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pH-stable Eu- and Tb-organic-frameworks mediated by ionic liquid for aqueous-phase detection of 2,4,6-trinitrophenol (TNP)

Jian-Hua Qin, Hua-Rui Wang, Min-Le Han, Xin-Hong Chang and Lu-Fang Ma*

College of Chemistry and Chemical Engineering, and Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, China,

Author for correspondence:

Prof. L-F Ma, E-mail: mazhuxp@126.com.

Supporting Information

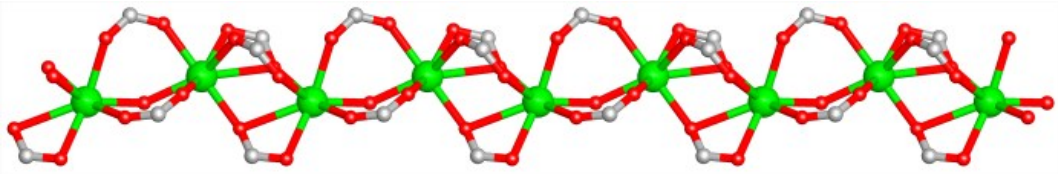

Fig. S1 View of the rod-shaped Eu(III)-carboxylate SBUs.

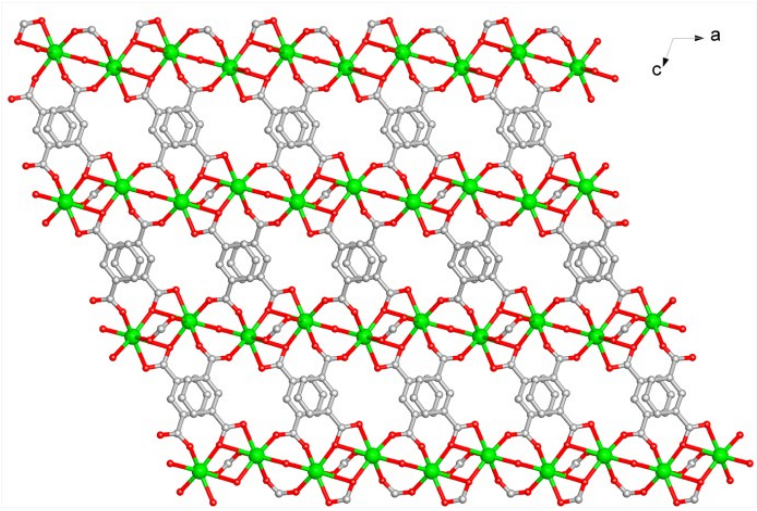

Fig. S2 View of 2D layer constructed by the isophthalic acid segment of L ligands.

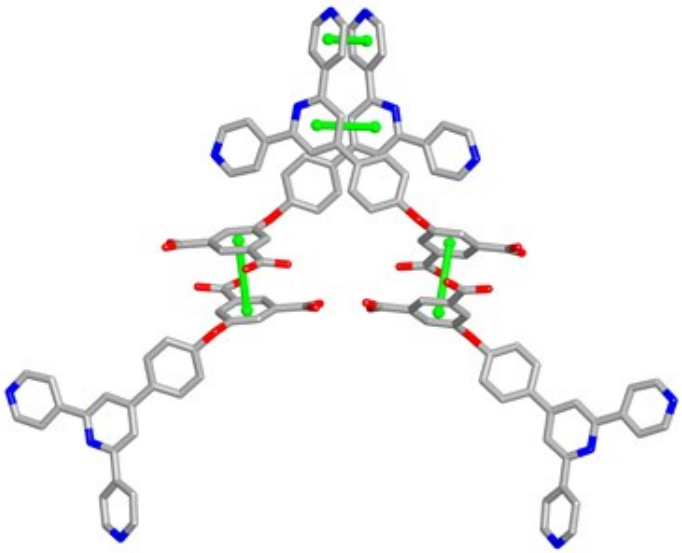

Fig. S3 View of π···π stacking between L ligands. H atoms are omitted for clarity.

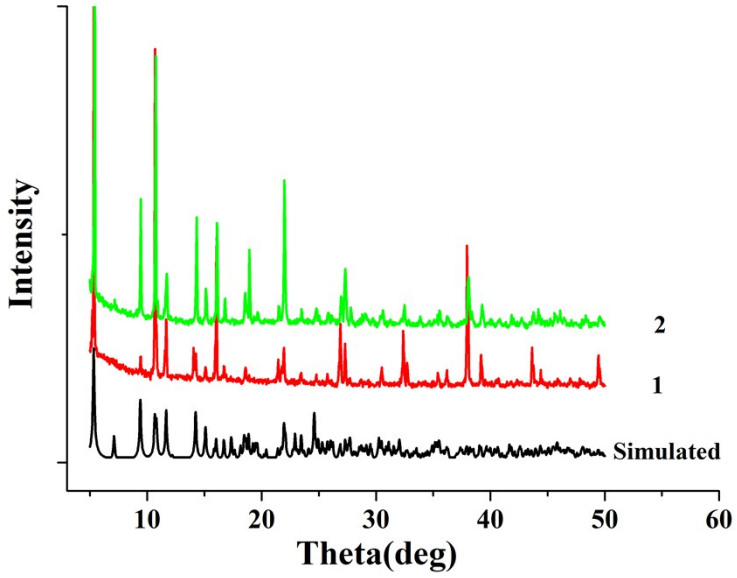

Fig. S4 PXRD patterns of **1** and **2**.

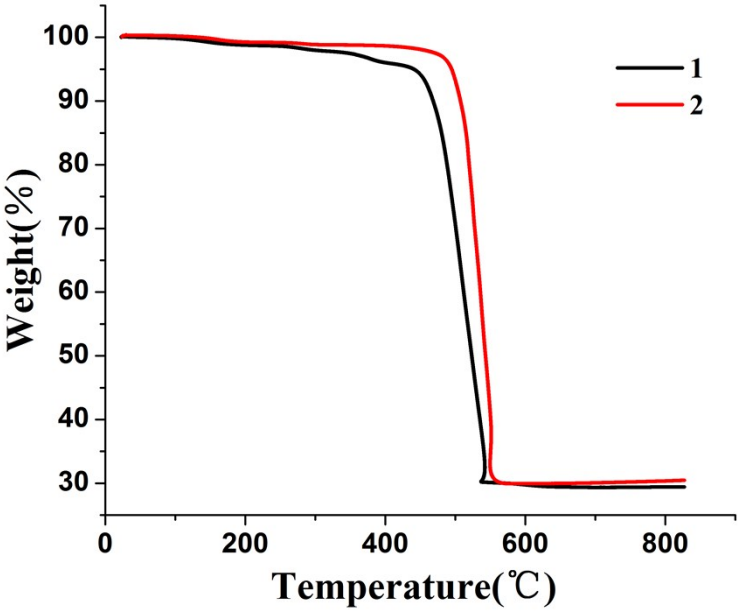

Fig. S5 Thermogravimetric curves of **1** and **2**.

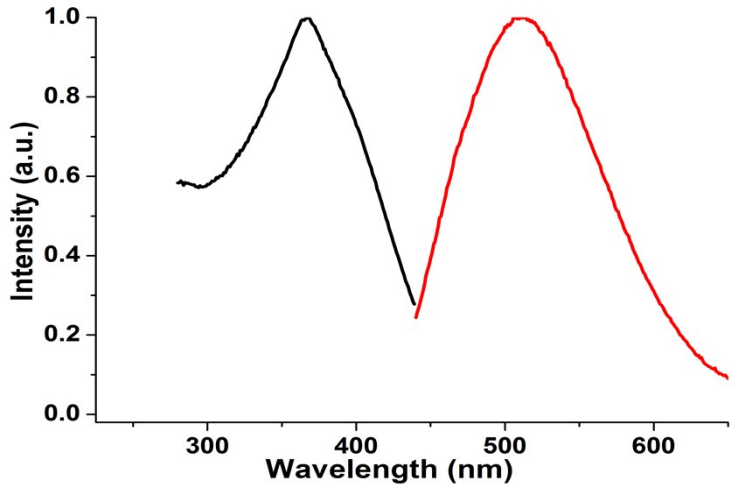

Fig. S6 Solid-state excitation and emission spectra for H_2L.

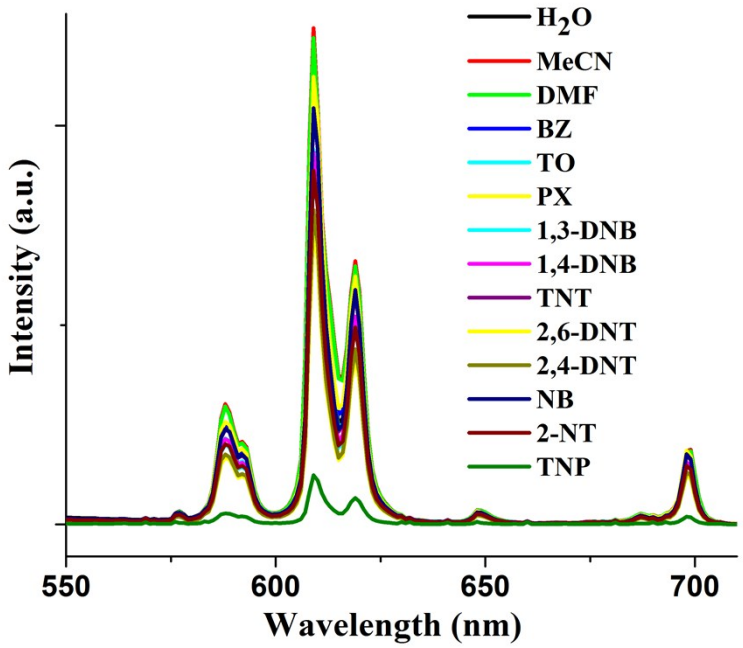

Fig. S7 The emission spectra for **1** dispersed in H_2O, MeCN, DMF, BZ, TO, PX and 1 mM or saturated aqueous solutions of seven different analytes at room temperature.

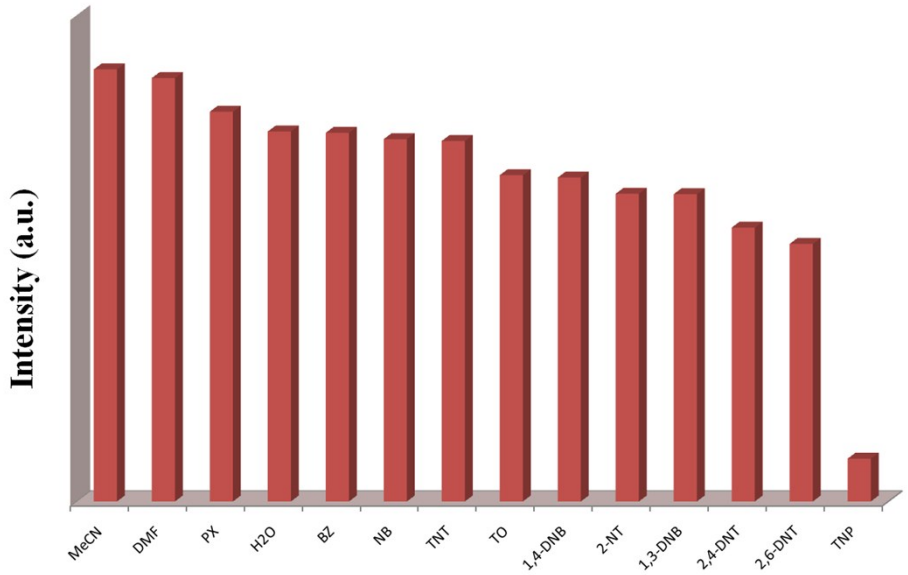

Fig. S8 The fluorescent intensity (609 nm) for **1** dispersed in H_2O, MeCN, DMF, BZ, TO, PX and 1 mM or saturated aqueous solutions of seven different analytes at room temperature.

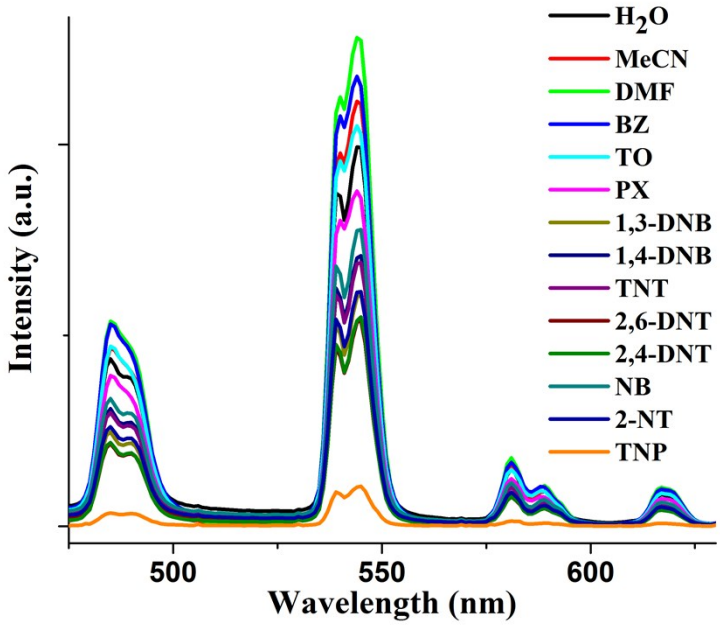

Fig. S9 The emission spectra for **2** dispersed in H_2O, MeCN, DMF, BZ, TO, PX and 1 mM or saturated aqueous solutions of seven different analytes at room temperature.

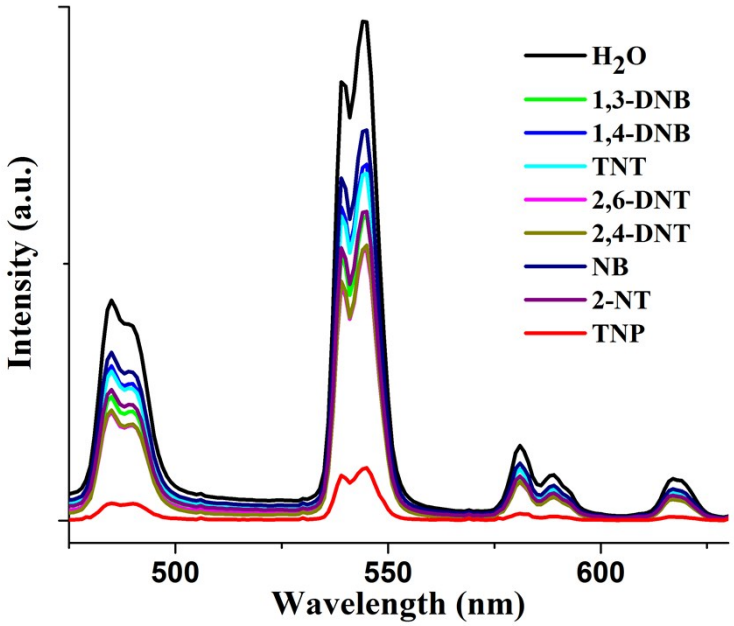

Fig. S10 The emission spectra for **2** dispersed in H_2O and 1 mM or saturated aqueous solutions of the selected analytes at room temperature.

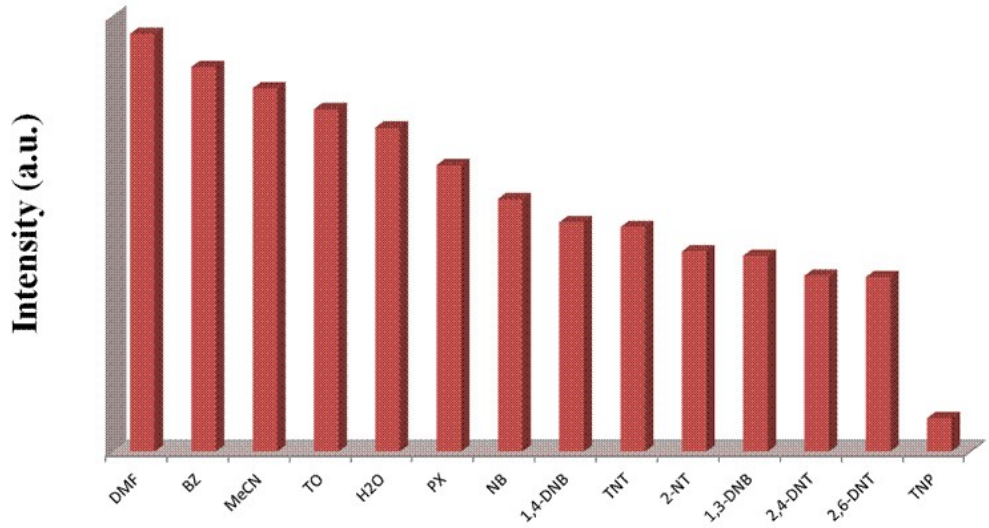

Fig. S11 The fluorescent intensity (544 nm) for **2** dispersed in H_2O, MeCN, DMF, BZ, TO, PX and 1 mM or saturated aqueous solutions of seven different analytes at room temperature.

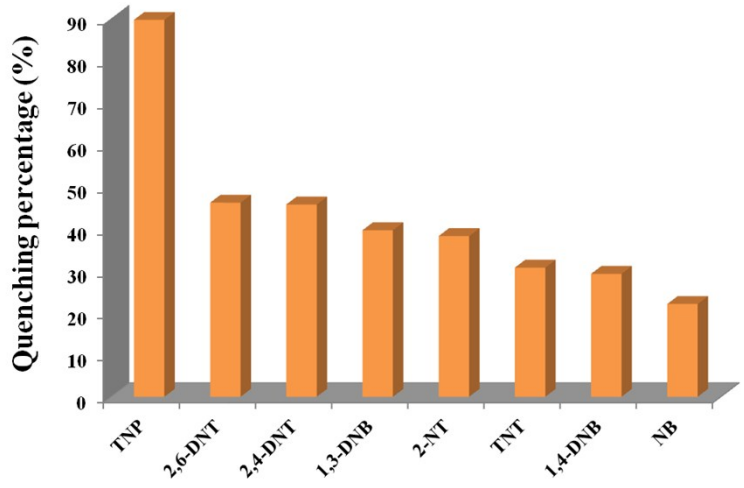

Fig. S12 Quenching efficiency of the fluorescent intensity for **2** dispersed in 1 mM or saturated aqueous solutions of the selected analytes at room temperature.

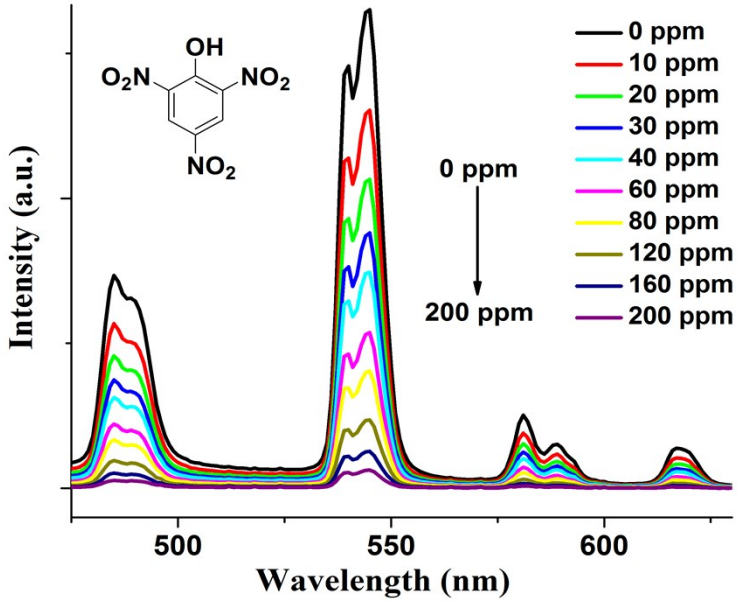

Fig. S13 Fluorescence titration of **2** dispersed in aqueous solution by gradual addition of TNP.

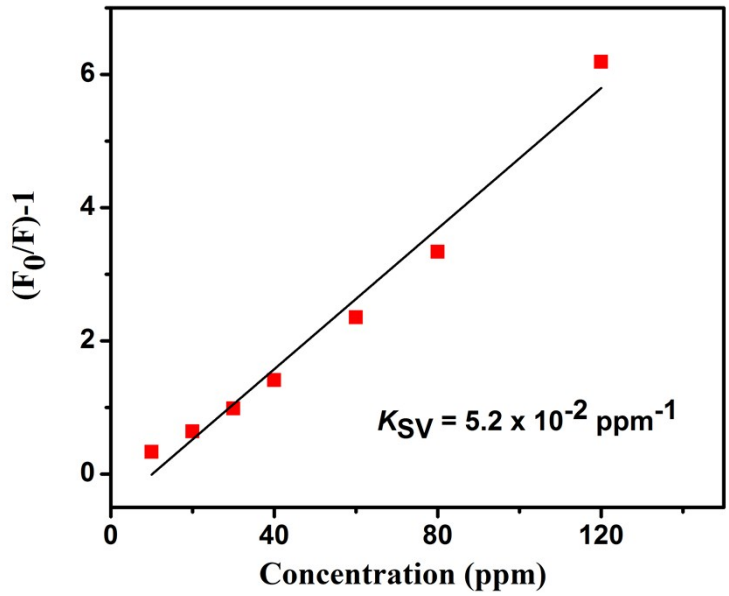

Fig. S14 Stern-Volmer plot of F_0/F *vs*. TNP concentration in aqueous solution for **1**.

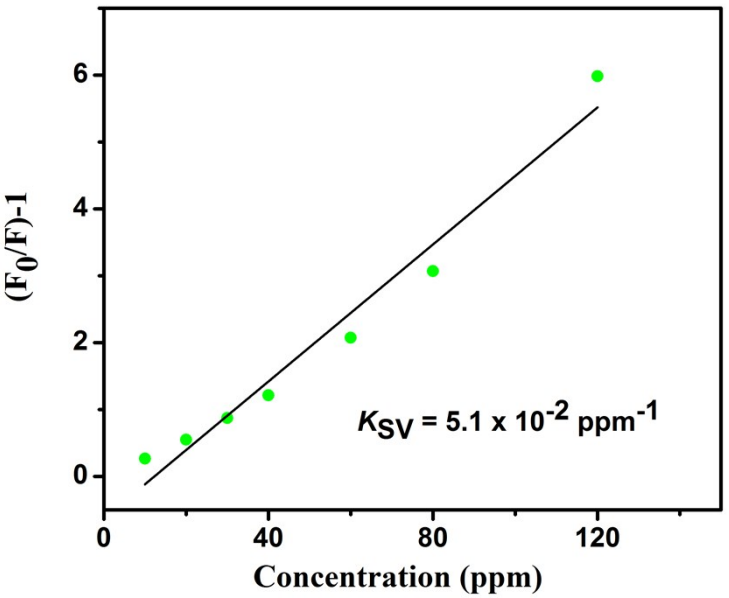

Fig. S15 Stern-Volmer plot of F_0/F *vs*. TNP concentration in aqueous solution for **2**.

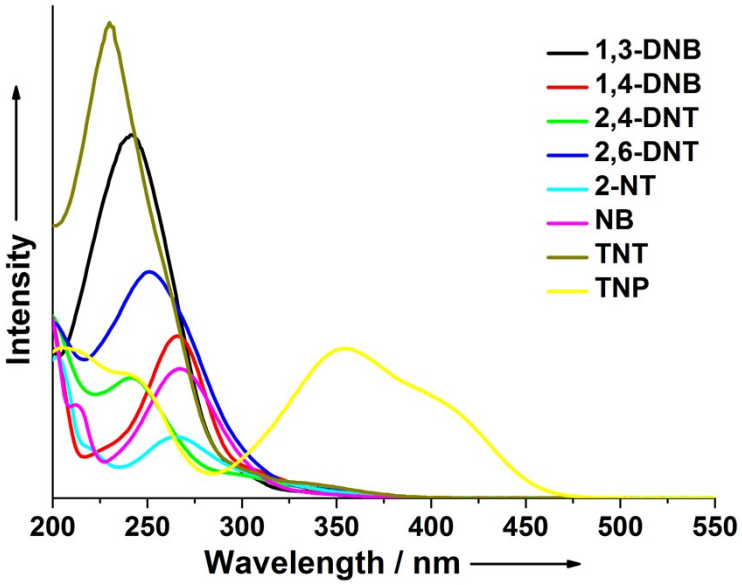

Fig. S16 The absorption spectrum of the selected analytes in water.

Table S1. Crystallographic data and experimental details for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{59}H_{38}Eu_2N_6O_{14}$	$C_{59}H_{38}N_6O_{14}Tb_2$
Formula weight	1358.87	1372.79
Crystal system	monoclinic	monoclinic
Space group	P2/c	P2/c
a/Å	8.0717(3)	8.0636(8)
b/Å	16.6471(6)	16.5777(17)
c/Å	19.9993(7)	20.0148(19)
α/°	90	90
β/°	109.831(3)	110.015(3)
γ/°	90	90
Volume/Å^3	2527.95(16)	2513.9(4)
Z	2	2
ρ_{calc}g/cm^3	1.785	1.814
μ/mm^{-1}	2.538	2.870
F(000)	1344.0	1352.0
2Θ range for data collection/°	5.898 to 54.998	4.98 to 54.998
Reflections collected	11618	20084
Independent reflections	5577 [R_{int} = 0.0300, R_{sigma} = 0.0482]	5677 [R_{int} = 0.0303, R_{sigma} = 0.0335]
Data/restraints/parameters	5577/47/367	5677/39/367
Goodness-of-fit on F^2	1.027	1.194
Final R indexes [I>=2σ (I)]	R_1 = 0.0294, wR_2 = 0.0586	R_1 = 0.0433, wR_2 = 0.0910
Final R indexes [all data]	R_1 = 0.0399, wR_2 = 0.0633	R_1 = 0.0515, wR_2 = 0.0938

$R = [\sum | |F_0| - |F_c| | / \sum |F_0|]$, $R_W = \sum_W [|F_0^2 - Fc^2|^2 / \sum_W (|F_w|^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Eu1	O1[1]	2.414(2)	Eu1	O4[4]	2.384(2)
Eu1	O2[1]	2.759(2)	Eu1	O6	2.384(3)
Eu1	O2	2.366(2)	Eu1	O7	2.3144(14)
Eu1	O3[3]	2.335(2)	Eu1	N1[5]	2.693(3)

[1]3-X,+Y,5/2-Z; [2]2-X,+Y,5/2-Z; [3]+X,2-Y,1/2+Z; [4]2-X,2-Y,2-Z; [5]1+X,1-Y,1/2+Z; [6]+X,2-Y,-1/2+Z; [7]-1+X,1-Y,-1/2+Z

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[1]	Eu1	O2[1]	49.94(7)	O6	Eu1	O1[1]	80.74(9)
O1[1]	Eu1	N1[3]	77.66(9)	O6	Eu1	O2[1]	71.95(9)
O2	Eu1	O1[1]	116.55(8)	O6	Eu1	O4[4]	71.45(9)
O2	Eu1	O2[1]	67.53(9)	O6	Eu1	N1[3]	144.68(9)
O2	Eu1	O4[4]	76.43(8)	O7	Eu1	O1[1]	119.72(7)
O2	Eu1	O6	90.64(9)	O7	Eu1	O2[1]	144.35(10)
O2	Eu1	N1[3]	74.78(9)	O7	Eu1	O2	103.62(7)
O3[5]	Eu1	O1[1]	74.71(8)	O7	Eu1	O3[5]	79.84(8)
O3[5]	Eu1	O2	162.40(9)	O7	Eu1	O4[4]	79.62(8)
O3[5]	Eu1	O2[1]	119.43(7)	O7	Eu1	O6	143.70(11)
O3[5]	Eu1	O4[4]	87.40(9)	O7	Eu1	N1[3]	71.61(10)
O3[5]	Eu1	O6	77.45(10)	O4[4]	Eu1	O2[1]	127.37(7)
O3[5]	Eu1	N1[3]	122.20(10)	O4[4]	Eu1	N1[3]	132.54(9)
O4[4]	Eu1	O1[1]	149.67(9)				

[1]3-X,+Y,5/2-Z; [2]2-X,+Y,5/2-Z; [3]1+X,1-Y,1/2+Z; [4]2-X,2-Y,2-Z; [5]+X,2-Y,1/2+Z; [6]+X,2-Y,-1/2+Z; [7]-1+X,1-Y,-1/2+Z

Table S3. Selected bond lengths (Å) and angles (°) for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Tb1	O1[1]	2.382(4)	Tb1	O4[3]	2.367(4)
Tb1	O2[1]	2.816(4)	Tb1	O6	2.342(4)
Tb1	O2	2.335(4)	Tb1	O7	2.281(2)
Tb1	O3[2]	2.306(4)	Tb1	N1[4]	2.664(5)

[1]3-X,+Y,5/2-Z; [2]+X,2-Y,1/2+Z; [3]2-X,2-Y,2-Z; [4]1+X,1-Y,1/2+Z; [5]+X,2-Y,-1/2+Z; [6]2-X,+Y,5/2-Z; [7]-1+X,1-Y,-1/2+Z

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[1]	Tb1	O2[1]	49.10(12)	O6	Tb1	N1[2]	144.28(16)
O1[1]	Tb1	N1[2]	77.04(15)	O7	Tb1	O1[1]	120.88(12)
O1[1]	Tb1	C1[1]	23.81(13)	O7	Tb1	O2	103.42(11)
O2	Tb1	O1[1]	115.31(13)	O7	Tb1	O2[1]	145.05(15)
O2	Tb1	O2[1]	67.24(13)	O7	Tb1	O3[4]	79.91(13)
O2	Tb1	O4[3]	76.88(14)	O7	Tb1	O4[3]	78.89(13)
O2	Tb1	O6	90.68(15)	O7	Tb1	O6	143.67(16)
O2	Tb1	N1[2]	74.77(16)	O7	Tb1	N1[2]	72.05(17)
O3[4]	Tb1	O1[1]	75.14(13)	N1[2]	Tb1	O2[1]	73.01(14)
O3[4]	Tb1	O2	163.33(15)	O4[3]	Tb1	O1[1]	150.01(15)
O3[4]	Tb1	O2[1]	119.07(12)	O4[3]	Tb1	O2[1]	127.28(12)
O3[4]	Tb1	O4[3]	87.91(14)	O4[3]	Tb1	N1[2]	132.78(15)
O3[4]	Tb1	O6	77.95(16)	O6	Tb1	O1[1]	80.36(15)
O3[4]	Tb1	N1[2]	121.39(17)	O6	Tb1	O2[1]	71.28(14)
O6	Tb1	O4[3]	71.89(14)	O6	Tb1	N1[2]	144.28(16)
O1[1]	Tb1	O2[1]	49.10(12)				

[1]3-X,+Y,5/2-Z; [2]1+X,1-Y,1/2+Z; [3]2-X,2-Y,2-Z; [4]+X,2-Y,1/2+Z; [5]+X,2-Y,-1/2+Z; [6]2-X,+Y,5/2-Z; [7]-1+X,1-Y,-1/2+Z

Table S4. Saturated vapor pressure and Reduction Potential for each of the analytes at room temperature (25 °C).

Analytes	Vapor Pressure (in mmHg)	Reduction Potential (in V *vs* SCE)
Nitrobenzene (NB)[1]	0.2416	−1.15
2-Nitrotoluene (2-NT)[1]	0.1602	−1.2
1,3-Dinitrobenzene(1,3-DNB)[2]	8.82×10^{-4}	−0.9
1,4-Dinitrobenzene (1,4-DNB)[1]	2.406×10^{-5}	−0.7
2,4-dinitrotoluene (2,4-DNT)[1]	1.44×10^{-4}	−1.0
2,6-dinitrotoluene (2,6-DNT)[1,3]	5.61×10^{-4}	−1.0
2,4,6-trinitrotoluene (TNT)[1,4]	8.02×10^{-6}	−0.7
2,4,6-trinitrophenol (TNP)[4]	5.8×10^{-9}	−0.63

1 J. S. Yang and T. M. Swager, *J. Am. Chem. Soc*., 1998, **120**, 11864.

2 R. Hoffmann, *J. Chem. Phys*., 1963, **39**, 1397.

3 A. J. Lan, K. H. Li, H. H. Wu, L. Z. Kong, N. Nijem, D. H. Olson, T. J. Emge, Y. J. Chabal, D. C. Langreth, M. C. Hong and J. Li, *Inorg. Chem*., 2009, **48**, 7165.

4 J. C. Sanchez and W. C. Trogler, *J. Mater. Chem*., 2008, **18**, 3143.

Table S5. Approximate sizes of the selected analytes.

Analytes	Approximate Size (D×W×L, Å)
NB	3.4 × 6.2 × 8.6
2-NT	5.0 × 7.7 × 8.6
1,3-DNB	5.6 × 7.7 × 8.1
1,4-DNB	5.6 × 7.7 × 9.1
2,4-DNT	5.6 × 7.7 × 10.1
2,6-DNT	5.6 × 7.7 × 9.5

TNT	5.6 × 7.7 × 10.2
TNP	5.0 × 6.2 × 7.1

Table S6. HOMO and LUMO energies calculated for H_2L and nitroaromatic explosives at B3LYP/6-31G** level of theory.

Analytes	**HOMO (eV)**	**LUMO (eV)**	**Band gap**
H_2L	-6.50706	-2.0414	4.46566
NB[6]	-7.5912	-2.4283	5.1629
2-NT[5]	-7.36454	-2.31722	5.04732
1,3-DNB[6]	-7.9855	-3.4311	4.5544
1,4-DNB[5]	-8.35250	-3.49679	4.85571
2,4-DNT[6]	-7.7645	-3.2174	4.5471
2,6-DNT[6]	-7.6448	-3.2877	4.3571
TNT[6]	-8.2374	-3.8978	4.3396
TNP[6]	-8.4592	-3.4926	4.9666

5 G. Y. Wang, C. Song, D. M. Kong, W. J. Ruan, Z. Chang and Y. Li, *J. Mater. Chem. A*., 2014, **2**, 2213.

6 S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem., Int. Ed*., 2013, **52**, 2881.