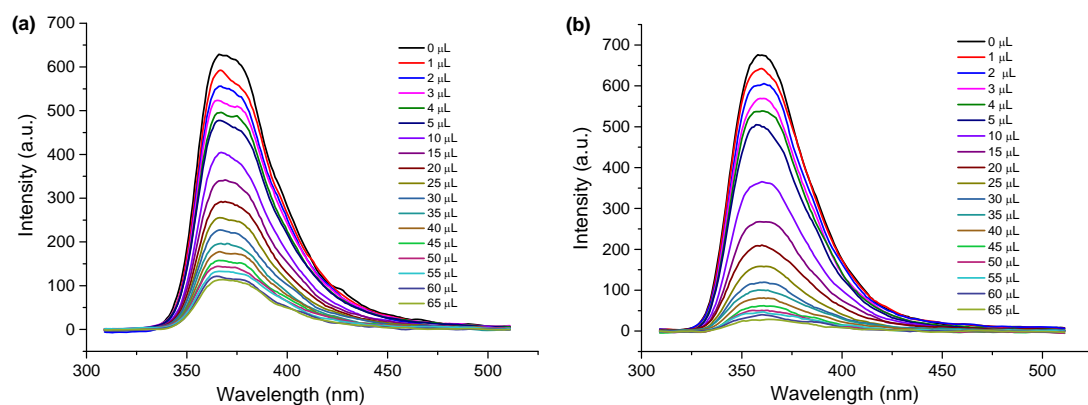


Fig. S10 Fluorescence titration of compounds (a) **1** and (b) **2** dispersed in acetonitrile (1 mg/mL) with the gradually addition of acetone, $\lambda_{\text{ex}} = 280$ nm.

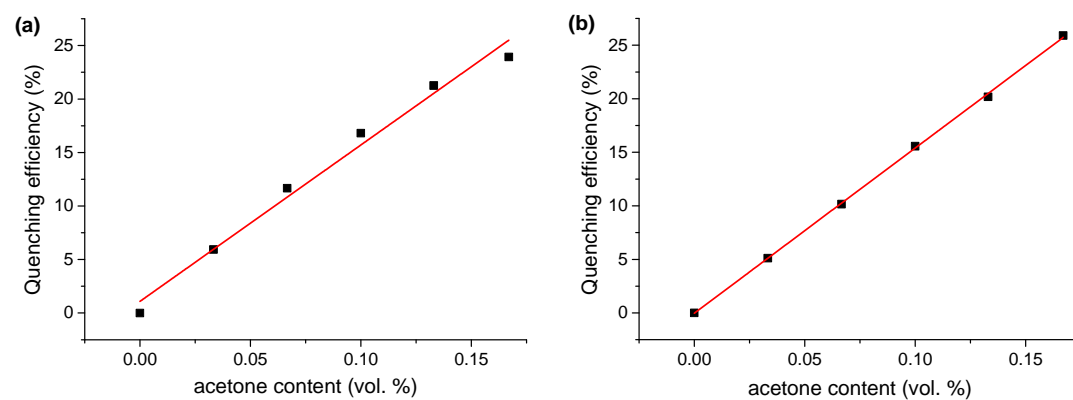


Fig. S11 Fitting plots of the quenching efficiencies of acetone (0-0.17 vol. %) on the emissions of the suspensions of compounds (a) **1** and (b) **2** (1 mg/mL), $\lambda_{\text{ex}} = 280$ nm.

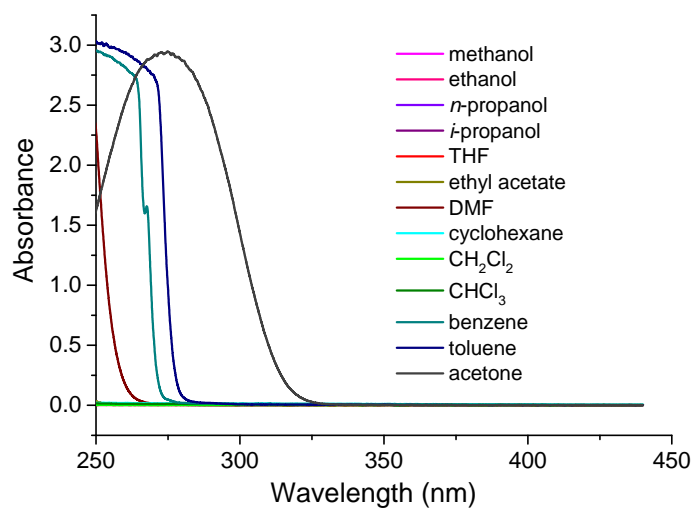


Fig. S12 UV-Vis spectra of the acetonitrile solutions containing 2.0% of different organics.

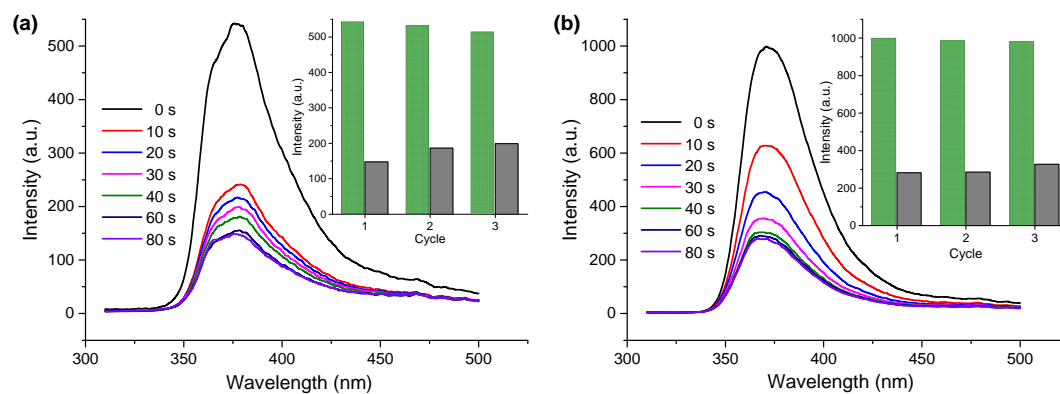


Fig. S13 Time-dependent photoluminescence spectra of compounds (a) **1** and (b) **2** upon exposure to acetone vapour, $\lambda_{\text{ex}} = 280$ nm. Inset: the change of emission intensity in three consecutive sensing-recovery cycles, green and gray volumes represent the emission intensity before and after exposure to acetone vapour.

References

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