# *Supplementary Information*

# Two metal-organic frameworks based on flexible benzimidazole carboxylic acid ligand: selective gas sorption and luminescence

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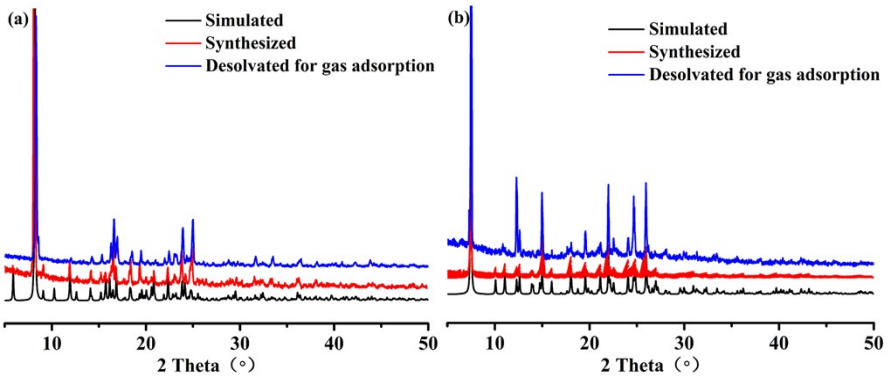



**Fig. S1** PXRD patterns of **1** (a) and **2** (b) simulated from the X-ray single-crystal structures, experimental samples and desolvated samples.

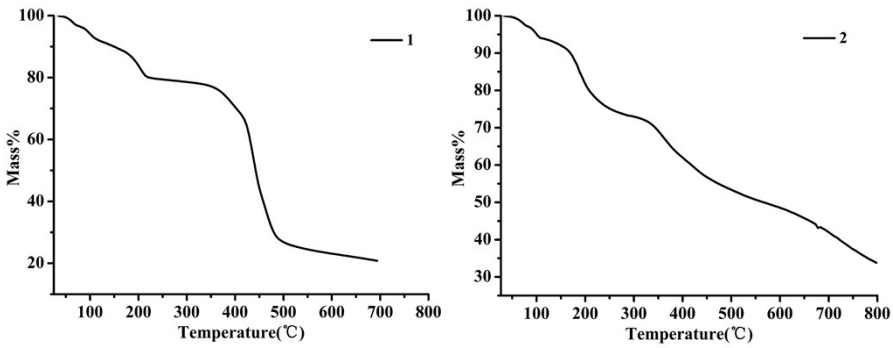



**Fig. S2** TGA plots of complexes **1** and **2**.

**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.

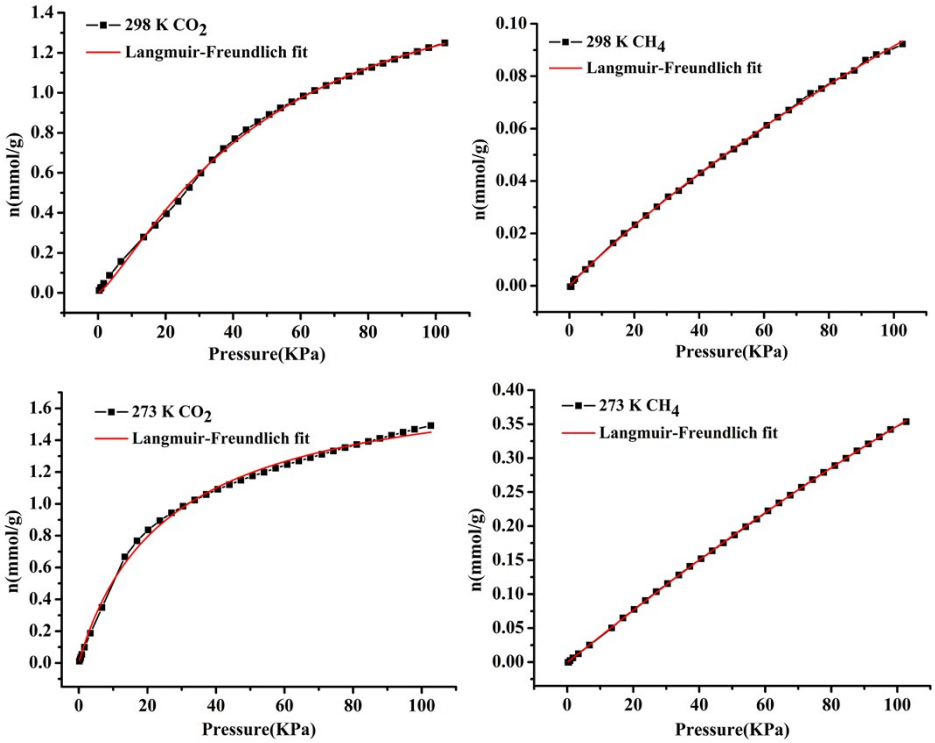



**Fig. S3** $CO_2$ adsorption isotherms of **1a** at 298K with fitting by L-F model: a =1.74802, b = 0.00689, c =1.27132, Chi^2 = $2.0513\times10^{-4}$, R^2 = 0.99882; $CH_4$ adsorption isotherms of **1a** at 298K with fitting by L-F model: a = 0.46111, b = 0.00292, c = 0.96391, Chi^2= $3.05\times10^{-7}$, R^2 = 0.99966; $CO_2$ adsorption isotherms of **1a** at 273K with fitting by L-F model: a =1.85073, b = 0.04204, c =0.96216, Chi^2 = $5.79\times10^{-4}$, R^2 = 0.99756; $CH_4$ adsorption isotherms of **1a** at 273K with fitting by L-F model: a = 2.07327, b = 0.00172, c = 1.03366, Chi^2 = $7.07\times10^{-7}$, R^2 =0.99995.

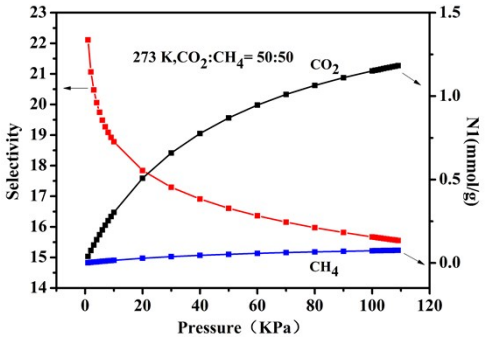



**Fig. S4** IAST adsorption selectivity of **1a** for the $CO_2/CH_4$ mixtures with components of 50:50 at 273 K.

**Calculation of Sorption Heat for $CO_2$ Uptake Using Virial 2 Model**

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} aiN^i + \sum_{i=0}^{n} biN^i \quad Q_{st} = -R \sum_{i=0}^{m} aiN^i$$

The above virial expression was used to fit the combined isotherm data for **1a** at 273, 298 K, where $P$ is the pressure, $N$ is the adsorbed amount, $T$ is the temperature, $a_i$ and $b_i$ are virial coefficients, and $m$ and $N$ are the number of coefficients used to describe the isotherms. $Q_{st}$ is the coverage-dependent enthalpy of adsorption and $R$ is the universal gas constant.

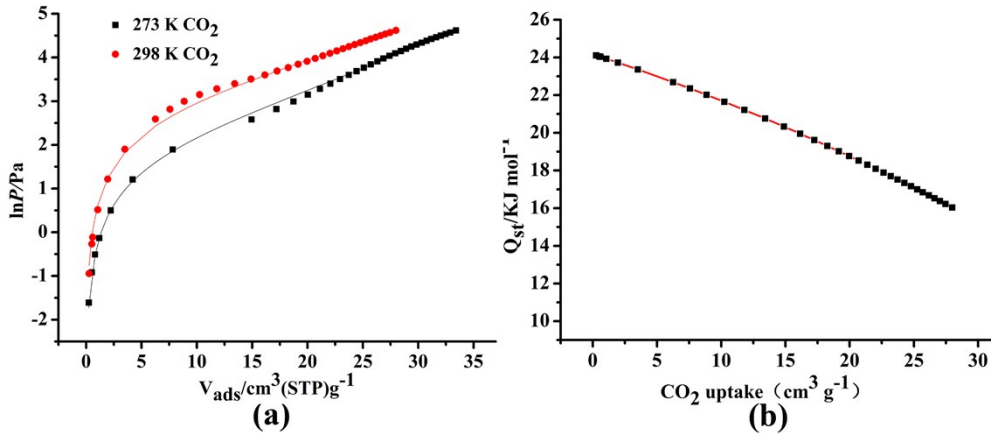
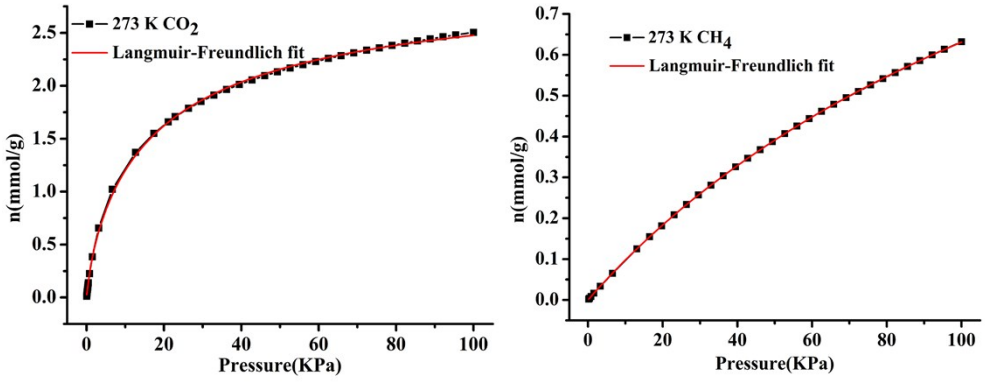



**Fig. S5** (a) Virial analysis of the $CO_2$ adsorption data at 273 and 298 K for **1a**. Fitting results: a0= -2906.84, a1 = 26.51, a2 = 0.30, a3 = 0, a4 = 0, Chi^2 = 0.00596,R^2 = 0.99788. (b) Isosteric heat of $CO_2$ adsorption for **1a** estimated by the virial equation from the adsorption isotherms at 273 and 298 K.



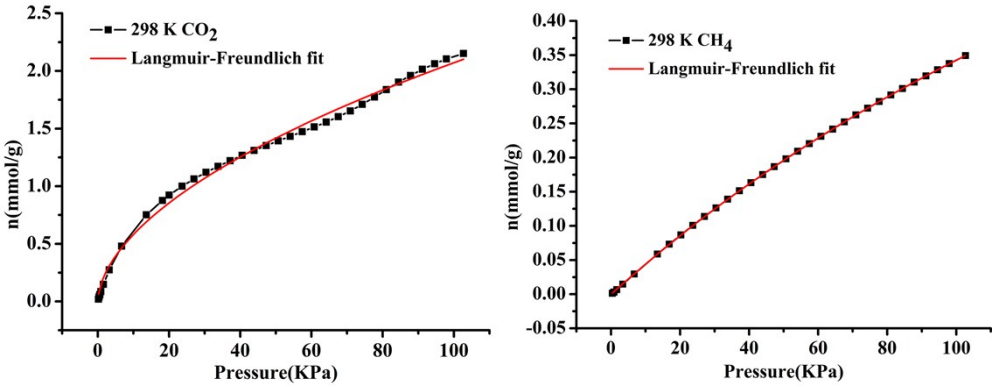



**Fig. S6** $CO_2$ adsorption isotherms of **2a** at 298K with fitting by L-F model: a =75.55824, b = 0.00213, c =0.56069, Chi^2=$2.59\times10^{-3}$, R^2 = 0.99399;$CH_4$ adsorption isotherms of **2a** at 298K with fitting by L-F model: a = 1.31743, b = 0.00339, c = 1.00758, Chi^2= $1.28\times10^{-7}$, R^2 = 0.99999; CO2 adsorption isotherms of **2a** at 273K with fitting by L-F model: a =3.10526, b = 0.10093, c =0.79582, Chi^2 = $3.76\times10^{-4}$, R^2 = 0.99958; $CH_4$ adsorption isotherms of **2a** at 273K with fitting by L-F model: a = 1.66684, b = 0.00637, c = 0.99014, Chi^2= $1.86\times10^{-7}$, R^2 = 1.

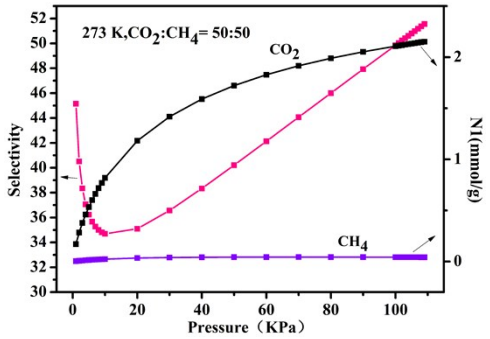



**Fig. S7** IAST adsorption selectivity of **2a** for the $CO_2/CH_4$ mixtures with different components at 273K.

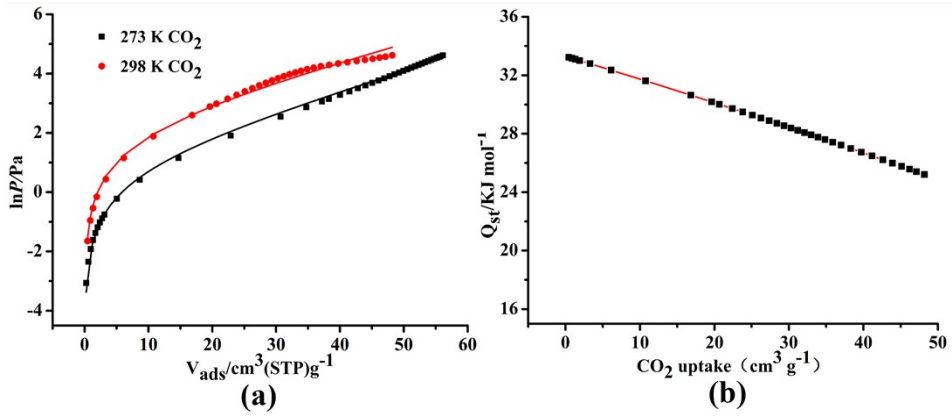



**Fig. S8** (a) Virial analysis of the $CO_2$ adsorption data at 273K and 298 K for **2a**. Fitting results: a0=-4004.85, a1 = 18.31, a2 = 0.0389, a3 = 0, a4 = 0, Chi^2 = 0.01242, R^2 = 0.99748. (b) Isosteric heat of $CO_2$ adsorption for **2a** estimated by the virial equation from the adsorption isotherms at 273 and 298 K.

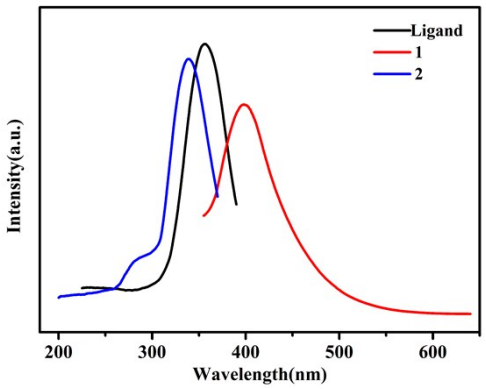



**Fig. S9** Solid-state excitation spectra of $H_4L$ ligand, **1** and **2**.

**Table S1** Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

| Complex **1** | | | |
|---|---|---|---|
| Cd(1)-O(1) | 2.534(6) | O(4)#1-Cd(1)-N(2)#3 | 101.0(2) |
| Cd(1)-O(1W) | 2.346(6) | O(8)#2-Cd(1)-O(1) | 94.6(2) |
| Cd(1)-O(2) | 2.330(6) | O(8)#2-Cd(1)-O(1W) | 85.0(2) |
| Cd(1)-O(4)#1 | 2.282(6) | O(8)#2-Cd(1)-O(2) | 146.2(2) |
| Cd(1)-O(8)#2 | 2.304(6) | N(2)#3-Cd(1)-O(1) | 96.2(2) |
| Cd(1)-N(2)#3 | 2.288(6) | N(2)#3-Cd(1)-O(1W) | 173.2(2) |
| Cd(2)-O(2W) | 2.333(6) | N(2)#3-Cd(1)-O(2) | 100.3(2) |
| Cd(2)-O(6)#4 | 2.189(5) | N(2)#3-Cd(1)-O(8)#2 | 91.2(2) |
| Cd(2)-O(7)#5 | 2.157(5) | O(6)#4-Cd(2)-O(2W) | 91.0(2) |
| Cd(2)-O(9) | 2.315(8) | O(6)#4-Cd(2)-O(9) | 83.6(3) |
| Cd(2)-N(4) | 2.246(6) | O(6)#4-Cd(2)-N(4) | 113.1(2) |
| O(1W)-Cd(1)-O(1) | 78.5(2) | O(7)#5-Cd(2)-O(2W) | 92.9(2) |
| O(2)-Cd(1)-O(1) | 52.8(2) | O(7)#5-Cd(2)-O(6)#4 | 124.8(2) |
| O(2)-Cd(1)-O(1W) | 80.1(2) | O(7)#5-Cd(2)-O(9) | 88.7(3) |
| O(4)#1-Cd(1)-O(1) | 162.5(2) | O(7)#5-Cd(2)-N(4) | 120.5(2) |
| O(4)#1-Cd(1)-O(1W) | 84.1(2) | O(9)-Cd(2)-O(2W) | 174.2(3) |
| O(4)#1-Cd(1)-O(2) | 125.6(2) | N(4)-Cd(2)-O(2W) | 98.5(2) |
| O(4)#1-Cd(1)-O(8)#2 | 82.3(2) | N(4)-Cd(2)-O(9) | 85.4(3) |
| Symmetry codes: #1 -x+1, -y+3, -z+1; #2 -x, -y+2, -z+1; #3 -x, -y+3, -z+1; #4 -x, -y, -z+2; #5 x+1, y, z; #6 x-1, y, z. | | | |
| Complex **2** | | | |
| Zn(1)-O(2)#1 | 1.925(5) | O(2)#1-Zn(1)-O(1W) | 94.6(3) |
| Zn(1)-N(1) | 1.976(6) | N(1)-Zn(1)-O(1W) | 100.9(3) |
| Zn(1)-O(3)#2 | 1.900(5) | O(3)#2-Zn(1)-O(2)#1 | 119.3(2) |
| Zn(1)-O(1W) | 2.006(6) | O(3)#2-Zn(1)-N(1) | 118.2(2) |
| O(2)#1-Zn(1)-N(1) | 115.3(2) | O(3)#2-Zn(1)-O(1W) | 101.4(3) |
| Symmetry codes: #1 -x+1, -y+2, -z; #2 x, -y+3/2, z-1/2; #3 -x+2, -y+1, -z; #4 x, -y+3/2, z+1/2. | | | |