Electronic Supplementary Information (ESI)

Solvent triggering structural changes for two terbium-based metal-

organic frameworks and their photoluminescent sensing

Dan Yue,*ab Yanyan Wang,ac Dong Chena and Zhenling Wang*a

^a School of Materials and Chemical Engineering, Henan International Joint Laboratory of Rare Earth Composite Materials, Henan University of Engineering, Zhengzhou, 451191, P. R. China.
^b State Key Laboratory of Silicon Materials, Cyrus Tang Center for Sensor Materials and Applications, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China.
^c College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China

E-mail: yuedan@haue.edu.cn; zlwang2007@hotmail.com

Experimental

All chemicals were analytical grade reagents and used directly without further purification, the organic linker 4,4'-(1H-pyrazole-1,3-diyl) dibenzoic acid (H₂PDBA) was obtained from Jinan Henghua Company and used as received.

Synthesis of TbPDBA-9

A mixture of Tb(NO₃)₃·6H₂O (0.1 mmol, 45 mg), H₂PDBA (0.096 mmol, 30 mg), DMF (5 mL), H₂O (10.5 mL) and HCOOH (100 μ L) were sealed in a 25 mL Teflonlined stainless-steel bomb at 160 °C for 72 h, which was then cooled to room temperature. After decanting the mother liquor, the white rhombus crystalline product was washed two times with DMF and dried at 60 °C for 20 min to obtain the sample. Elemental analysis calcd (%) for TbPDBA-9 Tb (PDBA)(COO)·(H₂O)_{0.5}: C, 42.24; H, 2.6; N, 5.44; Found: C, 42.36; H, 2.18; N, 5.34.

Synthesis of TbPDBA-8

A mixture of Tb(NO₃)₃·6H₂O (0.05 mmol, 22.5 mg), H₂PDBA (0.048 mmol, 15 mg), DMF (0.5 mL), H₂O (15 mL) and HCOOH (100 μ L) were sealed in a 25 mL Teflonlined stainless-steel bomb at 160 °C for 72 h, which was then cooled to room temperature. After decanting the mother liquor, the white rhombus crystalline product was washed two times with DMF and dried at 60 °C for 20 min to obtain the sample. Yield: 52.9%. Elemental analysis calcd (%) for TbPDBA-8 Tb₂(PDBA)₃·(H₂O)₄: C, 45.49; H, 2.66; N, 6.10; Found: C, 45.41; H, 2.67; N, 6.14.

The influence of H₂O content on the structure of TbPDBA-9 and TbPDBA-8

Based on the same ligand (H₂PDBA), two different crystal structures (TbPDBA-9 and TbPDBA-8) were obtained. Whether there is a certain relationship between the two configurations was explored in the process of crystal synthesis. A mixture of Tb(NO₃)₃·6H₂O (0.05 mmol, 22.5 mg), H₂PDBA (0.048 mmol, 15 mg), DMF (0.5 mL) and HCOOH (100 μ L) were sealed in a 25 mL Teflon-lined stainless-steel bomb at 160 °C for 72 h, then the different concentrations of H₂O solution were added to the above solution. The effect of H₂O concentrations on the structure of TbPDBA-9 and TbPDBA-8 was explored through XRD results.

Furthermore, sodium formate (NaCOOH) was added to the synthesis process, and the concentration of H₂O solution was adjusted. The effect of NaCOOH on the structure of TbPDBA-9 and TbPDBA-8 was explored through XRD results.

Crystallography

Single-crystal data of TbPDBA-9 and TbPDBA-8 were recorded on a Bruker APEX-II diffractometer with an CCD detector using graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. The determination of the unit cells and data collections of TbPDBA-9 and TbPDBA-8 were performed using CrysAlisPro. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure was determined by direct methods, refined by the full-matrix least-square method with the SHELX-2013 and Olex 2 program package¹⁻³. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all H atoms on C atoms were generated geometrically and refined with isotropic thermal parameters. Selected crystal parameters, data collection, and refinement are summarized in Table S1. CCDC 1968061 (TbPDBA-9) and CCDC 1968060 (TbPDBA-8) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Characterization

All solvents and reagents were obtained from commercial sources and used without further purification. PXRD data were taken on a Shimadzu XRD7000 powder X-ray diffractometer with the recording rate 5°/min in the 2θ =3-40 degree at room temperature. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 10 K min⁻¹ under N₂ atmosphere. Before the TGA measurement, the fresh samples were guest-exchanged with dry acetone at least 10 times, then filtered and degassed at 373 K for 2 h under high vacuum to obtain the activated samples. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyser. The emission and excitation spectra for the samples were recorded by a Hitachi F4600 fluorescence spectrometer.

Detection performance of TbPDBA-9

The dried powder of TbPDBA-9 (1.00 mg) in 1 mL deionized water was ultrasonicated for 30 min. For the detection of AA, different concentrations of AA solutions were added into the TbPDBA-9 suspension.

In order to investigate the recyclability of TbPDBA-9, the TbPDBA-9 (1 mg/mL) was dispersed into deionized water to form a suspension, and the emission intensity of TbPDBA-9 was recorded. After detection of AA (150 μ M), the suspensions of TbPDBA-9/AA were centrifuged and washed three times with ethanol, then the TbPDBA-9 was dried at 60 °C and ready for another cyclic test.

Detection performance of TbPDBA-8

The dried powder of TbPDBA-8 (1.00 mg) in 1 mL dioxane was ultrasonicated for 30 min. For the detection of H_2O , different volumes of H_2O were added into the TbPDBA-8 in dioxane.

In order to investigate the recyclability of TbPDBA-8, the TbPDBA-8 (1 mg/mL) was dispersed into dioxane to form a suspension, and the emission intensity of TbPDBA-8 was recorded. After detection of H₂O (100 μ L), the suspensions of TbPDBA-8/H₂O were centrifuged and washed three times with ethanol, then the TbPDBA-8 was dried at 60 °C and ready for another cyclic test.



Fig. S1 Coordination environments around (a)Tb atom and (b) ligand of TbPDBA-9; coordination environments around (c) Tb atom and (d)ligand of TbPDBA-8. Tb green ball, O red, N blue, C gray, H atoms are omitted for clarity.



Fig. S2 The hydrogen bond interactions indicated by dashed lines in TbPDBA-8 (O21-H21B…O1, 2.267 Å). Tb green ball; O red; N blue; C gray; H atoms in coordinate H₂O, sky blue.



Fig. S3 PXRD patterns of TbPDBA-9 and TbPDBA-8 in water with the pH of 6.8 for 7 days.



Fig. S4 TGA curves for TbPDBA-9 and TbPDBA-8 under nitrogen.



Fig. S5 Emission spectra of TbPDBA-9 and TbPDBA-8 (a) solid and (b) suspension.



Fig. S6 (a) The excitation (black line) and emission (red line) spectra of TbPDBA-9 suspension.(b) The excitation (black line) and emission (red line) spectra of TbPDBA-9 after suspension filtration.

When the TbPDBA-9 was dispersed into deionized water, the fluorescence spectrum of TbPDBA-9 was recorded (Fig. S6a). When excited at 310 nm, the emission spectrum of TbPDBA-9 shows a strong emission band at 390 nm. And then, TbPDBA-9 was centrifuged and washed three times with ethanol, then the TbPDBA-9 was dried to test its fluorescence spectrum, as shown in Fig. S6b. It can be seen that, the emission spectrum of TbPDBA-9 is composed of emission bands of H₂PDBA (390 nm) and Tb³⁺ ions' characteristic sharp emissions.



Fig. S7 Emission spectra of (a) TbPDBA-9 and (b) TbPDBA-8 towards various solution $(\lambda_{ex}=310 \text{ nm}).$



Fig. S8 Luminescent intensity of TbPDBA-9 at 390 nm with different time (0~5.5 min) after adding 150 μ M AA.



Fig. S9 (a) The luminescence intensity of TbPDBA-9 at 390 nm after three recycles. (b) PXRD patterns of TbPDBA-9 after three cycles for AA sensing.



Fig. S10 PXRD patterns of TbPDBA-9, which exhibit stability in 150 µM AA.

Fig.S10 shows that TbPDBA-9 exhibited stability in AA, it can be seen that quenching of the fluorescence intensity of TbPDBA-9 is not caused by the collapse of the framework during the detection of AA. In our previous study ⁴, we calculated the HOMO and LUMO energy levels of AA and H₂PDBA, the LUMO of H₂PDBA has a lower energy than the LUMO of AA, which means the excited electron of ligand could not be transferred to AA. The UV-Vis spectra of AA and H₂PDBA show that a large overlap between the absorption spectra of the ligand and AA, so the strong competitive absorption between AA and ligand is existed ^{5,6}. Hence, the possible mechanism for AA sensing is elucidated by the strong competitive absorption between ligand and AA.



Fig. S11 PXRD patterns of TbPDBA-8, which exhibit stability in dioxane solution.



Fig. S12 Excitation (black line) and emission (red line) spectra of TbPDBA-8 in dioxane solution.



Fig. S13 Luminescent intensity ratio (I_{380}/I_{543}) of TbPDBA-8 in dioxane solution with different time (0~5 min) after adding 100 µL H₂O.



Fig. S14 PXRD patterns of TbPDBA-8 after there recycles of detecting H₂O in dioxane solution (C1-3: cycles).

	TbPDBA-9	TbPDBA-8
Empirical formula	$TbC_{18}H_{11}N_2O_6$	$Tb_2C_{51}H_{39}N_6O_{16}$
Formula weight	510.21	1270.41
Temperature/K	293(2)	293(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	Pna2 ₁
a/Å	17.4278(5)	12.071(2)
b/Å	12.1359(3)	33.798(7)
c/Å	7.4214(2)	11.609(2)
$\alpha/^{\circ}$	90	90
β/°	92.6440(10)	90
γ/°	90	90
Ζ	4	4
Density (calculated g cm ⁻³)	2.161	1.870
Absorption coefficient/ mm ⁻¹	4.553	3.193
Reflections collected	16659	46578
Independent reflections	3068 [R(int) = 0.1082]	8866 [R(int) = 0.0428]
F(000)	984	2424
Goodness of fit on F ²	1.107	1.028
R1,wR2(I>2 σ (I)) ^a	0.0245, 0.0654	0.0343, 0.0774
R1,wR2(all date) ^a	0.0311, 0.0848	0.0488, 0.0875
$aR1=\Sigma(Fo - Fc)/\Sigma Fo ;$		

Table S1. Crystallographic data collection and refinement result for TbPDBA-9 and TbPDBA-8.

 ${}^{a}\mathbf{K}\mathbf{I} = \Sigma(|\mathbf{F}\mathbf{O}| - |\mathbf{F}\mathbf{C}|)/\Sigma|\mathbf{F}\mathbf{O}|;$

 $wR2=[\Sigma w(|Fo|-|Fc|^2)/\Sigma wFo^2]^{1/2}.$

References

- 1 A. L. Spek, Acta Crystallogr., Sect. D: Biol. Crystallogr., 2009, 65, 148-155.
- 2 A. L. Spek, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 9-18.
- 3 O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. *Appl. Cryst.*, 2009, **42**, 339-341.
- 4 D. Yue, Y. Huang, J. Zhang, X. Zhang, Y. Cui, Y. Yang, G. Qian, *Eur. J. Inorg. Chem.*, 2018, **2**, 173-177.
- 5 J. N. Hao, B. Yan. Adv. Funct. Mater., 2017, 27, 1603856.
- 6 M. Pan, W. M. Liao, S. Y. Yin, S. S. Sun, C. Y. Su, Chem. Rev., 2018, 118, 8889-8935.