Supporting Information for

Selective CO$_2$ adsorption in a microporous metal–organic framework

with suitable pore sizes and open metal sites

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**Fig. S1** The coordination environment of Zn$^{2+}$ ions in 1·DMF; the hydrogen atoms and solvent molecules are omitted.
**Fig. S2** The two coordination modes of the L^5^- ligands in 1·DMF, one exhibits μ¹⁻η¹, syn-syn-μ¹⁻η¹:η¹, syn-syn-μ²⁻η¹:η¹, and syn-anti-μ²⁻η¹:η¹ (left), the other adopts μ¹⁻η¹, and syn-anti-μ²⁻η¹:η¹ (right).

**Fig. S3** The coordination environment of Zn²⁺ ions in 1·DMA.

**Fig. S4** PXRD patterns (from bottom to top) for 1·DMF (Simulated), 1·DMF (As-synthesized), 1·DMA (Simulated), and 1·DMA (As-synthesized).
Fig. S5 PXRD patterns of 1-DMF simulated from the X-ray single-crystal structure, experimental samples, desolvated samples, and after gas adsorption samples.

Fig. S6 TGA plots of complexes 1-DMF (black), 1-DMA (blue), and 1a (red).

Fig. S7 IR spectra of the as-synthesized (1-DMF) and desolvated (1a).
IAST adsorption selectivity calculation:

The experimental isotherm data for pure CO$_2$, CH$_4$ and N$_2$ (measured at 298) were fitted using a Langmuir-Freundlich (L-F) model:

$$q = \frac{a \cdot b \cdot P^c}{1 + b \cdot P^c}$$

Where $q$ and $p$ are adsorbed amounts and pressures of component i, respectively.

The adsorption selectivities for binary mixtures of CO$_2$/CH$_4$ and CO$_2$/N$_2$, defined by

$$S_{ij} = \frac{x_i \cdot y_j}{x_j \cdot y_i}$$

were calculated using the Ideal Adsorption Solution Theory (IAST) of Myers and Prausnitz.

Where $x_i$ is the mole fraction of component i in the adsorbed phase and $y_i$ is the mole fraction of component i in the bulk.

Fig. S8 CO$_2$ adsorption isotherms of 1a with fitting by L-F model: a = 5.06407, b = 0.01767, c = 0.89890, Chi$^2$ = 1.41 $\times$ 10$^{-4}$, R$^2$ = 0.99982; CH$_4$ adsorption isotherms of 1a with fitting by L-F model: a = 1.97982, b = 0.00471, c = 1.01417, Chi$^2$ = 4.69 $\times$ 10$^{-7}$, R$^2$ = 0.99999; N$_2$ adsorption isotherms of 1a with fitting by L-F model: a = 0.57497, b = 0.00125, c = 94615, Chi$^2$ = 2.17 $\times$ 10$^{-7}$, R$^2$ = 0.99983.

Calculation of sorption heat for CO$_2$ uptake using Virial 2 model
\[
\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \quad Q_{st} = -R \sum_{i=0}^{m} a_i N^i
\]

The above equation was applied to fit the combined CO\(_2\) isotherm data for desolvated 1a at 273 and 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. S9 CO\(_2\) adsorption isotherms for 1a with fitting by Virial 2 model. Fitting results: \(a_0 = -3616.97213, a_1 = 207.96409, a_2 = -107.43727, a_3 = 34.35126, a_4 = 2.99692, b_0 = 21.79273, b_1 = -0.85783, b_2 = 0.79230, b_3 = -0.23580, \) Chi^2 = 0.00006, R^2 = 0.99983.

Fig. S10 CH\(_4\) adsorption isotherms for 1a with fitting by Virial 2 model. Fitting results: \(a_0 = -2635.48544, a_1 = 2968.21695, a_2 = -10730.33007, a_3 = 9400.63156, a_4 = 485.17455, b_0 = 20.64613, b_1 = -12.02875, b_2 = 43.76530, b_3 = -39.25892, \) Chi^2 = 0.00203, R^2 = 0.99921.
**Fig. S11** Excitation spectra of 1·DMF and 1·DMA in the solid state at room temperature.