Electronic Supplementary Material (ESI) for

Functionalization of MOFs via mixed-ligand strategy: enhanced CO_2 uptake by pore surface modification

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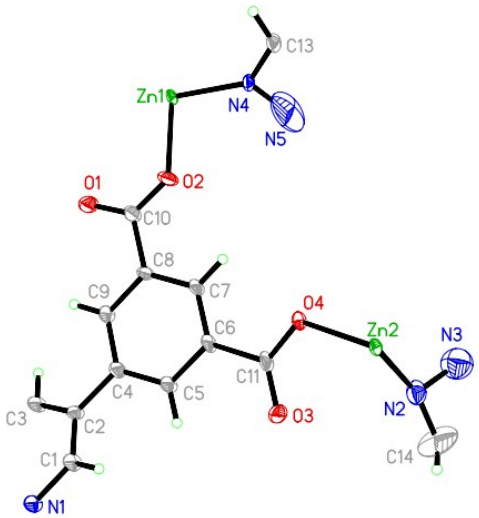


Figure S1. The asymmetric unit of **1** with the thermal ellipsoids shown at the 30% probability level.

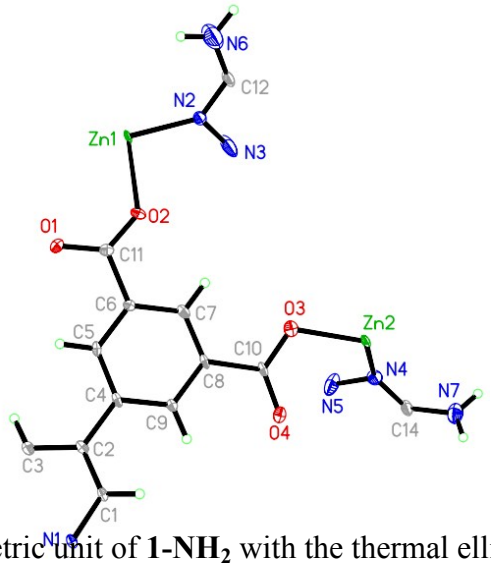


Figure S2. The asymmetric unit of **1-NH$_2$** with the thermal ellipsoids shown at the 30% probability level.

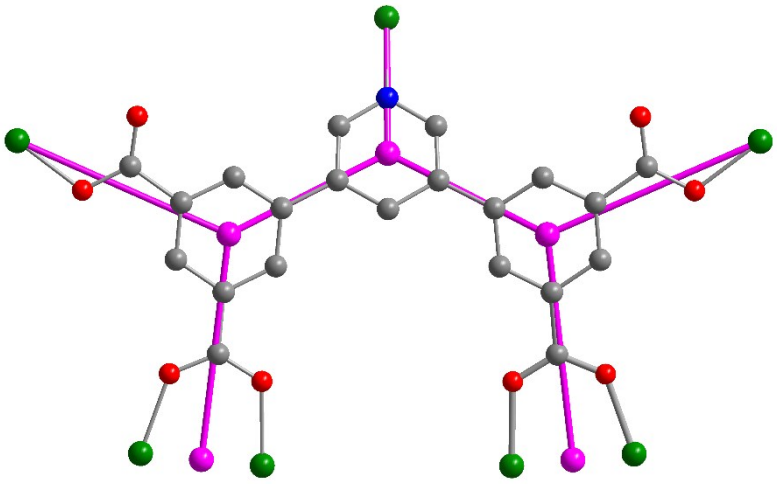


Figure S3. The BDPP^{4-} ligand viewed as two kinds of 3-c nodes.

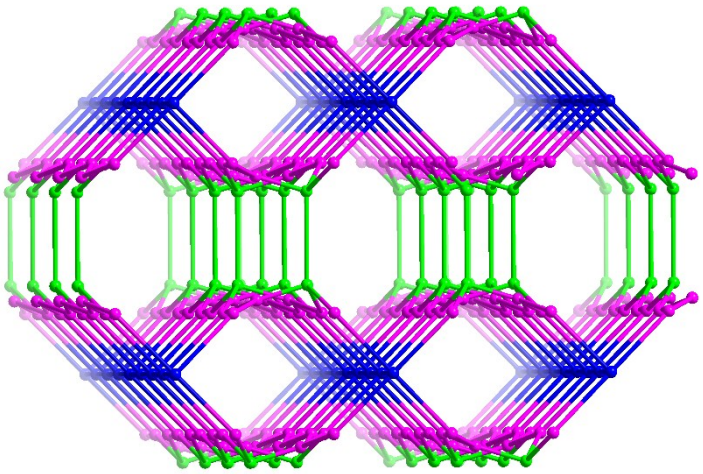


Figure S4. The (3,3,4,6)-connected topological representation for **1**.

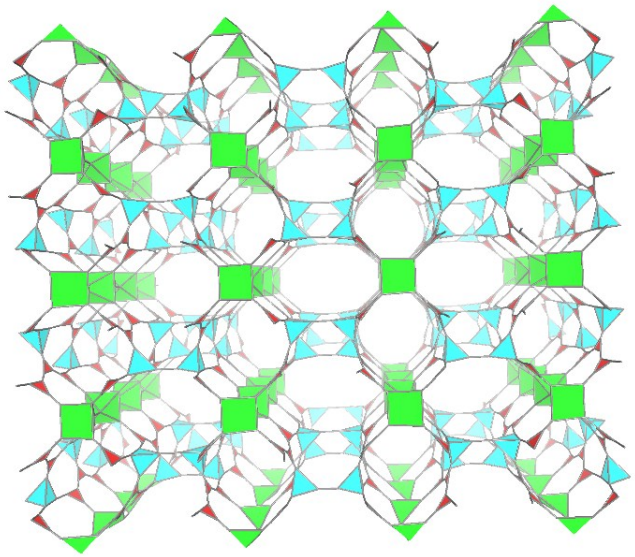
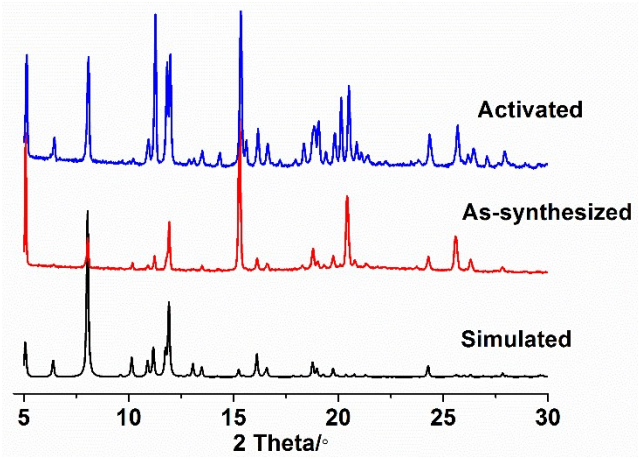
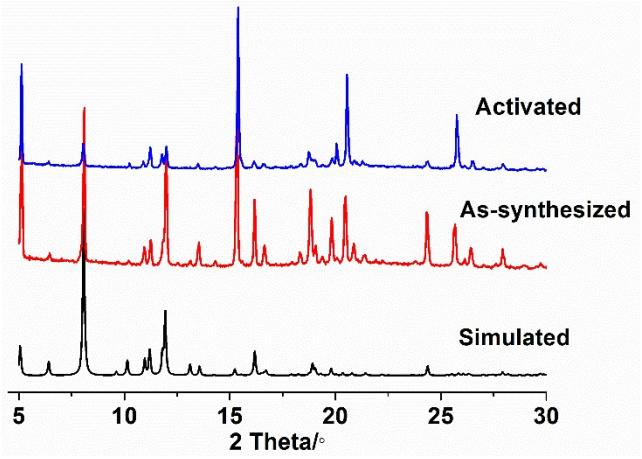


Figure S5. Polyhedral view of the (3,3,4,6)-connected topological network for **1**.



(a)



(b)

Figure S6. PXRD patterns of **1** (a) and **1-NH_2** (b) from simulated by single-crystal structure, as-synthesized, and activated samples.

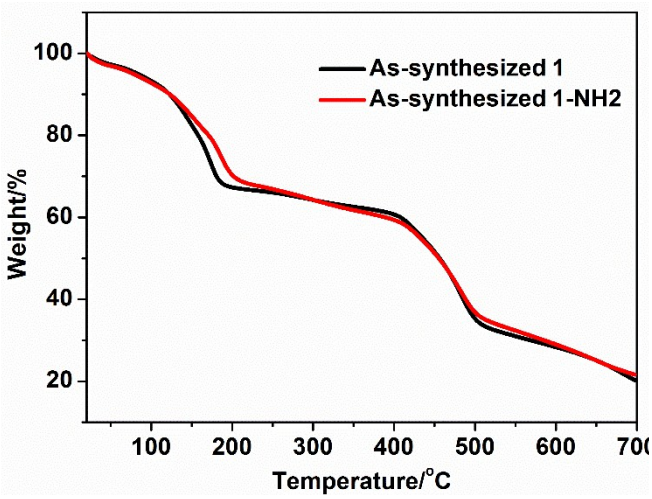


Figure S7. TGA plots of the as-synthesized **1** (black) and as-synthesized **1-NH$_2$** (red).

IAST adsorption selectivity calculation:

The experimental isotherm data for pure CO_2 and CH_4 (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, defined by

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

was 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.

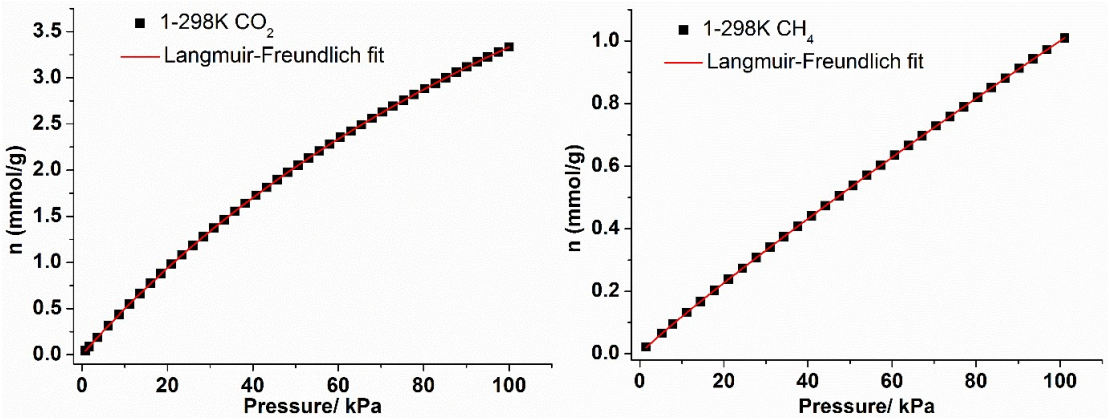


Figure S8. CO_2 adsorption isotherms of **1** with fitting by L-F model: a = 9.42961, b = 0.00566, c = 0.99263, Chi^2 = 1.5948×10^{-6}, R^2 = 1; CH_4 adsorption isotherms of **1** with fitting by L-F model: a = 26.71959, b = 5.12354×10^{-4}, c = 0.94016, Chi^2 = 3.93394×10^{-7}, R^2 = 1.

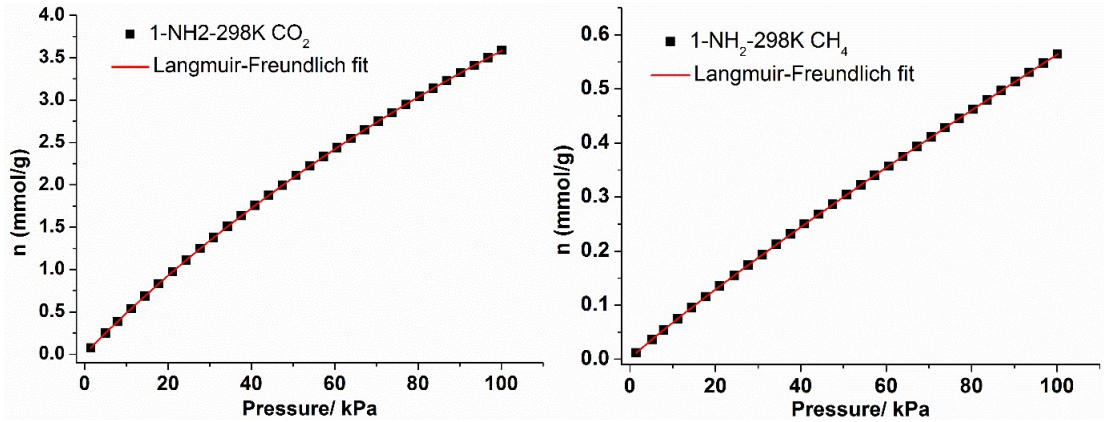


Figure S9. CO_2 adsorption isotherms of **1-NH_2** with fitting by L-F model: a = 13.2721, b = 0.00388, c = 0.98949, Chi^2 = 2.61712×10^{-6}, R^2 = 1; CH_4 adsorption isotherms of **1-NH_2** with fitting by L-F model: a = 15.27186, b = 5.16741×10^{-4}, c = 0.93495, Chi^2 = 2.24948×10^{-7}, R^2 = 0.99999.

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** and **1-NH$_2$** 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.

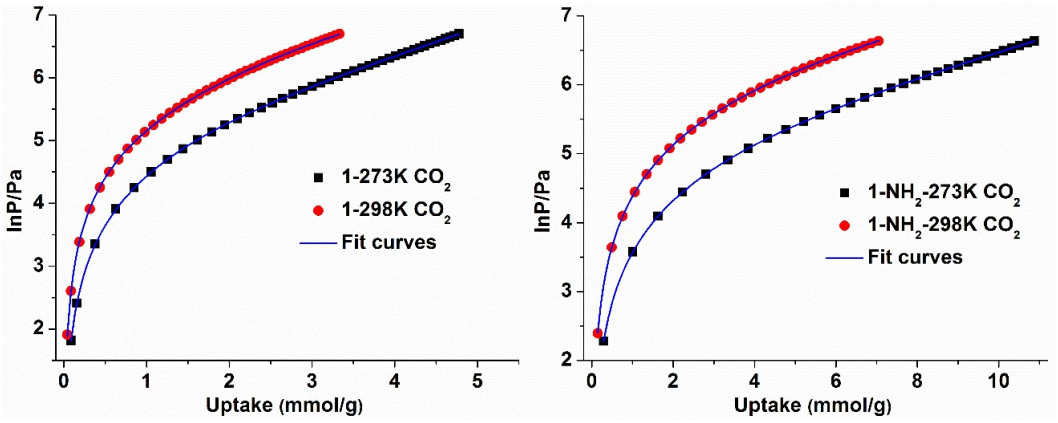


Figure S10. CO_2 adsorption isotherms for **1** and **1-NH$_2$** with fitting by Virial 2 model. Fitting results for **1**: a0 = -2690.92245, a1 = 532.47729, a2 = -232.3643, a3 = 36.63609, a4 = -0.3078, b0 = 14.07969, b1 = -1.69208, b2 = 0.78722 b3 = -0.11842, Chi^2 = 2.82305×10^{-5}, R^2 = 0.99998. Fitting results for **1-NH$_2$**: a0 = -2662.97499, a1 = 12.8101, a2 = 2.65671, a3 = 0.0521, a4 = -0.00904, b0 = 13.25475, b1 = 0.02509, b2 = -0.01589, b3 = 7.04865×10^{-5}, Chi^2 = 8.54265×10^{-6}, R^2 = 0.99999.