Electronic supplementary information (ESI)

Fluorescent sensing and selective adsorption properties of metal-organic frameworks with mixed tricarboxylate and 1H-imidazol-4-yl-containing ligands

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Table S1 Selected Bond Lengths (Å) and Angles (°) for **1** and **2**.

Compound **1**			
Co(1)-O(7)	1.972(5)	Co(3)-N(4)#5	2.006(5)
Co(1)-O(13)	1.980(3)	Co(3)-O(9)#3	1.968(4)
Co(1)-O(2)	2.005(5)	Co(3)-O(11)#4	1.972(4)
Co(1)-O(6)#1	2.019(4)	Co(3)-O(16)	1.946(4)
Co(2)-O(4)#2	2.045(4)	Co(4)-O(3)#2	2.146(4)
Co(2)-O(10)#3	2.072(4)	Co(4)-O(5)#1	2.059(4)
Co(2)-N(1)	2.097(5)	Co(4)-O(13)	2.078(3)
Co(2)-O(13)	2.105(3)	Co(4)-O(14)	2.101(4)
Co(2)-O(17)	2.137(4)	Co(4)-O(15)	2.175(4)
Co(2)-O(16)	2.160(3)	Co(4)-O(16)	2.068(4)
O(7)-Co(1)-O(13)	118.1(2)	O(16)-Co(3)-O(9)#3	110.77(16)
O(7)-Co(1)-O(2)	107.2(2)	O(16)-Co(3)-O(11)#4	112.54(17)
O(13)-Co(1)-O(2)	108.30(19)	O(9)#3-Co(3)-O(11)#4	102.98(18)
O(7)-Co(1)-O(6)#1	101.9(2)	O(16)-Co(3)-N(4)#5	110.79(18)

O(13)-Co(1)-O(6)#1	108.76(15)	O(9)#3-Co(3)-N(4)#5	98.65(18)
O(2)-Co(1)-O(6)#1	112.6(2)	O(11)#4-Co(3)-N(4)#5	119.63(19)
O(4)#2-Co(2)-O(10)#3	171.50(16)	O(5)#1-Co(4)-O(16)	173.75(15)
O(4)#2-Co(2)-N(1)	87.92(16)	O(5)#1-Co(4)-O(13)	91.69(15)
O(10)#3-Co(2)-N(1)	92.26(17)	O(16)-Co(4)-O(13)	84.00(13)
O(4)#2-Co(2)-O(13)	93.47(14)	O(14)-Co(4)-O(15)	82.37(18)
O(10)#3-Co(2)-O(13)	87.20(15)	O(5)#1-Co(4)-O(14)	89.84(18)
N(1)-Co(2)-O(13)	174.16(16)	O(16)-Co(4)-O(14)	95.03(17)
O(4)#2-Co(2)-O(17)	86.64(16)	O(13)-Co(4)-O(14)	172.31(17)
O(10)#3-Co(2)-O(17)	84.88(16)	O(5)#1-Co(4)-O(3)#2	87.37(15)
N(1)-Co(2)-O(17)	95.24(17)	O(16)-Co(4)-O(3)#2	88.86(14)
O(13)-Co(2)-O(17)	90.50(15)	O(13)-Co(4)-O(3)#2	99.30(14)
O(4)#2-Co(2)-O(16)	90.21(14)	O(14)-Co(4)-O(3)#2	88.30(16)
O(10)#3-Co(2)-O(16)	98.26(15)	O(5)#1-Co(4)-O(15)	89.85(16)
N(1)-Co(2)-O(16)	93.21(16)	O(16)-Co(4)-O(15)	94.67(16)
O(13)-Co(2)-O(16)	81.13(13)	O(13)-Co(4)-O(15)	90.09(16)
O(17)-Co(2)-O(16)	170.86(15)	O(3)#2-Co(4)-O(15)	170.28(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y-1, -z+2 #2 x, y, z+1 #3 x-1, y-1, z-1 #4 x, y+1, z+1 #5 x-1, y-1, z.

Compound **2**

Cd(1)-O(1)	2.234(2)	Cd(2)-O(9)#3	2.332(2)
Cd(1)-N(1)	2.252(3)	Cd(2)-O(10)#3	2.383(2)
Cd(1)-O(6)#1	2.292(3)	Cd(2)-O(3)	2.472(3)
Cd(1)-O(5)#1	2.368(3)	Cd(3)-N(5)	2.196(3)
Cd(1)-O(11)#2	2.392(2)	Cd(3)-O(8)	2.198(2)
Cd(1)-O(13)	2.404(2)	Cd(3)-O(12)#4	2.373(3)
Cd(2)-N(7)	2.255(3)	Cd(3)-O(11)#4	2.388(2)
Cd(2)-N(4)#3	2.286(3)	Cd(3)-O(13)#5	2.466(3)
Cd(2)-O(4)	2.296(2)		
O(1)-Cd(1)-N(1)	139.99(10)	O(4)-Cd(2)-O(9)#3	148.33(9)
O(1)-Cd(1)-O(6)#1	118.10(11)	N(7)-Cd(2)-O(10)#3	146.32(9)
N(1)-Cd(1)-O(6)#1	97.69(11)	N(4)#3-Cd(2)-O(10)#3	91.32(11)
O(1)-Cd(1)-O(5)#1	92.82(11)	O(4)-Cd(2)-O(10)#3	98.88(9)

N(1)-Cd(1)-O(5)#1	123.96(12)	O(9)#3-Cd(2)-O(10)#3	55.32(8)
O(6)#1-Cd(1)-O(5)#1	54.77(11)	N(7)-Cd(2)-O(3)	88.83(11)
O(1)-Cd(1)-O(11)#2	84.23(9)	N(4)#3-Cd(2)-O(3)	149.00(9)
N(1)-Cd(1)-O(11)#2	87.28(10)	O(4)-Cd(2)-O(3)	54.43(8)
O(6)#1-Cd(1)-O(11)#2	77.01(9)	O(9)#3-Cd(2)-O(3)	101.35(9)
O(5)#1-Cd(1)-O(11)#2	123.11(10)	O(10)#3-Cd(2)-O(3)	85.70(11)
O(1)-Cd(1)-O(13)	80.69(9)	N(5)-Cd(3)-O(8)	147.72(10)
N(1)-Cd(1)-O(13)	83.52(10)	N(5)-Cd(3)-O(12)#4	122.99(11)
O(6)#1-Cd(1)-O(13)	138.99(9)	O(8)-Cd(3)-O(12)#4	89.29(10)
O(5)#1-Cd(1)-O(13)	90.58(10)	N(5)-Cd(3)-O(11)#4	92.28(10)
O(11)#2-Cd(1)-O(13)	143.70(8)	O(8)-Cd(3)-O(11)#4	109.00(9)
N(7)-Cd(2)-N(4)#3	109.48(11)	O(12)#4-Cd(3)-O(11)#4	54.71(9)
N(7)-Cd(2)-O(4)	104.75(10)	N(5)-Cd(3)-O(13)#5	97.53(11)
N(4)#3-Cd(2)-O(4)	95.85(9)	O(8)-Cd(3)-O(13)#5	85.95(10)
N(7)-Cd(2)-O(9)#3	93.56(9)	O(12)#4-Cd(3)-O(13)#5	81.63(9)
N(4)#3-Cd(2)-O(9)#3	102.18(10)	O(11)#2-Cd(3)-O(13)	132.40(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, y+1/2, -z+3/2 #2 -x+1, -y+1, -z+1 #3 x+1, y, z-1 #4 -x+1, y+1/2, -z+1/2 #5 x, y, z-1.

Table S2 Adsorption of MO for **1**.

Time/h	Absorbance	Concentration/mg·L^{-1}
0	0.714	10
12	0.118	1.65
24	0.018	0.26

Table S3 Adsorption of MO for **2**.

Time/h	Absorbance	Concentration/mg·L^{-1}
0	0.714	10
12	0.220	3.08
24	0.038	0.53

Table S4 Adsorption of MB for **1**.

Time/h	Absorbance	Concentration/mg·L^{-1}
0	1.829	10
12	1.190	6.51
24	1.121	6.13

Table S5 Adsorption of MB for **2**.

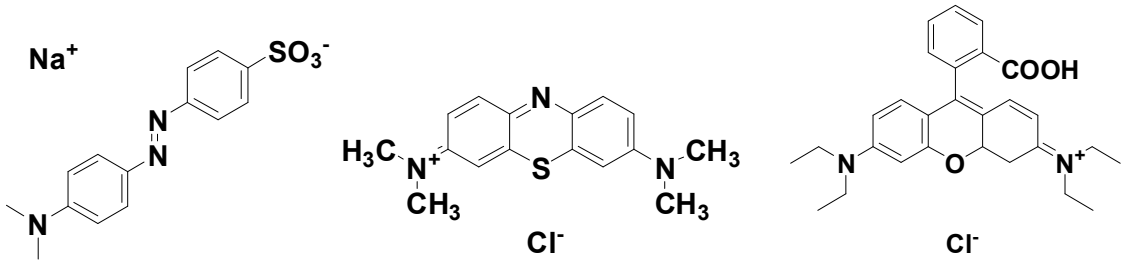
Time/h	Absorbance	Concentration/mg·L^{-1}
0	1.829	10
12	1.155	6.31
24	0.8437	4.61

Table S6 Adsorption of RhB for **1**.

Time/h	Absorbance	Concentration/mg·L^{-1}
0	1.641	10
12	1.512	9.21
24	1.484	9.04

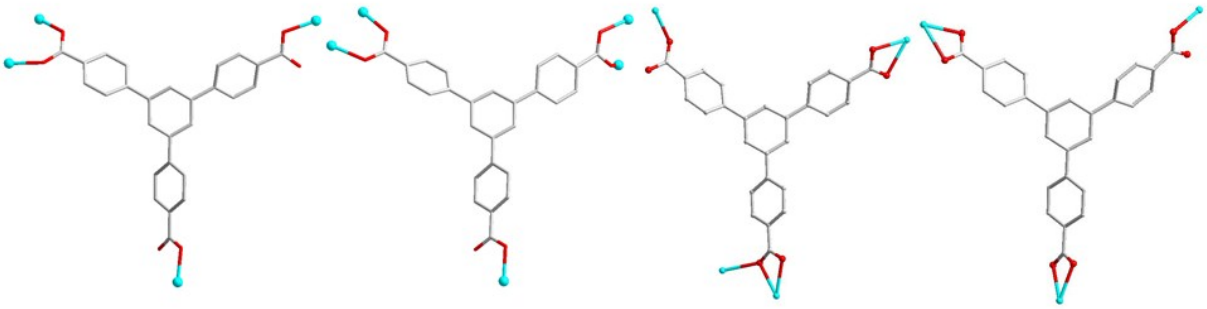
Table S7 Adsorption of RhB for **2**.

Time/h	Absorbance	Concentration/mg·L^{-1}
0	1.641	10
12	1.627	9.91
24	1.610	9.81



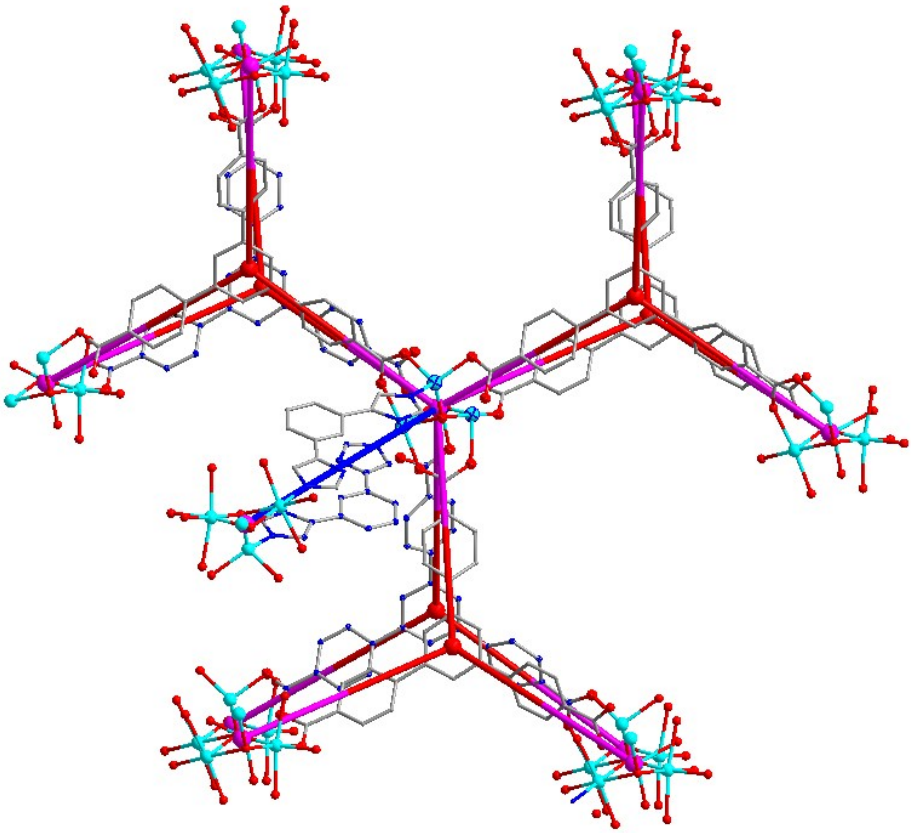
MO **(3.1** Å× **4.3** Å × **14.5** Å**)** MB **(4.2** Å × **5.0** Å × **13.4** Å) RhB **(5.4 Å × 9.8 Å × 14.1 Å)**

Scheme S1 Schematic drawing of dyes.

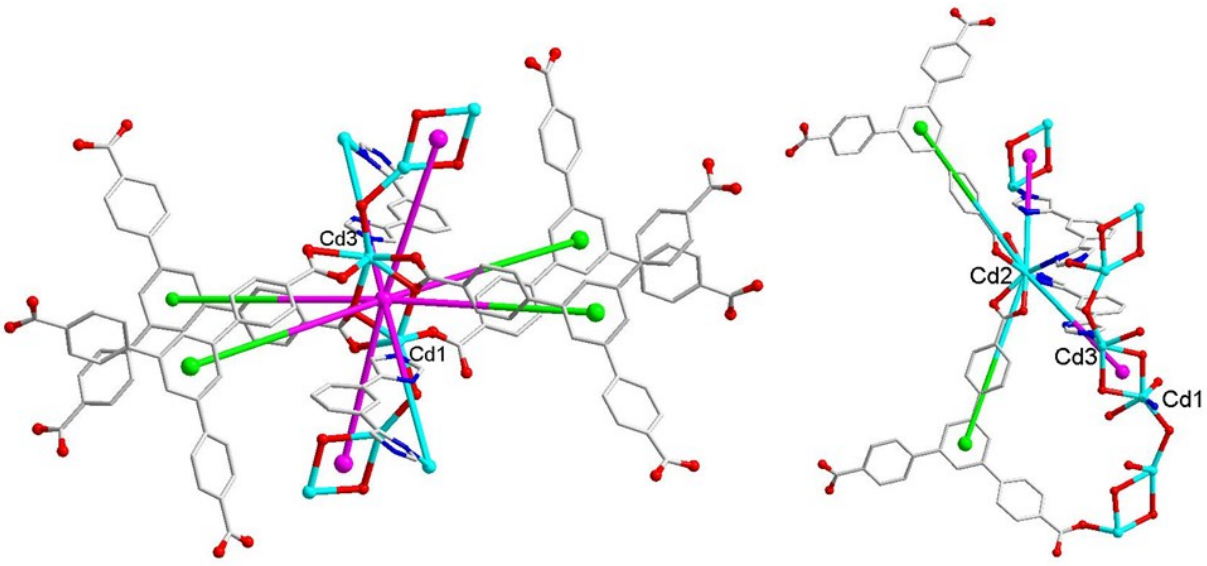


(a) (b) (c) (d)

Fig. S1 Coordination modes of BTB^{3-} appeared in **1** and **2**.

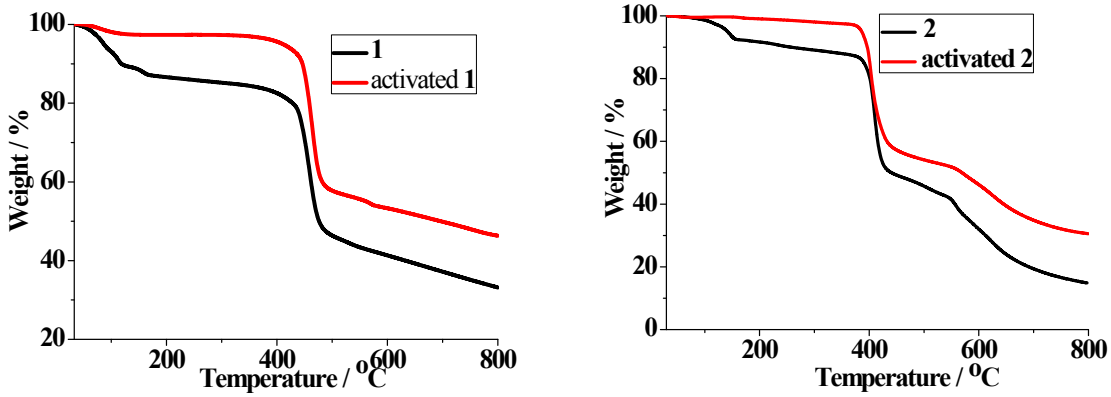


(a)



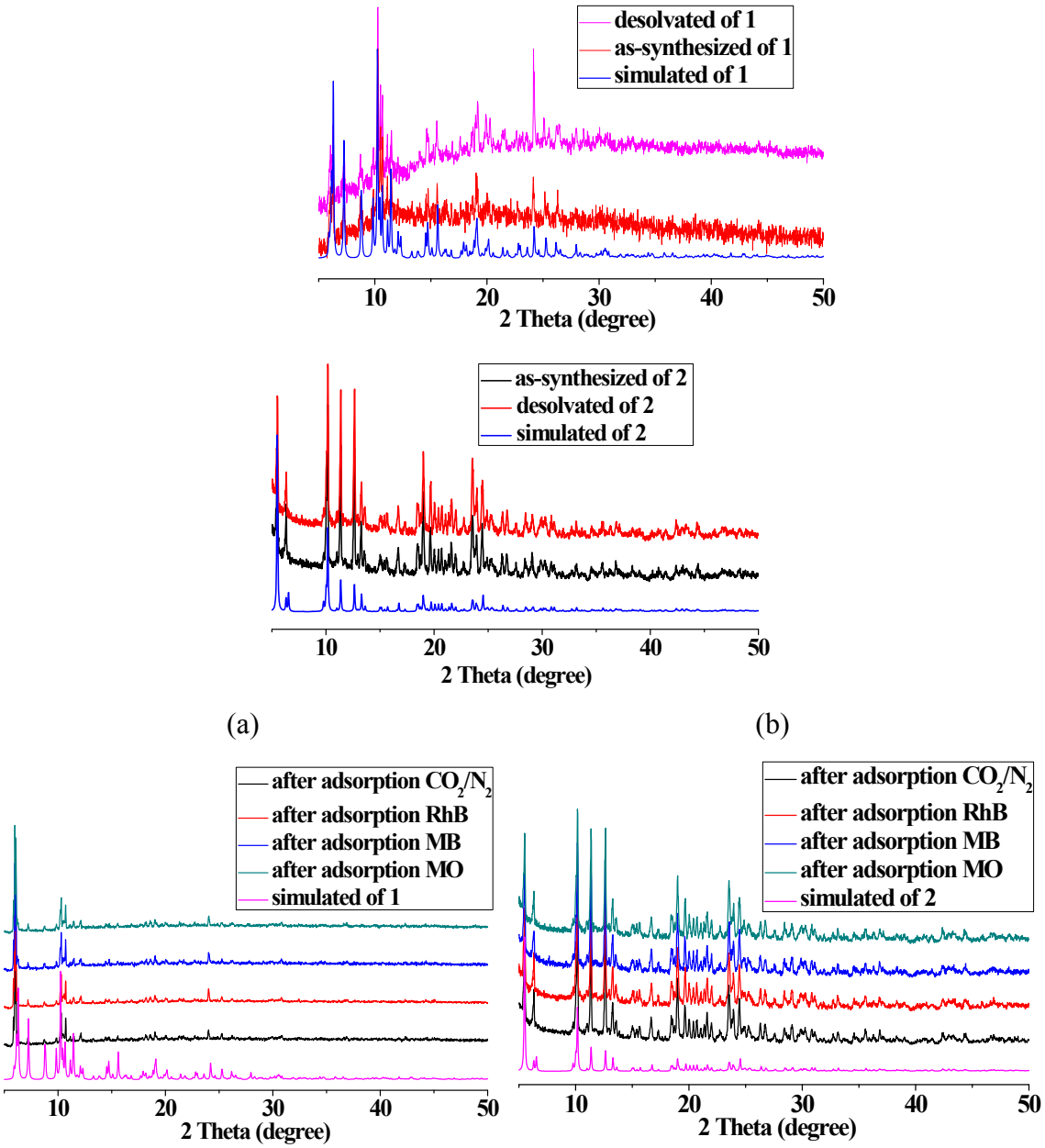
(b)

Fig. S2 (a) Simplified (3, 7)-connected bimodal of Co(II) in **1**. (b) Simplified (3, 4, 8)-connected 3-nodal in **2**.



(a) (b)

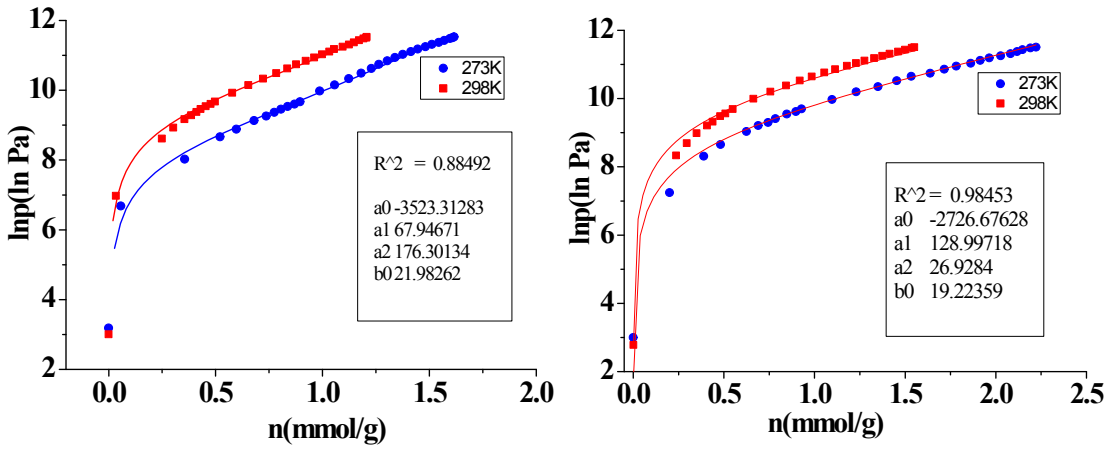
Fig. S3 TG curves of **1** (a) and **2** (b)



(a) (b)

(c) (d)

Fig. S4 PXRD patterns of **1** and **2** under varied conditions.



(a) (b)

Fig. S5 The calculated virial equation isotherms parameters fit to the experimental CO_2 data of **1'** (a) and **2'** (b).

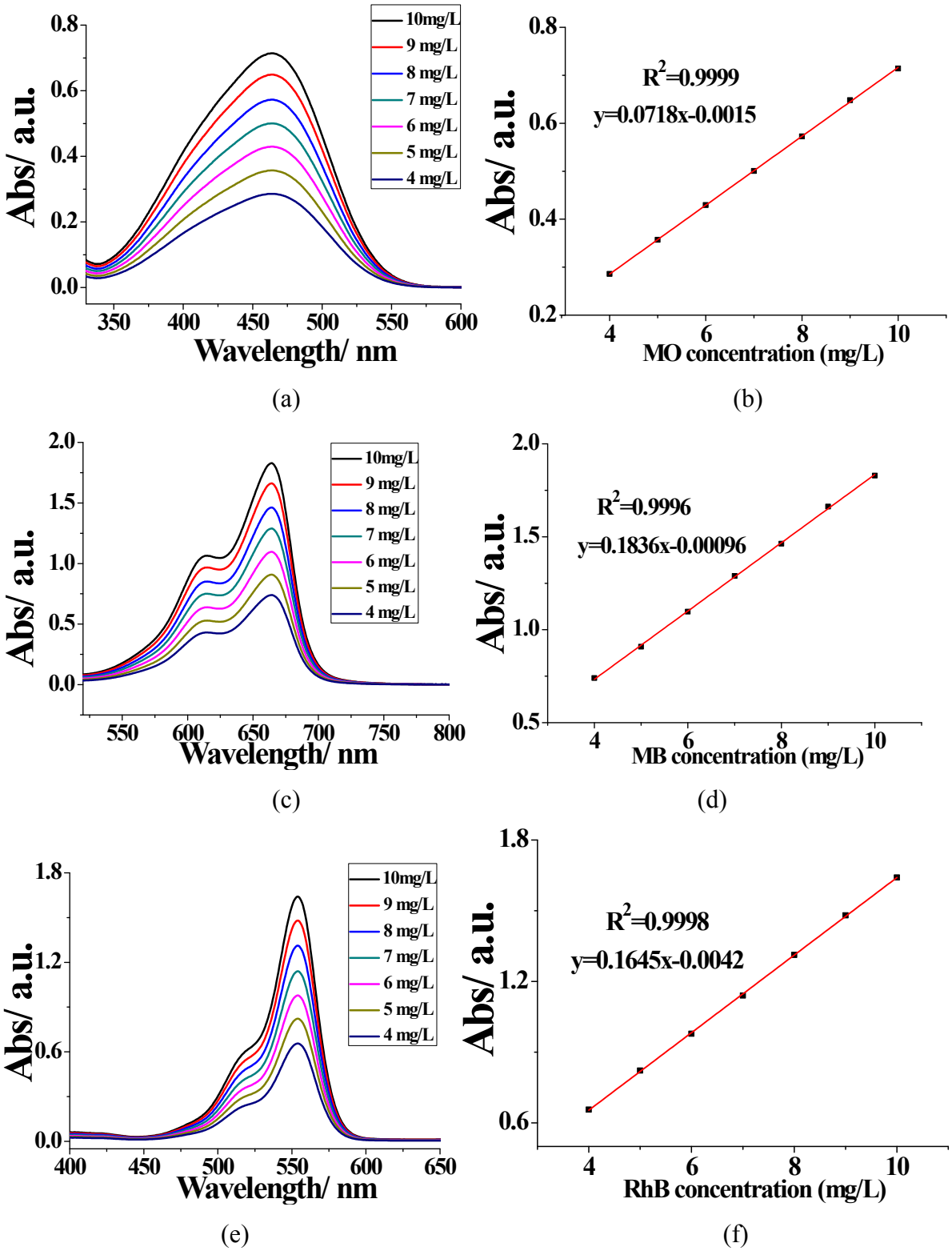


Fig. S6 UV-vis spectra of a solution of Methyl Orang (a), Methylene blue (c), Rhodamine B (e) at different concentration, standard curves for MO (b), standard curves for MB (d), standard curves for RhB (f).

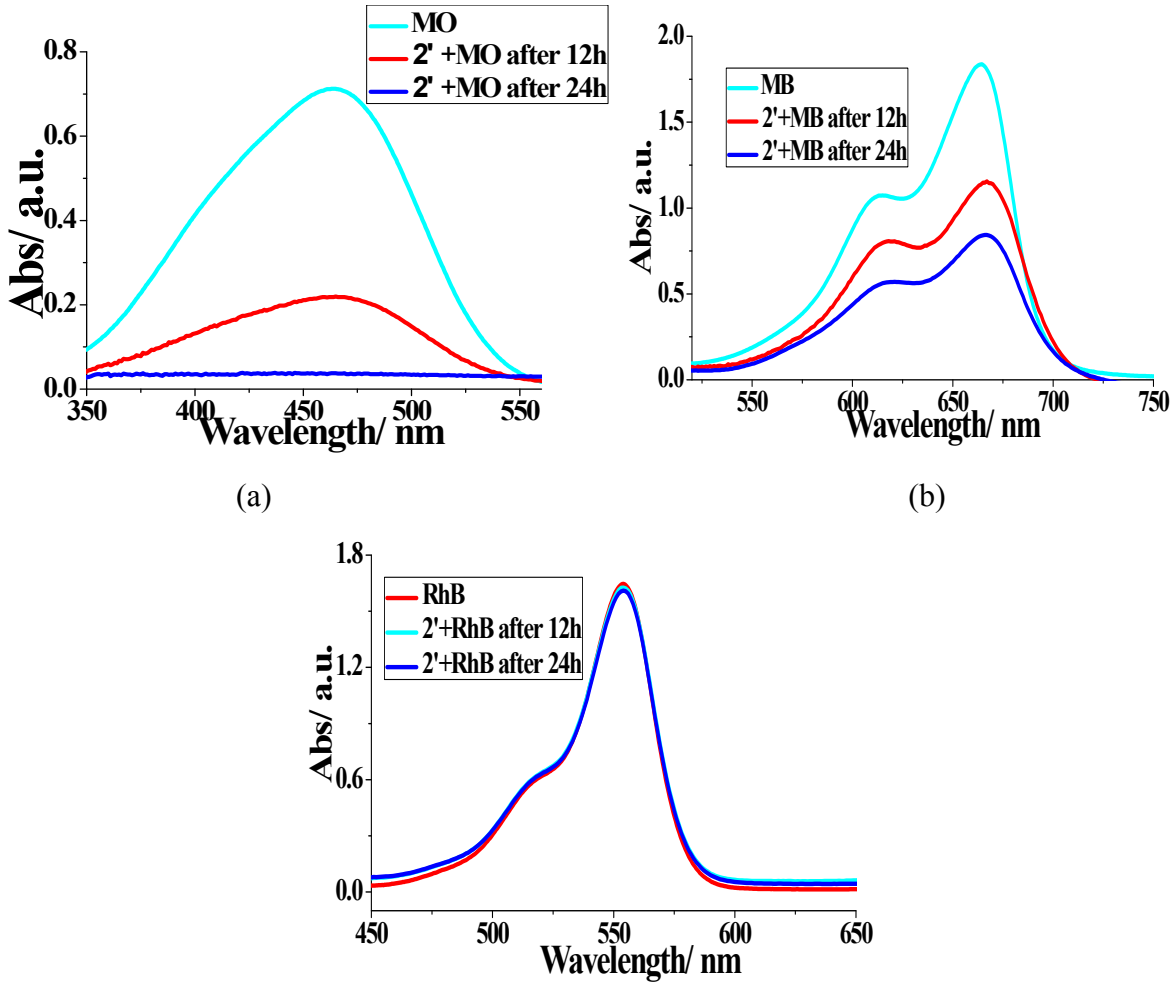


Fig. S7 Adsorption capability of **2'** toward MO (a), MB (b) and RhB (c) (experiment conditions: C_0 (MB): 10 mg L^{-1}, C_0 (MO): 10 mg L^{-1}, adsorbent dose: 10 mg/20 mL).

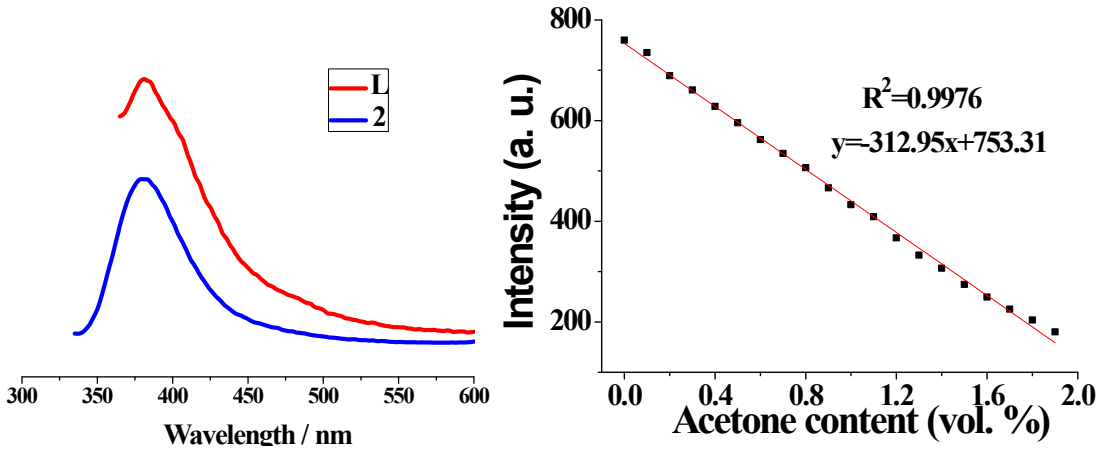


Fig. S8 (a) Solid-state photoluminescent spectra of free L ligand and **2** at room temperature. (b) Photoluminescence intensities of **2** in CH_3CN as a function of acetone content.

Calculations of the Adsorption Selectivity.

Adsorption isotherms from experimental data were analyzed using Ideal Adsorbed Solution Theory (IAST), using the pyIAST code.2 Each isotherm was fit with a quadratic isotherm model, and loadings from a representative 50:50 mixture of CO_2:N_2 were calculated for mixture feed pressures of 0.1 bar−1.0 bar. The selectivity $S(CO_2/N_2)$ of CO_2 with respect to N_2 in each mixture was calculated from

$$S\left(\frac{CO_2}{N_2}\right) = \frac{\left(\frac{x_{CO_2}}{x_{N_2}}\right)}{\left(\frac{y_{CO_2}}{y_{N_2}}\right)}$$

where xi represents the mole fraction of gas in the adsorbed phase, and yi represents the mole fraction in the bulk gas phase.[1,2]

Estimation of the isosteric heats of gas adsorption

A virial-type [3] expression comprising the temperature-independent parameters a_i and b_i was employed to calculate the enthalpies of adsorption for CO_2 (at 273 and 298 K) on **1'** and **2'**. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{m} b_i N^i$$

Here, P is the pressure expressed in Pa, N is the amount adsorbed in mmol g^{-1}, T is the temperature in K, a_i and b_i are virial coefficients, and m, n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

References

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2 C.-M. Simon, B. Smit, M. Haranczyk, *Comput. Phys. Commun*. **2016**, *200*, 364−380.

3 J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 1304–1315.