Supporting information

Cluster-based metal-organic framework as sensitive and selective luminescent probes for sensing nitro explosives

Xiao-Li Hu, Chao Qin,* Xin-Long Wan, Kui-Zhan Shao and Zhong-Min Su*

Institute of Functional Material Chemistry; Faculty of Chemistry, Northeast Normal University, Changchun, 130024, People's Republic of China; E-mail: qinc703@nenu.edu.cn; zmsu@nenu.edu.cn.

S1. Materials and measurements

All chemical materials were purchased from commercial sources and used without further purification. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. XRPD patterns were recorded on a Siemens D5005 diffractometer with Cu $K\alpha$ (λ = 1.5418 Å) radiation in the range of 3−60° at a rate of 5°/min. The UV-Vis absorption spectra were examined on a Shimadzu UV-2550 spectrophotometer in the wavelength range of 200-800 nm. The C, H, and N elemental analyses were conducted on a Perkin-Elmer 2400CHN elemental analyzer. TG curves were performed on a Perkin–Elmer TG-7 analyzer heated from room temperature to 1000 ºC at a ramp rate of 5 °C/min under nitrogen. The photoluminescence spectra were measured on a Perkin-Elmer FLS-920 Edinburgh Fluorescence Spectrometer.

S2. X-ray crystallography

Single-crystal X-ray diffraction data for compound **1** were recorded by using a Bruker Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) at 293 K. Absorption corrections were applied by using a multi-scan technique. All the structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program within WINGX. Non-hydrogen atoms were refined with anisotropic temperature parameters.

The detailed crystallographic data and structure refinement parameters for compound **1** are summarized in Table S1.

S3. The solvent sensing experiment

The solvent sensing experiment has been performed as follows: finely ground samples of **1a** was immersed in different organic solvents (3 mL), treated by ultrasonication for 30 minutes, and then aged to form stable emulsions before fluorescence was measured.

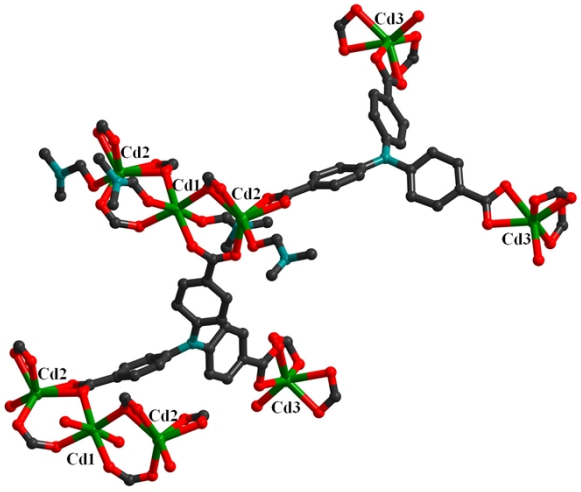

Fig. S1 The coordination environment of the Cd(II) center and the coordination mode of H_3NTB in **1**. The hydrogen atoms are omitted for clarity (Zn, pink; N, blue; C, gray; O, red).

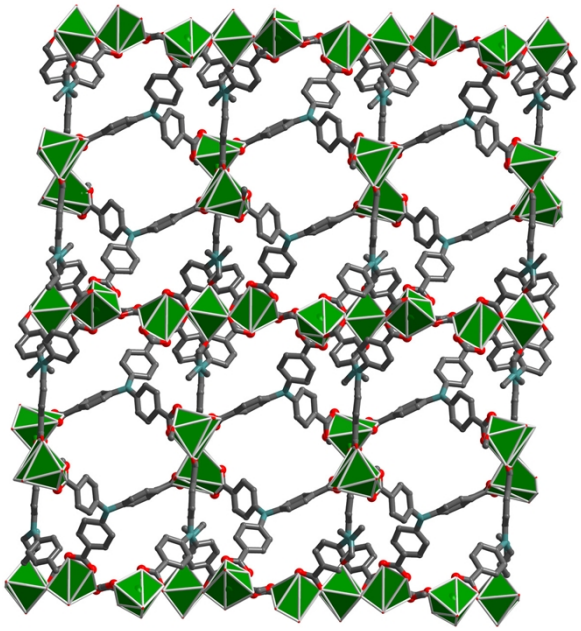

Fig. S2 View of the 3D framework of **1** along the *b* axis.

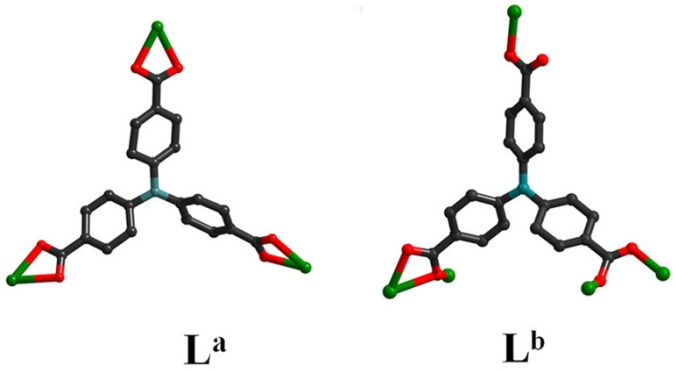

Fig. S3 Coordination Modes of the NTB Ligands in **1** (L^a and L^b)

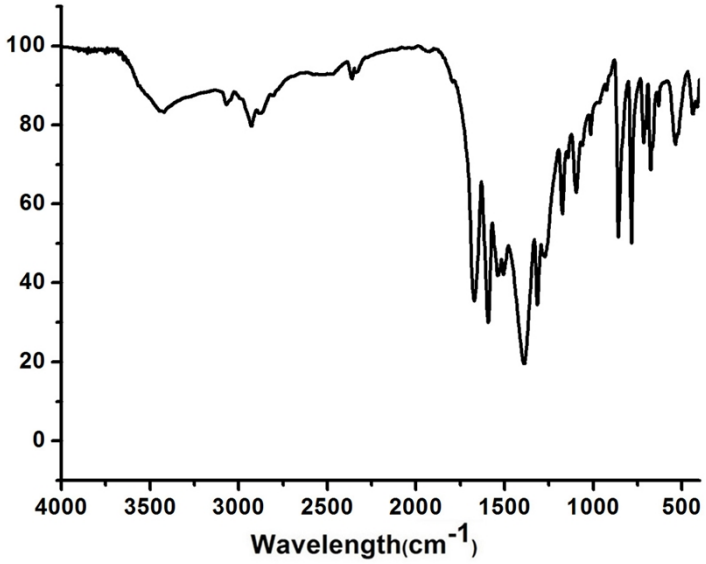

Fig. S4 FT-IR spectra of **1**.

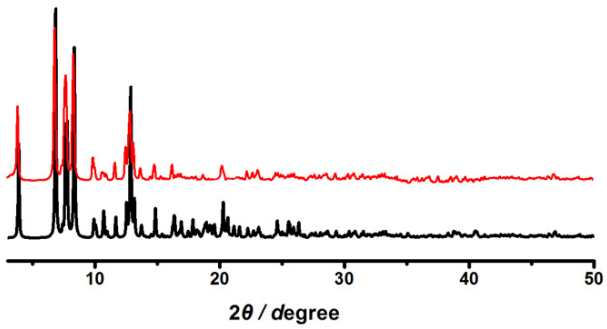

Fig. S5 X-ray powder diffraction patterns of **1**: simulated (black) and as-synthesized

(red).

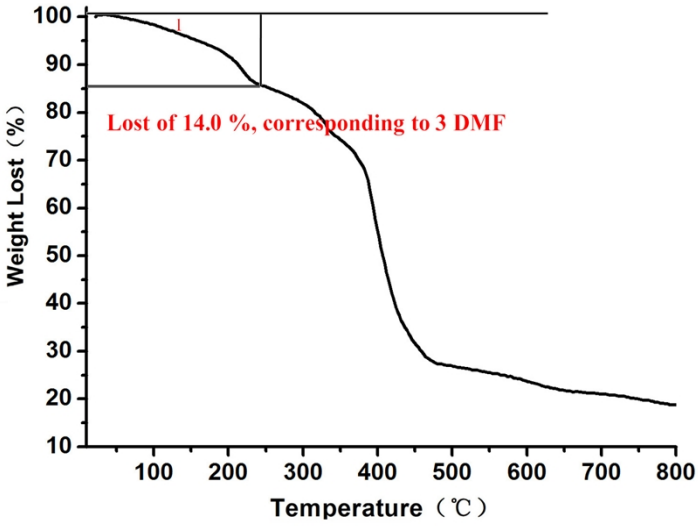

Fig. S6 TG curve of MOF **1**

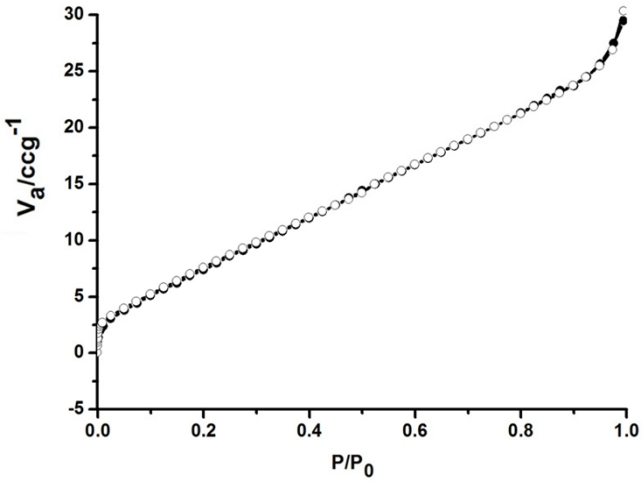

Fig. S7 N_2 sorption isotherms for 1a at 77K.

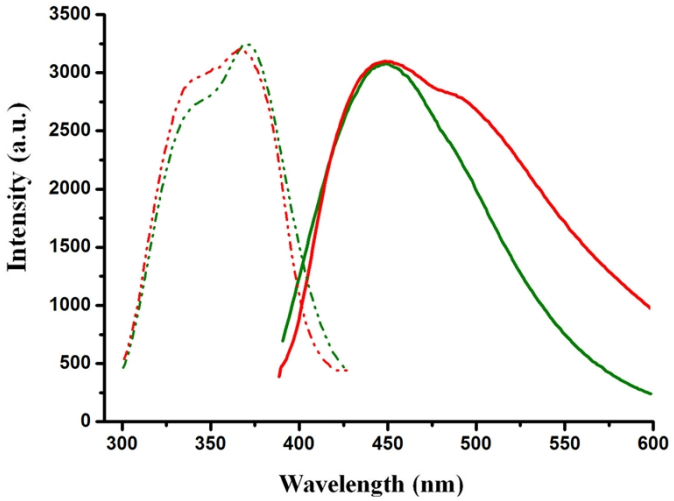

Fig. S8 Excitation and Emission spectra of the NTB ligand (red) and **1** (green).

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

	1
Formula	$C_{63}H_{73}N_9O_{19}NaCd_{2.5}$
Formula weight	1564.3
Crystal system	monoclinic
Space group	*P*2/*c*
a (Å)	25.450(5)
b (Å)	11.928(5)
c (Å)	25.835(5)
α (°)	90
β (°)	116.777(5)
γ (°)	90
V (Å^3)	7002(4)
Z	4
$D_{calcd.}$[gcm^{-3}]	1.484
F(000)	3188
Reflections collected	39241/12312
R(int)	0.1824
Goodness-of-fit on F^2	1.006
R_1[a] [$I>2\sigma(I)$]	0.0979
wR_2[b]	0.2440

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

Table S2 Selected bond lengths [Å] and angles [°] for **1**

Cd(1)-O(6)#1	2.283(11)	Cd(1)-O(6)	2.283(11)
Cd(1)-O(1)#2	2.301(10)	Cd(1)-O(1)#3	2.301(10)
Cd(1)-O(01)	2.302(8)	Cd(1)-O(01)#1	2.302(8)
Cd(2)-O(5)	2.199(12)	Cd(2)-O(02)	2.300(8)
Cd(2)-O(3)	2.301(12)	Cd(2)-O(2)#3	2.320(11)
Cd(2)-O(4)	2.434(13)	Cd(2)-O(1)#3	2.459(10)
Cd(3)-O(7)#4	2.263(11)	Cd(3)-O(03)	2.299(8)
Cd(3)-O(11)	2.311(11)	Cd(3)-O(10)#5	2.375(12)
Cd(3)-O(12)	2.379(11)	Cd(3)-O(9)#5	2.384(12)
O(6)#1-Cd(1)-O(6)	98.5(7)	O(6)#1-Cd(1)-O(1)#2	84.4(4)
O(6)-Cd(1)-O(1)#2	169.6(4)	O(6)#1-Cd(1)-O(01)	92.1(5)
O(6)-Cd(1)-O(01)	83.6(4)	O(1)#2-Cd(1)-O(01)	86.3(4)
O(1)#3-Cd(1)-O(01)	98.2(4)	O(6)#1-Cd(1)-O(01)#1	83.6(4)
O(6)-Cd(1)-O(01)#1	92.1(5)	O(1)#2-Cd(1)-O(01)#1	98.2(4)
O(1)#3-Cd(1)-O(01)#1	86.3(4)	O(01)-Cd(1)-O(01)#1	173.4(7)
O(5)-Cd(2)-O(02)	88.7(5)	O(5)-Cd(2)-O(3)	119.7(5)
O(02)-Cd(2)-O(3)	83.8(5)	O(5)-Cd(2)-O(2)#3	141.3(5)
O(02)-Cd(2)-O(2)#3	93.2(5)	O(3)-Cd(2)-O(2)#3	98.9(5)
O(5)-Cd(2)-O(4)	92.4(5)	O(02)-Cd(2)-O(4)	133.6(5)
O(3)-Cd(2)-O(4)	55.9(4)	O(2)#3-Cd(2)-O(4)	113.2(5)
O(5)-Cd(2)-O(1)#3	104.1(4)	O(02)-Cd(2)-O(1)#3	142.7(4)
O(3)-Cd(2)-O(1)#3	117.3(5)	O(2)#3-Cd(2)-O(1)#3	55.2(4)
O(4)-Cd(2)-O(1)#3	81.6(4)	O(7)#4-Cd(3)-O(03)	85.8(5)
O(7)#4-Cd(3)-O(11)	104.7(5)	O(03)-Cd(3)-O(11)	94.1(5)
O(7)#4-Cd(3)-O(10)#5	105.4(5)	O(03)-Cd(3)-O(10)#5	100.8(5)
O(11)-Cd(3)-O(10)#5	147.1(4)	O(7)#4-Cd(3)-O(12)	107.1(5)
O(03)-Cd(3)-O(12)	149.1(4)	O(11)-Cd(3)-O(12)	55.9(4)
O(10)#5-Cd(3)-O(12)	102.4(4)	O(7)#4-Cd(3)-O(9)#5	156.7(5)
O(03)-Cd(3)-O(9)#5	86.5(5)	O(11)-Cd(3)-O(9)#5	97.7(4)
O(10)#5-Cd(3)-O(9)#5	54.7(4)	O(12)-Cd(3)-O(9)#5	90.5(5)