Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

A chiral metal–organic framework with polar channels: unique interweaving six-fold helices and high CO_2/CH_4 separation

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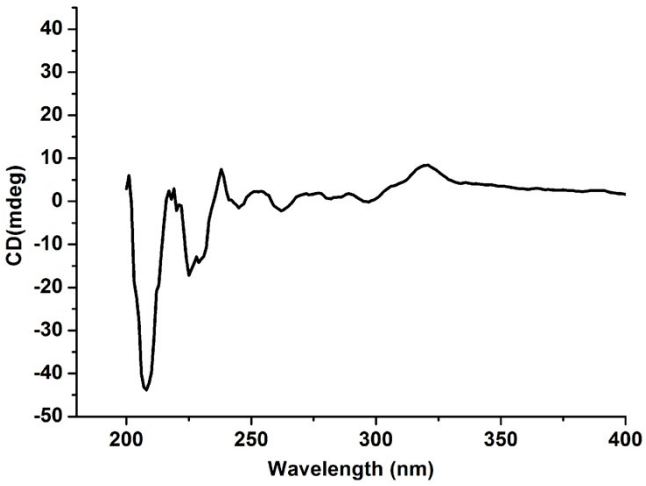

Fig. S1 The solid-state CD spectra for **1**.

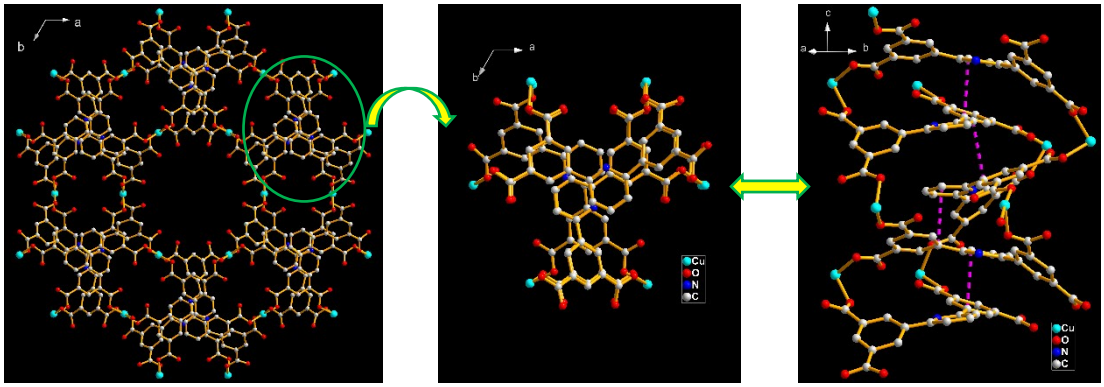

Fig. S2 π···π stacking in **1**, the vertical distance of adjacent pyridyl ring and isophthalate subunit is 3.367 Å, measured between the atoms of C8 and C10.

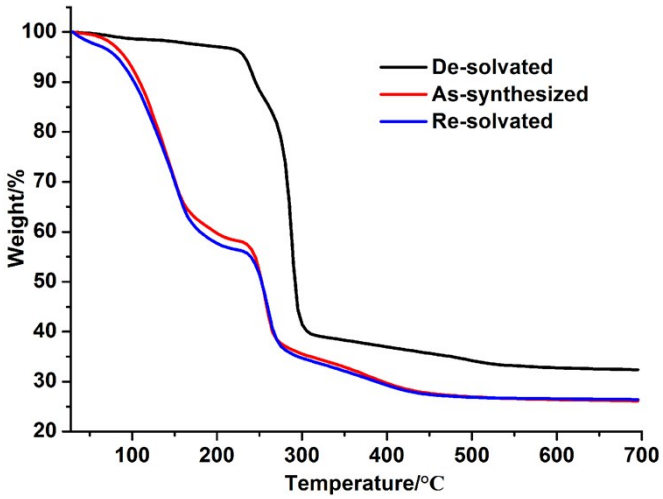

Fig. S3 TGA curves for as-synthesized, desolvated, and resolvated samples of **1**.

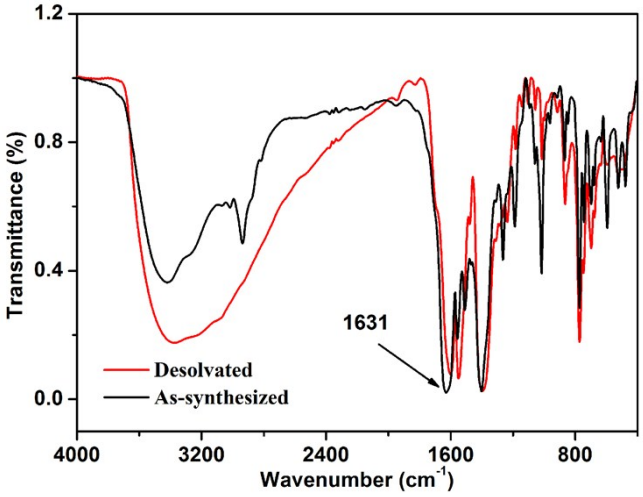

Fig. S4 IR spectras for as-synthesized and desolvated sample of **1**.

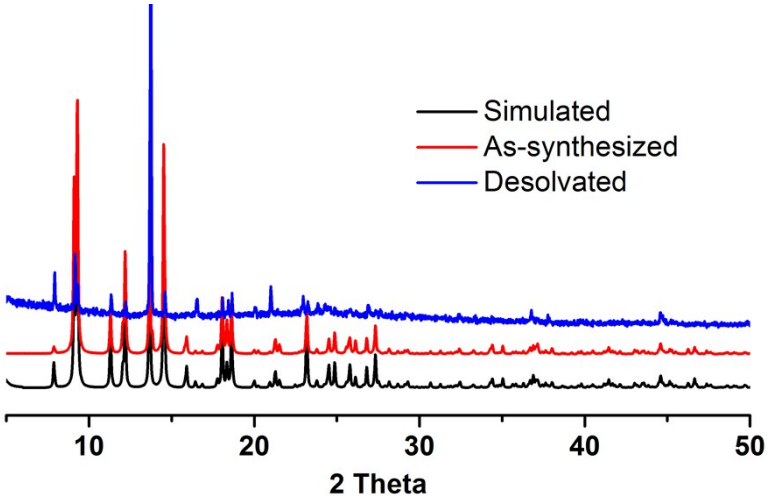

Fig. S5 PXRD patterns of simulated, as-synthesized and desolvated sample of **1**.

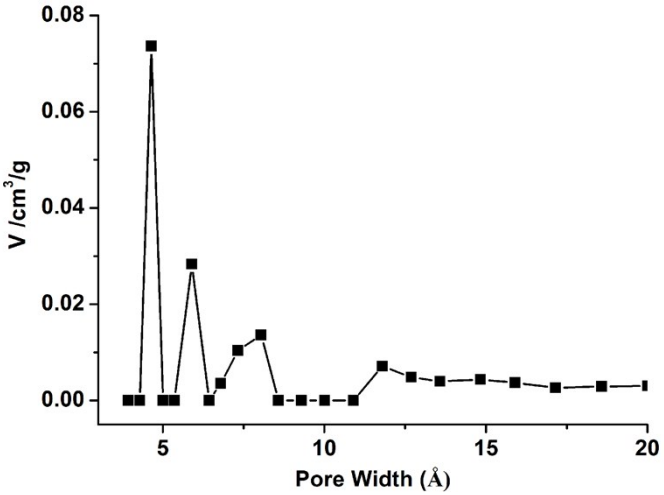

Fig. S6 Incremental surface area as a function of pore width for **1a** calculated from the adsorption branch of 77 K N_2 using the NLDFT model.

IAST adsorption selectivity calculation:

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

$$q = \frac{a_1 * b_1 * P^{1/c1}}{1 + b_1 * P^{1/c1}} + \frac{a_2 * b_2 * P^{1/c2}}{1 + b_1 * P^{1/c1}}$$

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.

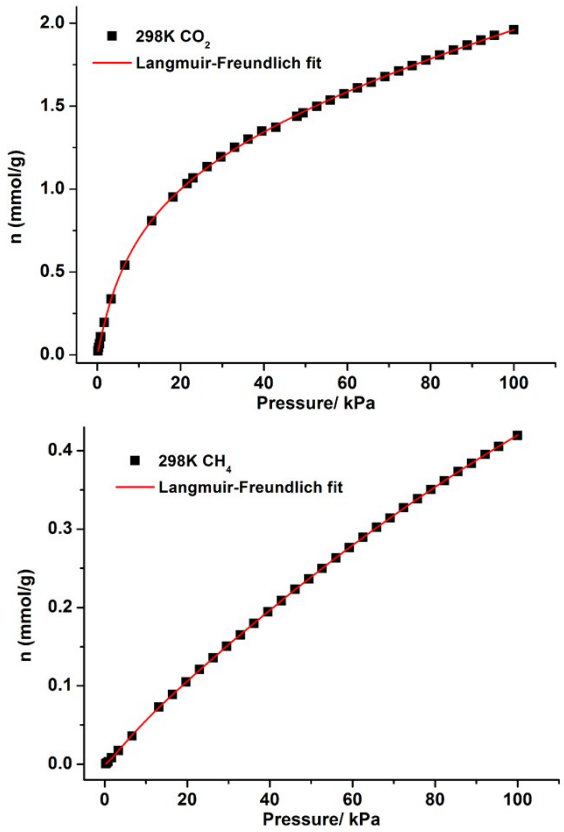

Fig. S7 CO_2 adsorption isotherms of **1a** with fitting by L-F model: a1 = 16.94769, b1 = 0.00227, c1 = 0.74336, a2 = 0.92357, b2 = 0.10130, c2 = 1.05120, Chi^2 = 3.33396×10^{-5}, R^2 = 0.99991; CH_4 adsorption isotherms of **1a** with fitting by L-F model: a1 = 0.05234, b1 = 0.04531, c1 = 1.34452, a2 = 1.09434, b2 = 0.00152, c2 = 1.26334, Chi^2 = 1.62179×10^{-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 **1a** at 273, 285 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.

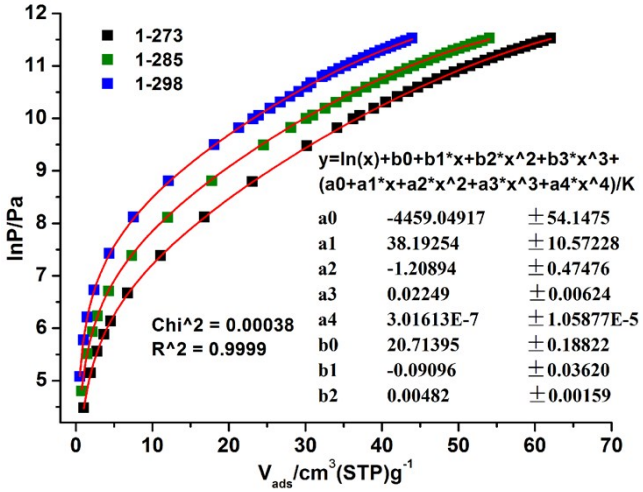

Fig. S8 Virial analysis of the CO_2 sorption data (273, 285 and 298 K, at 1 atm) for **1a**.

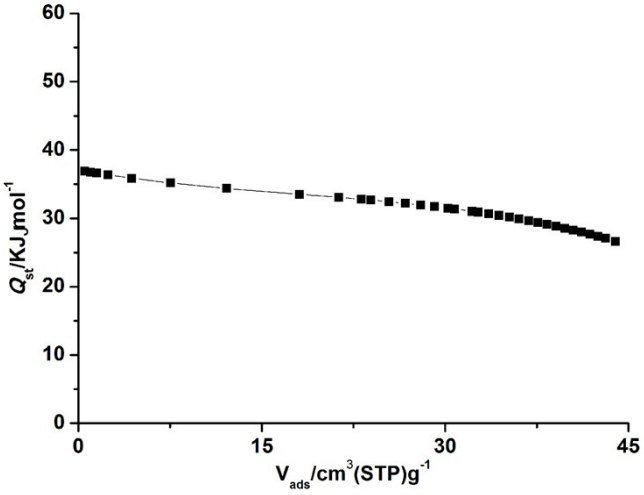

Fig. S9 Isosteric heat of CO_2 for **1a**.

GCMC Simulation Methodlody

Grand canonical Monte Carlo (GCMC) simulations were performed for the adsorption of CO_2 in **1a** at 298 K by the Sorption module of Material Studio.[1] The framework and CO_2 molecule were considered to be rigid. The partial charges for carbon and oxygen atoms of CO_2 molecules were 0.576*e* and -0.288*e*, respectively.[2] The partial charges for atoms of **1a** were derived from QEq method and QEq_neutral1.0 parameter (Table S2). One unit cell was used during the simulations. The interaction energies between CO_2 and framework were computed through the Coulomb and Lennard-Jones 6-12 (LJ) potentials. All parameters for CO_2 molecule and atoms of **1a** were modeled with the universal forcefield (UFF) embedded in the MS modeling package. A cutoff distance of 12.5 Å was used for LJ interactions, and the Coulombic interactions were calculated by using Ewald summation. For each run, the 5×10^6 maximum loading steps and 1×10^7 production steps were employed.

References

(1) *Accelrys, Materials Studio Getting Started, release 5.0*; Accelrys Software, Inc.: San Diego, CA, 2009.

(2) A. Hirotani, K. Mizukami, R. Miura, H. Takaba, T. Miya, A. Fahmi, A. Stirling, M. Kuboand, A. Miyamoto, *Appl. Surf. Sci*., 1997, **120**, 81–84.

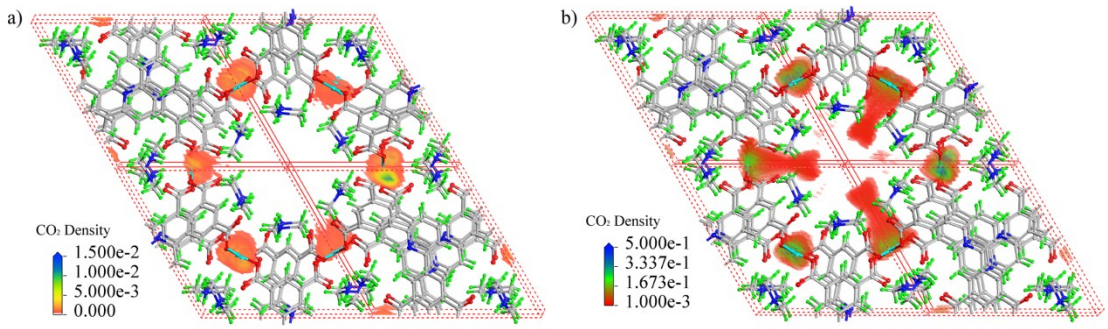

Fig. S10 Density contours of CO_2 adsorption in the pores of **1a** obtained from GCMC simulations at 298 K under pressure 0.1 kPa (a) and 100 kPa (b), respectively.

Table S1 Crystal Data and Refinement Results for **1**.

empirical formula	$C_{25}H_{25}CuN_3O_8$
formula weight	559.02
crystal system	Trigonal
space group	$P3_12_1$
T (K)	296(2)
a (Å)	22.4258(16)
b (Å)	22.4258(16)
c (Å)	10.9190(15)
α (deg)	90
β (deg)	90
γ (deg)	120
V (Å^3)	4755.6(8)
Z	6
D_c/g·cm^{-3}	1.171
μ/mm^{-1}	0.732
reflns collected	25299
reflns unique	6211
R(int)	0.0400
GOF	1.045
$R_1{}^a$, $wR_2{}^b$ [I > 2σ(I)]	0.0803, 0.2218
R_1, wR_2 (all data)	0.0875, 0.2286
Flack parameter	0.12(3)

$^aR_1 = \Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $^bwR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2 The atomic partial charges (e) in **1a**.

Cu1	4.09328	C9	0.180654	H3B	0.266463
Cu2	4.08499	C10	-0.0940951	H5	0.165829
N1	-0.350699	C11	-0.145150	H7	0.134186
N2	-0.740649	C12	-0.135383	H10	0.102208
N3	-0.771971	C13	0.175235	H11	0.128473
O1	-0.703096	C14	0.00242796	H12	0.0948875
O2	-0.686856	C15	-0.137768	H15	0.130874
O3	-0.707388	C16	-0.0226645	H17	0.180816
O4	-0.692748	C17	-0.125944	H19	0.105114
O5	-0.683639	C18	-0.00463972	H22A	0.198510
O6	-0.697394	C19	-0.172015	H22B	0.148480
O7	-0.694135	C20	0.395671	H22C	0.136154
O8	-0.697622	C21	0.385468	H23A	0.172598
C1	0.389721	C22	-0.403951	H23B	0.186650
C2	-0.0168210	C23	-0.444410	H23C	0.159782
C3	-0.178901	C24	-0.392220	H24A	0.164466
C4	-0.0249610	C25	-0.371810	H24B	0.185389
C5	-0.119213	H2A	0.338814	H24C	0.143638
C6	0.0121158	H2B	0.269841	H25A	0.159154
C7	-0.133158	H3	0.128054	H25B	0.139772
C8	0.388314	H3A	0.300550	H25C	0.189858