

Electronic Supplementary Information (ESI)

Luminescent Lanthanide-Organic Polyrotaxane Framework as a Turn-Off Sensor for nitrobenzene and Fe³⁺

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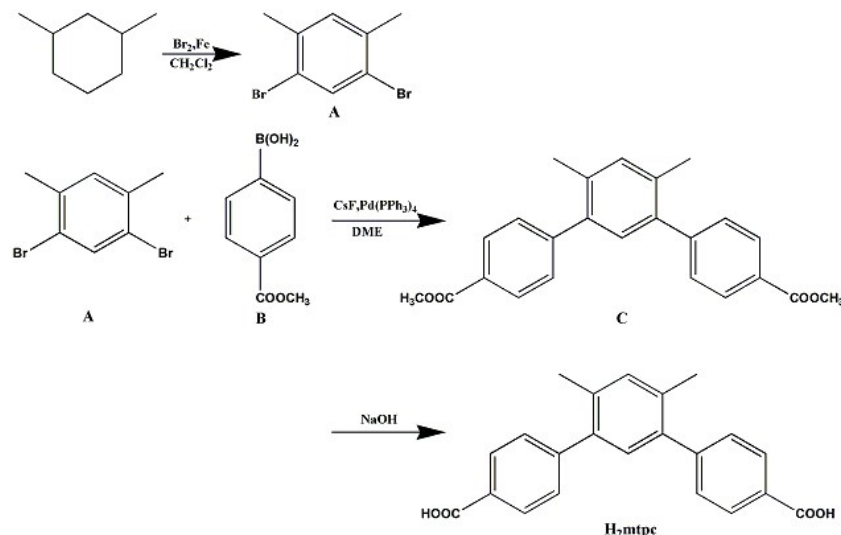
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Materials and general methods	

All solvents and starting materials for synthesis were purchased commercially and were used as received. The FT-IR spectra were recorded from KBr pellets in the 4000-400 cm^{-1} range on a Nicolet 5DX spectrometer. The C, H, and N microanalyses were carried out with Perkin-Elmer 240 elemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 advanced automated diffractometer with Cu-K radiation. Thermogravimetric analyses (TGA) were taken on a Perkin-Elmer Pyris1 (20–800 $^{\circ}\text{C}$, 10 $^{\circ}\text{C}/\text{min}^{-1}$, flowing $\text{N}_2(\text{g})$). Luminescencespectra for the solid samples and liquid samples were investigated with a HitachiF-4500 fluorescence spectrophotometer and Varian Cary Eclipse Fluorescence spectrophotometer, respectively.

Synthesis of H_2mtpc



1. Synthesis of compound A (Suzuki-coupling reaction)

To a solution of m-xylene (148 mL, 127 g, 1.20 mol) in CH_2Cl_2 (150 mL), iron powder (2.40 g) was added. At 0 $^{\circ}\text{C}$, bromine was slowly added dropwise and stirred for 16 hr at room temperature. It was washed with 2 N NaOH (300 mL) and saturated NaCl solution, dried over Na_2SO_4 and the solvent was removed under vacuum. The crude product was washed with ethanol and then recrystallized from ethanol in 39 % yield. $^1\text{H-NMR}$ (CDCl_3): 2.35 (s, 6H), 6.64 (s, 1H), 7.36 (s, 1H).

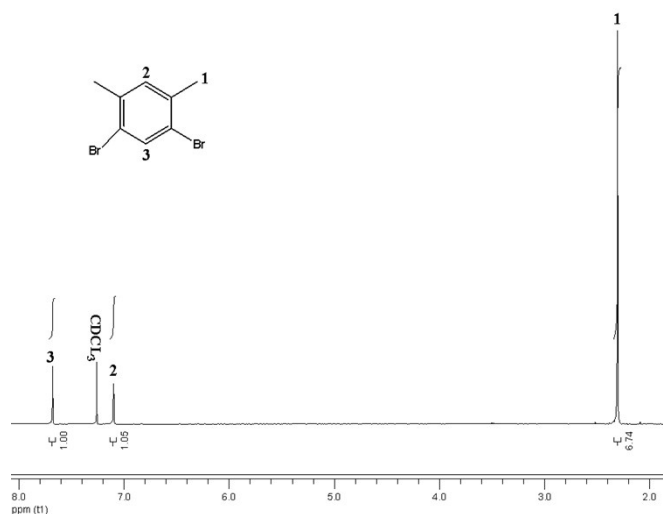


Fig. S1 $^1\text{H-NMR}$ (300 MHz, CDCl_3 , r.t.) of compound A.

2. Synthesis of compound C (Suzuki-coupling reaction)

A (1.79 g, 6.8 mmol) and B (2.8 g, 15.6 mmol) (mol/mol = 1 : 2.3), CsF (3 g, 19.7 mmol) and Pd(PPh₃)₄ (0.17 g, 0.15 mmol) were mixed in a 250 mL two-necked flask and pumped for 30 minutes. 100 mL degassed CH₃OCH₂CH₂OCH₃ (DME) was added through a syringe. The mixture was heated to reflux under the protection of N₂ for 48 hours. Water was added after the mixture was cooled to room temperature. The water phase was extracted thrice with CH₂Cl₂. The mixed organic phases were dried with anhydrous MgSO₄ overnight, and filtered. After the solvent was removed, the crude product was purified by column chromatography (silica, CHCl₃) to give the pure product. ¹H-NMR (CDCl₃): 2.35 (s, 6H), 3.88 (s, 6H), 6.98 (s, 1H), 7.46 (s, 1H), 7.59 (d, 4H), 8.03 (d, 4H).

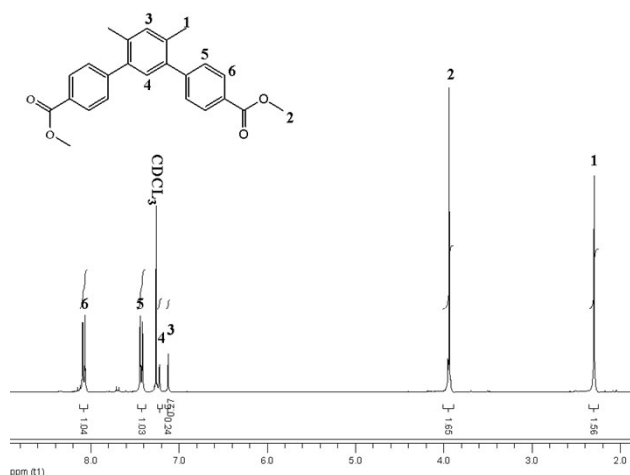


Fig. S2 ¹H-NMR (300 MHz, CDCl₃, r.t.) for compound C.

3. Synthesis of H₂mtpc ligand

C was dissolved in mixture of THF (70mL) and MeOH (70ml, v/v = 1:1), 50 mL 4N NaOH aqueous solution was added. Heated to reflux and add moderate water until completely dissolved, then the mixture was stirred at this temperature overnight. After the mixture being cooled to room temperature, The mixture was acidified with add concentrated HCl with stirred to give yellow flocculent precipitate, which was filtered and washed with water several times.

Synthesis of 1, 2 and 3

[Tb(mtpc)_{1.5}(DMA)(H₂O)]·2H₂O (1) A mixture of Tb(NO₃)₃·6H₂O (0.033 mmol, 0.015 g), H₂mtpc (0.014 mmol, 0.005 g), DMA (1.5 mL) and H₂O (0.5 mL) was stirred for 10 minutes in glass vial at room temperature, which was heated in an oven to 358 K for 3 days, followed by slowly cooling (5 K h⁻¹). The resulting crystals were washed with DMA and dried in air. C₃₇H₃₄NO₈Tb (%), C: 57.00; H: 4.40; N: 1.80; found: C: 57.02; H: 4.43; N: 1.78. IR (KBr Pellets, cm⁻¹): 3434(s), 1671(s), 1592(m), 1545(m), 1396(s), 1323(m), 1276(m), 1164(w), 968(w), 775(m), 707(m).

[Dy(mtpc)_{1.5}(DMA)(H₂O)]·2H₂O (2) The colorless block crystals of 2 was synthesized similarly to that of 1 except that Tb(NO₃)₂·6H₂O (0.033 mmol, 0.015 g) was used instead of Dy(NO₃)₃·6H₂O (0.033 mmol, 0.015 g). Yield: ca. 67 %. Anal. calcd for C₃₇H₃₄NO₈Dy (%): C: 56.74; H: 4.38; N: 1.79; found: C: 56.80; H: 4.33; N: 1.82. IR (KBr Pellets, cm⁻¹): 3434(s), 1671(s), 1592 (m), 1545(m), 1396(s), 1323(m), 1276 (m), 1164(w), 968(w), 775 (m), 707(m).

[Er(mtpc)_{1.5}(DMA)(H₂O)]·2H₂O (3) The colorless block crystals of 2 was synthesized similarly to that

of **1** except that Dy(NO₃)₃·6H₂O (0.033 mmol, 0.015 g) was used instead of Er(NO₃)₂·6H₂O (0.033 mmol, 0.015 g). C₃₇H₃₄NO₈Er (%), C: 56.40; H: 4.35; N: 1.78; found: C: 56.52; H: 4.38; N: 1.81. IR (KBr Pellets, cm⁻¹): 3434(s), 1671(s), 1592(m), 1545(m), 1396(s), 1323(m), 1276(m), 1164(w), 968(w), 775(m), 707(m).

X-ray crystallography

Crystallographic data of compounds **1-3** were collected at room temperature with a Bruker APEX-II diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and graphite monochromator using the ω -scan mode. The structures were solved by direct methods and refined of F^2 by full-matrix least squares using SHELXTL⁹. Crystallographic data and experimental details for structural analyses are summarized in Table S1. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC 1421607-1421609 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

PXRD patterns

The powder PXRD patterns of **1**, **2** and **3** are shown in Fig. S12. The as-synthesized powder XRD patterns are similar to the corresponding simulated ones from single-crystal data, indicating that the purity of phases.

Thermogravimetric analysis

The thermogravimetric analysis were carried out, shown in Fig. S13. The TGA curves of the three compounds are similar, all show two great weight loss. The first weight loss of 17.57% (ca. 17.31%), 17.04% (ca. 17.23%) and 17.58% (ca. 17.13%) are connected with the loss of the one coordinated water molecules, one coordinated DMA and two water lattice water molecule in the lattice from 20°C to 372°C. The second weight loss begins at 490°C and is related to the decomposition of organic ligand. The frameworks of complexes were stable up to 490°C and then began to decompose upon further heating.

Table S1 Crystallographic data for **1**, **2** and **3**.

	1	2	3
Empirical formula	C ₃₇ H ₃₄ NO ₈ Tb	C ₃₇ H ₃₄ NO ₈ Dy	C ₃₇ H ₃₄ NO ₈ Er
Formula weight	779.57	783.15	787.91
Wavelength/ Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2/ <i>C</i>	<i>P</i> 2/ <i>C</i>	<i>P</i> 2/ <i>C</i>
<i>a</i> / Å	10.8481 (10)	10.7467(5)	10.8349 (5)
<i>b</i> / Å	15.9105 (13)	15.8854(7)	15.8724 (8)
<i>c</i> / Å	19.5148 (16)	19.3945(10)	19.5158 (12)
β /°	92.135 (2)	91.363(2)	92.229 (2)
<i>V</i> /Å ³	3365.9 (5)	3310.0(3)	3353.7 (3)
<i>Z</i>	4	4	4
μ / mm ⁻¹	2.148	2.311	2.555
<i>F</i> (000)	1420	1572	1574
Range for data collection/°	26.36	26.373	25.373
<i>T</i> / K	293(2)	173(2)	293(2)
<i>R</i> _{int}	0.0880	0.0888	0.0687
Goodness-of-fit on <i>F</i> ²	1.038	1.014	1.026
Data/restraints/parameters	6868/0/424	6615/24/446	6053/19/413
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> ₁ = 0.0513, w <i>R</i> ₂ = 0.1168	<i>R</i> ₁ = 0.0525, w <i>R</i> ₂ = 0.1124	<i>R</i> ₁ = 0.0527, w <i>R</i> ₂ = 0.1262
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1151, w <i>R</i> ₂ = 0.1452	<i>R</i> ₁ = 0.1015, w <i>R</i> ₂ = 0.1329	<i>R</i> ₁ = 0.1049, w <i>R</i> ₂ = 0.1516
Largest diff. peak and hole(e Å ⁻³)	2.178, -1.394	2.561, -0.968	2.159, -1.189
Unique reflections	6868	6615	6053

^a $R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|$; $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$

Table S2 Selected bond lengths (Å) and angles (deg.) for **1, 2 and 3**.

Compound 1			
Bond		D, Å	
Tb(1)-O(4)#1	2.290(5)	Tb(1)-O(7)	2.390(6)
Tb(1)-O(3)#2	2.307(6)	Tb(1)-O(5)	2.427(6)
Tb(1)-O(2)#3	2.318(5)	Tb(1)-O(1W)	2.465(6)
Tb(1)-O(1)	2.338(5)	Tb(1)-O(6)	2.486(6)
Angle		ω , deg	
O(1)-Tb(1)-O(7)	80.8(2)	O(5)-Tb(1)-O(1W)	104.4(2)
O(1)-Tb(1)-O(5)	149.1(2)	O(1)-Tb(1)-O(6)	153.6(2)
O(7)-Tb(1)-O(5)	75.3(2)	O(7)-Tb(1)-O(6)	101.2(2)
O(1)-Tb(1)-O(1W)	83.2(2)	O(5)-Tb(1)-O(6)	52.9(2)
O(7)-Tb(1)-O(1W)	66.6(2)	O(1W)-Tb(1)-O(6)	73.8(2)
Compound 2			
Bond		D, Å	
Dy(1)-O(4)#1	2.278(5)	Dy(1)-O(7)	2.379(5)
Dy(1)-O(3)#2	2.304(5)	Dy(1)-O(5)	2.424(5)
Dy(1)-O(2)#3	2.310(5)	Dy(1)-O(1w)	2.424(6)
Dy(1)-O(1)	2.330(5)	Dy(1)-O(6)	2.471(6)
Angle		ω , deg	
O(1)-Dy(1)-O(7)	81.56(19)	O(5)-Dy(1)-O(1w)	104.4(2)
O(1)-Dy(1)-O(5)	149.79(19)	O(1)-Dy(1)-O(6)	153.75(19)
O(7)-Dy(1)-O(5)	75.69(19)	O(7)-Dy(1)-O(6)	101.8(2)
O(1)-Dy(1)-O(1w)	84.0(2)	O(5)-Dy(1)-O(6)	52.96(19)
O(7)-Dy(1)-O(1w)	66.5(2)	O(1w)-Dy(1)-O(6)	74.0(2)
Compound 3			
Bond		D, Å	
Er(1)-O(4)#1	2.268(7)	Er(1)-O(7)	2.356(7)
Er(1)-O(3)	2.292(7)	Er(1)-O(6)	2.386(7)
Er(1)-O(2)#2	2.296(6)	Er(1)-O(1W)	2.423(7)
Er(1)-O(1)#3	2.310(7)	Er(1)-O(5)	2.453(8)
Angle		ω , deg	
O(3)-Er(1)-O(7)	147.2(2)	O(6)-Er(1)-O(1W)	104.2(3)
O(3)-Er(1)-O(6)	76.4(3)	O(3)-Er(1)-O(5)	75.3(3)
O(7)-Er(1)-O(6)	76.1(3)	O(7)-Er(1)-O(5)	101.6(3)
O(3)-Er(1)-O(1W)	138.6(3)	O(6)-Er(1)-O(5)	53.0(2)
O(7)-Er(1)-O(1W)	66.4(3)	O(1W)-Er(1)-O(5)	73.2(3)

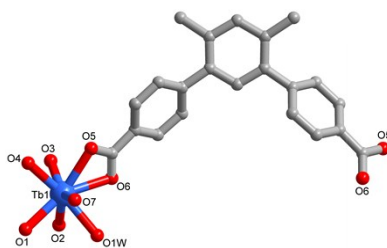


Fig. S3 Coordination environment of Tb^{III} center in **1**.

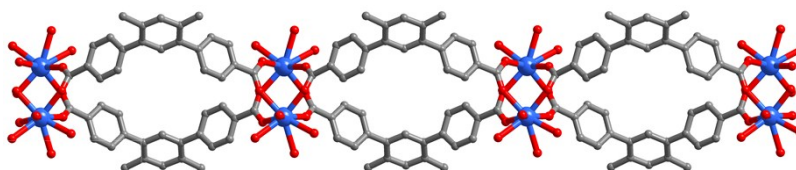


Fig. S4 The coordination modes of mtpc ligand in **1**.

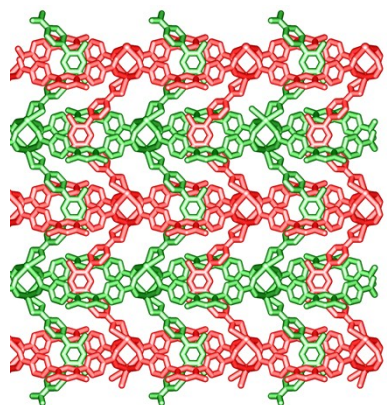


Fig. S5 The 2D polyrotaxane sheets in **1**.

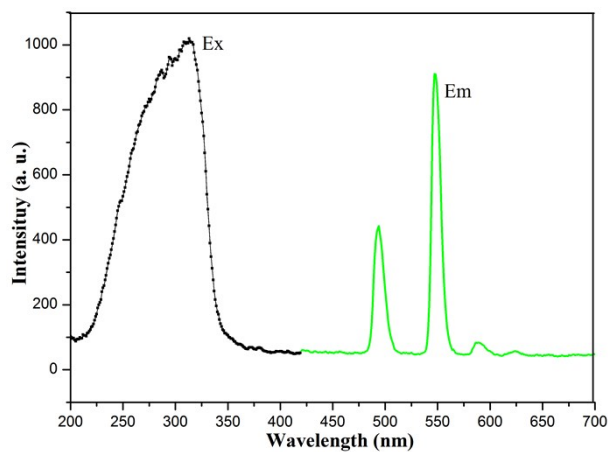


Fig. S6 Excitation (at 314 nm) and emission (at 545 nm) spectra of **1** in the solid state at room temperature.

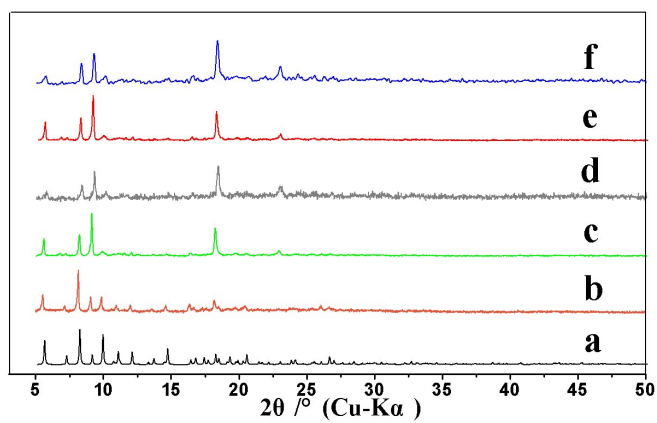


Fig. S7 Chemical stability tests for **1** after introduction of various solvents: (a) simulated from the X-ray single structure of **1**, (b) CH₃OH, (c) DMF, (d) H₂O, (e) C₂H₅OH, (f) DMA by PXRD analysis.

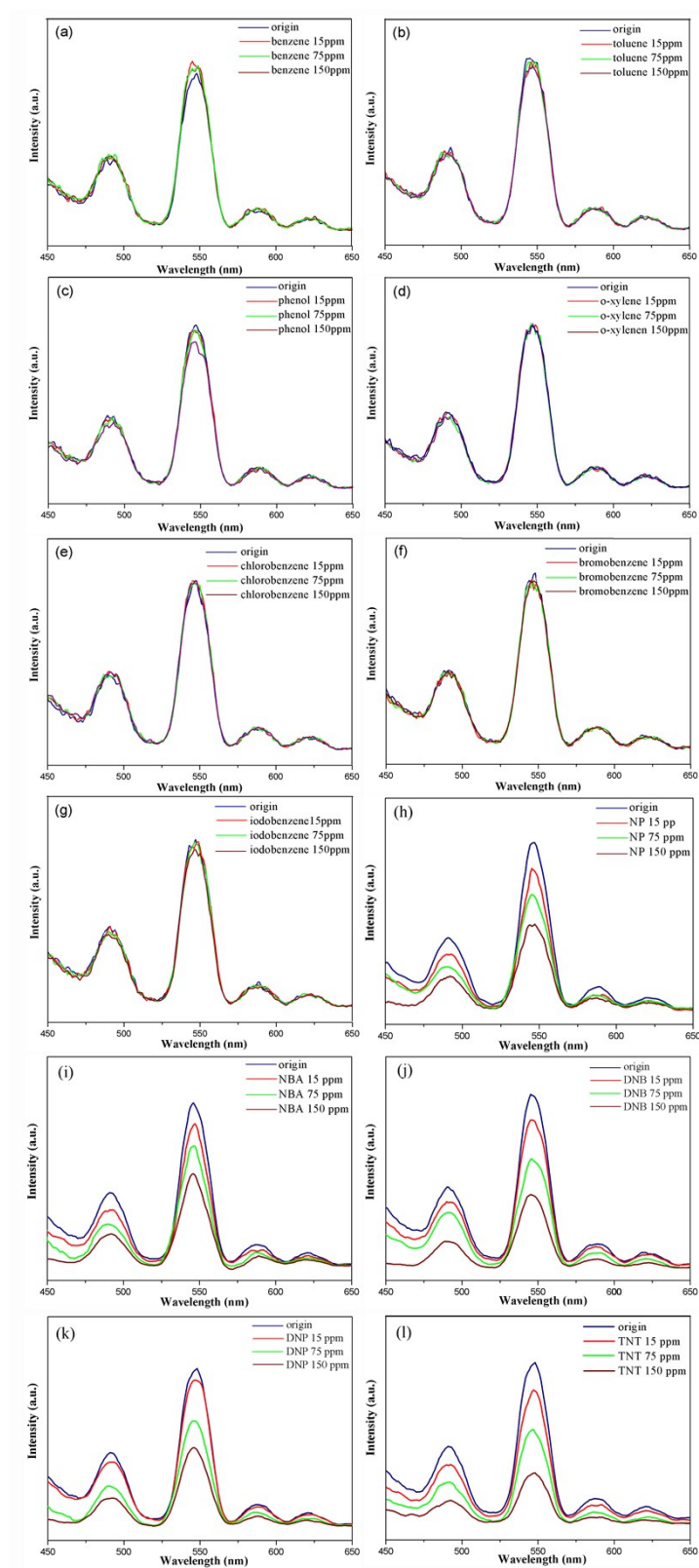


Fig. S8 The luminescent intensity of **1** in different concentration of analytes (a) benzene (BZ), (b) toluene (TO), (c) phenol (PhOH), (d) o-xylene (OX), (e) chlorobenzene (Cl-BZ), (f) bromobenzene (Br-BZ), (g) iodobenzene (I-BZ), (h) o-nitrobenzaldehyde (NP), (i) m-nitrobenzoic acid (NBA), (j) 1,3-dinitrobenzene (DNB), (k) 2,4-dinitrophenol (DNP), (l) 2,4,6-trinitrotoluene (TNT) ($\lambda_{\text{ex}} = 314 \text{ nm}$).

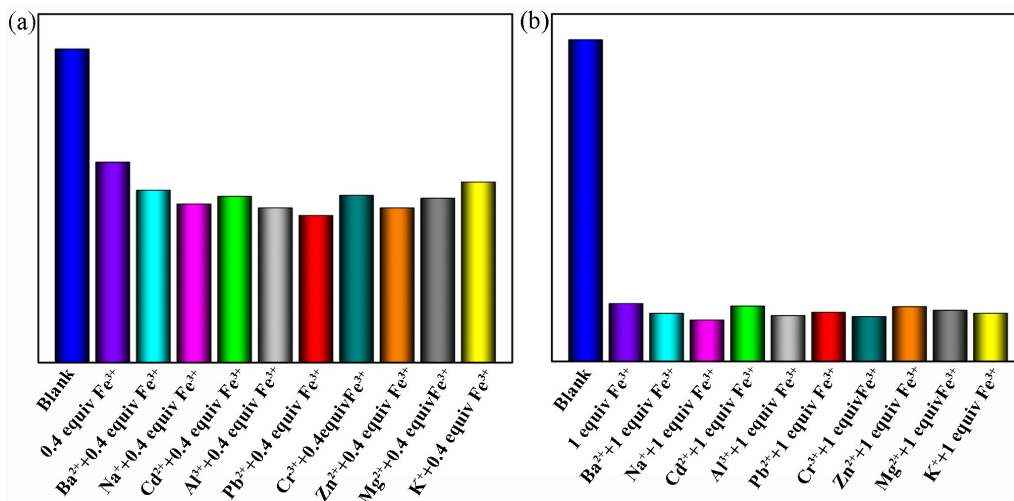


Fig. S9 Room-temperature luminescent intensity of **1** upon addition of 0.4 equiv of Fe³⁺ and 0.4 equiv of various metal ions (a) and with adding 1 equiv of Fe³⁺ and 1 equiv of other metal ions (b) in methanol ($\lambda_{\text{ex}}=314$ nm).

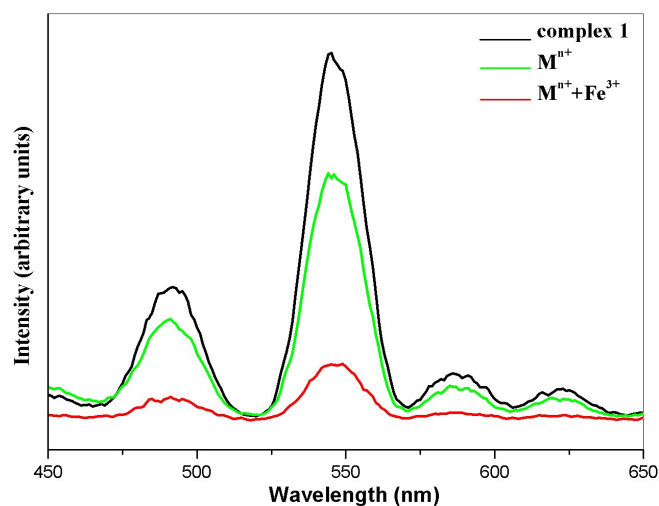


Fig. S10 Comparison of the photoluminescence intensity of **1** in methanol suspension with the introduction of other Mⁿ⁺ ions (Ba²⁺, Na⁺, Cd²⁺, Al³⁺, Pb²⁺, Cr³⁺, Zn²⁺, Mg²⁺, K⁺) in the absence and presence of 1 equiv. Fe³⁺ ($\lambda_{\text{ex}}=314$ nm).

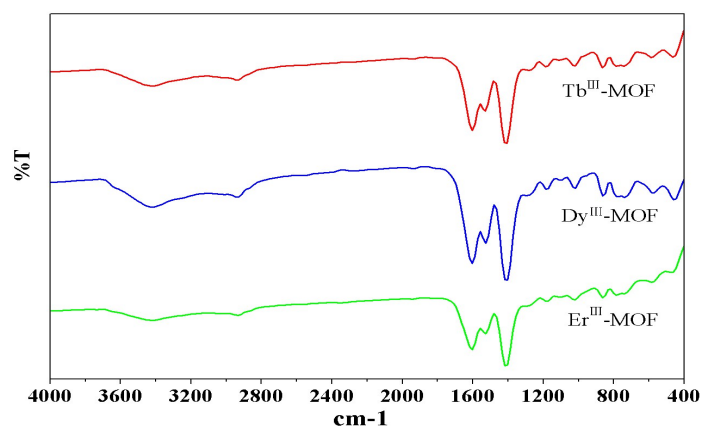


Fig. S11 IR spectra for **1**, **2** and **3**.

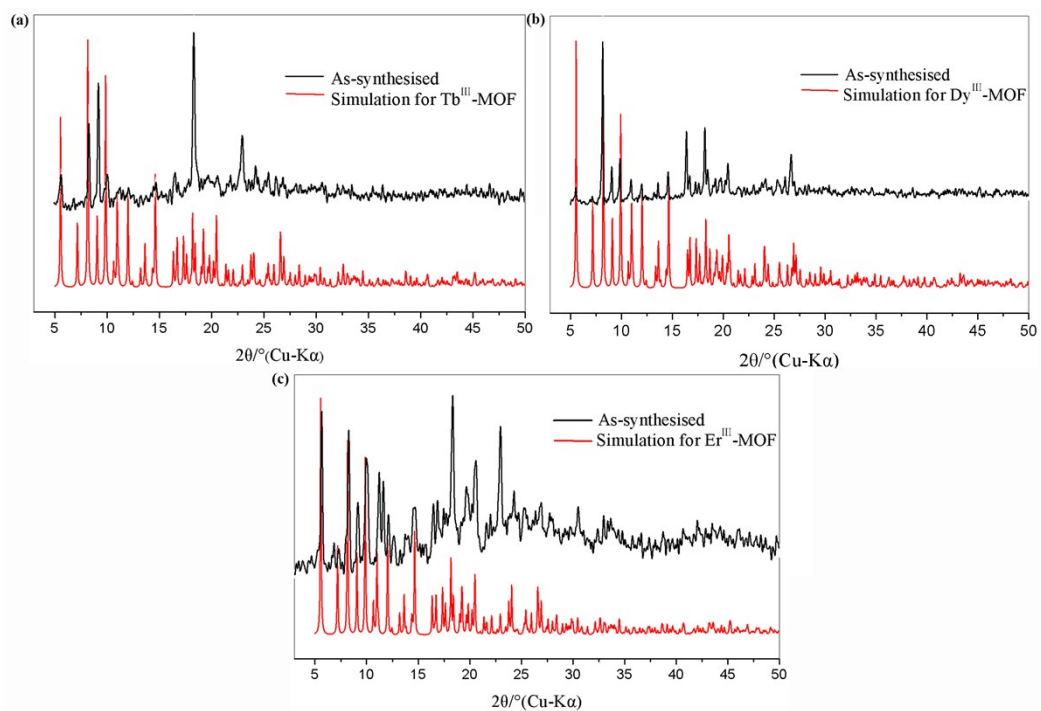


Fig. S12 Simulated and experimental X-ray powder diffraction patterns for **1**, **2** and **3**.

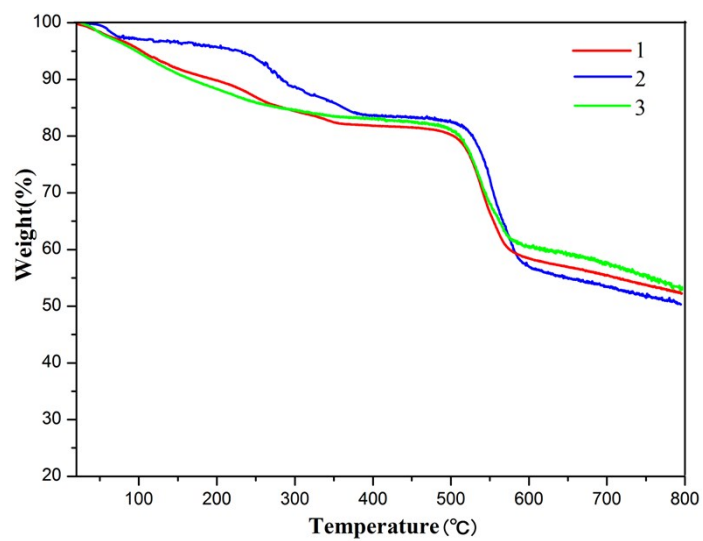


Fig. S13 TGA curves of compounds **1**, **2** and **3**.