

Supplementary information

New luminescent complexes for recognition and reversible sensing small molecules

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Materials and instrumentation

All chemicals were obtained from commercial sources and used as received. 0.5M Ln(ClO₄)₃ solution were prepared by dissolving lanthanide oxide in excess perchloric acid. Compounds **1-4** were synthesized in 25ml Teflon-lined stainless steel vessels under autogenous pressure. The reactants were stirred homogeneously before heating. Elemental analyses were carried out on a Vario EL III element analyzer. Infrared spectra were obtained on a PerkinElmer Spectrum FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449C under a nitrogen gas flow at a heating rate of 10 °C·min⁻¹ from room temperature to 800 °C. Powder X-ray diffraction (XRD) patterns were acquired on a DMAX-2500 diffractometer and a XPERT-PRO diffractometer using CuK α radiation at ambient environment. Magnetic measurements for **1** were carried out with a Quantum Design PPMS model 6000 magnetometer from 2 K to room temperature under an applied field of 5 KOe. Photoluminescent properties for these solids were investigated in solid state at room temperature. Photoluminescence analyses were performed with an Edinburgh FLS920 and LifeSpec-ps fluorescence spectrometers, as well as a F-7000 FL spectrophotometer.

Synthesis

[Mn(1,10-phen)(L)(H₂O)] (1). A mixture of Mn(CH₃COO)₂·4H₂O (0.0646 g, 0.264 mmol), 1.10-phenanthroline·H₂O (0.0483 g, 0.244 mmol), Na₂L (1.5237 g, 2.7086 mmol), and H₂O (10.0 ml, 556 mmol) was heated at 180 °C for 144 hours. After the mixture was cooled slowly to ambient temperature, orange prismatic single crystals were obtained. The final pH value of the solution is 3.70. Experimental PXRD patterns were in agreement with those of simulated from single crystal X-ray data, which indicated the homogenous phase of the product. The yield was 53 % (0.0997 g) based on 1.10-phenanthroline·H₂O. Anal. Calc. For C₄₀H₃₀N₂O₇S₂Mn **1**: C 62.42, H 3.93, N 3.64 %. Found: C 62.26, H 4.15, N 3.41 %. IR (KBr pellet, cm⁻¹):

3461w, 3278w, 3196w, 3044w, 3033w, 3018w, 1622m, 1589m, 1517m, 1494m, 1427m, 1246s, 1215m, 1184s, 1160s, 1136s, 1104m, 1083m, 1043w, 1021s, 1003m, 965m, 951w, 865w, 851m, 808m, 761m, 750m, 729m, 697m, 641m, 614s, 593m, 563m, 538w, 523m.

{[Pr(1,10-phen)₂(H₂O)₂][Pr(1,10-phen)(H₂O)₃](L)₃}·2.5H₂O (2). A mixture of 0.5M Pr(ClO₄)₃ (0.4 mL, 0.2 mmol), Na₂L (0.1700 g, 0.3022 mmol), 1.10-phenanthroline·H₂O (0.0730 g, 0.368 mmol) and H₂O (10.0 ml, 556 mmol) was heated at 120 °C for 96 hours. After the mixture was cooled slowly to ambient temperature, orange prismatic single crystals of **2** were obtained. The pH value of the final solution was 5.74. Experimental PXRD patterns for as-prepared **2** were in agreement with those of simulated from single crystal X-ray data of **2**, which indicated the homogenous phase of the product. Yield: 0.0753 g (30 %). Anal. Calc. For C₁₂₀H₉₉N₆O_{25.5}S₆Pr₂ **2**: C 57.48, H 3.98, N 3.35 %. Found: C 57.05, H 3.98, N 3.31 %. IR (KBr pellet, cm⁻¹): 3393m, 3059w, 3028w, 2974w, 2925w, 2348w, 1627m, 1589m, 1520m, 1496m, 1463m, 1424m, 1385m, 1343w, 1249m, 1232w, 1160s, 1128s, 1103m, 1079s, 1046m, 1014s, 967m, 880w, 863m, 845m, 813m, 756m, 730m, 698m, 637m, 612m, 595m, 574m, 562m, 537m. In addition, pure phase of **2** can also be obtained as follows. A mixture of Pr₆O₁₁ (0.0340 g, 0.0333 mmol), perchloric acid (0.08 mL, 1.4 mmol) and H₂O (10.0 ml, 556 mmol) was previously heated at 120 °C for 20 hours. After cooled to room temperature, 1.10-phenanthroline·H₂O (0.0741 g, 0.374 mmol) and Na₂L [(0.5555 g, 0.9875 mmol), or (0.4032 g, 0.7167 mmol)] were added in the above mixture and heated at 180 °C for 120 hours. After the mixture was cooled slowly to ambient temperature, orange prismatic single crystals of **2** were obtained.

{[Nd(1,10-phen)₂(H₂O)₂][Nd(1,10-phen)(H₂O)₃](L)₃}·2.5H₂O (3). A mixture of 0.5M Nd(ClO₄)₃ (0.2 mL, 0.1 mmol), Na₂L (0.0850 g, 0.150 mmol), 1.10-phenanthroline·H₂O (0.0365 g, 0.184 mmol) and H₂O (10.0 ml, 556 mmol) was heated at 120 °C for 96 hours. After the mixture was cooled slowly to ambient temperature, orange prismatic single crystals of **3** were obtained. The pH value of the final solution was 5.97. Experimental PXRD patterns for as-prepared **3** were in agreement with those of simulated from single crystal X-ray data of **2**, which indicated the homogenous phase of the product. Yield: 0.0285 g (23 %). Anal. Calc. For C₁₂₀H₉₉N₆O_{25.5}S₆Nd₂ **3**: C 57.33, H 3.97, N 3.34 %. Found: C 57.05, H 3.98, N 3.31 %. IR (KBr pellet, cm⁻¹): 3394m, 3059w, 3029w, 2346w, 1627m, 1589m, 1520m, 1496m, 1464m, 1425m, 1385m, 1343w, 1248m, 1154s, 1129s, 1104m, 1080s, 1044m, 1014s, 967m, 864m, 846m, 813m, 756m, 730m, 698m, 638m, 613m, 595m, 575m, 562m, 538m.

{[La(1,10-phen)₂(H₂O)₂][La(1,10-phen)(H₂O)₃](L)₃}·2.5H₂O (4). Pure phase of **4** was synthesized by the same procedure as **2** except for the replacement of

Pr(ClO₄)₃ with La(ClO₄)₃. The pH value of the final solution is 5.73. Experimental PXRD patterns for as-prepared **4** was in agreement with those of simulated from single crystal X-ray data of **2**, which indicated the homogenous phase of the product. Yield: 0.0870 g (35 %). Anal. Calc. For C₁₂₀H₉₉N₆O_{25.5}S₆La₂ **4**: C 57.58, H 3.99, N 3.36 %. Found: C 57.74, H 3.93, N 3.48 %. IR (KBr pellet, cm⁻¹): 3394m, 3059w, 3029w, 2344w, 1627m, 1589m, 1520m, 1496m, 1464m, 1425m, 1385m, 1344w, 1247m, 1154s, 1129s, 1103m, 1080s, 1044m, 1014s, 967m, 863m, 846m, 813m, 756m, 730m, 720m, 698m, 637m, 613m, 595m, 574m, 562m, 537m.

X-Ray crystallography

X-ray data for **1** and **2** were collected on a Rigaku Mercury CCD/AFC diffractometer using graphite-monochromated Mo K α radiation ($\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$). Data were reduced with CrystalClear v1.3. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL-97.¹ All non-hydrogen atoms were treated anisotropically. Hydrogen atoms, which bonded to carbon atoms, were generated geometrically. Whereas hydrogen atoms of water molecule in **1** were from the difference Fourier map and fixed with O-H = 0.90 \AA . While no attempt was made to locate the hydrogen atoms of water in **2**. Crystallographic data for compounds **1** and **2** are summarized in Table S1. CCDC-775029 (**1**) and 736313 (**2**). Selected bond lengths and angles for compounds **1** and **2** are listed in Table S2 and S3, respectively. .

Sensing experiment:

Each small molecules, ammonia solution and formaldehyde solution with about 1 ml has been placed into respective 40mm \times 70mm capped weighing bottles in advance. And then each open 25mm \times 25mm weighing bottles containing about 0.05g **1a**, are placed into respective capped bottle for 0.5 hour to 30 days

Relative luminescent intensity

Coin-like of **1a** and **1a**(2-methylpyrazine) with about 1.2 cm diameter were prepared under room temperature. First, **1a** was excited at 380 nm to obtain the emission spectrum, and all the experimental conditions (including optical set up, focalization point, illuminated cross-section, sample holder, and emission and excitation slits width) were held constant, then **1a**(2-methylpyrazine) was also excited at 380 nm to obtain the emission spectrum.

Table S1. Crystallographic data for compounds **1** and **2**.

Compounds	1	2
Formula	C ₄₀ H ₃₀ N ₂ O ₇ S ₂ Mn	C ₁₂₀ H ₉₉ N ₆ O _{25.5} S ₆ Pr ₂
FW	769.72	2507.23
Space group	P-1	P2(1)/n
a/ (Å)	10.842(3)	24.0813(15)
b (Å)	11.194(3)	16.5778(7)
c (Å)	14.953(5)	28.3107(18)
α (°)	93.155(3)	90
β (°)	96.372(3)	100.055(3)
γ (°)	102.207(6)	90
V (Å ³)	1757.0(9)	11128.5(11)
Z	2	4
T(K)	293(2)	293(2)
Measured/unique/observed reflections	13289/7816/6814	84400/25373/18727
D _{calcd} (g cm ³)	1.455	1.496
μ (mm ⁻¹)	0.550	1.056
GOF on F ²	1.053	1.133
R _{int}	0.0221	0.0467
R1 ^a [I>2σ(I)]	0.0417	0.0636
wR2 ^b [all data]	0.1233	0.1656
^a R1 = Σ(F _o - F _c) / Σ F _o . ^b wR2 = {Σw [(F ² _o - F ² _c)] / Σw [(F ² _o) ²]} ^{0.5} .		

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

Mn(1)-O(1)	2.1517(13)	S(1)-O(2)	1.4628(15)
Mn(1)-O(2) ^b	2.2369(14)	S(1)-O(3)	1.4404(15)
Mn(1)-O(4) ^a	2.2237(15)	S(1)-C(13)	1.7779(19)
Mn(1)-O(7W)	2.1239(18)	S(2)-O(4)	1.4651(15)
Mn(1)-N(1)	2.2387(17)	S(2)-O(5)	1.4548(14)
Mn(1)-N(2)	2.2457(17)	S(2)-O(6)	1.4421(15)
S(1)-O(1)	1.4620(14)	S(2)-C(40)	1.781(2)
O(1)-Mn(1)-O(2) ^b	95.05(6)	O(2) ^b -Mn(1)-N(2)	85.53(6)
O(1)-Mn(1)-O(4) ^a	90.05(6)	O(4) ^a -Mn(1)-O(7W)	90.25(9)
O(1)-Mn(1)-O(7W)	94.99(7)	O(4) ^a -Mn(1)-N(1)	89.29(6)
O(1)-Mn(1)-N(1)	88.61(6)	O(4) ^a -Mn(1)-N(2)	89.35(6)
O(1)-Mn(1)-N(2)	163.28(6)	O(7W)-Mn(1)-N(1)	176.37(7)
O(2) ^b -Mn(1)-O(4) ^a	174.84(5)	O(7W)-Mn(1)-N(2)	101.71(8)
O(2) ^b -Mn(1)-O(7W)	90.15(9)	N(1)-Mn(1)-N(2)	74.68(7)
O(2) ^b -Mn(1)-N(1)	89.99(6)		
Symmetry code: <i>a</i> 1 + x, y - 1, z; <i>b</i> 1 - x, - y, - z.			

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

Pr(1)-O(1) ^a	2.400(4)	Pr(2)-O(4)	2.502(3)
Pr(1)-O(2)	2.495(4)	Pr(2)-O(10) ^a	2.449(4)
Pr(1)-O(7)	2.372(4)	Pr(2)-O(21)	2.508(4)
Pr(1)-O(13)	2.421(4)	Pr(2)-O(22)	2.565(4)
Pr(1)-O(19)	2.530(4)	Pr(2)-O(23)	2.543(4)
Pr(1)-O(20)	2.481 (4)	Pr(2)-N(3)	2.673(4)
Pr(1)-N(1)	2.634(4)	Pr(2)-N(4)	2.699(4)
Pr(1)-N(2)	2.656(4)	Pr(2)-N(5)	2.625(4)
		Pr(2)-N(6)	2.661(4)
O(1) ^a -Pr(1)-O(2)	95.51(14)	O(4)-Pr(2)-N(3)	135.23(13)
O(1) ^a -Pr(1)-O(7)	142.98(14)	O(4)-Pr(2)-N(4)	76.41(12)
O(1) ^a -Pr(1)-O(13)	141.40(14)	O(4)-Pr(2)-N(5)	75.44(13)
O(1) ^a -Pr(1)-O(19)	70.09(14)	O(4)-Pr(2)-N(6)	72.39(13)
O(1) ^a -Pr(1)-O(20)	74.48(14)	O(10) ^a -Pr(2)-O(21)	69.81(13)
O(1) ^a -Pr(1)-N(1)	82.78(13)	O(10) ^a -Pr(2)-O(22)	132.10(12)
O(1) ^a -Pr(1)-N(2)	76.19(14)	O(10) ^a -Pr(2)-O(23)	134.54(13)
O(2)-Pr(1)-O(7)	99.03(14)	O(10) ^a -Pr(2)-N(3)	68.10(13)
O(2)-Pr(1)-O(13)	80.26(14)	O(10) ^a -Pr(2)-N(4)	102.91(13)
O(2)-Pr(1)-O(19)	67.50(14)	O(10) ^a -Pr(2)-N(5)	78.26(14)
O(2)-Pr(1)-O(20)	74.03 (13)	O(10) ^a -Pr(2)-N(6)	68.09(13)
O(2)-Pr(1)-N(1)	144.76(13)	O(21)-Pr(2)-O(22)	66.88(13)
O(2)-Pr(1)-N(2)	151.55(13)	O(21)-Pr(2)-O(23)	88.04(15)
O(7)-Pr(1)-O(13)	74.94(14)	O(21)-Pr(2)-N(3)	81.13(14)
O(7)-Pr(1)-O(19)	146.83(14)	O(21)-Pr(2)-N(4)	140.29(13)
O(7)-Pr(1)-O(20)	77.13(15)	O(21)-Pr(2)-N(5)	82.50(15)
O(7)-Pr(1)-N(1)	103.27(15)	O(21)-Pr(2)-N(6)	129.35(15)
O(7)-Pr(1)-N(2)	74.87(14)	O(22)-Pr(2)-O(23)	63.11(13)
O(13)-Pr(1)-O(19)	72.97(14)	O(22)-Pr(2)-N(3)	122.51(14)
O(13)-Pr(1)-O(20)	138.14(14)	O(22)-Pr(2)-N(4)	123.39(14)
O(13)-Pr(1)-N(1)	79.63(13)	O(22)-Pr(2)-N(5)	76.82(15)
O(13)-Pr(1)-N(2)	123.07(14)	O(22)-Pr(2)-N(6)	130.04(15)
O(19)-Pr(1)-O(20)	123.62(14)	O(23)-Pr(2)-N(3)	69.61(14)
O(19)-Pr(1)-N(1)	79.05(14)	O(23)-Pr(2)-N(4)	69.31(14)
O(19)-Pr(1)-N(2)	131.09(14)	O(23)-Pr(2)-N(5)	139.28(15)
O(20)-Pr(1)-N(1)	137.46(13)	O(23)-Pr(2)-N(6)	142.32(15)
O(20)-Pr(1)-N(2)	77.53(14)	N(3)-Pr(2)-N(4)	60.80(14)
N(1)-Pr(1)-N(2)	62.19(14)	N(3)-Pr(2)-N(5)	145.94(15)
O(4)-Pr(2)-O(10) ^a	139.33(12)	N(3)-Pr(2)-N(6)	107.32(15)
O(4)-Pr(2)-O(21)	135.01(13)	N(4)-Pr(2)-N(5)	135.69(15)
O(4)-Pr(2)-O(22)	70.12(12)	N(4)-Pr(2)-N(6)	76.65(15)
O(4)-Pr(2)-O(23)	84.13(13)	N(5)-Pr(2)-N(6)	62.57(17)

Symmetry code: $a - x + 1, -y, -z$.

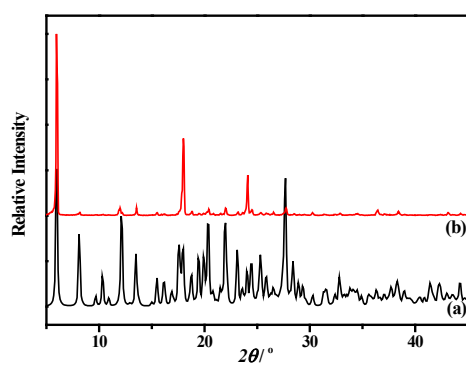


Fig. S1 Powder XRD patterns of **1** simulated from single-crystal X-ray data (a) and experimental (b).

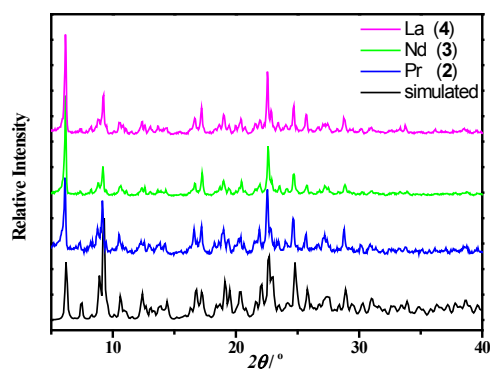


Fig. S2 Powder XRD patterns of simulated from single-crystal X-ray data of compound **2** and experimental data for solids **2-4**.

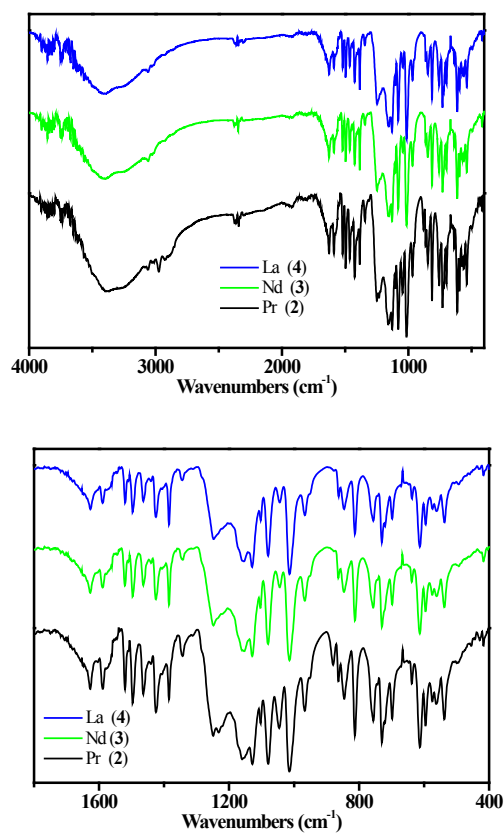


Fig. S3 IR spectra of solids 2-4.

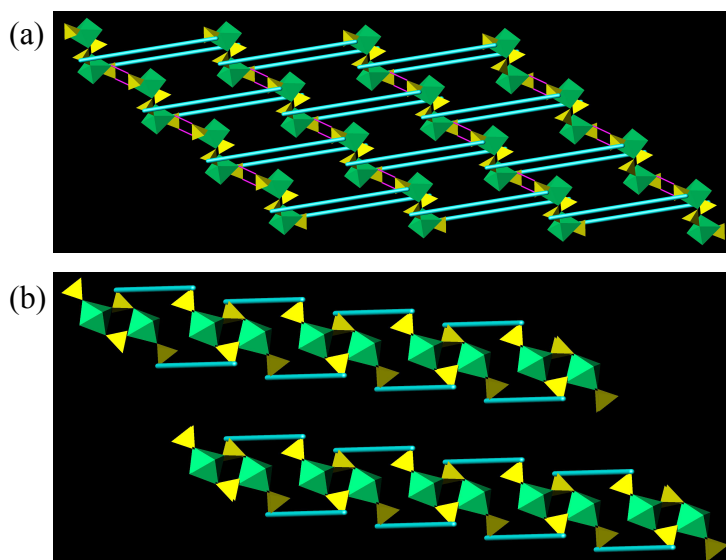


Fig. S4 Polyhedral views of layer (a) and 3D structure (b) in **1**. The rose thin line indicates hydrogen bonding. Green octahedron, $[\text{MnN}_2\text{O}_4]$; yellow tetrahedron, $[\text{SCO}_3]$; blue-green thick line, L group.

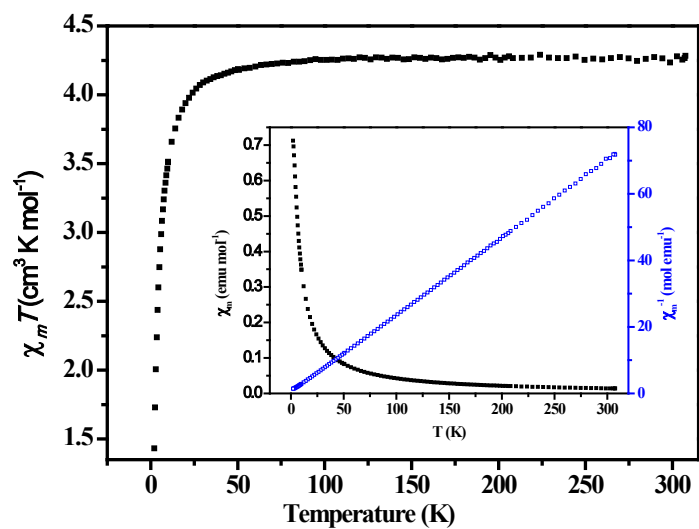


Fig. S5 Thermal dependence of the $\chi_m T$ value (solid squares) for **1**. Inset: the magnetic susceptibility (χ_m , solid squares) and inverse magnetic susceptibility (χ_m^{-1} , blue hollow squares) plotted as a function of temperature.

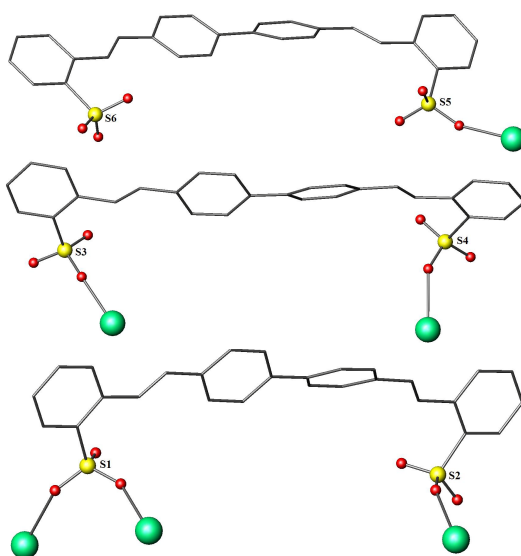


Fig. S6 The coordination modes of L anions in compound **2**.

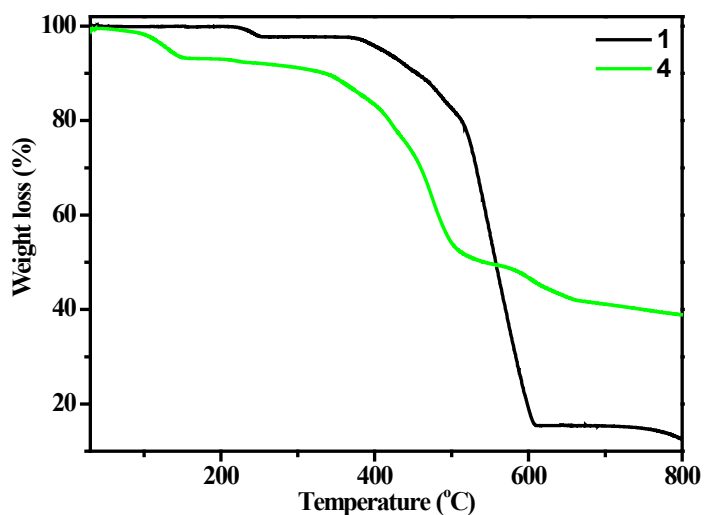


Fig. S7 TGA curves of compounds 1 and 4.

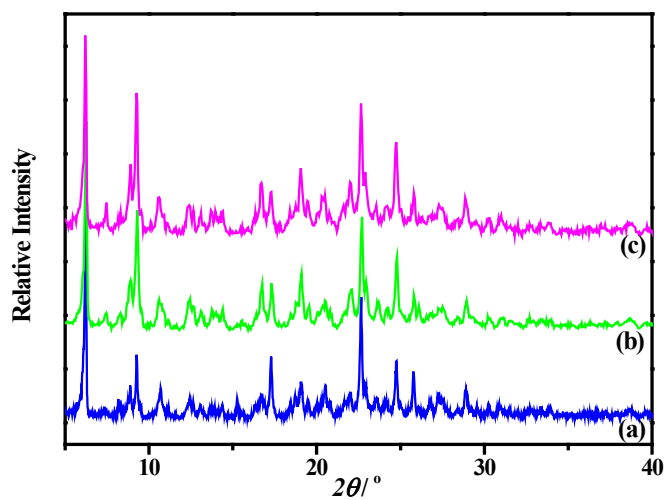


Fig. S8 Powder XRD patterns of as-prepared 2 (a), and as-prepared 2 was previously heated at 160 (b) and 250 °C (c) for 2 h under an air atmosphere.

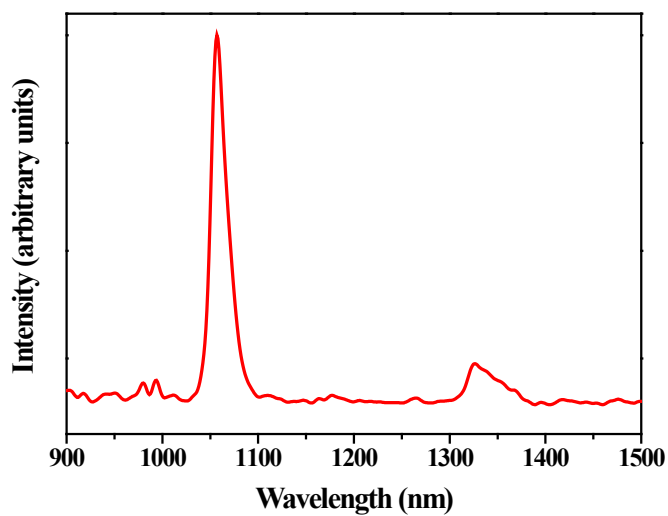


Fig. S9 NIR emission spectrum for 3.

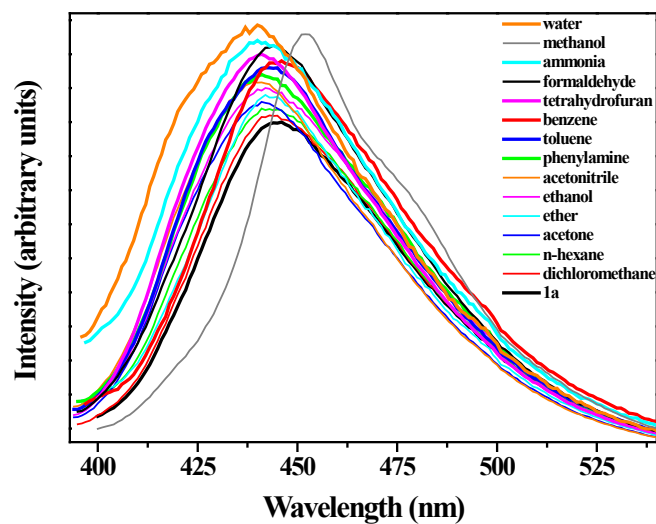


Fig. S10 Normalized emission spectra upon excitation at 380 nm for **1a**, as well as **1a** has been exposed to the equilibrated vapors of respective small molecules.

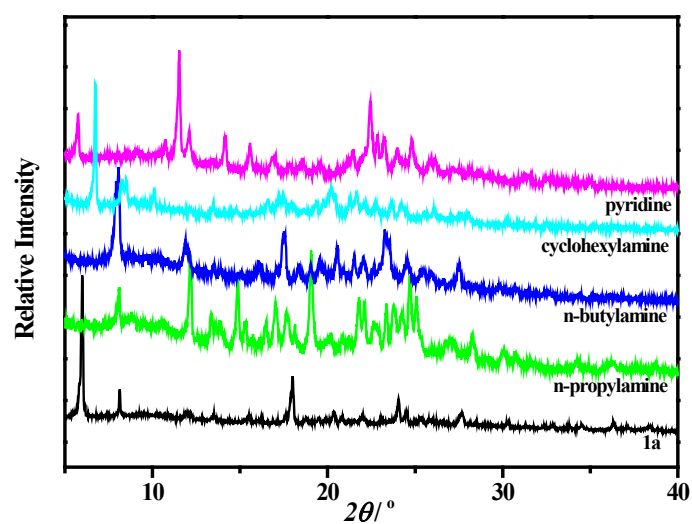


Fig. S11 Powder XRD patterns of **1a**, as well as **1a** has been exposed to the equilibrated vapors of n-propylamine, n-butylamine, cyclohexylamine and pyridine, respectively.

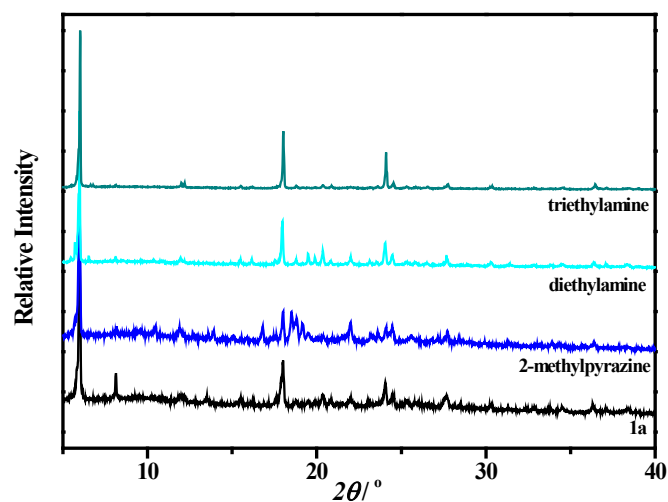


Fig. S12 Powder XRD patterns of **1a**, as well as **1a** has been exposed to the equilibrated vapors of 2-methylpyrazine, diethylamine and triethylamine, respectively.

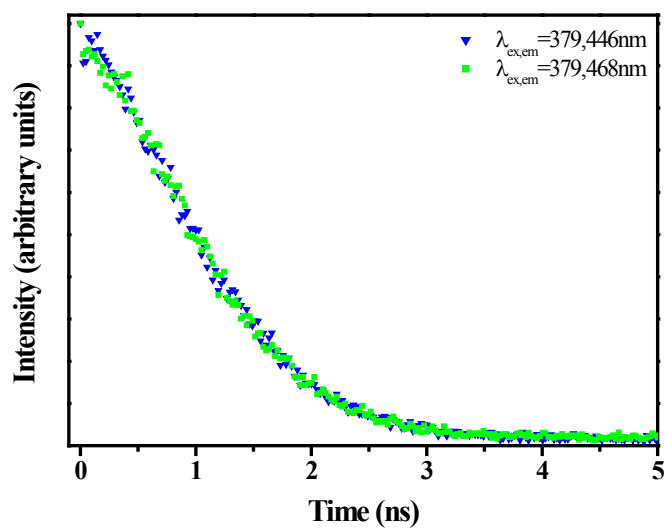


Fig. S13 Fluorescent intensity as a function of time for **1a**(2-methylpyrazine).

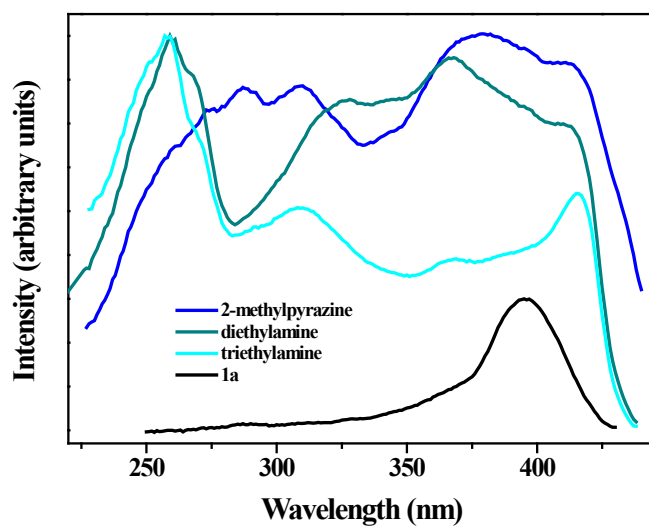


Fig. S14 Normalized excitation spectra for **1a**, as well as **1a** has been exposed to the equilibrated vapors of 2-methylpyrazine, diethylamine and triethylamine, respectively.

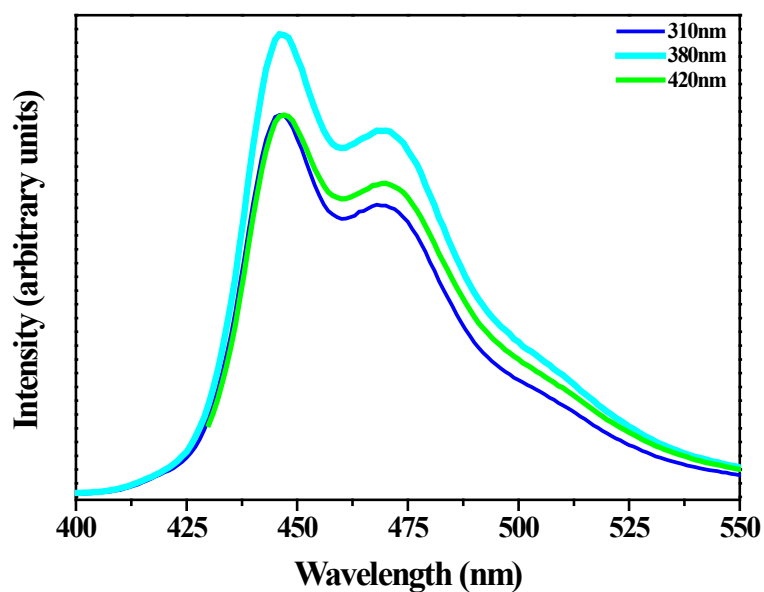


Fig. S15 Normalized emission spectra for **1a**(2-methylpyrazine) upon excitation at 310, 380 and 420 nm, respectively.

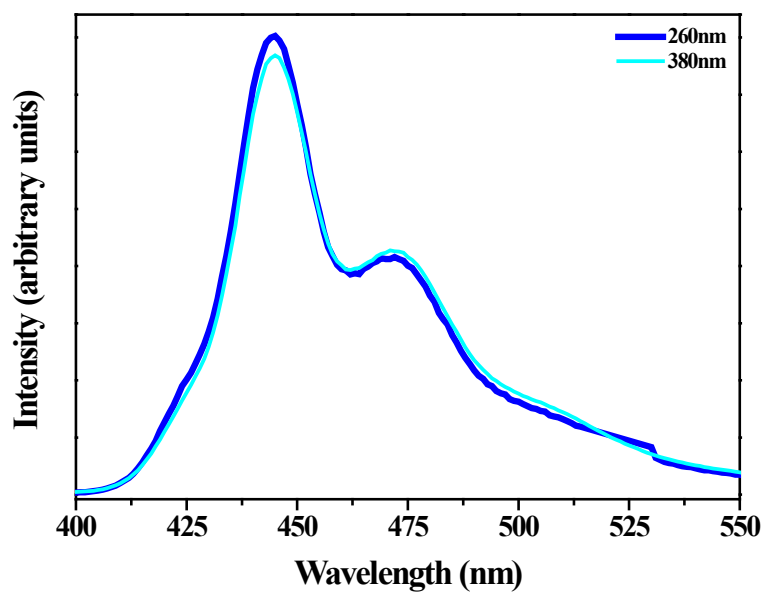


Fig. S16. Normalized emission spectra for **1a**(diethylamine) upon excitation at 260 and 380 nm, respectively.

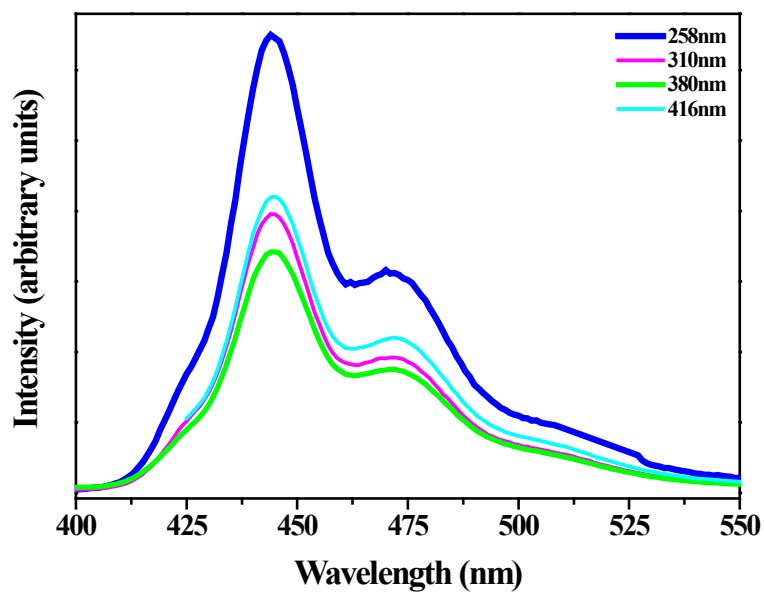


Fig. S17 Normalized emissions spectra for **1a**(triethylamine) upon excitation at 258, 310, 380 and 416 nm, respectively.

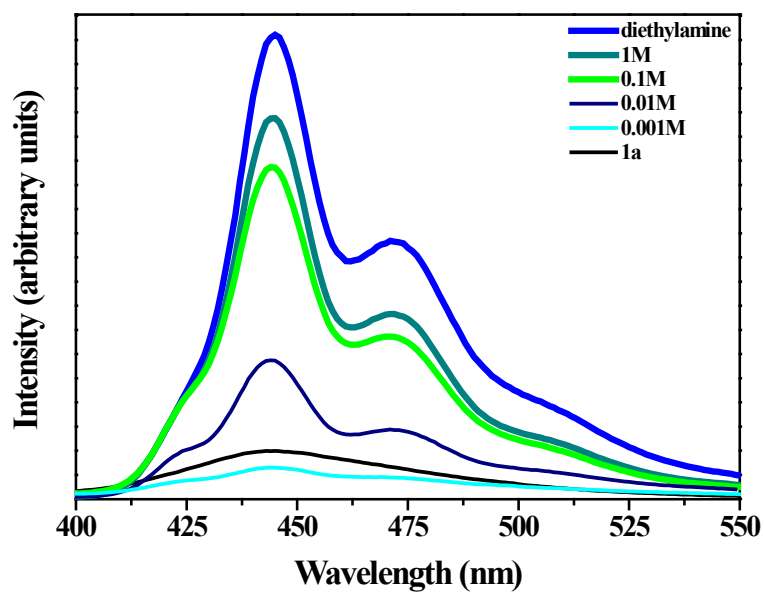


Fig. S18 Normalized emission spectra upon excitation at 380 nm for **1a**, as well as **1a** has been exposed to diethylamine, as well as 5ml 1M, 50ml 0.1M and 500ml 0.01M diethylamine in ethanol, respectively.

References

- (1) G. M. Sheldrick, SHELXT 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.