Supporting information for

A highly stable dynamic fluorescent metal-organic framework with selective sensing of nitroaromatic explosives

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Experimental section

General methods. All of the chemicals are commercially available and used without further purification. Fluorescent spectra were measured using a Shimadzu RF-5301PC spectrofluorophotometer. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. The IR spectra was recorded in the 4000 to 400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 spectrometer. The thermogravimetric analyses (TGA) were carried out on Netzsch TG-209 Thermogravimetry Analyzer in N_2 atmosphere. The thermogravimetric-mass spectrometric (TG-MS) analysis was performed using a NETZSCH STA449C instrument in N_2 atmosphere. The Powder X-ray diffraction patterns were recorded on D8 ADVANCE X-Ray Diffractometer.

Synthesis of [Tb(TTCA)(DMA)(H_2O)]·7DMA·9.5H_2O (1): A mixture of $Tb(NO_3)_3·6H_2O$ (0.045 g, 0.1 mmol), H_3TTCA (0.018 g, 0.05 mmol), triethylamine (1 drop) and DMA (8.0 mL) was heated at 80 °C for 72 h in a sealed Teflon-lined autoclave. The autoclave was cooled to room temperature. Colorless block-shaped crystals of **1** were collected by filtration. Yield: 30 %. Anal. Calcd for [Tb(TTCA)(DMA)(H_2O)]·5DMA·6H_2O ($C_{45}H_{77}N_6O_{19}Tb$): C, 46.39; H, 6.66; N,

7.21 %; Found: C,45.92; H, 6.30; N, 7.33 %. IR (KBr, cm^{-1}): 3404 (s), 1614 (vs), 1546 (m), 1421 (s), 1389 (vs), 1329 (m), 1295 (w), 1262 (w), 1022 (m), 899 (w), 792 (m), 770 (s), 595 (m), 493 (m).

Preparation of 1a-1d. To prepare the guest-exchanged samples of **1a-1d**, crystals of **1** were immersed in methanol, ethanol, 1-prapanol and 1-butanol for 7 days, respectively, and the guest solutions refreshed two times daily. The crystals of $[Tb(TTCA)(MeOH)_2(H_2O)]\cdot 27MeOH$ (**1a**), $[Tb(TTCA)(EtOH)(H_2O)]\cdot 17.5EtOH$ (**1b**), $[Tb(TTCA)(PrOH)(H_2O)]\cdot 11PrOH$ (**1c**), $[Tb(TTCA)(BuOH)(H_2O)]\cdot 6.33BuOH$ (**1d**) were produced. Elemental analysis: Calcd for $[Tb(TTCA)(MeOH)_2(H_2O)]\cdot 6MeOH$ ($C_{29}H_{43}O_{15}Tb$): C, 44.06; H, 5.48 %; Found: C, 44.42; H, 5.36 %; Calcd for $[Tb(TTCA)(C_2H_5OH)(H_2O)]\cdot 5C_2H_5OH$ ($C_{33}H_{47}O_{13}Tb$): C, 48.89; H, 5.84 %; Found: C, 49.23; H, 5.95 %; Calcd for $[Tb(TTCA)(C_3H_7OH)(H_2O)]\cdot 5C_3H_7OH$ ($C_{39}H_{59}O_{13}Tb$): C, 52.35; H, 6.65 %; Found: C, 52.72; H, 6.36 %; Calcd for $[Tb(TTCA)(C_4H_9OH)(H_2O)]\cdot 3C_4H_9OH$ ($C_{37}H_{51}O_{11}Tb$): C, 53.50; H, 6.19 %; Found: C, 53.13; H, 6.56 %.

X-ray crystallography. The single-crystal data of **1** and **1a-1d** were collected on Agilent Technologies Gemini A Ultra system, with Cu/Kα radiation (λ = 1.54178 Å). All empirical absorption corrections were applied using the SCALE3 ABSPACK program.[1] The structures were solved by direct method and refined by full-matrix least-squares analysis on F^2 using the SHELX97 program package. All the hydrogen atoms (except those of coordinated water and alcohol molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The H atoms bonded to the oxygen atoms of coordinated water and alcohol molecules were located in

Fourier-difference electron density maps. All non-hydrogen atoms were refined anisotropically. The electron density of disordered DMA, methanol, ethanol, 1-prapanol, 1-butanol and H_2O molecules in **1** and **1a-1d** were treated as a diffuse contribution using the program SQUEEZE.[2] All calculations were performed using the SHELXTL system of computer programs.[3]

Table S1. Crystal Data and Structure Refinements for **1** and **1a-1d.**

	1	**1a**	**1b**	**1c**	**1d**
Formula	$C_{53}H_{102}N_8O_{24.5}Tb$	$C_{50}H_{127}O_{36}Tb$	$C_{58}H_{122}O_{25.5}Tb$	$C_{57}H_{107}O_{19}Tb$	$C_{50.33}H_{84.33}O_{14.33}Tb$
Fw.	1402.35	1463.44	1386.48	1255.35	1077.69
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C2/c*	*C2/c*	*C2/c*	*C2/c*	*C2/c*
a (Å)	25.6621(2)	24.7463(2)	27.162(3)	25.9498(2)	26.8247(8)
b (Å)	16.1587(2)	16.9612(2)	13.2751(16)	15.6298(2)	14.1562(5)
c (Å)	26.5745(2)	25.1036(2)	27.128(2)	26.8239(2)	27.3046(10)
α (°)	90	90	90	90	90
β (°)	113.210(2)	116.887(2)	108.438(9)	114.532(2)	112.393(4)
γ (°)	90	90	90	90	90
V (Å^3)	10127.69(17)	9397.64(15)	9279.6(16)	9897.41(17)	9586.7(6)
Z	8	8	8	8	8
D_c (g·cm^{-3})	1.839	2.069	1.985	1.685	1.493
Reflections/	21685/	27753/	17860/	19714/	16897/
Unique	8028	7567	7755	7964	7662
R(int)	0.0763	0.0777	0.0900	0.0704	0.0329
F(000)	5896	6240	5912	5328	4527
GOF on F^2	1.094	0.940	1.076	1.024	0.974
$R_1[I \geq 2\sigma(I)]^a$	0.0777	0.0678	0.0777	0.0696	0.0533
$wR_2[I \geq 2\sigma(I)]^b$	0.1746	0.1601	0.1979	0.1520	0.1354
CCDC deposit number	955652	955653	955654	955655	955656

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$

Table S2. Selected bond distances (Å) and angles (^{o}) for **1** and **1a-1d**.

1					
Tb(1)-O(1)	2.375(6)	O(1)-Tb(1)-O(2)	53.75(16)	O(3)#1-Tb(1)-O(1)	104.6(2)
Tb(1)-O(2)	2.438(5)	O(1)-Tb(1)-O(5)#3	81.5(2)	O(3)#1-Tb(1)-O(4)#2	80.14(17)
Tb(1)-O(3)#1	2.315(4)	O(1)-Tb(1)-O(6)#3	78.5(3)	O(4)#2-Tb(1)-O(1W)	147.9(2)
Tb(1)-O(4)#2	2.326(6)	O(2)-Tb(1)-O(5)#3	120.22(18)	O(4)#2-Tb(1)-O(1)	76.9(2)
Tb(1)-O(5)#3	2.471(4)	O(2)-Tb(1)-O(6)#3	77.76(19)	O(4)#2-Tb(1)-O(2)	117.5(2)
Tb(1)-O(6)#3	2.456(5)	O(3)#1-Tb(1)-O(5)#3	158.35(18)	O(4)#2-Tb(1)-O(6)#3	131.19(18)
Tb(1)-O(1W)	2.341(8)	O(3)#1-Tb(1)-O(6)#3	147.29(17)	O(4)#2-Tb(1)-O(5)#3	81.15(18)
Tb(1)-O(7)	2.303(9)	O(3)#1-Tb(1)-O(2)	78.44(17)	O(6)#5-Tb(1)-O(5)#3	53.86(17)
O(1W)-Tb(1)-O(5)#3	114.4(2)	O(3)#1-Tb(1)-O(1W)	77.6(2)	O(7)-Tb(1)-O(3)#1	88.0(4)
O(1W)-Tb(1)-O(1)	131.1(2)	O(7)-Tb(1)-O(1)	150.4(3)	O(7)-Tb(1)-O(6)#3	105.3(4)
O(7)-Tb(1)-O(4)#2	79.2(3)	O(7)-Tb(1)-O(2)	155.7(3)	O(7)-Tb(1)-O(5)#3	77.9(3)
O(7)-Tb(1)-O(1W)	77.2(3)	O(1W)-Tb(1)-O(2)	80.2(2)	O(1W)-Tb(1)-O(6)#3	76.5(2)
Symmetry codes: #1: - x, y, - z + 1/2; #2: x, - y + 2, z - 1/2; #3: - x + 1/2, y - 1/2, - z + 1/2.					
1a					
Tb(1)-O(1)	2.533(4)	O(2)-Tb(1)-O(3)#3	83.94(17)	O(5)#2-Tb(1)-O(4)#3	72.92(15)
Tb(1)-O(2)	2.427(5)	O(3)#3-Tb(1)-O(1)	70.91(13)	O(5)#2-Tb(1)-O(6)#1	82.59(17)
Tb(1)-O(3)#3	2.470(4)	O(3)#3-Tb(1)-O(8)	141.77(16)	O(6)#1-Tb(1)-O(1)	69.19(14)
Tb(1)-O(4)#3	2.451(4)	O(4)#3-Tb(1)-O(1)	104.66(16)	O(6)#1-Tb(1)-O(8)	69.66(17)
Tb(1)-O(5)#2	2.321(4)	O(4)#3-Tb(1)-O(8)	123.01(18)	O(6)#1-Tb(1)-O(3)#3	139.93(14)
Tb(1)-O(6)#1	2.380(4)	O(4)#3-Tb(1)-O(3)#3	52.78(14)	O(6)#1-Tb(1)-O(4)#3	143.9(2)
Tb(1)-O(7)	2.423(5)	O(5)#2-Tb(1)-O(3)#3	125.54(13)	O(6)#1-Tb(1)-O(2)	74.79(19)
Tb(1)-O(8)	2.503(4)	O(5)#2-Tb(1)-O(8)	70.13(15)	O(6)#1-Tb(1)-O(7)	135.9(2)
Tb(1)-O(1W)	2.378(5)	O(5)#2-Tb(1)-O(1)	126.31(15)	O(7)-Tb(1)-O(1)	137.44(17)
O(2)-Tb(1)-O(1)	52.22(14)	O(5)#2-Tb(1)-O(2)	77.16(16)	O(7)-Tb(1)-O(8)	68.06(19)
O(2)-Tb(1)-O(8)	133.91(19)	O(5)#2-Tb(1)-O(7)	94.47(18)	O(7)-Tb(1)-O(3)#3	75.59(18)
O(2)-Tb(1)-O(4)#3	74.22(19)	O(5)#2-Tb(1)-O(1W)	148.29(17)	O(7)-Tb(1)-O(4)#3	73.4(2)
O(1W)-Tb(1)-O(6)#1	86.47(19)	O(7)-Tb(1)-O(2)	147.56(19)	O(1W)-Tb(1)-O(3)#3	80.51(17)
O(1W)-Tb(1)-O(7)	73.24(13)	O(8)-Tb(1)-O(1)	132.14(15)	O(1W)-Tb(1)-O(8)	78.16(17)
O(1W)-Tb(1)-O(2)	128.17(15)	O(1W)-Tb(1)-O(4)#5	127.68(19)	O(1W)-Tb(1)-O(1)	75.98(14)
Symmetry codes: #1: - x + 1, y, - z + 1/2; #2: x - 1/2, - y + 3/2, z - 1/2; #3: - x + 1/2, y + 1/2, - z + 1/2.					
1b					
Tb(1)-O(1)	2.424(9)	O(1)-Tb(1)-O(5)#3	89.0(3)	O(5)#3-Tb(1)-O(2)	122.5(3)
Tb(1)-O(2)	2.445(8)	O(1)-Tb(1)-O(2)	53.8(3)	O(6)#3-Tb(1)-O(2)	74.3(3)
Tb(1)-O(3)#1	2.241(8)	O(3)#1-Tb(1)-O(4)#2	85.5(3)	O(7)-Tb(1)-O(2)	154.5(4)
Tb(1)-O(4)#2	2.326(9)	O(3)#1-Tb(1)-O(1W)	78.0(6)	O(6)#3-Tb(1)-O(5)#3	54.0(3)

Tb(1)-O(5)#3	2.431(8)	O(3)#1-Tb(1)-O(1)	103.2(4)	O(7)-Tb(1)-O(5)#3	77.6(4)
Tb(1)-O(6)#3	2.431(9)	O(3)#1-Tb(1)-O(6)#3	146.4(3)	O(4)#2-Tb(1)-O(7)	75.8(4)
Tb(1)-O(7)	2.431(12)	O(3)#1-Tb(1)-O(7)	82.7(4)	O(4)#2-Tb(1)-O(6)#3	125.8(3)
Tb(1)-O(1W)	2.376(16)	O(3)#1-Tb(1)-O(5)#3	157.7(3)	O(4)#2-Tb(1)-O(1W)	150.4(5)
O(1)-Tb(1)-O(6)#3	77.6(4)	O(3)#1-Tb(1)-O(2)	79.4(3)	O(4)#2-Tb(1)-O(1)	74.9(3)
O(1)-Tb(1)-O(7)	149.5(4)	O(4)#2-Tb(1)-O(2)	120.3(3)	O(4)#2-Tb(1)-O(5)#3	79.6(3)
O(1W)-Tb(1)-O(7)	77.8(6)	O(6)#3-Tb(1)-O(7)	113.9(4)	O(1W)-Tb(1)-O(6)#3	77.6(6)
O(1W)-Tb(1)-O(5)#3	107.6(7)	O(1W)-Tb(1)-O(2)	80.9(6)	O(1W)-Tb(1)-O(1)	132.6(5)

Symmetry codes: #1: - x, y, - z + 1/2; #2: x, - y + 1, z - 1/2; #3: - x + 1/2, y - 1/2, - z + 1/2.

1c

Tb(1)-O(1)	2.392(7)	O(3)#1-Tb(1)-O(7)	83.2(3)	O(4)#2-Tb(1)-O(1W)	151.8(2)
Tb(1)-O(2)	2.447(5)	O(3)#1-Tb(1)-O(4)#2	87.05(18)	O(5)#3-Tb(1)-O(2)	122.12(18)
Tb(1)-O(3)#1	2.248(5)	O(3)#1-Tb(1)-O(1W)	83.4(3)	O(7)-Tb(1)-O(2)	147.6(2)
Tb(1)-O(4)#2	2.307(6)	O(3)#1-Tb(1)-O(1)	93.9(2)	O(6)#3-Tb(1)-O(2)	73.35(18)
Tb(1)-O(5)#3	2.440(4)	O(3)#1-Tb(1)-O(6)#3	146.03(16)	O(6)#3-Tb(1)-O(7)	115.7(3)
Tb(1)-O(6)#3	2.404(6)	O(3)#1-Tb(1)-O(2)	76.37(16)	O(6)#3-Tb(1)-O(5)#3	52.02(17)
Tb(1)-O(7)	2.407(8)	O(4)#2-Tb(1)-O(2)	124.0(2)	O(7)-Tb(1)-O(5)#3	81.3(3)
Tb(1)-O(1W)	2.366(8)	O(3)#1-Tb(1)-O(5)#3	161.26(18)	O(1W)-Tb(1)-O(1)	132.7(2)
O(1)-Tb(1)-O(5)#3	95.3(2)	O(4)#2-Tb(1)-O(5)#3	79.8(2)	O(1W)-Tb(1)-O(6)#3	76.2(3)
O(1)-Tb(1)-O(7)	153.4(3)	O(4)#2-Tb(1)-O(7)	79.1(3)	O(1W)-Tb(1)-O(7)	73.5(3)
O(1)-Tb(1)-O(6)#3	80.8(3)	O(4)#2-Tb(1)-O(6)#3	122.8(2)	O(1W)-Tb(1)-O(5)#3	102.0(3)
O(1)-Tb(1)-O(2)	54.48(17)	O(4)#2-Tb(1)-O(1)	74.3(2)	O(1W)-Tb(1)-O(2)	79.3(2)

Symmetry codes: #1: - x, y, - z + 1/2; #2: x, - y, z - 1/2; #3: - x + 1/2, y + 1/2, - z + 1/2.

1d

Tb(1)-O(1)	2.414(6)	O(3)#1-Tb(1)-O(4)#2	89.49(19)	O(5)#3-Tb(1)-O(2)	124.84(19)
Tb(1)-O(2)	2.464(5)	O(3)#1-Tb(1)-O(7)	79.1(6)	O(6)#3-Tb(1)-O(2)	71.59(19)
Tb(1)-O(3)#1	2.266(5)	O(3)#1-Tb(1)-O(1W)	92.0(4)	O(7)-Tb(1)-O(2)	142.8(7)
Tb(1)-O(4)#2	2.289(6)	O(3)#1-Tb(1)-O(5)#3	157.0(2)	O(7)-Tb(1)-O(5)#3	79.6(5)
Tb(1)-O(5)#3	2.446(5)	O(3)#1-Tb(1)-O(2)	77.96(18)	O(6)#3-Tb(1)-O(1)	77.2(3)
Tb(1)-O(6)#3	2.407(6)	O(4)#2-Tb(1)-O(2)	126.9(2)	O(7)-Tb(1)-O(1)	154.3(9)
Tb(1)-O(7)	2.354(14)	O(4)#2-Tb(1)-O(7)	81.5(9)	O(7)-Tb(1)-O(6)#3	123.1(7)
Tb(1)-O(1W)	2.394(10)	O(4)#2-Tb(1)-O(1W)	155.0(4)	O(7)-Tb(1)-O(1W)	74.3(10)
O(1)-Tb(1)-O(2)	53.60(19)	O(4)#2-Tb(1)-O(6)#3	113.5(2)	O(1W)-Tb(1)-O(2)	77.7(5)
O(1)-Tb(1)-O(5)#3	106.2(2)	O(4)#2-Tb(1)-O(1)	75.3(2)	O(1W)-Tb(1)-O(5)#3	90.4(5)
O(3)#1-Tb(1)-O(1)	89.8(2)	O(4)#2-Tb(1)-O(5)#3	79.0(2)	O(1W)-Tb(1)-O(6)#3	75.9(4)
O(3)#1-Tb(1)-O(6)#3	148.94(19)	O(6)#3-Tb(1)-O(5)#3	53.3(2)	O(1W)-Tb(1)-O(1)	129.7(4)

Symmetry codes: #1: - x, y, - z + 1/2; #2: x,- y, z - 1/2; #3: – x + 1/2, y + 1/2,- z + 1/2.

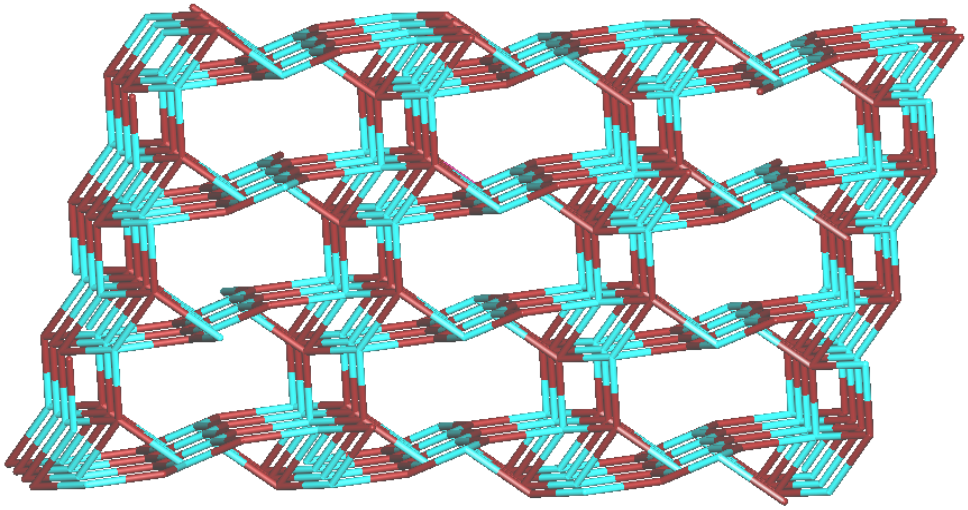


Fig. S1 4,4-Connected 3D net derived from the structure of **1**. Brown and blue 4-connected nodes represent TTCA ligands and Tb ions, respectively.

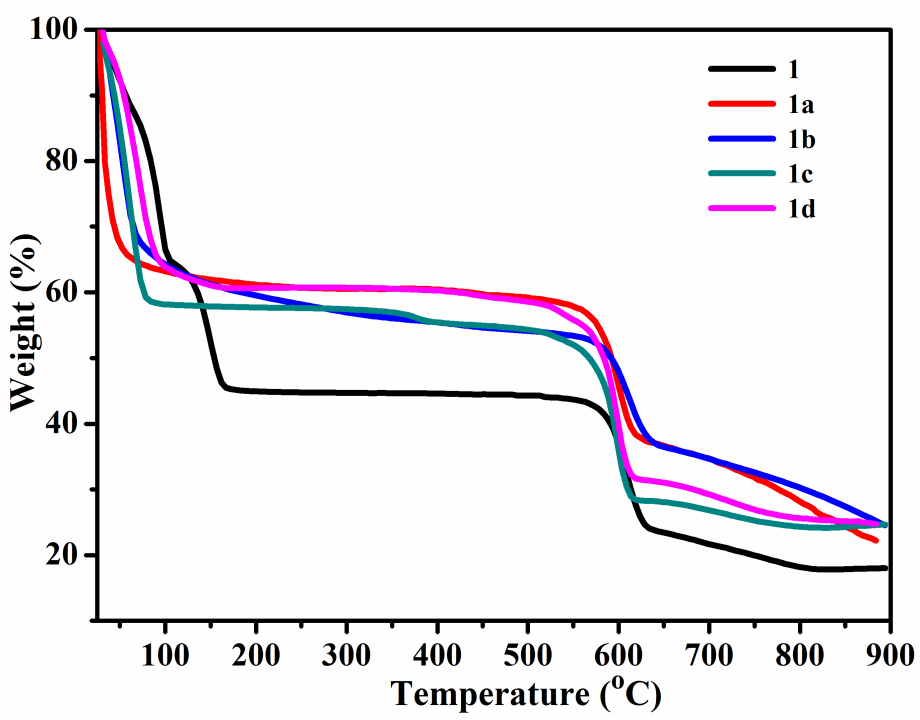


Fig. S2 TGA curves for **1** and **1a-1d**.

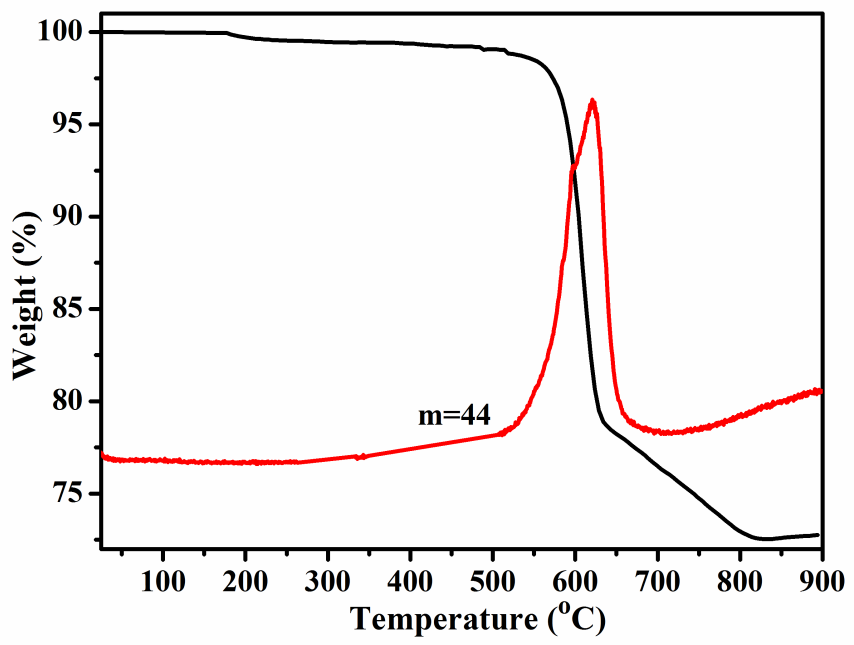


Fig. S3 TG-MS curves for desolvated **1**.

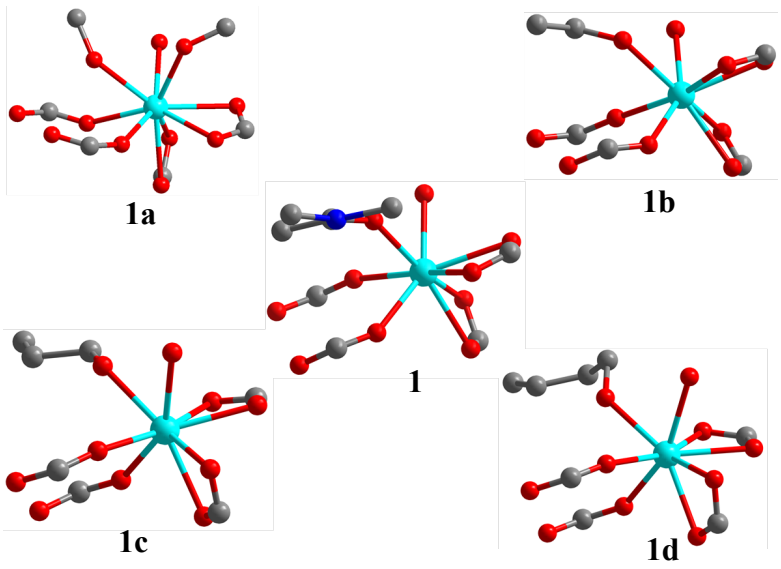


Fig. S4 The coordination environments of Tb1 in **1** and **1a-1d**, indicating the DMA molecule in **1** was exchanged to two methanol molecules in **1a**, and one ethanol, 1-propanol, and 1-butanol molecules in **1b-1d**, respectively.

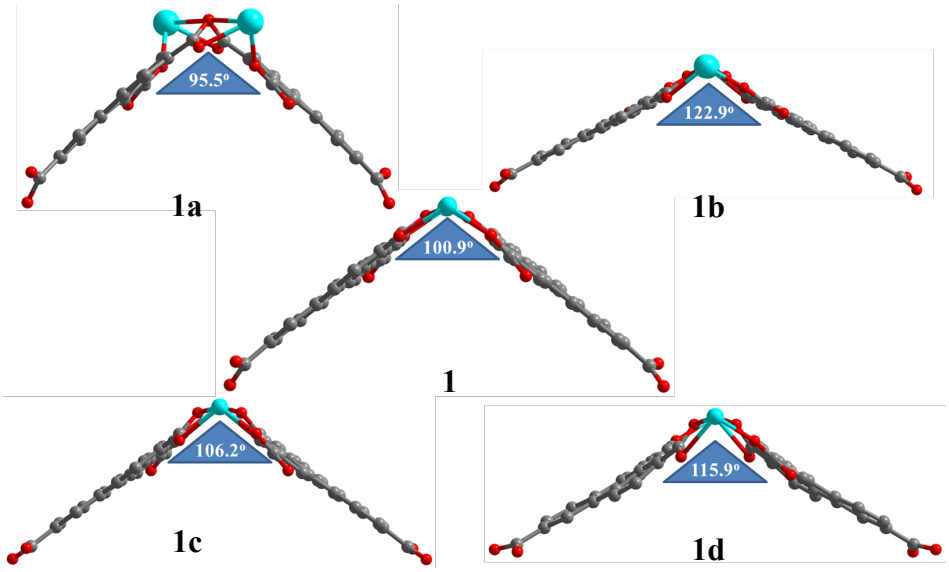


Fig. S5 The dihedral angles between neighbor TTCA ligands of **1** and **1a-1d**.

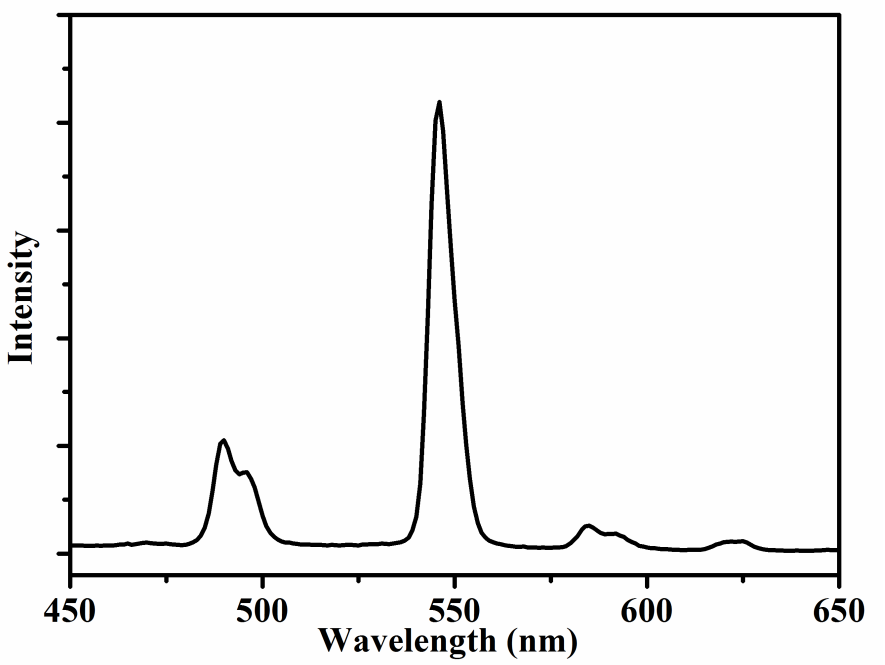
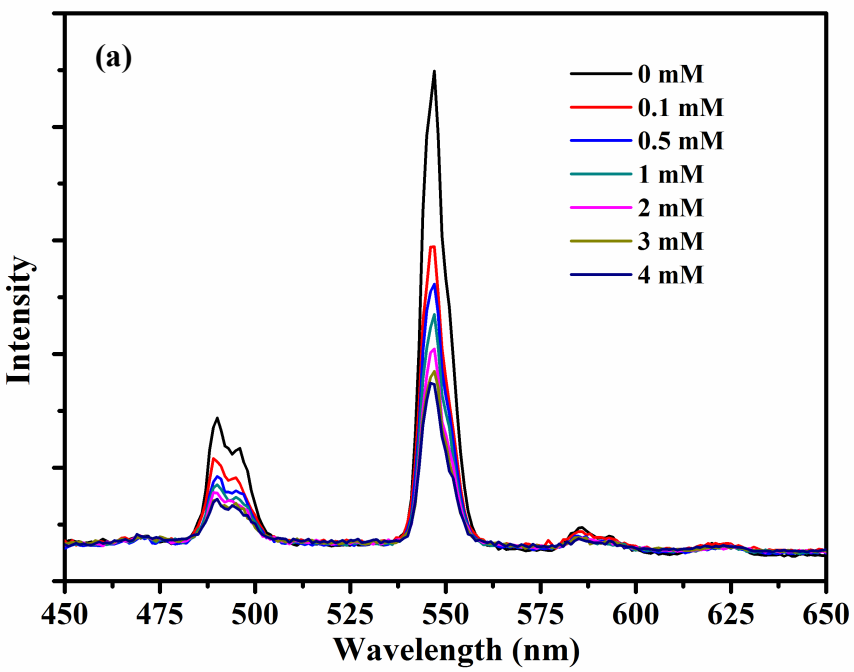
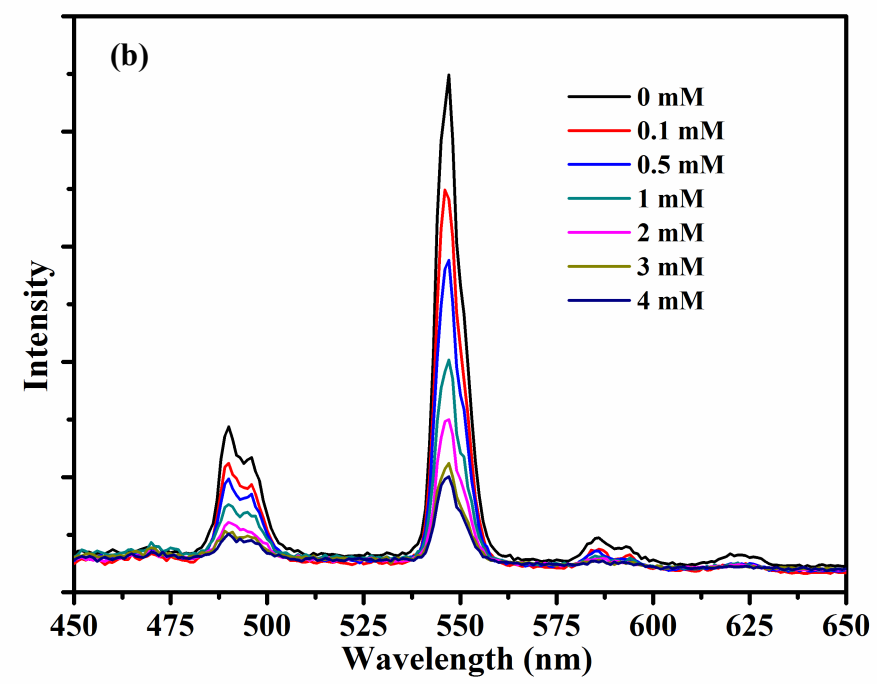


Fig. S6 Emission spectra of **1**.





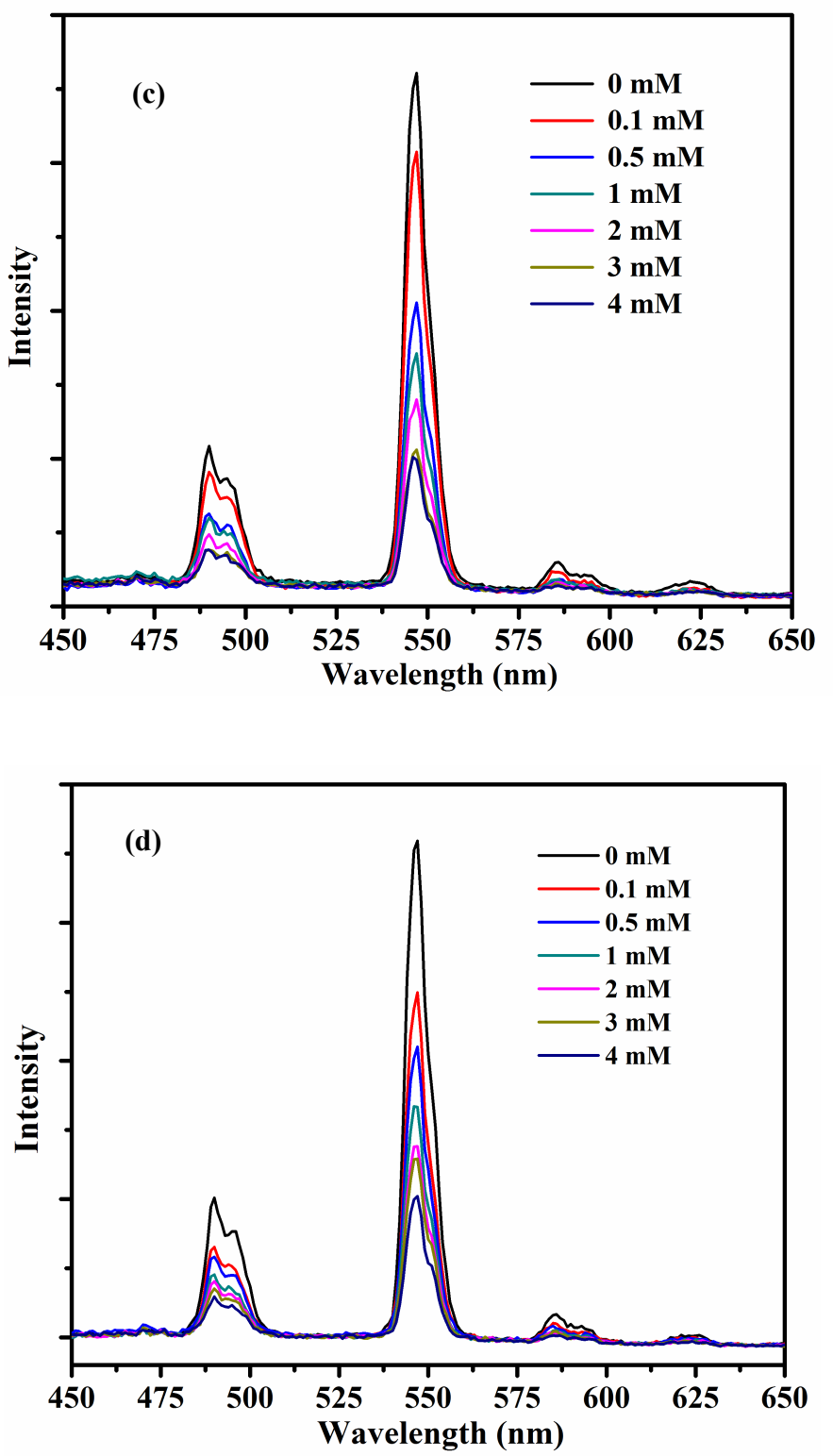


Fig. S7 Luminescence quenching of **1** by gradual addition of ethanol solutions of TNP (a), 2,4-DNT (b), 2,6-DNT (c), and NB (d), respectively.

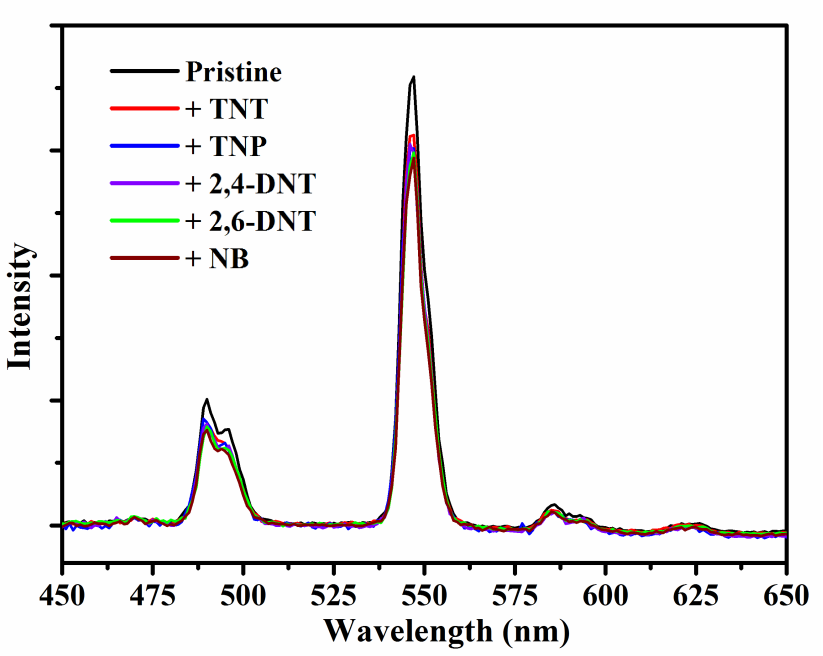


Fig. S8 Luminescence quenching of **1** by adding 5 ppm (0.025 mM) ethanol solutions of TNT, TNP, 2,4-DNT, 2,6-DNT, and NB, respectively, the maximum fluorescent intensity of **1** at 546 nm was reduced to 80.6-86.7%.

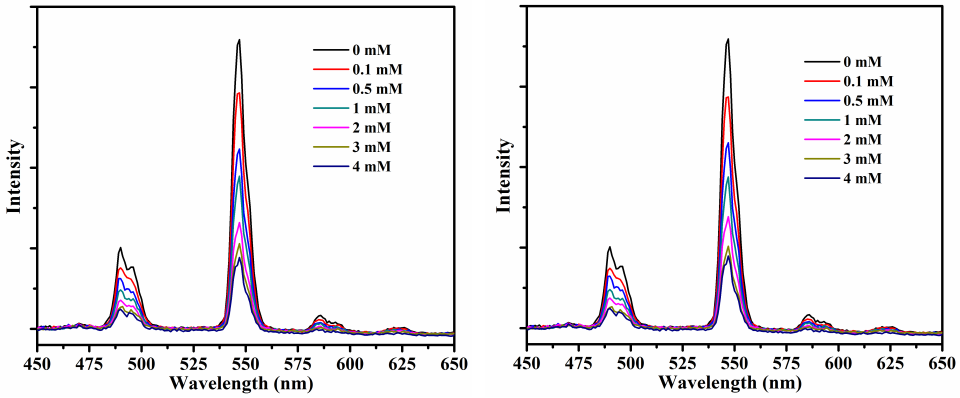


Fig. S9 Luminescence quenching of **1** by gradual addition of ethanol solutions of TNT without (left) and with (right) addition of water (9.2 %) in the solutions, the percentage of fluorescence quenching slightly changed from 18.9 (0.1 mM), 37.8 (0.5 mM), 47.2 (1 mM), 63.3 (2 mM), 70.5 (3 mM) and 75.6% (4 mM) to 19.3 (0.1 mM), 36.6 (0.5 mM), 48.1 (1 mM), 61.4 (2 mM), 71.2 (3 mM) and 73.3% (4 mM) after addition of water, demonstrating the sensing ability of **1** was not interfered by the presence of water.

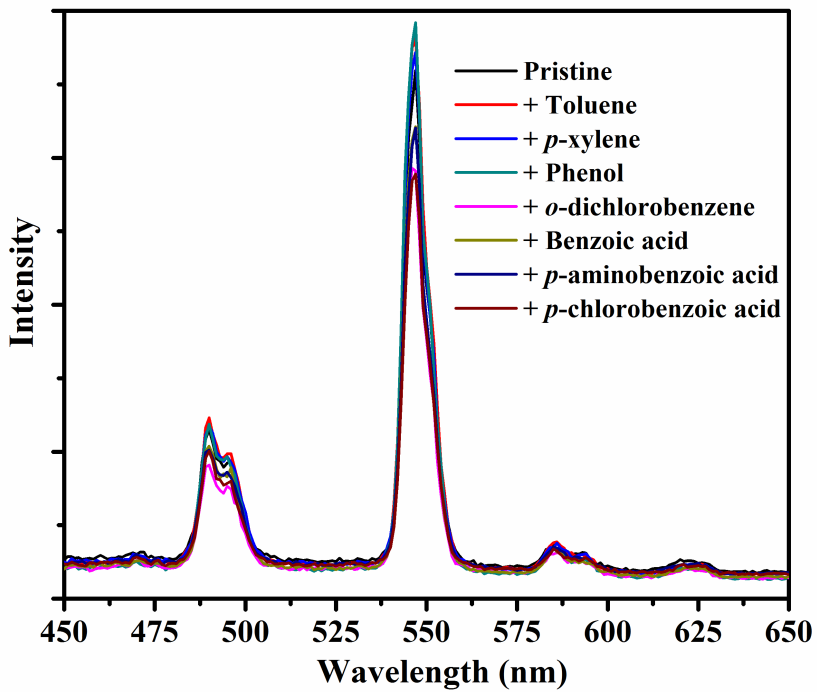


Fig. S10 Luminescence changes of **1** by addition of 4 mM ethanol solutions of toluene, *p*-xylene, phenol, *o*-dichlorobenzene, benzoic acid, *p*-aminobenzoic acid and *p*-chlorobenzoic acid.

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