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Supporting Information for

Amide-containing zinc(II) metal–organic layer networks: structure–CO_2 capture relationship

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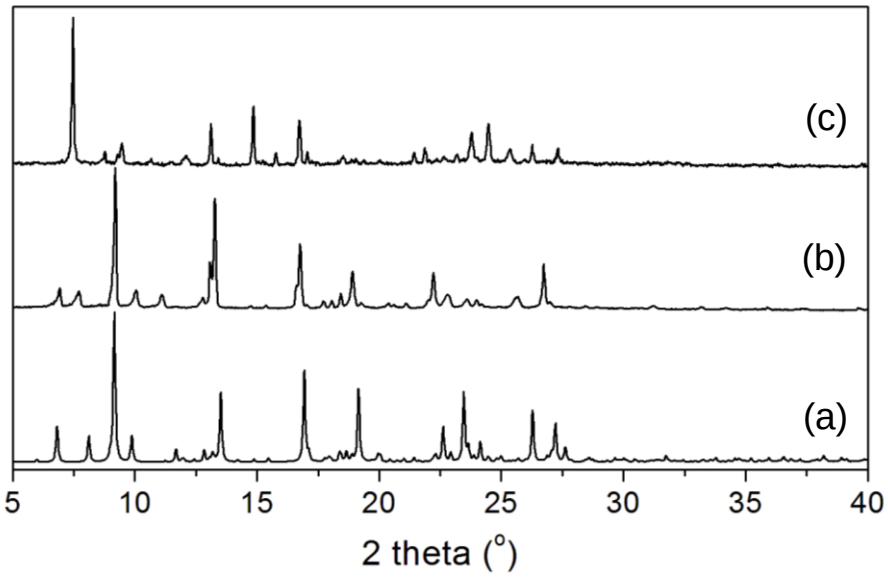


Fig. S1 Powder X-ray diffractions of (a) simulated pattern of **1** from the single-crystal diffraction data and experimental patterns of (b) as-synthesized **1** and (c) dried **1** (**1′**) prepared after the heating at 120 °C for 2 h.

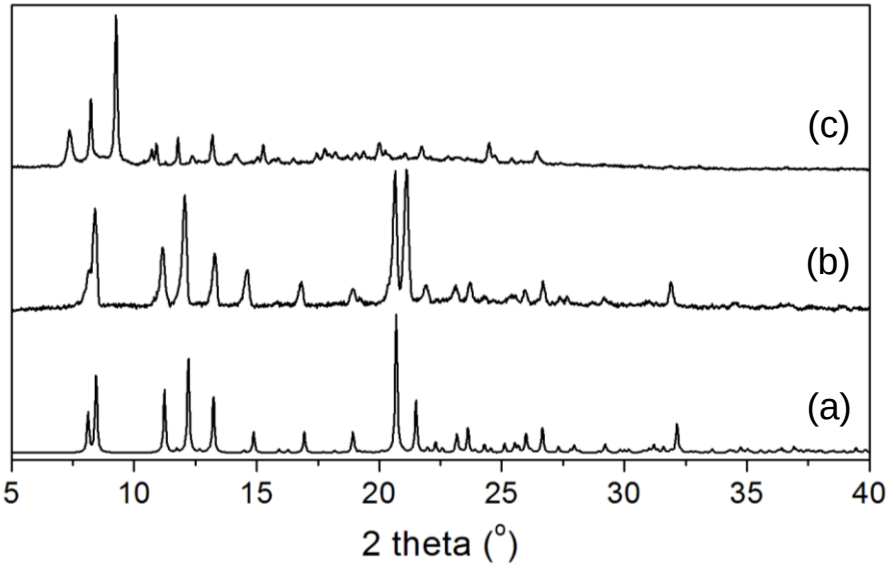
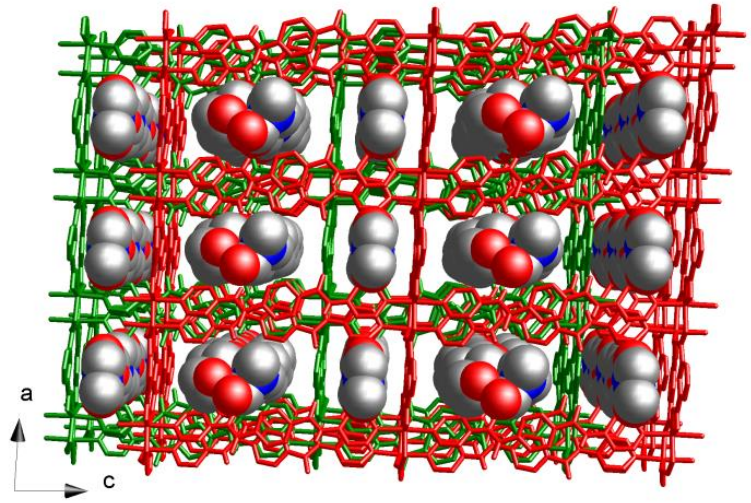
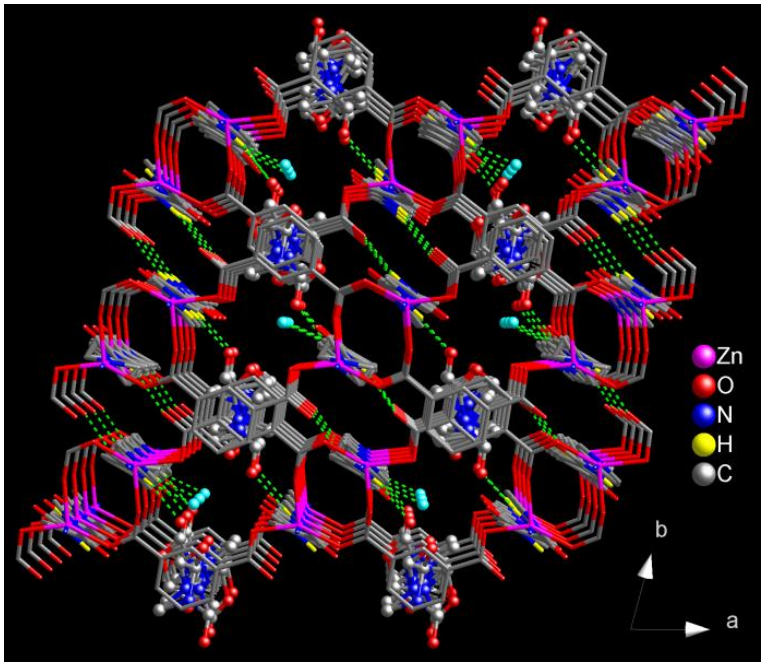


Fig. S2 Powder X-ray diffractions of (a) simulated pattern of **2** from the single-crystal diffraction data and experimental patterns of (b) as-synthesized **2** and (c) thermal-activated **2** (**2′**) prepared after the heating at 120 °C for 2 h.



(a)



(b)

Fig. S3 Views of the crystal packing in **1** (a) along the crystallographic [010] direction, showing 1D open channels in two different sizes where lattice DMF and H_2O molecules reside, and (b) along the crystallographic [001] direction, showing the net-to-net and net-to-guest N−H···O hydrogen-bonding interactions (green dashed lines). Cyan color balls represent the lattice H_2O molecules.

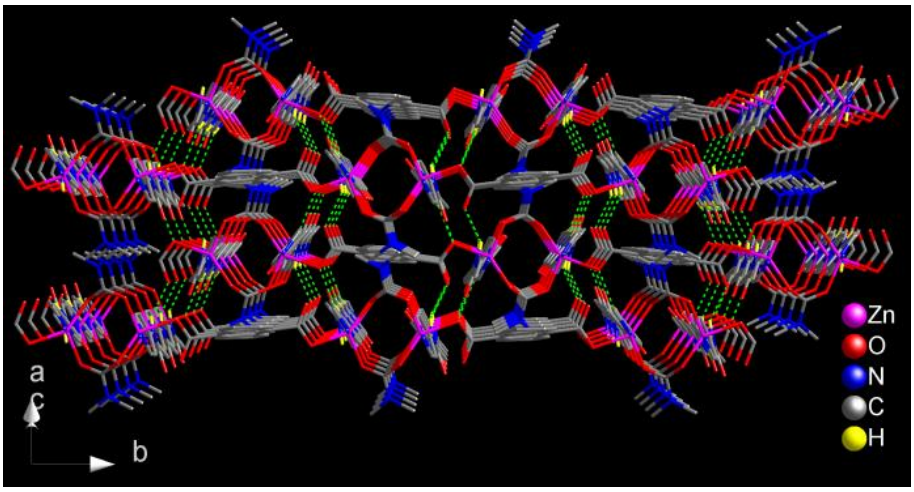


Fig. S4 View of the crystal packing in **2** along the crystallographic [10$\bar{1}$] direction, showing the net-to-net N−H···O hydrogen-bonding interactions (green dashed lines).

Table S1 Crystallographic data for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{61}H_{58}N_{11}O_{15.5}Zn_2$	$C_{27}H_{22}N_5O_6Zn$
M_w	1323.92	577.87
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.0677(3)	10.5340(2)
b (Å)	15.6039(5)	15.0561(2)
c (Å)	20.1092(5)	15.8443(3)
α (°)	78.1845(10)	90
β (°)	83.2542(11)	96.9290(10)
γ (°)	73.8005(13)	90
V (Å^3)	2963.24(15)	2494.57(7)
Z	2	4
T (K)	150(2)	100.0(1)
λ (Å)	0.71073	0.71073
D_{calc} (g cm^{-3})	1.484	1.539
F_{000}	1370	1188
μ (mm^{-1})	0.889	1.039
θ_{min}, θ_{max} (deg)	1.04, 27.50	1.87, 26.37
Refl collected	29444	19536
Unique refl, R_{int}	13415, 0.0428	5082, 0.0333
Obs refl [$I > 2\sigma(I)$]	10720	4151
Parameters	793	380
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0669, 0.1773	0.0356, 0.0841
R_1,[a] wR_2[b] (all data)	0.0844, 0.1893	0.0484, 0.0903
GOF on F^2	1.067	1.032
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.851, –1.139	0.586, –0.364

[a] $R_1 = \sum\left\|F_o\right|-\left|F_c\right\| / \sum\left|F_o\right|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0792P)^2 + 10.0791P]$ where $P = (F_o^2 + 2F_c^2)/3$ for **1**; $w = 1/[\sigma^2(F_o^2)+(0.0416P)^2 + 1.6073P]$ where $P = (F_o^2 + 2F_c^2)/3$ for **2**.

Table S2 Hydrogen-bond parameters in compounds **1** and **2**[a]

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
		1		
Net-to-net H-bonds				
N3–H···O12#1	0.88	2.05	2.90	160
N7–H···O8#2	0.88	2.04	2.88	159
Net-to-guest H-bonds				
N2–H···O13#3	0.88	2.16	3.02	163
N6–H···O16#4	0.88	2.12	2.96	160
N6–H···O17#4	0.88	2.02	2.90	156
		2		
Net-to-net H-bonds				
N2–H···O1#1	0.84	2.23	3.03	160
N4–H···O4#2	0.86	2.13	2.88	145

[a]Symmetry codes: For **1**: #1, $-x + 1, -y, -z + 2$; #2, $-x - 1, -y + 1, -z + 2$; #3, $x - 1, y, z$; #4, $x, y, z + 1$. For **2**: #1, $x, -y + 1/2, z - 1/2$; #2, $x, -y + 1/2, z + 1/2$.

Estimation of isosteric heats of gas adsorption

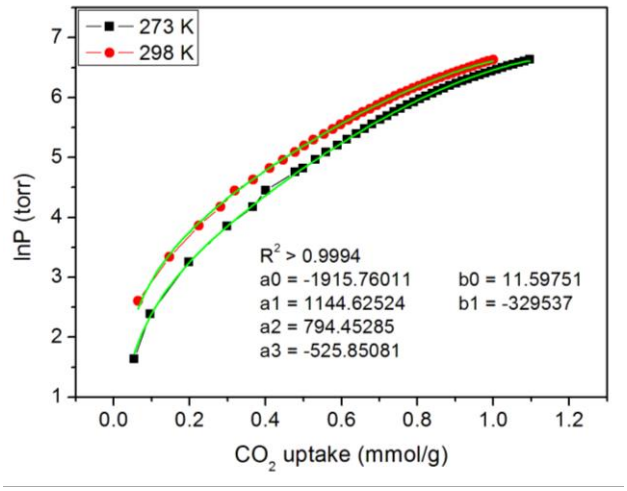
A virial-type expression comprising the temperature independent parameters a_i and b_i was employed to calculate the enthalpies of adsorption for CO_2 (at 273 and 298 K) on **1′** and **2′**. In this case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

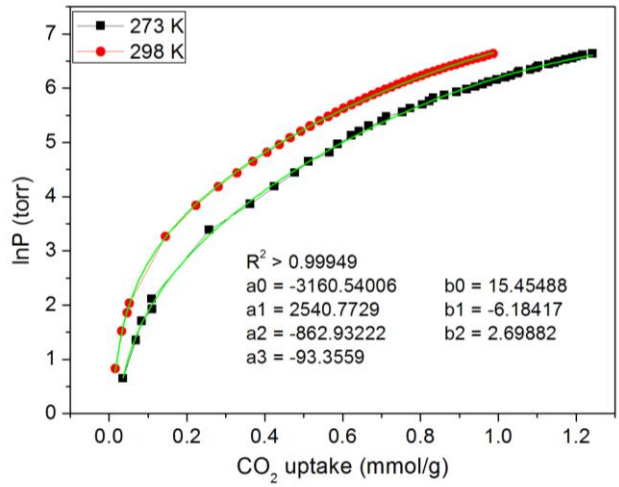
Here, P is pressure, N is the amount adsorbed (or uptake), T is temperature, a_i and b_i are virial coefficients, and m, n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the enthalpies heats of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i \qquad (2)$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant. The heat of CO_2 sorption for **1′** and **2′** in this manuscript is determined by using the excess sorption data in the pressure range from 0–1 atm (273 and 298 K), which is fitted by the virial-equation very well ($R^2 > 0.999$, Fig. S5).



(a)



(b)

Fig. S5 The CO_2 isotherms of (a) **1′** and (b) **2′** measured at 273 K and 298 K and the virial equation fits (lines).