Supporting Information

Three new solvent-directed 3D lead(II)–MOFs displaying the unique properties of luminescence and selective CO_2 sorption

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Table S1. Crystallographic Data of **1**–**3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{20}H_{10}N_6Pb_2O_8$	$C_{30}H_{14}N_9Pb_3O_{12}$	$C_{10}H_4N_3PbO_5$
Formula weight	876.72	1314.10	453.36
Crystal system	Orthorhombic	Monoclinic	Tetragonal
Space group	*Pbca*	$P2_1/c$	$I4_1/a$
T/K	296(2)	296(2)	296(2)
a/Å	15.506(17)	15.3197(14)	17.262(8)
b/Å	11.458(7)	15.6843(15)	17.262(8)
c/Å	24.859(3)	15.1838(14)	21.956(10)
α/°	90	90	90
β/°	90	116.386	90
γ/°	90	90	90
V/Å^3	4416.7(9)	3268.3(5)	6542(5)
Z	8	4	16
D_c/g.cm^{-3}	2.637	2.768	1.776
μ/mm^{-1}	15.290	15.472	10.322
Reflns collected	20156	16284	18375
Reflns unique	3932	5811	3486
Rint	0.0895	0.0559	0.0487
GOF	1.068	0.934	1.036
R_1[a], wR_2[b] [$I>2\sigma(I)$]	0.0573,0.1584	0.0392,0.1034	0.0318,0.0980
R_1, wR_2 (all data)	0.0663,0.1751	0.0642,0.1368	0.0476,0.1032

Table S2. Selected bond lengths (Å) and bond angles (º) for **1**–**3**

Compound **1**

Pb(1)–N(5)#1	2.407(9)	Pb(1)–N(1)	2.464(11)
Pb(1)–N(6)#1	2.501(11)	Pb(1)–O(6)	2.654(9)
Pb(1)–O(1)	2.712(9)	Pb(1)–N(3)	2.904(9)
Pb(2)–O(4)#2	2.423(8)	Pb(2)–O(5)	2.483(9)
Pb(2)–N(2)#2	2.537(10)	Pb(2)–N(4)	2.650(10)
Pb(2)–O(3)#3	2.735(9)	Pb(2)–O(8)	2.837(11)
N(5)#1–Pb(1)–N(1)	128.4(3)	N(5)#1–Pb(1)–N(6)#1	66.1(3)
N(1)–Pb(1)–N(6)#1	84.3(4)	N(5)#1–Pb(1)–O(6)	77.7(3)
N(1)–Pb(1)–O(6)	133.1(3)	N(6)#1–Pb(1)–O(6)	71.8(3)
N(5)#1–Pb(1)–O(1)	74.4(3)	N(1)–Pb(1)–O(1)	62.4(3)
N(6)#1–Pb(1)–O(1)	87.5(3)	O(6)–Pb(1)–O(1)	150.3(3)
N(1)–Pb(1)–N(3)	58.71(4)	O(6)–Pb(1)–N(3)	78.84(3)
N(3)–Pb(1)–N(6) #1	84.62(3)	N(3)–Pb(1)– N(5)#1	147.80(3)
O(1)– Pb(1)– N(3)	121.09(3)	O(4)#2–Pb(2)–N(4)	76.2(3)
O(4)#2–Pb(2)–O(5)	74.7(3)	O(4)#2–Pb(2)–N(2)#2	68.4(3)
O(5)–Pb(2)–N(4)	65.6(3)	N(2)#2–Pb(2)–N(4)	115.1(3)
O(4)#2–Pb(2)–O(3)#3	123.3(3)	O(5)–Pb(2)–O(3)#3	107.1(3)
N(2)#2–Pb(2)–O(3)#3	78.1(3)	N(4)–Pb(2)–O(3)#3	160.4(3)
O(8)–Pb(2)–O(3)#3	75.67(3)	O(8)–Pb(2)–N(4)	74.59(3)
O(5)–Pb(2)–O(8)	175.10(3)	O(4)–Pb(2)–O(8)	110.51(3)
O(5)–Pb(2)–N(2)#2	74.7(3)		

Compound **2**

Pb(1)–N(6)#1	2.374(10)	Pb(1)–O(4)	2.496(8)
Pb(1)–O(5)	2.693(9)	Pb(1)–O(1)#2	2.700(9)
Pb(1)–N(4)#1	2.744(12)	Pb(1)–N(3)	2.756(9)
Pb(2)–N(9)	2.346(10)	Pb(2)–O(8)	2.400(8)
Pb(2)–N(7)	2.647(11)	Pb(2)–N(5)	2.709(10)

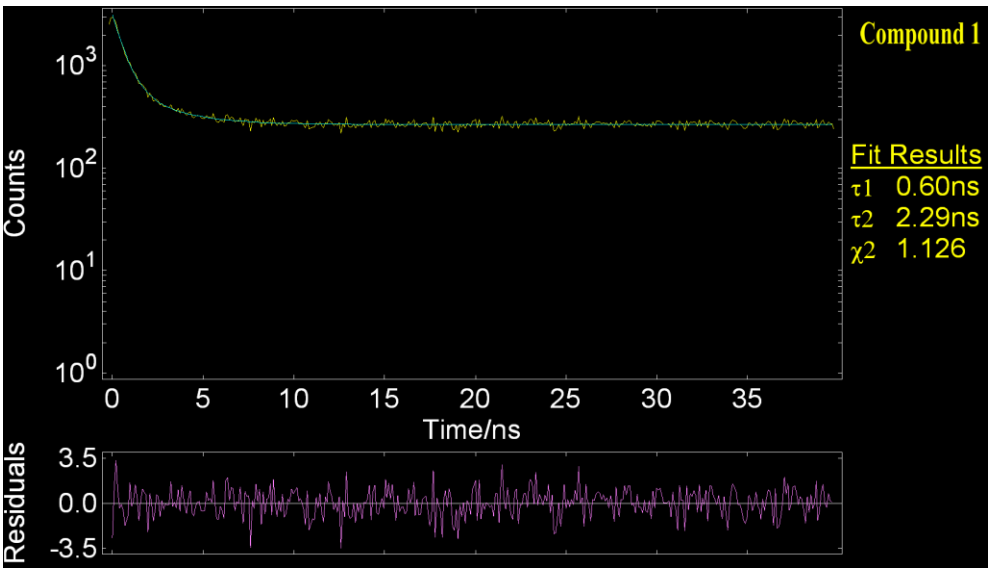
Pb(2)–O(9)	2.889(10)	Pb(3)–N(2)#3	2.333(9)
Pb(3)–O(12)	2.399(9)	Pb(3)–N(8)	2.616(10)
Pb(3)–N(1)#3	2.732(10)	Pb(3)–O(1)	2.862(10)
Pb(3)–O(5)	2.898(11)		
N(6)#1–Pb(1)–O(4)	74.7(3)	N(6)#1–Pb(1)–O(5)	90.3(3)
O(4)–Pb(1)–O(5)	164.1(3)	N(6)#1–Pb(1)–O(1)#2	113.0(3)
O(4)–Pb(1)–O(1)#2	84.6(3)	O(5)–Pb(1)–O(1)#2	96.8(3)
N(6)#1–Pb(1)–N(4)#1	62.9(3)	O(4)–Pb(1)–N(4)#1	77.3(3)
O(5)–Pb(1)–N(4)#1	100.9(3)	O(1)#2–Pb(1)–N(4)#1	161.9(3)
N(6)#1–Pb(1)–N(3)	125.0(3)	O(4)–Pb(1)–N(3)	63.8(3)
O(5)–Pb(1)–N(3)	131.3(3)	O(1)#2–Pb(1)–N(3)	97.8(3)
N(4)#1–Pb(1)–N(3)	73.7(3)	N(9)–Pb(2)–O(8)	71.7(3)
N(9)–Pb(2)–N(7)	64.4(3)	O(8)–Pb(2)–N(7)	77.4(3)
N(9)–Pb(2)–N(5)	127.7(3)	O(8)–Pb(2)–N(5)	66.3(3)
N(7)–Pb(2)–N(5)	77.0(3)	O(9)–Pb(2)–N9	61.02(3)
O(8)–Pb(2)–O(9)	88.36(3)	O(9)–Pb(2)–N(5)	142.79(3)
O(9)–Pb(2)–N(7)	125.33(3)	N(2)#3–Pb(3)–O(12)	73.9(3)
N(2)#3–Pb(3)–N(8)	120.7(3)	O(12)–Pb(3)–N(8)	67.6(3)
N(2)#3–Pb(3)–N(1)#3	63.4(3)	O(12)–Pb(3)–N(1)#3	90.3(3)
N(8)–Pb(3)–N(1)#3	73.4(3)	O(1)–Pb(3)–O(5)	60.21(3)
O(12)–Pb(3)–O(1)	71.28(3)	O(1)–Pb(3)–N(2) #3	61.78(3)
O(1)–Pb(3)–N(1)#3	125.0(3)	N(8)–Pb(3)–O(1)	134.95(3)
O(5)–Pb(3)–N(8)	141.52(3)	N(1)#3–Pb(3)–O(5)	132.67(3)
O(5)–Pb(3)–O(12)	127.73(3)	N(2)#3–Pb(3)–O(5)	97.67(3)

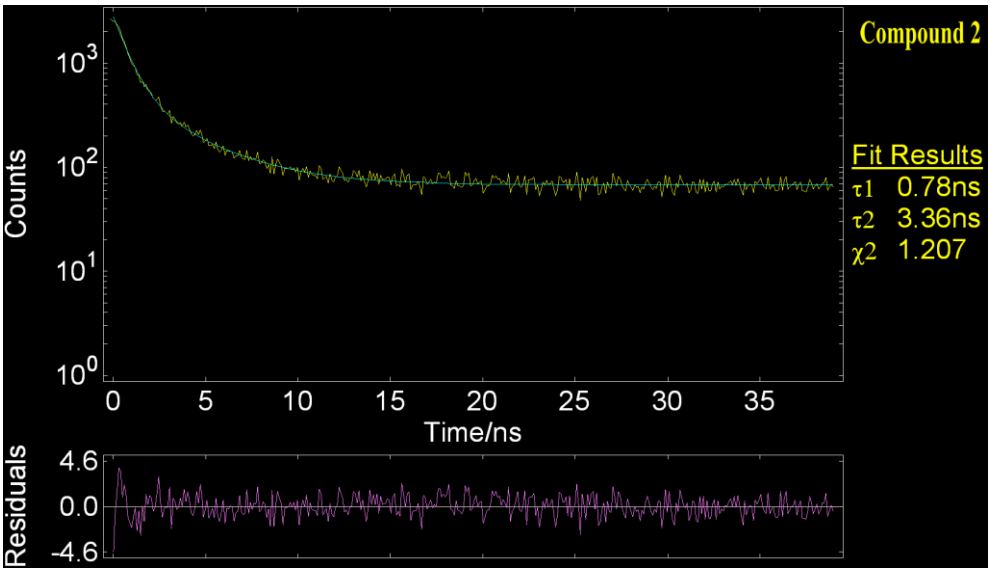
Compound **3**

Pb(1)–N(2)#1	2.332(5)	Pb(1)–O(1)	2.493(5)
Pb(1)–O(4)#2	2.490(5)	Pb(1)–N(3)#1	2.603(7)
Pb(1)–O(4)#1	2.815(7)	Pb(1)–N(1)	2.806(5)
N(2)#1–Pb(1)–O(1)	79.85(19)	N(2)#1–Pb(1)–O(4)#2	73.77(18)

O(1)–Pb(1)–O(4)#2	152.57(19)	N(2)#1–Pb(1)–N(3)#1	65.46(19)
O(1)–Pb(1)–N(3)#1	87.4(2)	O(4)#2–Pb(1)–N(3)#1	75.0(2)
O(4)#1–Pb(1) –N(2)#1	61.12(2)	O(4)#1–Pb(1)–O(1)	84.94(18)
O(4)#1–Pb(1)–O(4)#2	88.82(17)	O(4)#1–Pb(1)–N(1)	141.42(19)
N(3)#1–Pb(1)–O(4)#1	126.57(5)	N(3)#1–Pb(1)–N(1)	76.47(3)
N(1)–Pb(1)–O(1)	63.7(17)	N(1) –Pb(1)–O(4)#2	129.34(19)
N(2)#1–Pb(1)–N(1)	127.89(17)		

[a]Symmetry codes: compound **1**: #1 –x + 1, y + 1/2, –z+1/2; #2 –x + 1, –y + 1, –z; #3 x – 1/2, –y + 3/2, –z. compound **2**: #1 –x + 2, –y + 1, –z+1; #2 –x + 2, y + 1/2, –z + 1/2; #3 –x + 1,–y + 1,– z. compound **3**: #1 –y + 5/4, x + 3/4, z – 1/4; #2 x, y + 1/2, –z + 1.





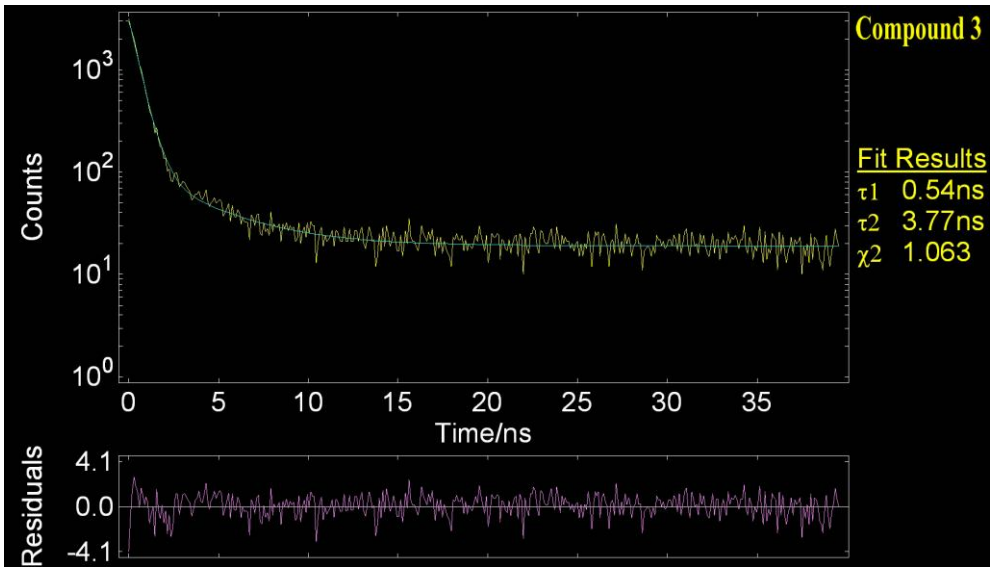


Fig S1. The emission lifetime of **1 – 3** fits a double-exponential decay.

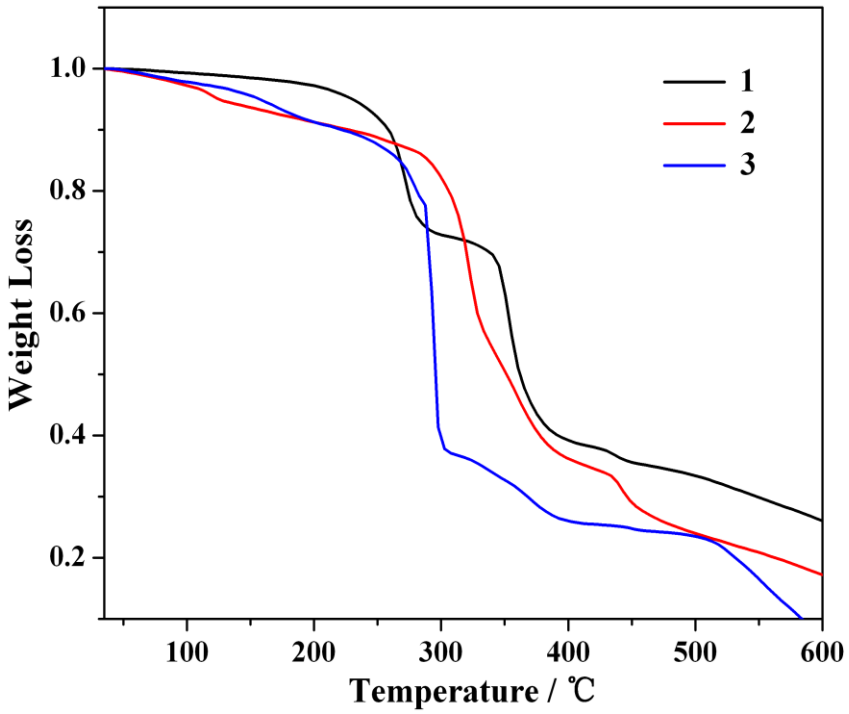


Figure S2. TGA curves of **1** – **3**.

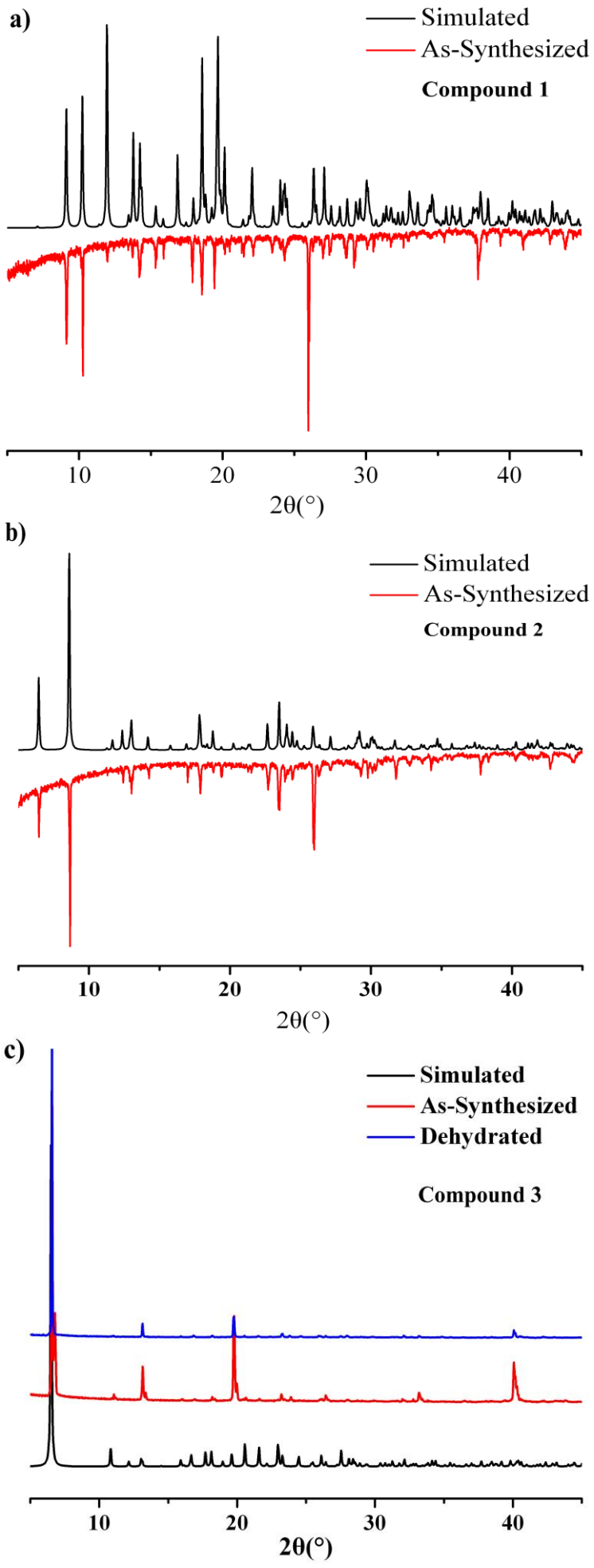
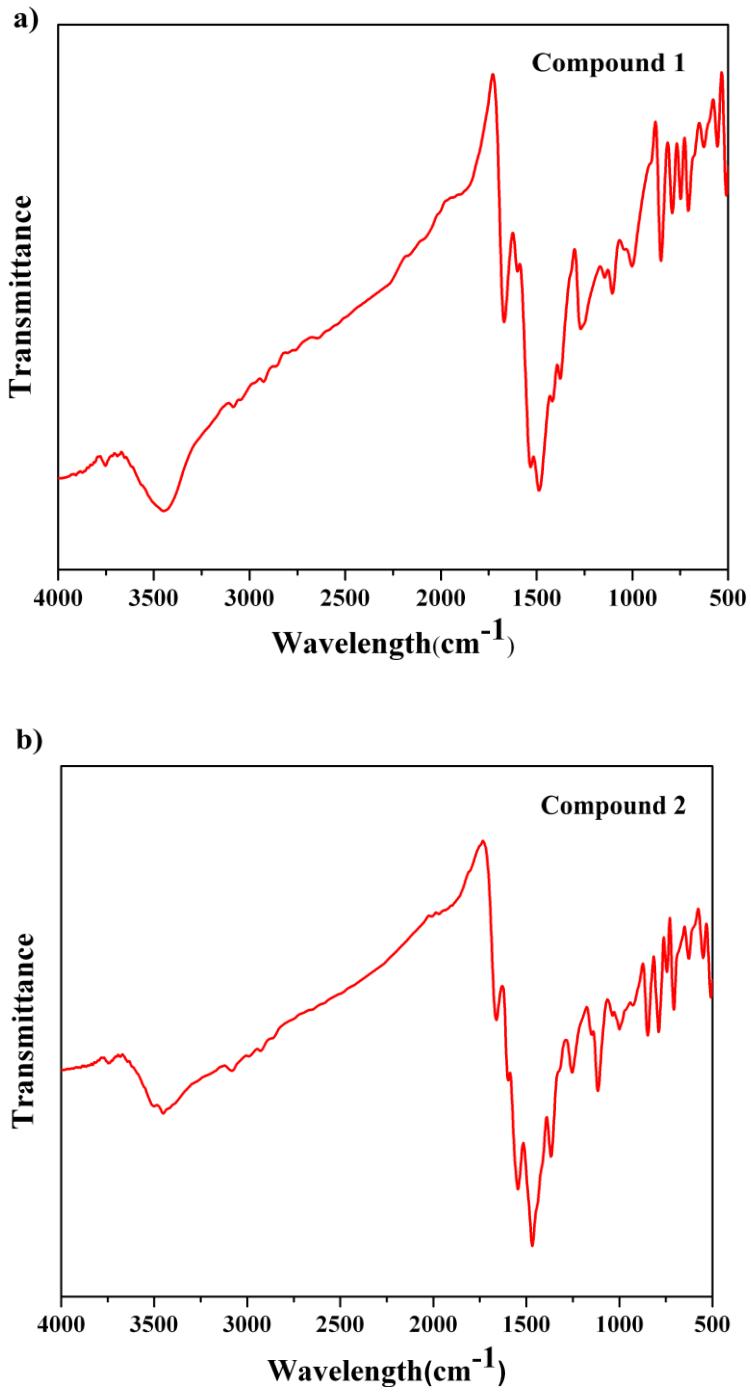


Figure S3. PXRD patterns of **1**–**3** simulated from the X–ray single–crystal structures and as–synthesized samples.



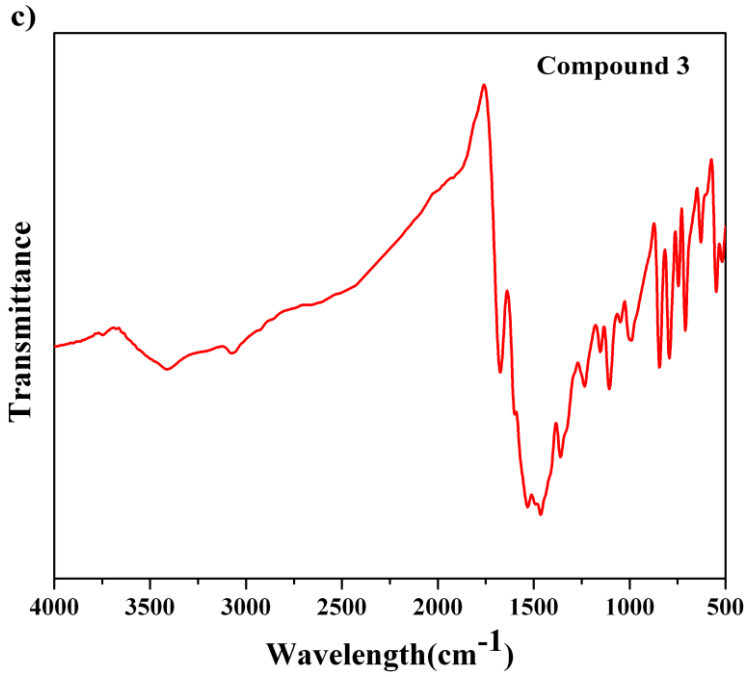


Figure S4. IR spectrum of **1**–**3** at room temperature.

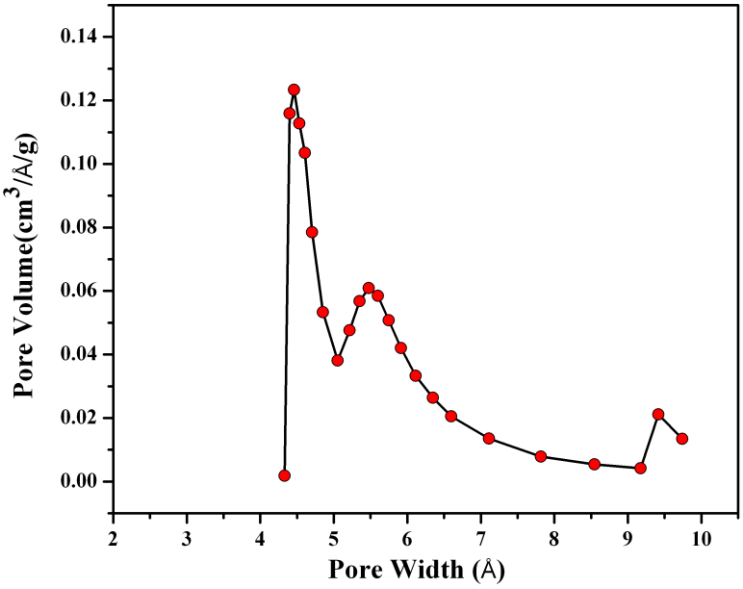


Figure S5. Pore size distribution of 3 calculated from the Horvath–Kawazoe (H–K) model.

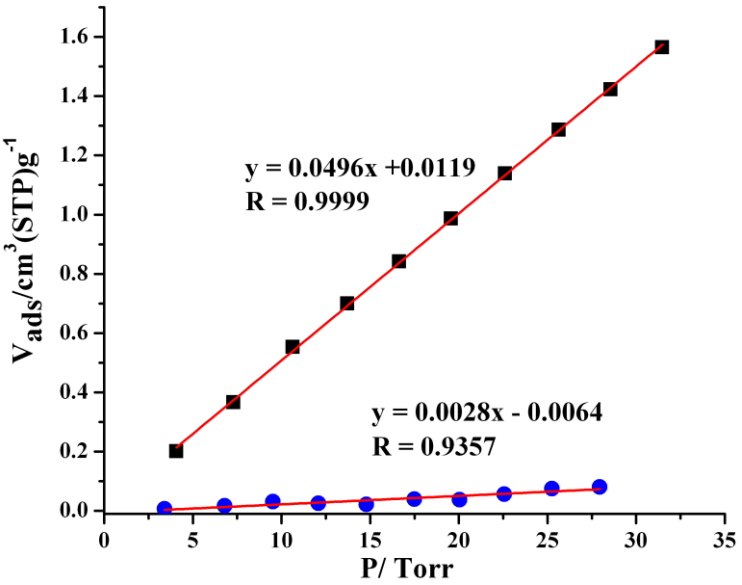


Figure S6. Initial slope calculation for CO_2 and N_2 isotherms collected at 293K (CO_2: black squares; N_2: blue circles)

Calculation of sorption heat for CO_2 uptake using Virial 2 model

The CO_2 adsorption isotherm data for **3** at 273 and 293 K were fitted using the Virial 2 expression, 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.

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

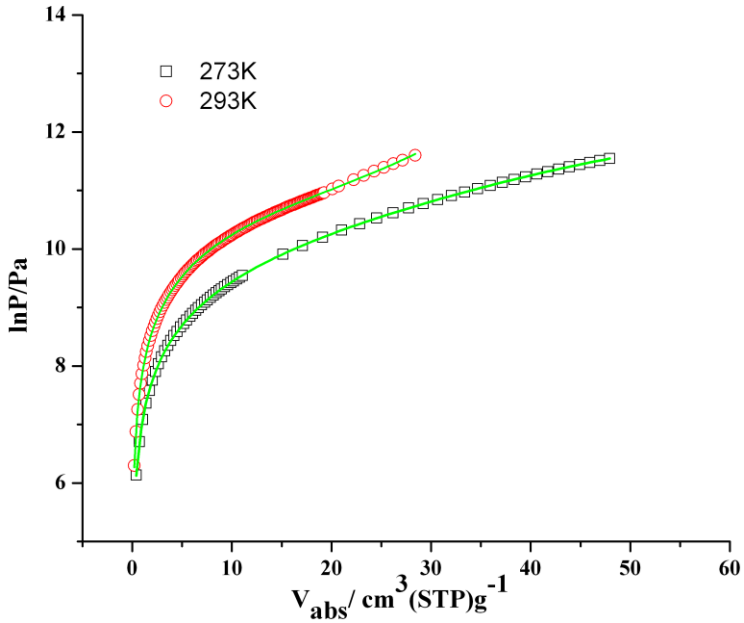


Figure S7. CO_2 adsorption isotherms for 3 with fitting by Virial 2 model. Fitting results: a0 = –3339.70214 ± 12.12776, a1 = ‾19.63059 ± 3.64291, a3 = 4.7942 ± 0.29431, a4 = ‾0.000024 ± 0.000007, b0 = 19.27005 ± 0.04234, b1 = 0.08149 ± 0.01271, b2 = ‾0.01757 ± 0.00102, b3 = 0.00056 ± 0.00002. Chi^2 = 0.00003, R^2= 0.99998.