Electronic Supplementary Information

Solvent-induced diversity of luminescent metal-organic frameworks based on different secondary building units

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Table S1 Selected bond lengths (Å) and bond angles (°) for **1**-**3**.

Complex**1**			
Cd(1)-O(4)#1	2.423(4)	Cd(1)-O(2)	2.248(4)
Cd(1)-O(1)#2	2.287(5)	Cd(1)-O(3)#1	2.436(4)
Cd(1)-O(3)#3	2.283(4)	Cd(1)-O(8)	2.310(5)
Cd(2)-O(6)	2.261(5)	Cd(2)-O(5)	2.332(6)
O(4)#1-Cd(1)-O(3)#1	53.37(12)	Cd(2)-O(7)	2.62(3)
O(2)-Cd(1)-O(1)#2	105.7(2)	Cd(2)-O(7A)	2.241(12)
O(2)-Cd(1)-O(3)#3	104.53(16)	O(2)-Cd(1)-O(4)#1	167.28(17)
O(1)#2-Cd(1)-O(4)#1	83.0(2)	O(2)-Cd(1)-O(3)#1	115.86(15)
O(1)#2-Cd(1)-O(8)	158.57(19)	O(2)-Cd(1)-O(8)	88.1(2)
O(3)#3-Cd(1)-O(1)#2	74.63(16)	O(1)#2-Cd(1)-O(3)#1	93.65(15)
O(3)#3-Cd(1)-O(8)	86.20(17)	O(3)#3-Cd(1)-O(4)#1	86.53(14)
O(8)-Cd(1)-O(3)#1	94.88(17)	O(3)#3-Cd(1)-O(3)#1	139.61(14)
O(5)-Cd(2)-O(7)#4	139.5(6)	O(8)-Cd(1)-O(4)#1	86.4(2)
O(6)#4-Cd(2)-O(5)	112.3(2)	O(5)#4-Cd(2)-O(5)	93.7(3)
O(6)#4-Cd(2)-O(6)	165.5(3)	O(5)-Cd(2)-O(7)	79.2(5)
O(6)#4-Cd(2)-O(7)	89.2(5)	O(6)-Cd(2)-O(5)	56.5(2)
O(7A)-Cd(2)-O(5)#4	156.6(4)	O(6)-Cd(2)-O(7)	96.9(5)
O(7A)-Cd(2)-O(6)	90.5(4)	O(7)#4-Cd(2)-O(7)	130.4(12)
O(7A)-Cd(2)-O(6)#4	100.2(4)	O(7A)-Cd(2)-O(5)	95.1(6)
O(7A)#4-Cd(2)-O(7A)	85.3(14)		

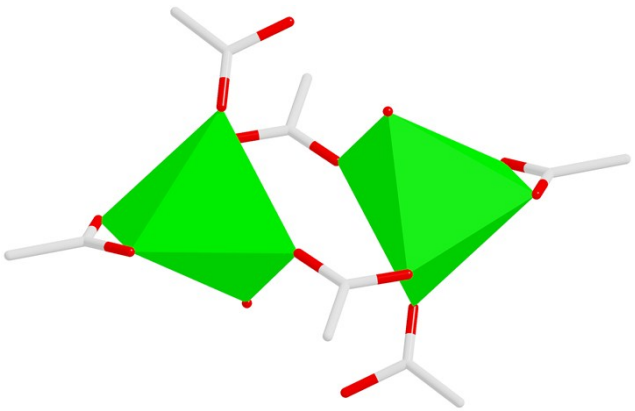
Symmetrical codes: #1 1.5-x, 0.5+y, 2.5-z;#2 x, 2-y, 0.5+z;#3 1.5-x, 1.5-y, 3-z;#4 1-x, y, -0.5-z.

Complex**2**			
Cd(2)-O(2)	2.280(7)	Cd(2)-O(7)#3	2.446(6)
Cd(2)-O(3)#1	2.259(10)	Cd(2)-O(3)	2.259(10)
Cd(1)-O(1)	2.194(8)	Cd(1)-O(7)#2	2.358(8)
Cd(1)-O(4)#1	2.290(8)	O(2)-Cd(2)-O(2)#1	92.9(4)
O(2)-Cd(2)-O(7)#2	106.9(3)	O(3)-Cd(2)-O(2)	86.2(3)
O(2)-Cd(2)-O(7)#3	160.0(3)	O(3)-Cd(2)-O(7)#3	89.3(3)
O(2)-Cd(2)-C(11)#2	133.5(2)	O(3)-Cd(2)-O(3)#1	178.2(4)
O(7)#3-Cd(2)-O(7)#2	53.5(3)	O(1)#4-Cd(1)-O(7)#5	80.6(4)
O(3)#1-Cd(2)-O(2)	95.1(4)	O(1)-Cd(1)-O(4)#1	87.5(4)
O(3)-Cd(2)-O(7)#2	89.1(3)	O(7)#2-Cd(1)-O(7)#5	180.0
O(1)#4-Cd(1)-O(1)	180.0	O(4)#6-Cd(1)-O(7)#2	89.8(3)
O(1)-Cd(1)-O(7)#5	99.4(4)	O(4)#1-Cd(1)-O(7)#2	90.2(3)
O(1)-Cd(1)-O(4)#6	92.5(4)	O(4)#6-Cd(1)-O(4)#1	180.0

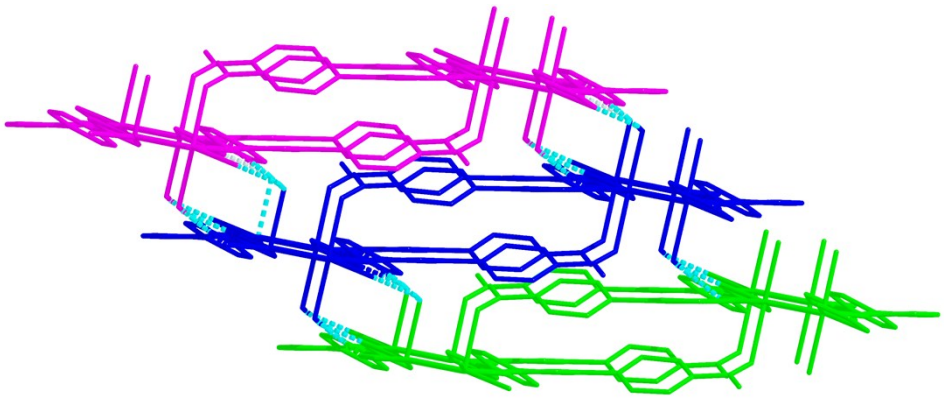
Symmetrical codes: #1 2-x, y, 1.5-z； #2 2-x, 1-y, 2-z;#3 1.5-x, 0.5-y, 2-z;#4 0.5+x, 0.5-y, 0.5+z;#5 1-x, y, 1.5-z； #6 -0.5+x, -0.5+y, z;#7 1.5-x, -0.5+y, 1.5-z.

Complex**3**			
Cd(1)-O(1)	2.194(8)	Cd(1)-O(2)#1	2.262(6)
Cd(1)-O(3)#2	2.375(7)	Cd(1)-O(4)#2	2.273(7)
Cd(1)-O(5)#3	2.366(8)	Cd(1)-O(7)	2.381(7)
O(1)-Cd(1)-O(2)#1	127.0(3)	O(1)-Cd(1)-O(3)#2	147.8(3)
O(1)-Cd(1)-O(4)#2	94.0(3)	O(1)-Cd(1)-O(5)#3	89.8(3)
O(1)-Cd(1)-O(7)	85.9(3)		

Symmetrical codes: #1 -x, -y, -z; #2 -1-x, -y, 1-z;#3 -1+x, -1+y, z.



(a)



(b)

Fig. S1 (a) The dimeric SBU in **3**. (b) The H-bonds [O7-H7B…O2 = 1.811 Å and O7-H7A…O3 = 2.667 Å] between the adjacent layers in **3.**

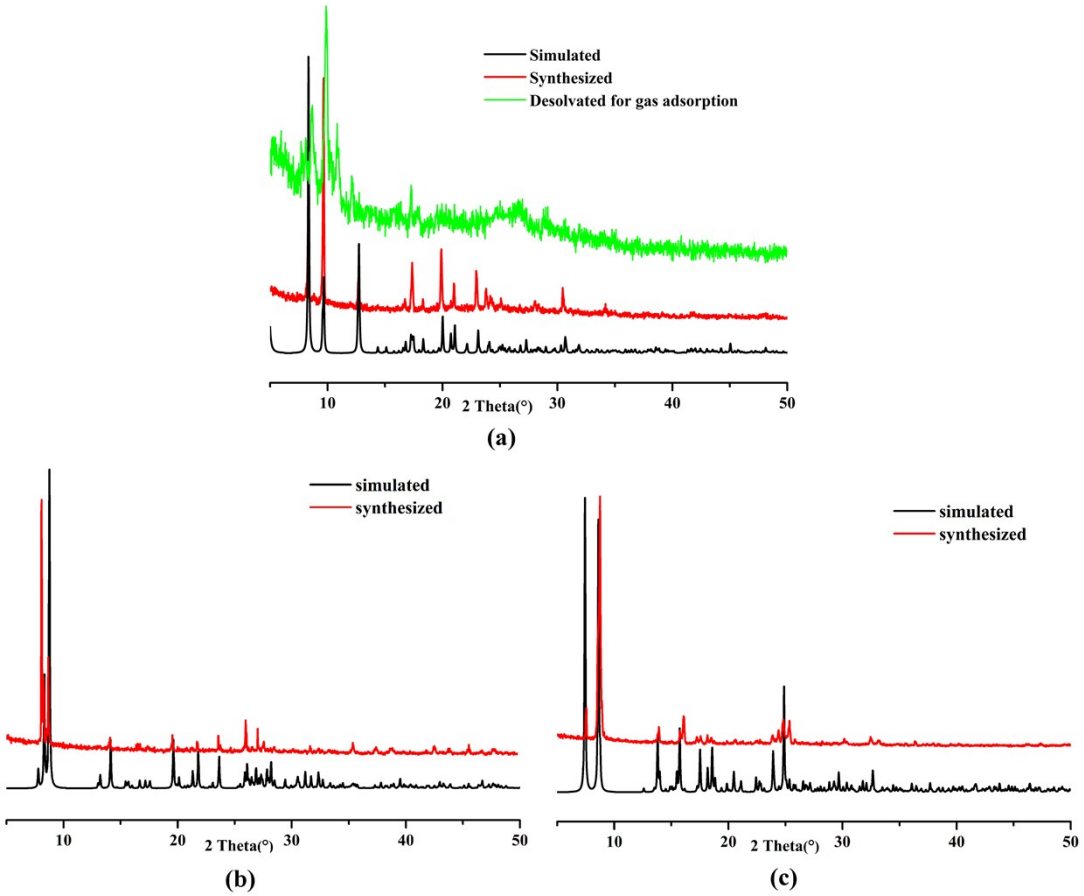
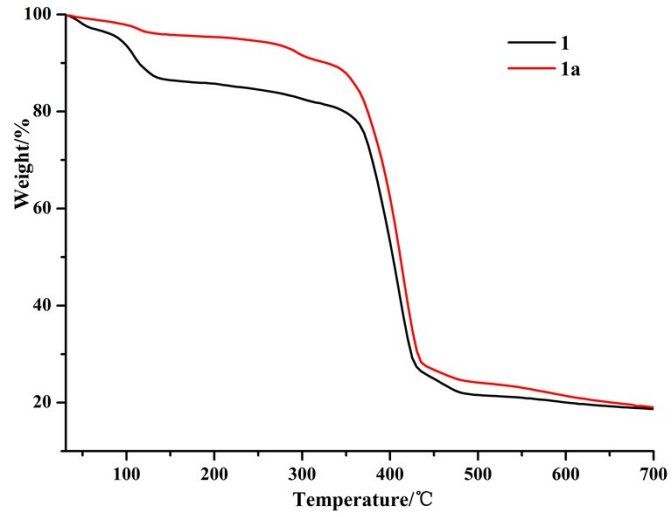
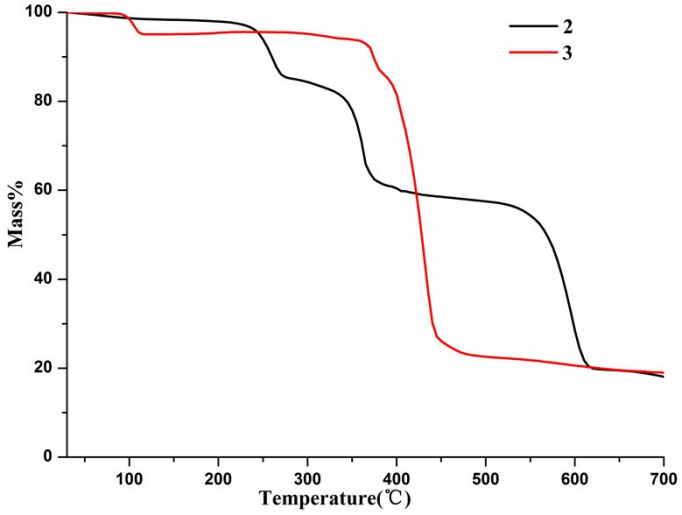


Fig. S2 PXRD patterns of **1-3** in (a-c) simulated from the X-ray single-crystal structure, experimental samples and desolvated samples.



(a)



(b)

Fig. S3 TGA plots of complexes **1-3.**

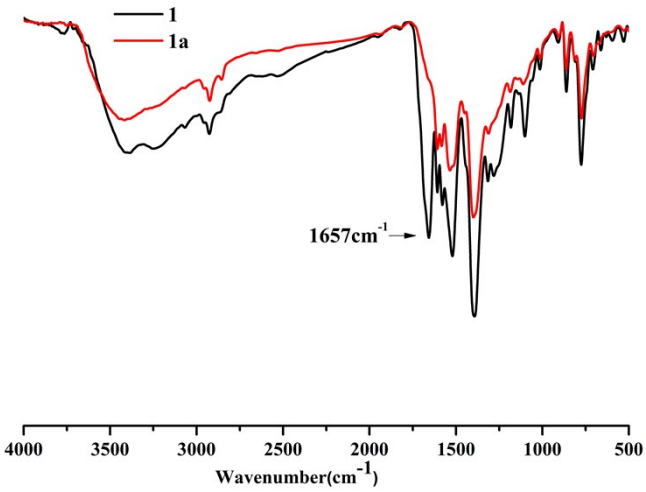


Fig. S4 IR spectra of the as-synthesized and desolvated **1** (**1a**). The characteristic C=O vibration at 1657 cm^{-1} of DMF in **1** is absent in **1a**, indicating the complete removal of DMF.

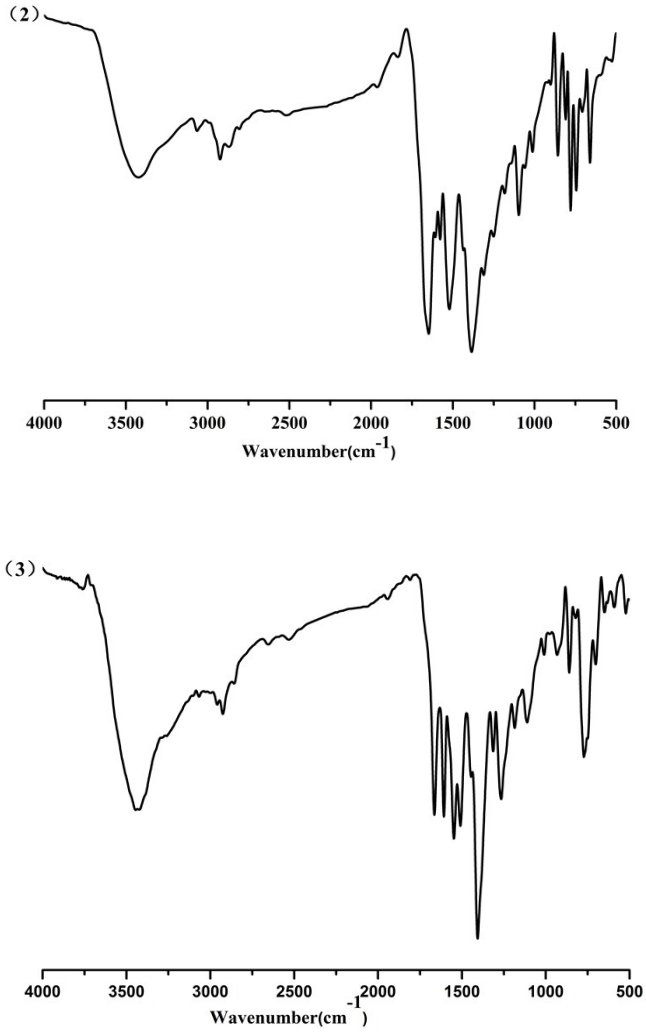


Fig. S5 IR spectra of the as-synthesized **2** and **3.**

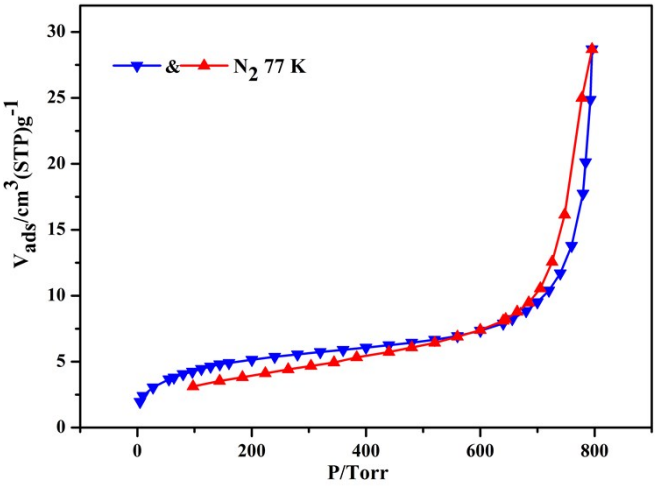


Fig. S6 The adsorption isotherms of **1a** (N_2) at 77 K.

IAST adsorption selectivity calculation:

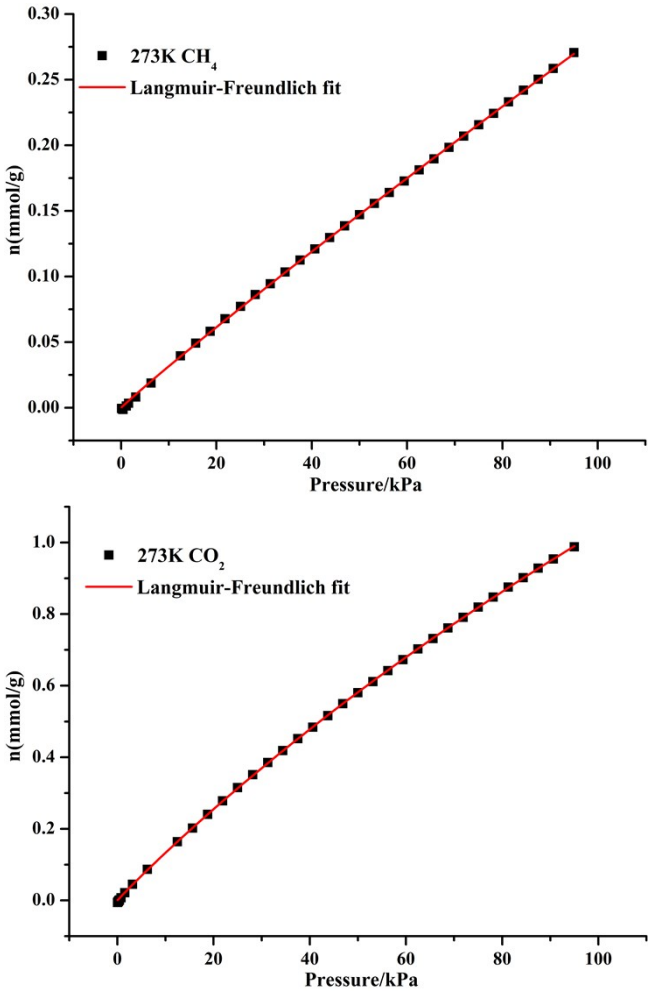
The experimental isotherm data for pure CO_2 and CH_4 (measured at 273 and 298 K) were fitted using a Langmuir-Freundlich (L-F) model:

$$q = \frac{a * b * p^c}{1 + b * p^c}$$

Where q and p are adsorbed amounts and pressures of component i, respectively. The adsorption selectivities for binary mixtures of CO_2/CH_4 at 273 and 298 K, defined by

$$S_{ads} = (q_1 / q_2) / (p_1 / p_2)$$

Where qi is the amount of i adsorbed and pi is the partial pressure of i in the mixture.



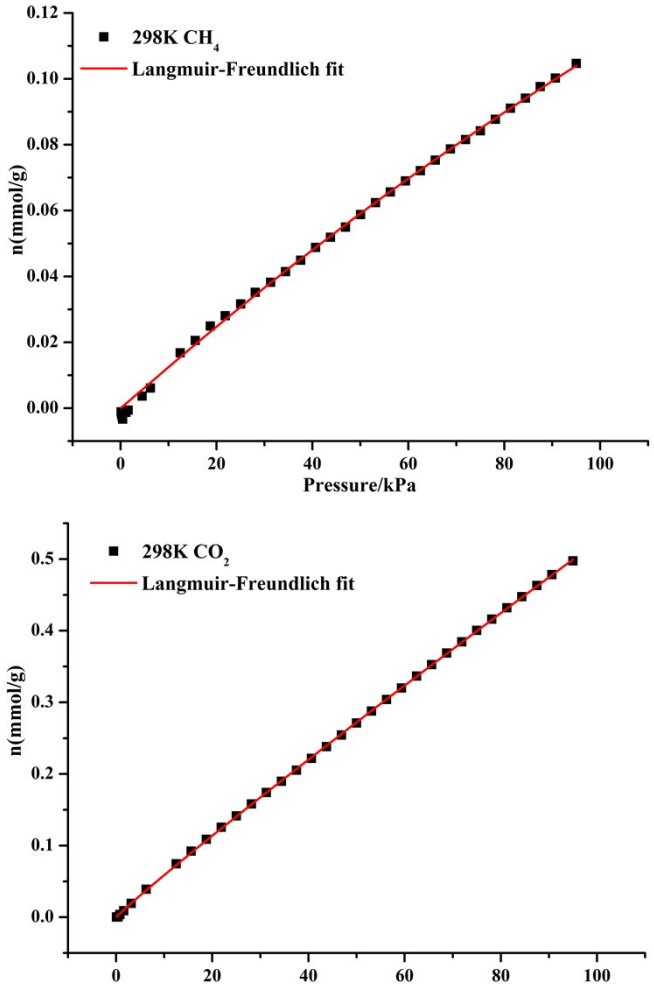


Fig. S7 CO_2 adsorption isotherms of **1a** at 298K with fitting by L-F model: a = 36.29522, b = 1.79197×10^{-4}, c = 0.95632, Chi^2 = 1.69 ×10^{-6}, R^2 = 0.99994; CO_2 adsorption isotherms of **1a** at 273K with fitting by L-F model: a = 5.16565, b = 0.0028, c =0.97488, Chi^2 = 7.91396 ×10^{-6}, R^2 = 0.99994; CH_4 adsorption isotherms of **1a** at 298K with fitting by L-F model: a = 0.58455, b = 0.00208, c = 1.01934, Chi^2 = 1.98953 ×10^{-6}, R^2 = 0.99838; CH_4 adsorption isotherms of **1a** at 273K with fitting by L-F model: a = 10.39661, b = 3.31485 ×10^{-4}, c = 0.96323, Chi^2 = 1.37919 ×10^{-6}, R^2 = 0.99982.