Electronic Supplementary Information (ESI)

Novel Double Layer Lanthanide Metal-Organic Networks for Sensing Applications

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Table S1. Selected Bond Lengths (Å) and Angles (˚) for **1**.

Tb1—Tb1^{i}	3.9054 (9)	Tb1—O1	2.345 (7)	Tb1—O2^{i}	2.326 (7)
Tb1—O3^{ii}	2.408 (6)	Tb1—O4^{ii}	2.488 (6)	Tb1—O7	2.473 (7)
Tb1—O8^{i}	2.328 (7)	C17—Tb1^{iii}	2.825 (10)	Tb1—O8	2.538 (6)
Tb1—N1	2.528 (8)	Tb1—N2	2.591 (8)	Tb1—C17^{ii}	2.825 (10)
Tb1—C29	2.881 (10)	O2—Tb1^{i}	2.326 (7)	O3—Tb1^{iii}	2.408 (6)
O4—Tb1^{iii}	2.488 (6)	O8—Tb1^{i}	2.328 (7)	O1—Tb1—Tb1^{i}	69.74 (15)
O1—Tb1—O3^{ii}	129.1 (2)	O1—Tb1—O4^{ii}	76.3 (2)	O1—Tb1—O7	77.8 (2)
O1—Tb1—O8	71.7 (2)	O1—Tb1—N1	79.5 (3)	O1—Tb1—N2	133.0 (3)
O1—Tb1—C17^{ii}	102.8 (3)	O1—Tb1—C29	72.4 (2)	O2^{i}—Tb1—Tb1^{i}	68.74 (15)
O2^{i}—Tb1—O1	138.5 (2)	O2^{i}—Tb1—O3^{ii}	78.8 (2)	O2^{i}—Tb1—O4^{ii}	119.2 (2)
O2^{i}—Tb1—O7	98.3 (3)	O2^{i}—Tb1—O8	73.9 (2)	O2^{i}—Tb1—O8^{i}	72.2 (2)
O2^{i}—Tb1—N1	140.1 (2)	O2^{i}—Tb1—N2	77.1 (3)	O3—C17—Tb1^{iii}	58.1 (5)
O2^{i}—Tb1—C17^{ii}	98.5 (3)	O2^{i}—Tb1—C29	86.5 (3)	O4—C17—Tb1^{iii}	61.7 (5)
O3^{ii}—Tb1—Tb1^{i}	126.74 (17)	O3^{ii}—Tb1—O4^{ii}	53.0 (2)	O3^{ii}—Tb1—O7	141.2 (2)
C16—C17—Tb1^{iii}	174.8 (7)	O3^{ii}—Tb1—O8	151.9 (2)	O3^{ii}—Tb1—N1	83.0 (3)
O3^{ii}—Tb1—N2	76.8 (2)	O3^{ii}—Tb1—C17^{ii}	26.5 (2)	O3^{ii}—Tb1—C29	158.0 (2)
O4^{ii}—Tb1—Tb1^{i}	109.80 (15)	O4^{ii}—Tb1—O8	139.3 (2)	O4^{ii}—Tb1—N1	73.9 (2)
O4^{ii}—Tb1—N2	117.4 (2)	O4^{ii}—Tb1—C17^{ii}	26.6 (2)	O4^{ii}—Tb1—C29	148.6 (3)
O7—Tb1—Tb1^{i}	85.90 (16)	O7—Tb1—O4^{ii}	142.3 (2)	O7—Tb1—O8	51.5 (2)
O7—Tb1—N1	74.9 (3)	O7—Tb1—N2	65.0 (2)	O7—Tb1—C17^{ii}	152.8 (3)
O7—Tb1—C29	25.6 (3)	O8—Tb1—Tb1^{i}	34.84 (15)	O8^{i}—Tb1—Tb1^{i}	38.51 (15)
O8^{i}—Tb1—O1	76.2 (2)	O8^{i}—Tb1—O3^{ii}	92.4 (2)	O8^{i}—Tb1—O4^{ii}	75.1 (2)
O8^{i}—Tb1—O7	124.0 (2)	O8^{i}—Tb1—O8	73.4 (2)	O8^{i}—Tb1—N1	144.1 (2)
O8^{i}—Tb1—N2	148.9 (3)	O8—Tb1—N2	102.8 (2)	O8—Tb1—C17^{ii}	155.0 (2)
O8^{i}—Tb1—C17^{ii}	81.7 (2)	O8^{i}—Tb1—C29	98.7 (3)	O8—Tb1—C29	25.9 (3)
N1—Tb1—Tb1^{i}	146.6 (2)	N1—Tb1—O8	122.7 (2)	N1—Tb1—N2	64.3 (3)
N1—Tb1—C17^{ii}	78.5 (3)	N1—Tb1—C29	98.5 (3)	O7—C29—Tb1	58.6 (5)
N2—Tb1—Tb1^{i}	130.90 (18)	N2—Tb1—C17^{ii}	98.4 (3)	N2—Tb1—C29	84.0 (3)
O8—C29—Tb1	61.7 (5)	C17^{ii}—Tb1—Tb1^{i}	120.18 (19)	C17^{ii}—Tb1—C29	174.8 (3)
C30—C29—Tb1	175.8 (8)	C29—Tb1—Tb1^{i}	60.4 (2)	C13—O1—Tb1	136.7 (6)
C13—O2—Tb1^{i}	139.6 (6)	C17—O3—Tb1^{iii}	95.4 (6)	C17—O4—Tb1^{iii}	91.8 (5)
C29—O7—Tb1	95.8 (6)	Tb1^{i}—O8—Tb1	106.6 (2)	C29—O8—Tb1	92.4 (6)
C29—O8—Tb1^{i}	157.3 (6)	C1—N1—Tb1	121.9 (7)	C1—N1—C5	117.1 (9)
C5—N1—Tb1	120.4 (7)	C6—N2—Tb1	117.4 (7)	C12—N2—Tb1	122.1 (7)

Symmetry codes: (i) −x+2, −y+1, −z+1; (ii) x+1/2, −y+1/2, z; (iii) x−1/2, −y+1/2, z.

Table S2. Selected Bond Lengths (Å) and Angles (˚) for **2**.

Eu1—Eu1^{i}	3.9341 (9)	Eu1—O1	2.375 (5)	Eu1—N1	2.562 (8)
Eu1—N2	2.600 (8)	Eu1—O7^{i}	2.345 (6)	Eu1—O7	2.569 (6)
O2—Eu1^{i}	2.358 (6)	Eu1—O8	2.504 (7)	Eu1—C17	2.914 (10)
Eu1—O2^{i}	2.359 (6)	Eu1—O3^{ii}	2.445 (6)	Eu1—O4^{ii}	2.512 (6)
Eu1—C8^{ii}	2.832 (9)	O3—Eu1^{iii}	2.445 (6)	O4—Eu1^{iii}	2.512 (6)
O7—Eu1^{i}	2.345 (6)	C8—Eu1^{iii}	2.832 (9)	O1—Eu1—Eu1^{i}	69.47 (15)
O1—Eu1—N1	79.6 (2)	C18—C17—Eu1	176.5 (7)	O1—Eu1—N2	132.9 (2)
O1—Eu1—O7	71.8 (2)	O1—Eu1—O8	78.1 (2)	O1—Eu1—C17	72.5 (2)
O1—Eu1—O3^{ii}	128.9 (2)	O1—Eu1—O4^{ii}	76.3 (2)	O1—Eu1—C8^{ii}	102.7 (2)
N1—Eu1—Eu1^{i}	146.43 (16)	N1—Eu1—N2	64.3 (2)	N1—Eu1—O7	122.7 (2)
N1—Eu1—C17	98.3 (3)	N1—Eu1—C8^{ii}	78.5 (3)	N2—Eu1—Eu1^{i}	130.87 (19)
N2—Eu1—C17	83.5 (2)	N2—Eu1—C8^{ii}	98.7 (2)	O7—Eu1—Eu1^{i}	34.91 (14)
O7^{i}—Eu1—Eu1^{i}	38.81 (16)	O7^{i}—Eu1—O1	75.8 (2)	O7^{i}—Eu1—N1	143.7 (2)
O7^{i}—Eu1—N2	149.4 (2)	O7—Eu1—N2	102.5 (2)	O7^{i}—Eu1—O7	73.7 (2)
O7^{i}—Eu1—O8	124.0 (2)	O7^{i}—Eu1—C17	99.3 (3)	O7—Eu1—C17	26.1 (2)
O7^{i}—Eu1—O2^{i}	72.8 (2)	O7^{i}—Eu1—O3^{ii}	92.4 (2)	O7^{i}—Eu1—O4^{ii}	75.2 (2)
O7^{i}—Eu1—C8^{ii}	81.4 (2)	O7—Eu1—C8^{ii}	155.1 (2)	O8—Eu1—Eu1^{i}	85.62 (16)
O8—Eu1—N1	75.3 (2)	O8—Eu1—N2	64.7 (2)	O8—Eu1—O7	51.2 (2)
O8—Eu1—C17	25.0 (2)	C1—O2—Eu1^{i}	137.9 (6)	O8—Eu1—O4^{ii}	142.3 (2)
O8—Eu1—C8^{ii}	153.1 (2)	C17—Eu1—Eu1^{i}	60.64 (19)	O2^{i}—Eu1—Eu1^{i}	68.93 (15)
O2^{i}—Eu1—O1	138.4 (2)	O2^{i}—Eu1—N1	140.0 (2)	O2^{i}—Eu1—N2	77.0 (2)
O2^{i}—Eu1—O7	73.7 (2)	O2^{i}—Eu1—O8	97.7 (2)	O2^{i}—Eu1—C17	86.4 (2)
O2^{i}—Eu1—O3^{ii}	79.3 (2)	O2^{i}—Eu1—O4^{ii}	119.8 (2)	O2^{i}—Eu1—C8^{ii}	98.8 (2)
C8—O3—Eu1^{iii}	94.2 (5)	O3^{ii}—Eu1—Eu1^{i}	127.11 (15)	C8—O4—Eu1^{iii}	91.1 (5)
O3^{ii}—Eu1—N1	82.6 (2)	C4—C8—Eu1^{iii}	173.8 (6)	O3^{ii}—Eu1—N2	77.1 (2)
O3—C8—Eu1^{iii}	59.4 (5)	O3^{ii}—Eu1—O7	152.3 (2)	O3^{ii}—Eu1—O8	141.2 (2)
O4—C8—Eu1^{iii}	62.5 (5)	O3^{ii}—Eu1—C17	158.0 (2)	O3^{ii}—Eu1—O4^{ii}	52.72 (19)
O3^{ii}—Eu1—C8^{ii}	26.4 (2)	O4^{ii}—Eu1—Eu1^{i}	110.29 (14)	O4^{ii}—Eu1—N1	73.3 (2)
O4^{ii}—Eu1—N2	117.2 (2)	O4^{ii}—Eu1—O7	139.79 (19)	O4^{ii}—Eu1—C17	148.6 (2)
O4^{ii}—Eu1—C8^{ii}	26.4 (2)	C8^{ii}—Eu1—Eu1^{i}	120.20 (18)	C8^{ii}—Eu1—C17	174.7 (2)
C1—O1—Eu1	136.3 (6)	C33—N1—Eu1	122.1 (6)	C43—N1—Eu1	118.0 (7)
C42—N2—Eu1	123.6 (7)	C44—N2—Eu1	117.4 (6)	Eu1^{i}—O7—Eu1	106.3 (2)
C17—O7—Eu1^{i}	157.7 (6)	C17—O7—Eu1	92.1 (6)	C17—O8—Eu1	96.3 (6)
O7—C17—Eu1	61.7 (5)	O8—C17—Eu1	58.6 (5)		

Symmetry codes: (i) −x, −y+1, −z; (ii) x+1/2, −y+3/2, z; (iii) x−1/2, −y+3/2, z.

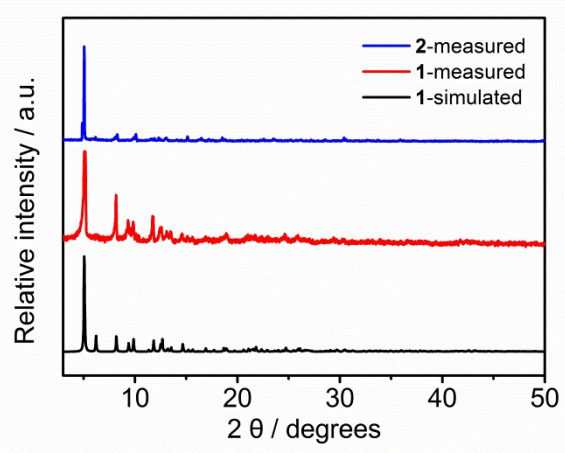

Fig. S1. PXRD patterns of **1** (simulated from the single crystal X-ray data) and as-synthesized samples of **1** and **2**.

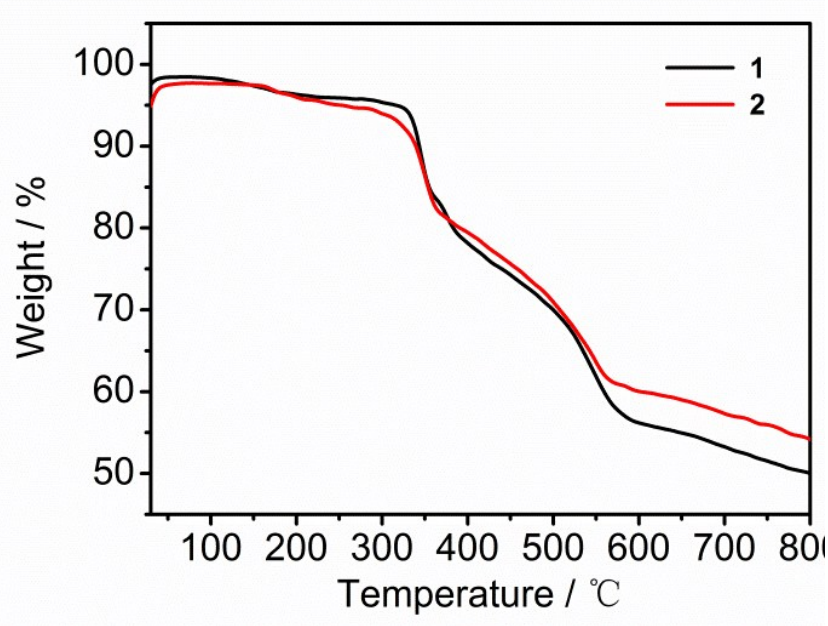

Fig. S2. TGA curves for compounds **1** and **2**.

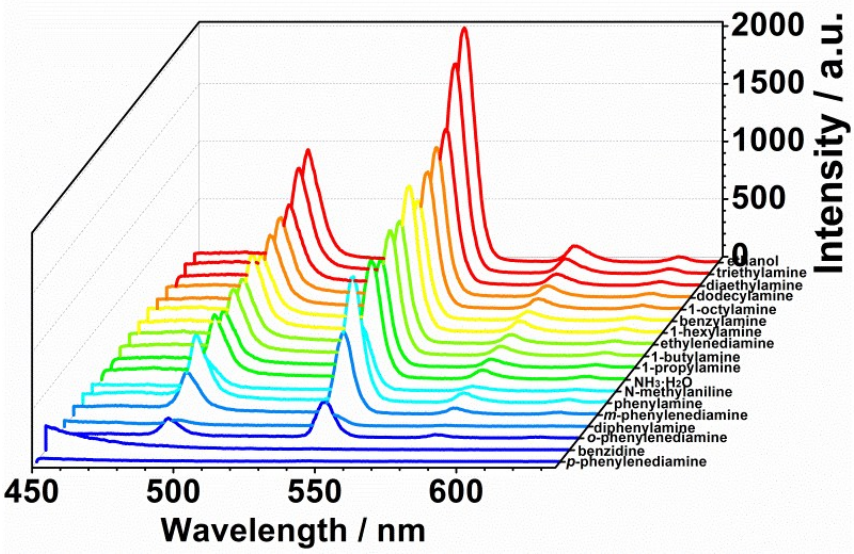

Fig. S3. Luminescence spectra of the dispersion of **1** in ethanol in the presence of various amines (10^{-2} M). Excitation: 320 nm.

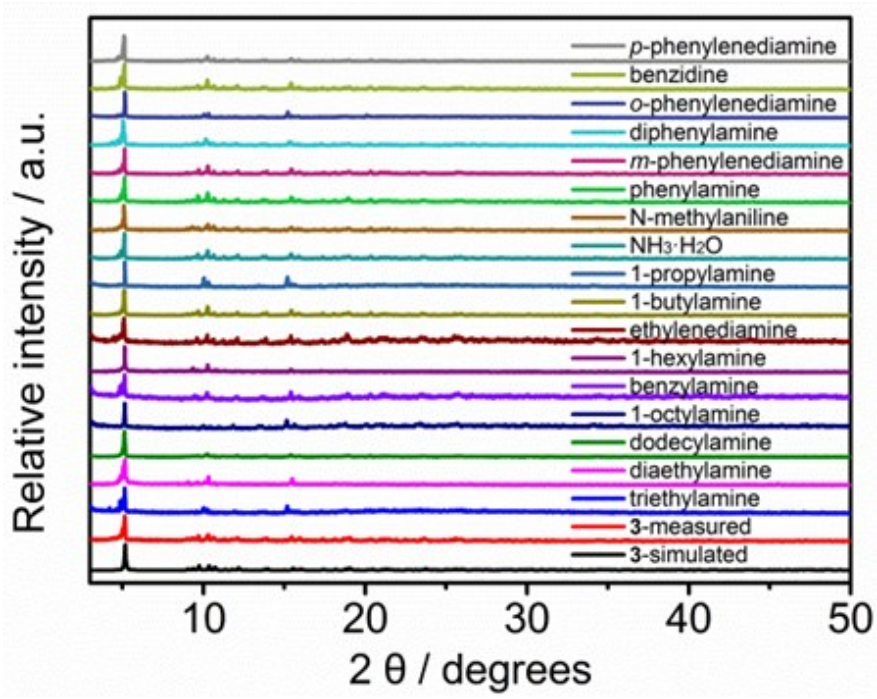

Fig. S4. PXRD patterns of **1** before and after being immersed in ethanol solutions of various amines.

(a) (b)

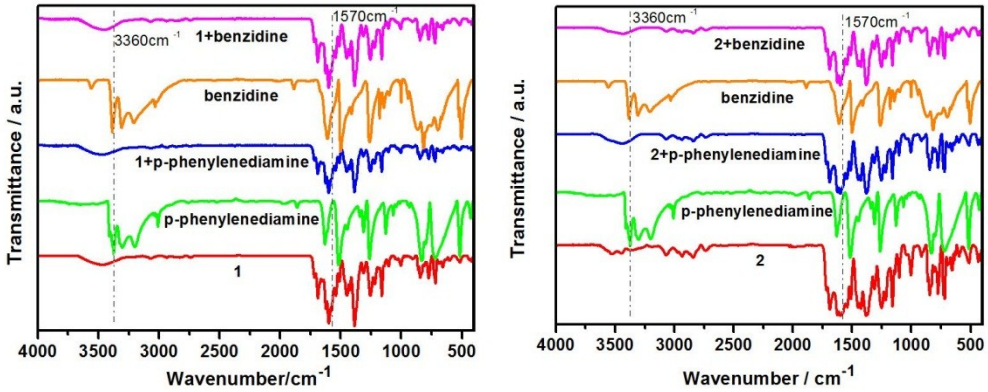

Fig. S5. FT-IR spectra of **1** (a) and **2** (b) before and after being immersed in ethanol solutions of *p*-phenylenediamine or benzidine.

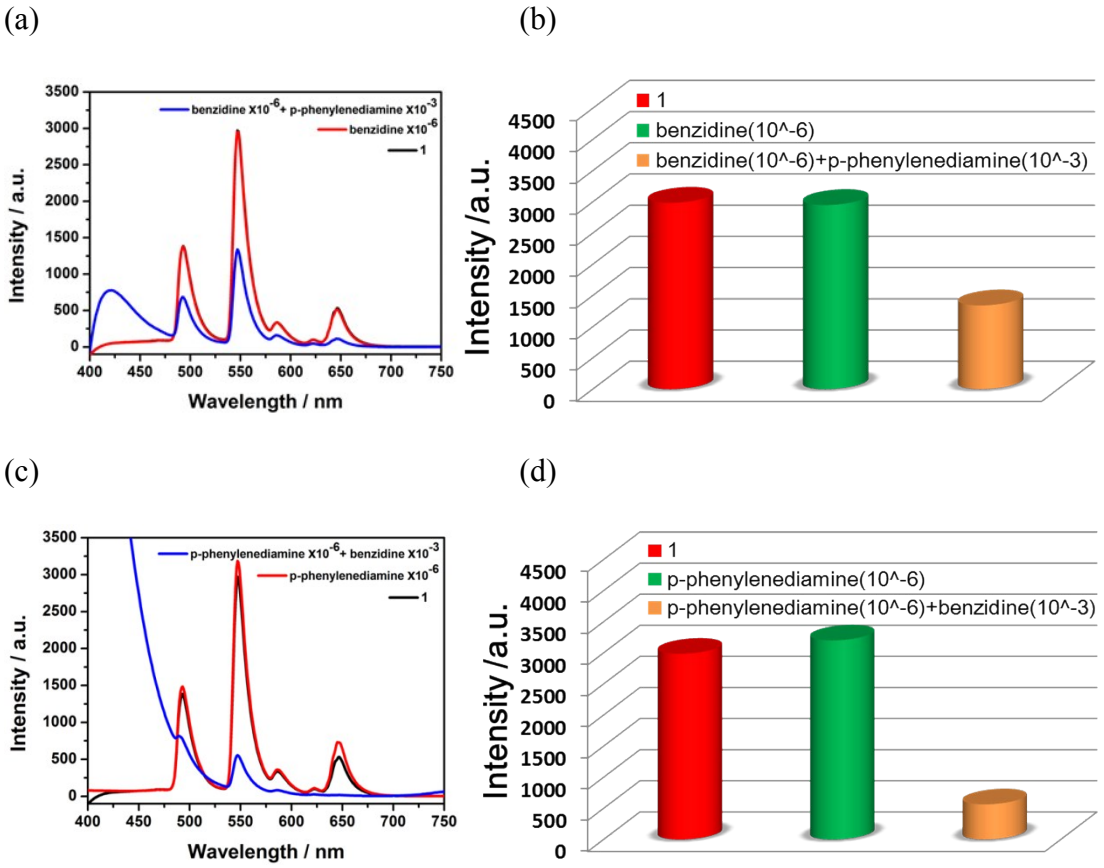

Fig. S6. Luminescence sensing selectivity measurements of **1** (dispersion in ethanol) toward *p*-phenylenediamine and benzidine analytes. (a, b) Luminescence spectra and bar diagrams of **1** in the presence of benzidine (10^{-6} M, red line) with and without added *p*-phenylenediamine (10^{-3}M, blue line). (c, d) Luminescence spectra and bar diagrams of **1** in the presence of *p*-phenylenediamine (10^{-6} M, red line) with and without added benzidine (10^{-6} M, blue line).

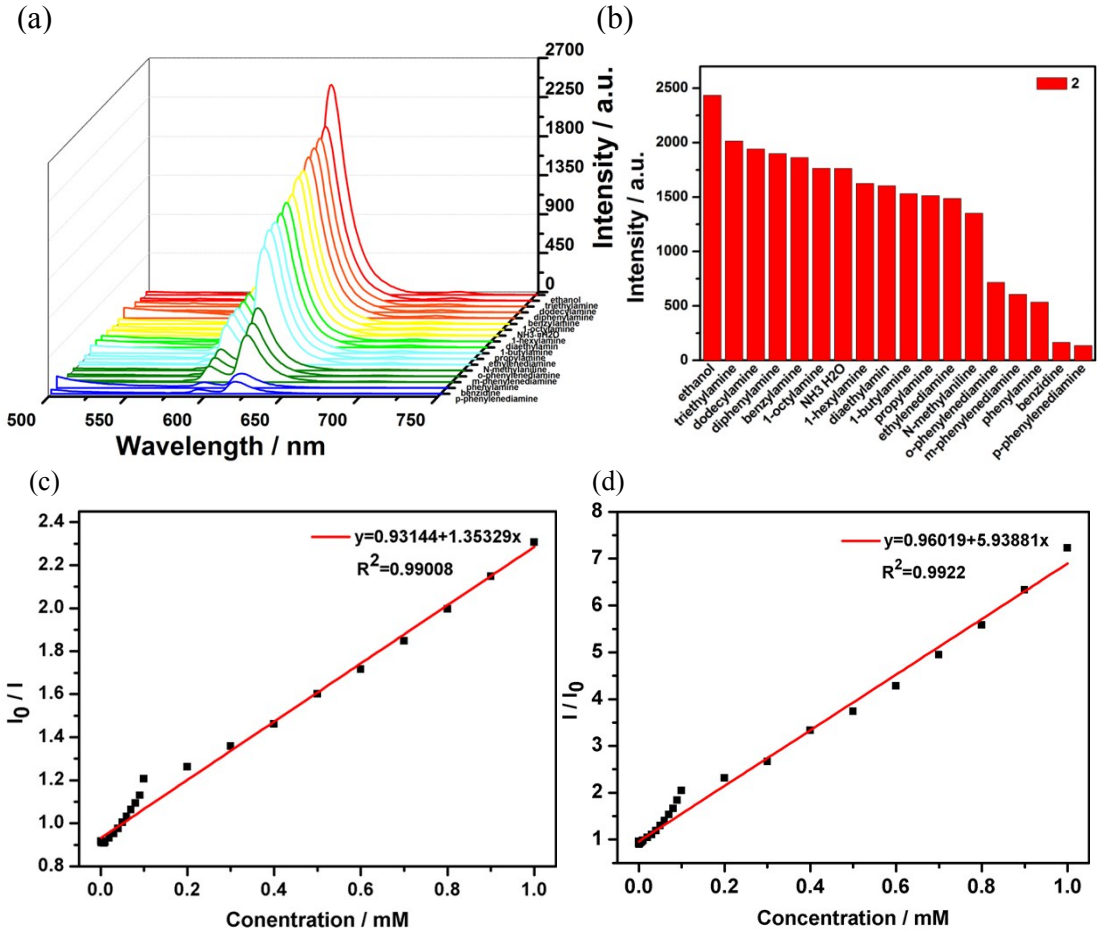

Fig. S7. (a, b) Luminescence spectra and relative intensities of the $^5D_0 \rightarrow {}^7F_2$ transition (616 nm band) of the dispersion of **2** in ethanol and in the presence of various amine analytes (excitation: 348 nm). (c,d) Linear relation between the quenching efficiency and the concentration of benzidine, *p*-phenylenediamine (0.01–1.0 mM) for a dispersion of **2**.

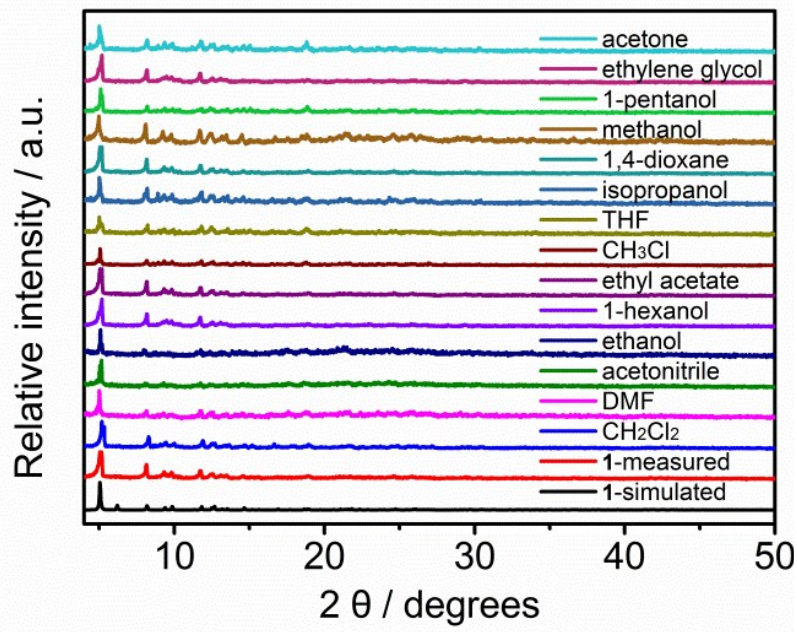

Fig. S8. PXRD patterns of **1** before and after being immersed in various organic solvents.

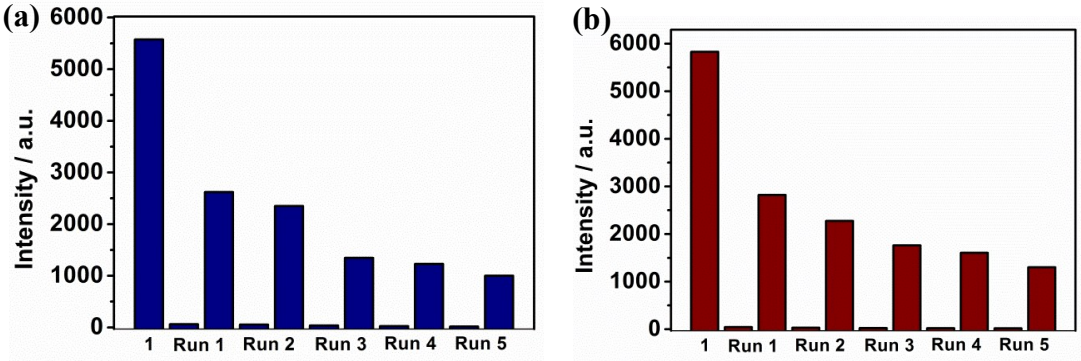

Fig. S9. Recycling luminescence sensing experiments. Quenching ability of regenerated samples of **1** (dispersion in EtOH) in the presence of (a) *p*-phenylenediamine (10 mM) and (b) benzidine (10 mM).