Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

Selective CO_2 adsorption in a microporous metal–organic framework with suitable pore sizes and open metal sites

Bo Liu,[a] Ya-Hui Jiang,[a] Zhi-Sen Li,[a] Lei Hou [a] and Yao-Yu Wang[*a]

[a]Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an 710069, China. E-mail: wyaoyu@nwu.edu.cn

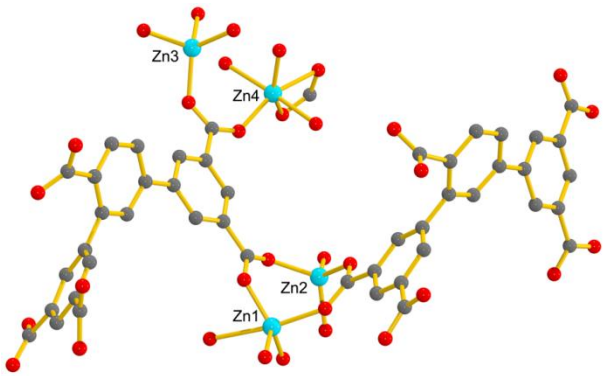

Fig. S1 The coordination environment of Zn^{2+} ions in **1**·DMF, the hydrogen atoms and solvent molecules are omitted.

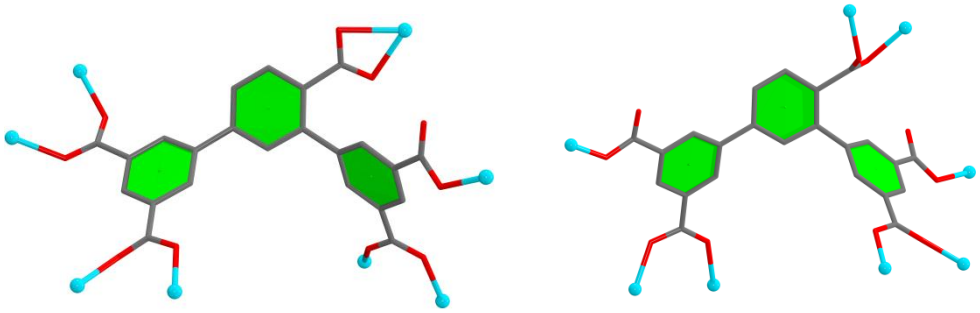

Fig. S2 The two coordination modes of the L^{5-} ligands in **1**·DMF, one exhibits μ^1-η^1, *syn-syn*-μ^1-η^1:η^1, *syn-syn*-μ^2-η^1:η^1, and *syn-anti*-μ^2-η^1:η^1 (left), the other adopts μ^1-η^1, and *syn-anti*-μ^2-η^1:η^1 (right).

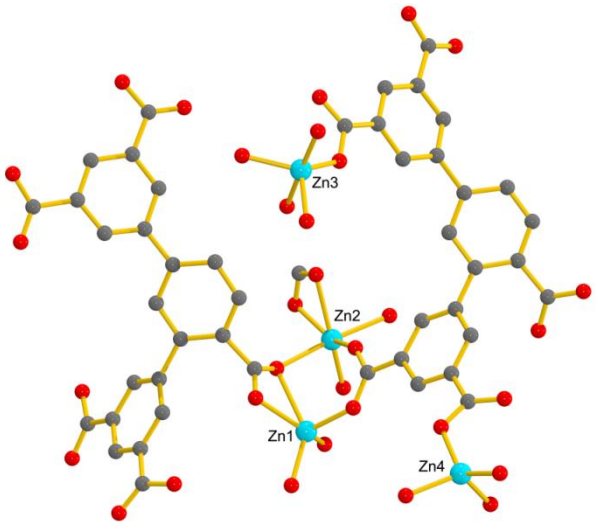

Fig. S3 The coordination environment of Zn^{2+} ions in **1**·DMA.

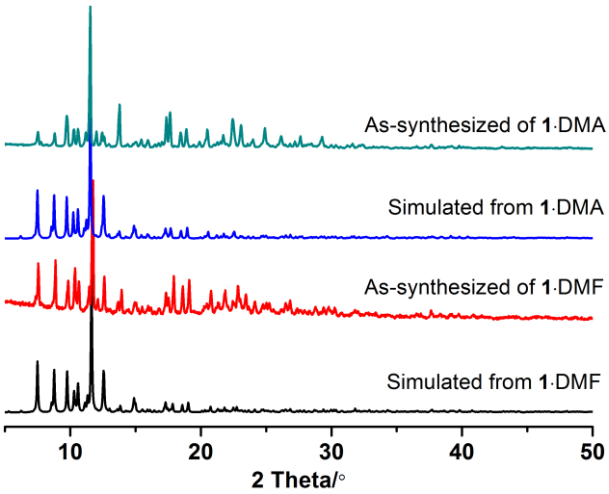

Fig. S4 PXRD patterns (from bottom to top) for **1** ĐMF (Simulated), **1** ĐMF (As-synthesized), **1** ĐMA (Simulated), and **1** ĐMA (As-synthesized).

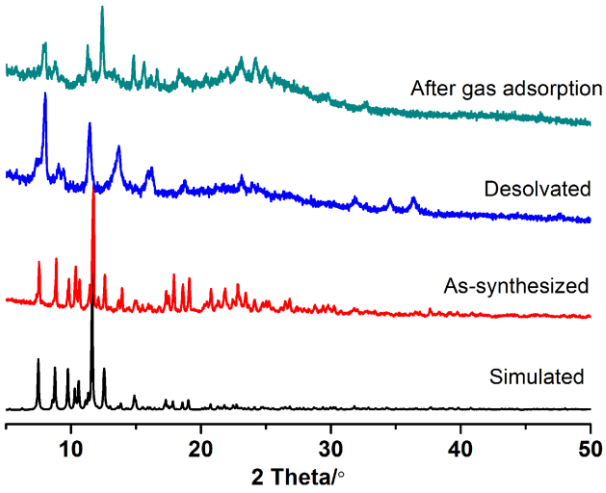

Fig. S5 PXRD patterns of **1**·DMF simulated from the X-ray single-crystal structure, experimental samples, desolvated samples, and after gas adsorption samples.

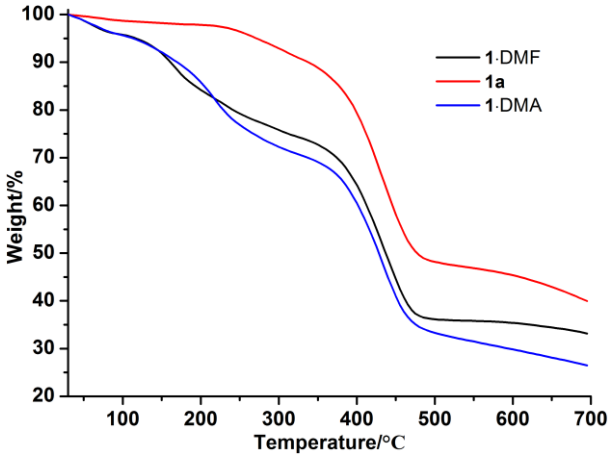

Fig. S6 TGA plots of complexes **1**·DMF (black), **1**·DMA (blue), and **1a** (red).

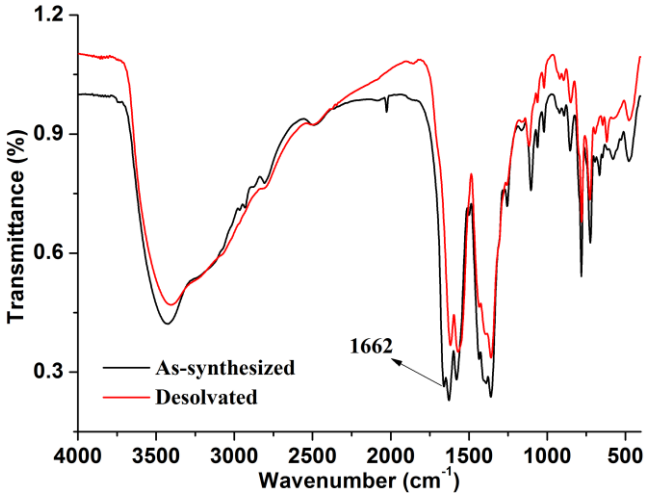

Fig. S7 IR spectra of the as-synthesized (**1**·DMF) and desolvated (**1a**).

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:

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

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

The adsorption selectivities for binary mixtures of CO_2/CH_4 and CO_2/N_2, defined by

$$S_{i/j} = \frac{x_i * y_j}{x_j * y_i}$$

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.

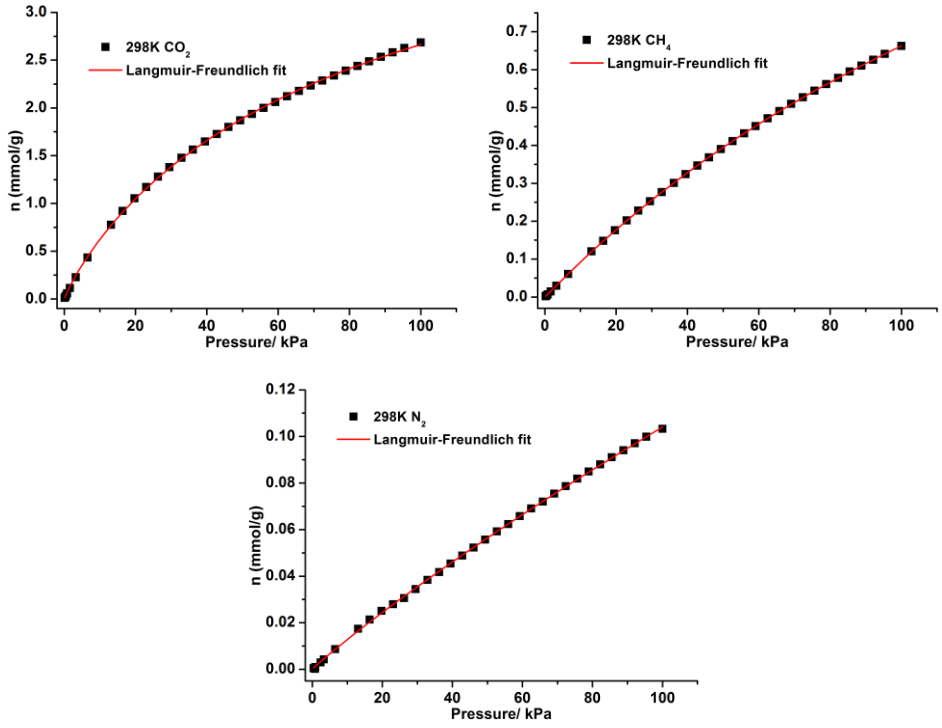

Fig. S8 CO_2 adsorption isotherms of **1a** with fitting by L-F model: a = 5.06407, b = 0.01767, c = 0.89890, Chi^2 = 1.41 × 10^{-4}, R^2 = 0.99982; CH_4 adsorption isotherms of **1a** with fitting by L-F model: a = 1.97982, b = 0.00471, c = 1.01417, Chi^2 = 4.69 × 10^{-7}, R^2 = 0.99999; N_2 adsorption isotherms of **1a** with fitting by L-F model: a = 0.57497, b = 0.00125, c = 94615, Chi^2 = 2.17 × 10^{-7}, R^2 = 0.99983.

Calculation of sorption heat for CO_2 uptake using Virial 2 model

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

The above equation was applied to fit the combined CO_2 isotherm data for desolvated **1**a at 273 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, *ai* and *bi* 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.

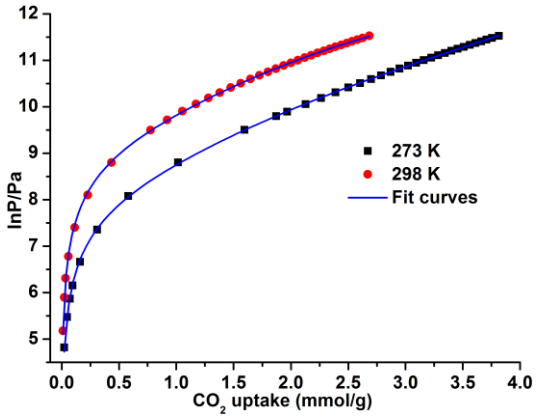

Fig. S9 CO_2 adsorption isotherms for **1a** with fitting by Virial 2 model. Fitting results: a0 = -3616.97213, a1 = 207.96409, a2 = -107.43727, a3 = 34.35126, a4 = 2.99692, b0 = 21.79273, b1 = -0.85783, b2 = 0.79230, b3 = -0.23580, Chi^2 = 0.00006, R^2 = 0.99983.

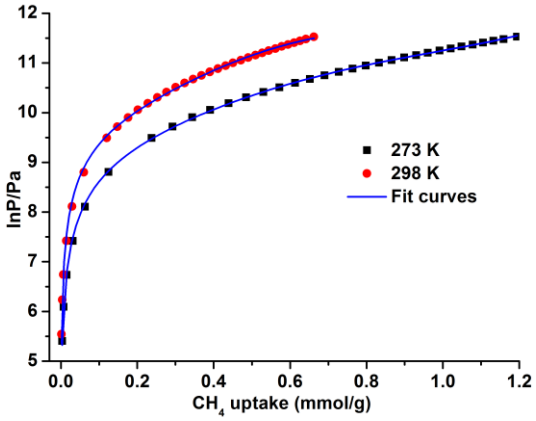

Fig. S10 CH_4 adsorption isotherms for **1a** with fitting by Virial 2 model. Fitting results: a0 = -2635.48544, a1 = 2968.21695, a2 = -10730.33007, a3 = 9400.63156, a4 = 485.17455, b0 = 20.64613, b1 = -12.02875, b2 = 43.76530, b3 = -39.25892, Chi^2 = 0.00203, R^2 = 0.99921.

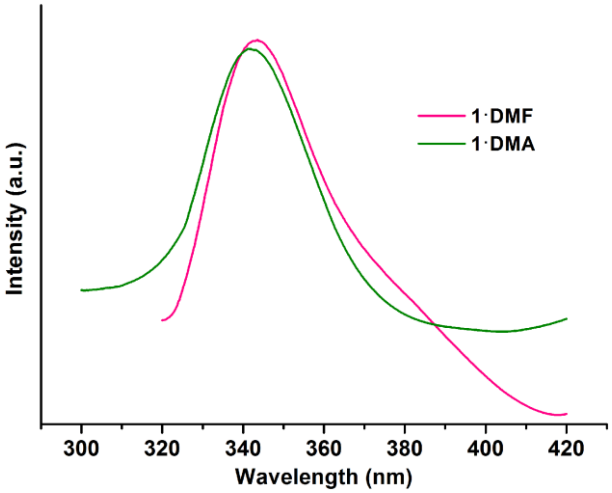

Fig. S11 Excitation spectra of **1**·DMF and **1**·DMA in the solid state at room temperature.