Electronic Supplementary Information for

The difference in CO_2 adsorption capacities of different functionalized pillar-layered metal-organic frameworks (MOFs)

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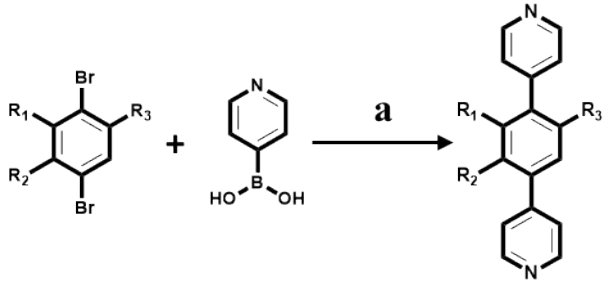
Section S1. The synthesis of the ligands

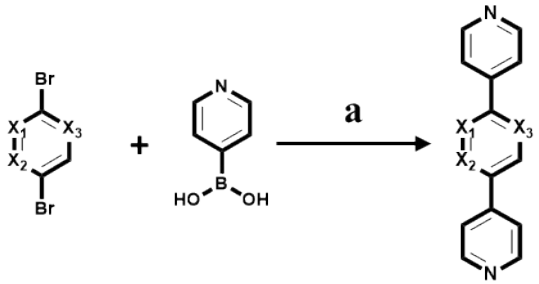
The name and the corresponding abbreviations of the ligands.

H_4L: 5',5''''-oxybis([1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid);
DPB: 1,4-di(pyridin-4-yl)benzene; 2-FDPB: 4,4'-(2-fluoro-1,4-phenylene)dipyridine;
2,3-FDPB: 4,4'-(2,3-difluoro-1,4-phenylene)dipyridine; 2,5-FDPB: 4,4'-(2,5-difluoro-1,4-phenylene)dipyridine;
2-NDPB: 4,2':5',4''-terpyridine; 2,3-NDPB: 3,6-di(pyridin-4-yl)pyridazine;
2,5-NDPB: 2,5-di(pyridin-4-yl)pyrazine; 2-NH_2DPB: 2,5-di(pyridin-4-yl)aniline.

The synthesis of the auxiliary N-based ligands

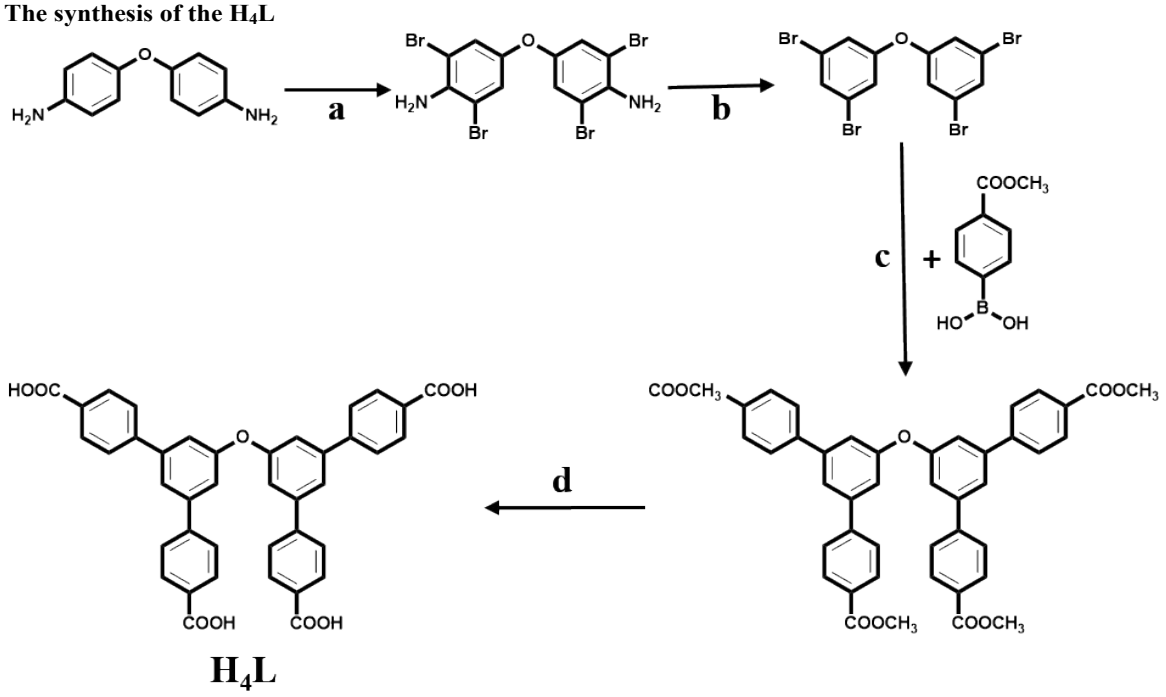


Scheme S1. Synthetic procedure for the auxiliary N-based ligands: DPB, $R_1 = R_2 = R_3 = H$; 2-FDPB, $R_1 = F$, $R_2 = R_3 = H$; 2,3-FDPB, $R_1 = R_2 = F$, $R_3 = H$; 2,5-FDPB, $R_1 = H$, $R_2 = R_3 = F$; 2-NH_2DPB, $R_1 = NH_2$, $R_2 = R_3 = H$. Reagents and conditions: a) K_2CO_3, $Pd[P(Ph)_3]_4$ (tetrakis(triphenylphosphine)palladium), 1,4-dioxane, H_2O, N_2 atmosphere, 95℃.



Scheme S2. Synthetic procedure for the auxiliary N-based ligands: 2-NDPB, $X_1 = N$, $X_2 = X_3 = CH$; 2,3-NDPB, $X_1 = X_2 = N$, $X_3 = CH$; 2,5-NDPB $X_1 = CH$ $X_2 = X_3 = N$. Reagents and conditions: a) K_3PO_4, $Pd_2(dba)_3$, tricyclohexylphosphonium tetrafluoroborate, 1,4-dioxane, H_2O, N_2 atmosphere, 90℃.

The synthesis of the H_4L



Scheme S3. Synthetic procedure for H_4L. Reagents and conditions: a) Br_2, CH_3COOH, 30℃, b) $NaNO_2$, H_2SO_4 (25% in H_2O), ethyl acetate, 55℃; c) $KF{\cdot}2H_2O$, $Pd_2(dba)_3$ (tris(dibenzylideneacetonyl)bis-palladium), P(o-tolyl)$_3$ tris(2-methylphenyl)phosphine, tetrahydrofuran, N_2 atmosphere, 55℃; d) $THF/H_2O/CH_3OH$, NaOH, reflux, HCl.

Section S2. The crystallographic data of compounds 1 – 8

Table S1 Crystal data and the structure refinement parameters for compound **1** – **4**

Compound	**1**[a]	**2**[a]	**3**[a]	**4**[a]
Empirical formula	$C_{72}H_{46}Co_2N_4O_9$	$C_{72}H_{44}Co_2F_2N_4O_9$	$C_{72}H_{42}Co_2F_4N_4O_9$	$C_{72}H_{42}Co_2F_4N_4O_9$
Formula weight	1228.99	1264.97	1300.95	1300.95
Temperature(K)	193	193	193	193
Radiation	Ga Kα	Ga Kα	Ga Kα	Ga Kα
Wavelength(Å)	1.34139	1.34139	1.34139	1.34139
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	15.6949(7)	15.6982(12)	15.6937(13)	15.7015(12)
b (Å)	16.2787(7)	16.1863(12)	16.1670(13)	16.0590(12)
c (Å)	17.4503(8)	17.4056(13)	17.3817(15)	17.3895(11)
α (°)	78.711(2)	78.553(3)	78.765(4)	78.572(6)
β (°)	80.290(2)	85.240(3)	81.283(4)	84.677(7)
γ (°)	72.523(3)	83.272(3)	82.367(4)	83.611(5)
V(Å^3)	4141.5(3)	4296.8(6)	4251.3(6)	4259.9(5)
Z	2	2	2	2
D_{calcd} (g·cm^{-3})	0.986	0.978	1.016	1.014
μ (mm^{-1})	2.408	2.382	2.405	2.400
F(000)	1264.0	1296.0	1328.0	1328.0
θ range (deg)	2.506 – 54.165	2.436 – 56.230	2.274 – 54.211	2.453 – 53.928
Index ranges *hkl*	$-18 \le h \le 18$ $-19 \le k \le 19$ $-21 \le l \le 21$	$-19 \le h \le 19$ $-20 \le k \le 20$ $-21 \le l \le 21$	$-18 \le h \le 18$ $-19 \le k \le 16$ $-21 \le l \le 20$	$-18 \le h \le 18$ $-19 \le k \le 19$ $-20 \le l \le 18$
Reflections collected/unique	58909/15185	80637/17038	46256/15614	55345/15562
Data/ restraints/ parameters	15185/0/784	17038/12/1153	15614/57/1138	15562/0/1165
GOF on F^2	1.042	1.023	1.006	1.074
Final R indices	R_1[b] = 0.0728	R_1[b] = 0.0755	R_1[b] = 0.1312	R_1[b] = 0.0535
[I > 2σ(I)]	wR_2[c] = 0.2005	wR_2[c] = 0.2349	wR_2[c] = 0.3543	wR_2[c] = 0.1746
R indices	R_1[b] = 0.0870	R_1[b] = 0.0917	R_1[b] = 0.1926	R_1[b] = 0.0621
(all data)	wR_2[c] = 0.2133	wR_2[c] = 0.2486	wR_2[c] = 0.3962	wR_2[c] = 0.1824
Largest diff. Peak and hole (e·Å^{-3})	2.52 and -0.77	1.21 and -0.43	1.28 and -0.56	1.36 and -0.51

[a]The lattice solvent molecules are squeezed by PLATON program. [b]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [c]$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

Table S2 Crystal data and the structure refinement parameters for compound **5** – **8**

Compound	**5**[a]	**6**[a]	**7**[a]	**8**[a]
Empirical formula	$C_{70}H_4Co_2N_6O_9$	$C_{68}H_{42}Co_2N_8O_9$	$C_{68}H_{42}Co_2N_8O_9$	$C_{72}H_{48}Co_2N_6O_9$
Formula weight	1230.97	1232.95	1232.95	1259.02
Temperature(K)	193	193	193	193
Radiation	Ga Kα	Ga Kα	Ga Kα	Ga Kα
Wavelength(Å)	1.34139	1.34139	1.34139	1.34139
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	15.6045(5)	15.479(2)	15.5470(5)	15.6660(6)
b (Å)	16.0443(5)	16.172(3)	16.0134(5)	16.2798(7)
c (Å)	17.3893(5)	17.414(3)	17.4005(6)	17.3799(7)
α (°)	78.7890(10)	78.489(13)	78.694(2)	78.3560(10)
β (°)	80.4680(10)_	84.732(11)	81.9740(10)	87.5780(10)
γ (°)	80.0540(10)	82.848(12)	79.5270(10)	86.226(2)
V(Å^3)	4166.9(2)	4228.2(12)	4152.8(2)	4330.0(3)
Z	2	2	2	2
D_{calcd} (g·cm^{-3})	0.981	0.968	0.986	0.966
μ (mm^{-1})	2.398	2.368	2.411	2.313
F(000)	1264.0	1264.0	1264.0	1296.0
θ range (deg)	2.469 – 53.880	2.440 – 53.979	2.480 – 53.969	2.415 – 53.883
Index ranges *hkl*	$-18 \le h \le 18$ $-19 \le k \le 19$ $-20 \le l \le 20$	$-18 \le h \le 18$ $-19 \le k \le 19$ $-20 \le l \le 20$	$-18 \le h \le 16$ $-19 \le k \le 19$ $-20 \le l \le 20$	$-18 \le h \le 18$ $-19 \le k \le 19$ $-20 \le l \le 18$
Reflections collected/unique	54200/15131	61919/15457	50567/15157	56757/15701
Data/ restraints/ parameters	15131/0/784	15457/6/1252	15157/0/784	15701/36/1159
GOF on F^2	1.046	1.033	1.032	1.042
Final R indices	R_1[b] = 0.0457	R_1[b] = 0.0769	R_1[b] = 0.0431	R_1[b] = 0.0654
[I > 2σ(I)]	wR_2[c] = 0.1262	wR_2[c] = 0.2318	wR_2[c] = 0.1140	wR_2[c] = 0.2069
R indices	R_1[b] = 0.0567	R_1[b] = 0.0911	R_1[b] = 0.0542	R_1[b] = 0.0781
(all data)	wR_2[c] = 0.1320	wR_2[c] = 0.2457	wR_2[c] = 0.1192	wR_2[c] = 0.2185
Largest diff. Peak and hole (e·Å^{-3})	0.93 and -0.39	1.48 and -0.43	0.44 and -0.35	0.77 and -0.46

[a]The lattice solvent molecules are squeezed by PLATON program. [b]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [c]$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

Section S3. The characterization of compounds 1 – 8.

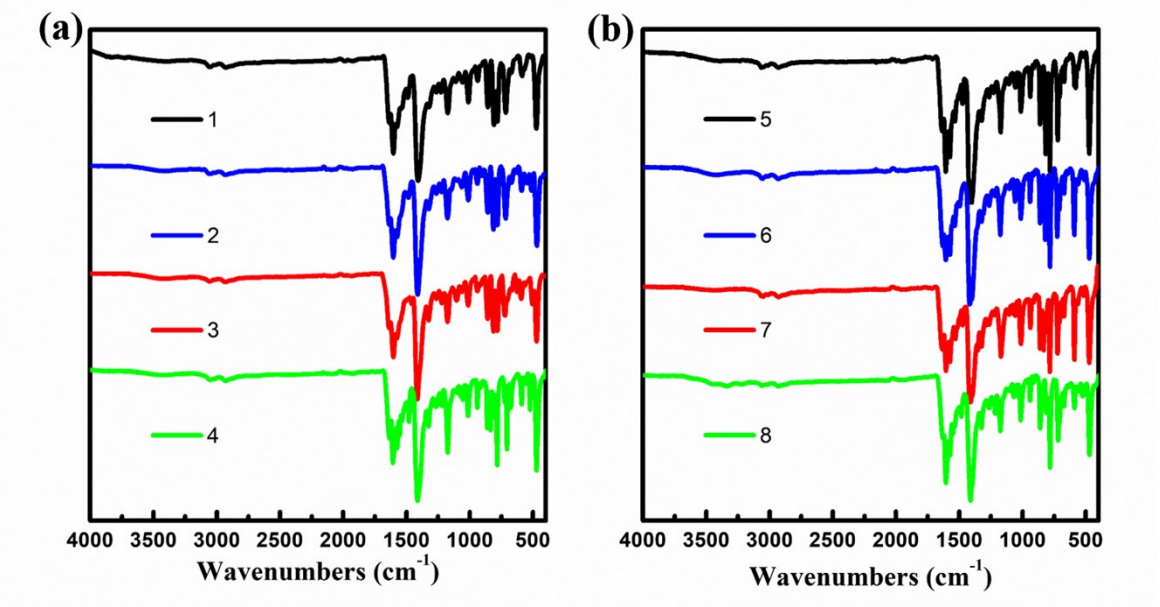


Figure S1. The IR spectra of compounds **1** – **4** (a), compounds **5** – **8** (b).

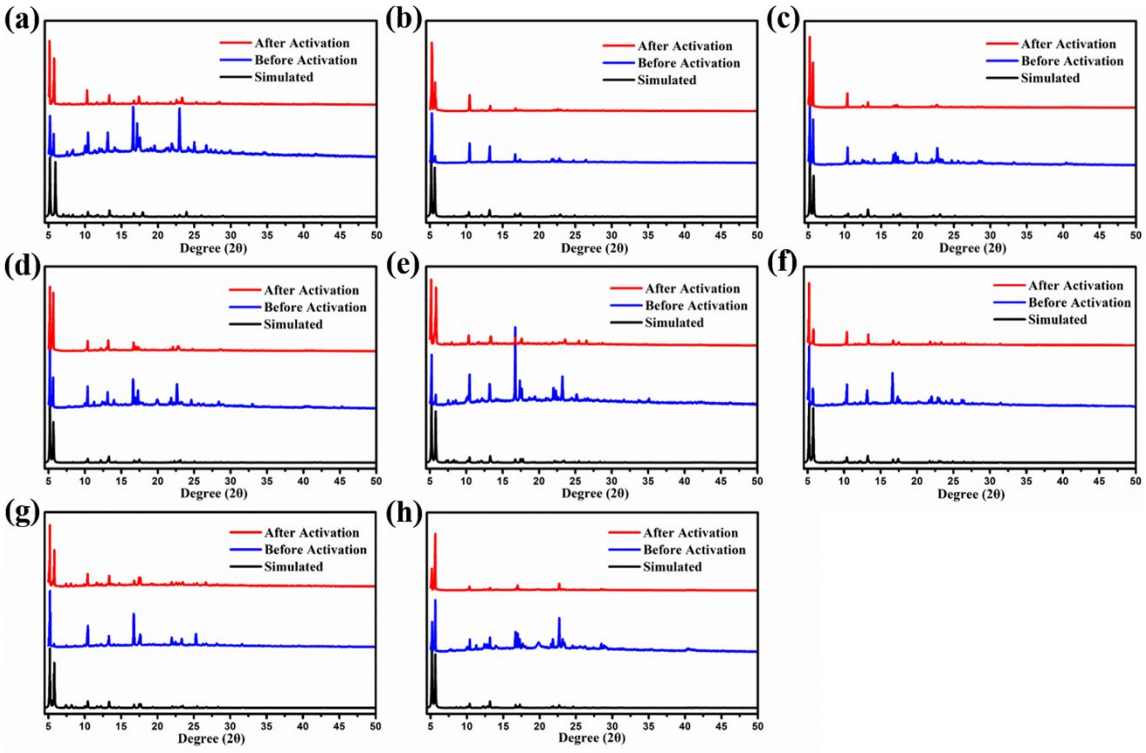


Figure S2. The PXRD patterns of compounds **1** (a), **2** (b), **3** (c), **4** (d), **5** (e), **6** (f), **7** (g), and **8** (h) before and after activation.

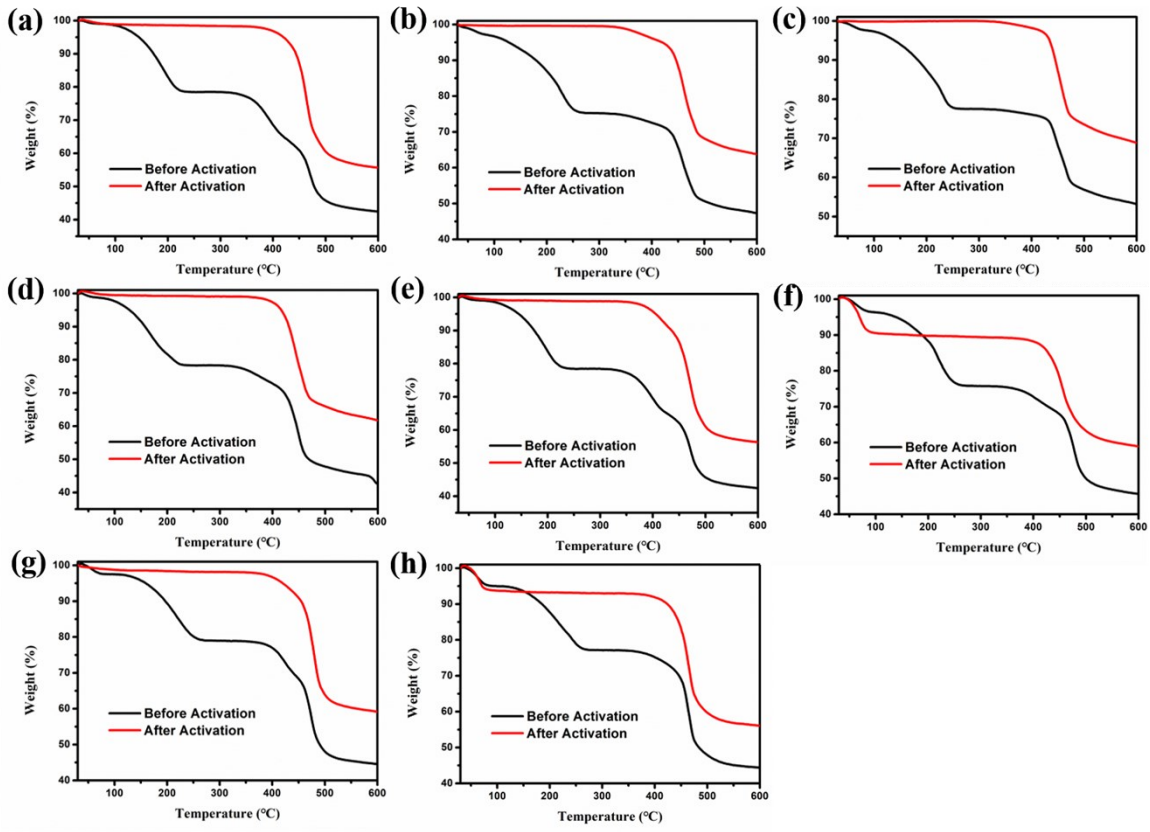


Figure S3. The TG diagrams of compounds **1** (a), **2** (b), **3** (c), **4** (d), **5** (e), **6** (f), **7** (g), and **8** (h) before and after activation.

Table S3 The weight loss percentage, weight loss temperature range and thermal destruction temperature of compounds **1** – **8**

	The first weight loss temperature range (℃)	The first weight loss percentage (%)	The second weight loss temperature range (℃)	The second weight loss percentage (%)	Thermal destruction temperature (℃)
1	30 – 238	21.5	—	—	321
2	30 – 272	24.7	—	—	340
3	30 – 78	2.3	96 – 261	19.8	340
4	30 – 239	21.6	—	—	317
5	30 – 244	21.6	—	—	326
6	30 – 89	3.5	109 – 273	20.4	347
7	30 – 80	2.4	115 – 274	18.4	360
8	30 – 91	5.0	117 – 275	17.6	359
1[a]	—	—	—	—	375
2[a]	—	—	—	—	340
3[a]	—	—	—	—	340
4[a]	—	—	—	—	370
5[a]	—	—	—	—	360
6[a]	30 – 105	9.6	—	—	376
7[a]	—	—	—	—	370
8[a]	30 – 98	6.2	—	—	374

[a]This sample is activated by soaking it in ACN for three days, and then vacuum-drying at 40℃ for 2 hours.

Section S4. Additional information of CO_2 adsorption tests

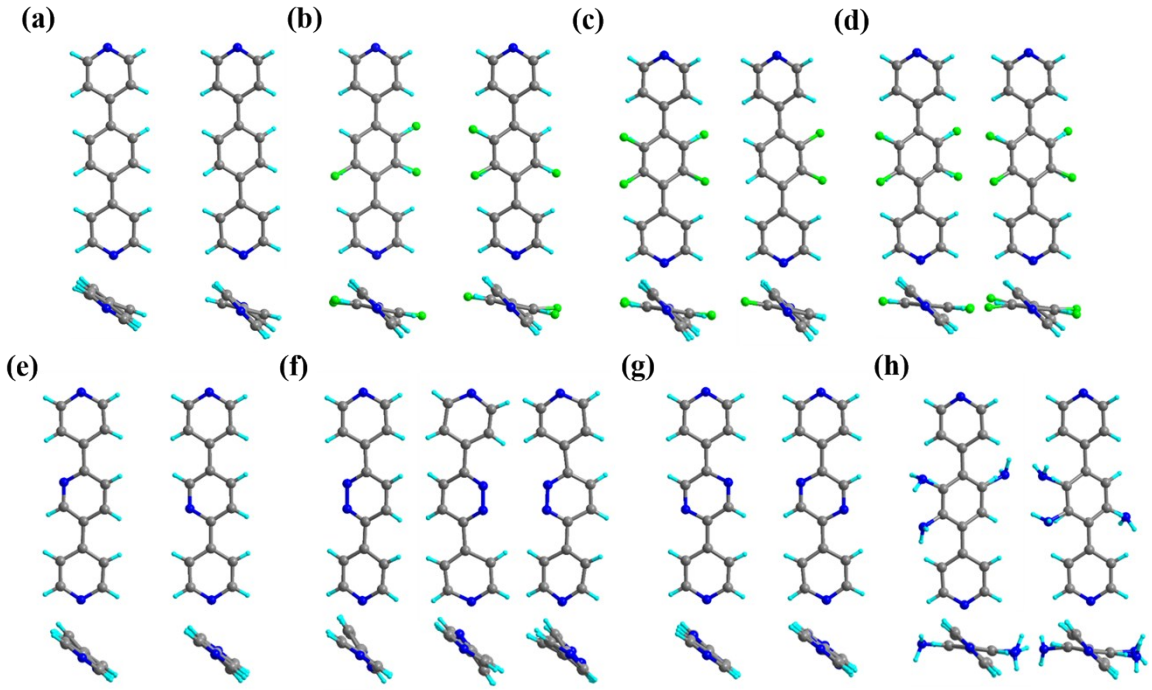


Figure S4. The conformations of the pillar-ligands in the single-crystal structures of compound **1** (a), **2** (b), **3** (c), **4** (d), **5** (e), **6** (f), **7** (g), and **8** (h) at 193 K (Gray, C; red, O; blue, N and turquoise H).

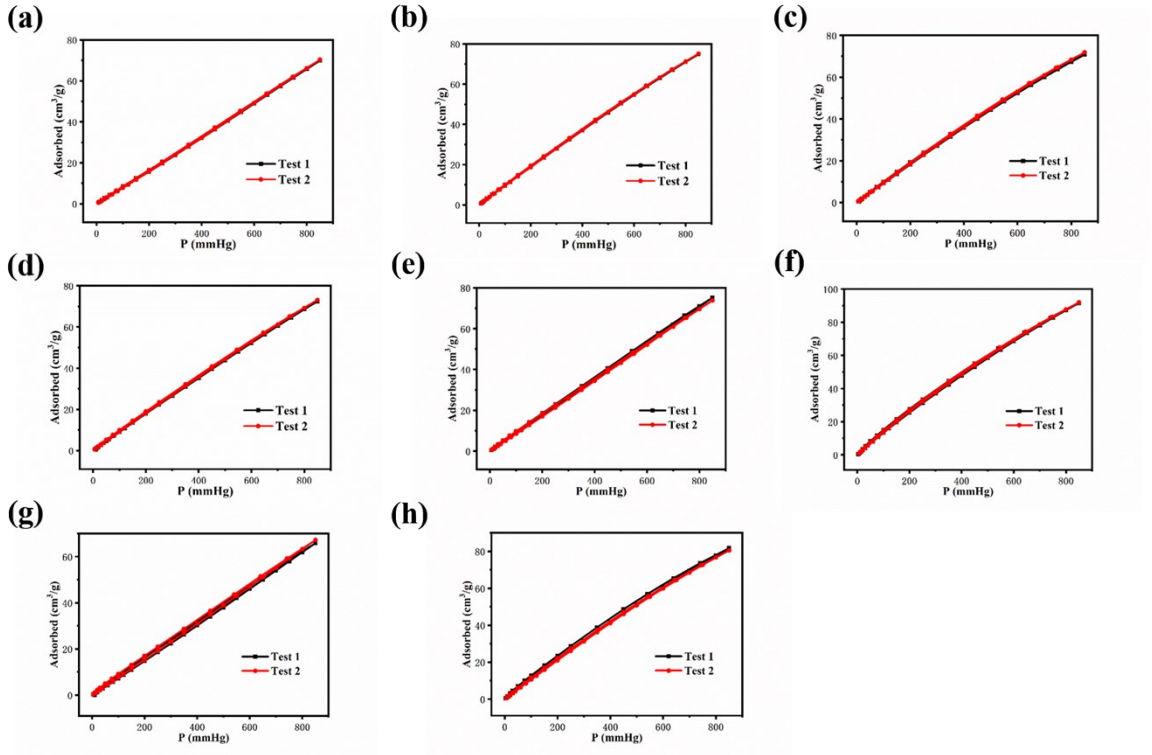


Figure S5. Low-pressure CO_2 isotherms of compound **1** (a), **2** (b), **3** (c), **4** (d), **5** (e), **6** (f), **7** (g), and **8** (h) at 273 K.

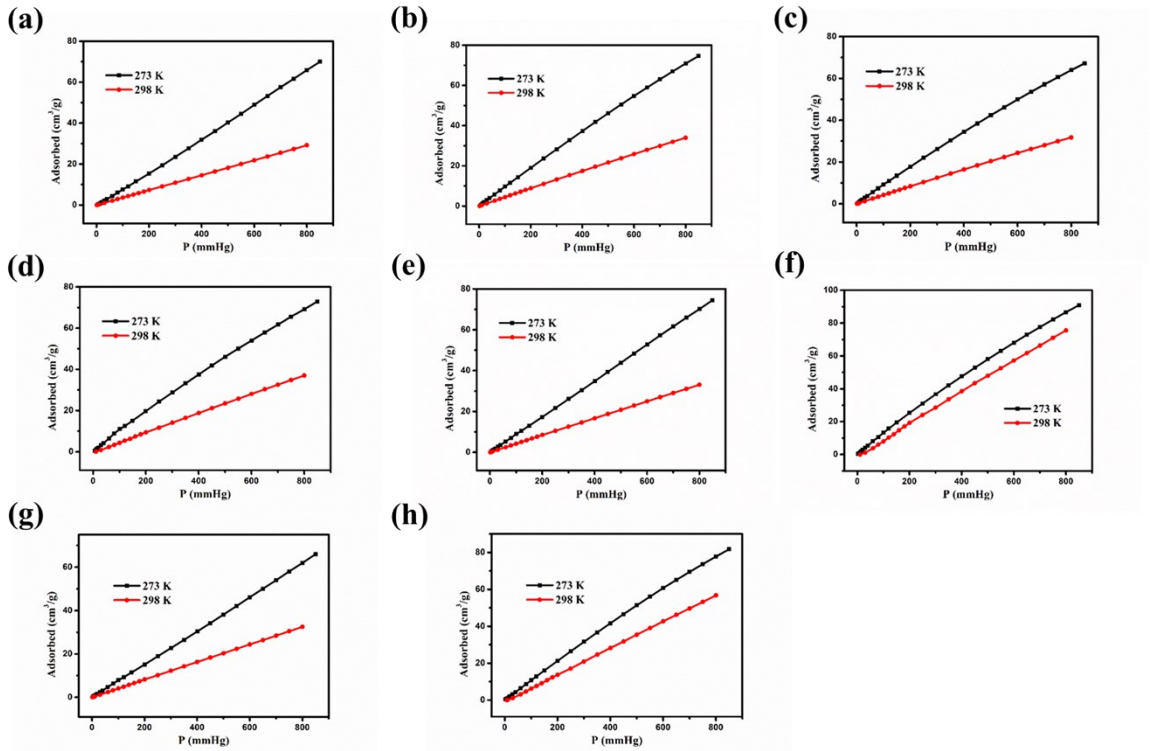


Figure S6. Low-pressure CO_2 adsorption isotherms of compound **1** (a), **2** (b), **3** (c), **4** (d), **5** (e), **6** (f), **7** (g), and **8** (h) at 273K and 298 K.

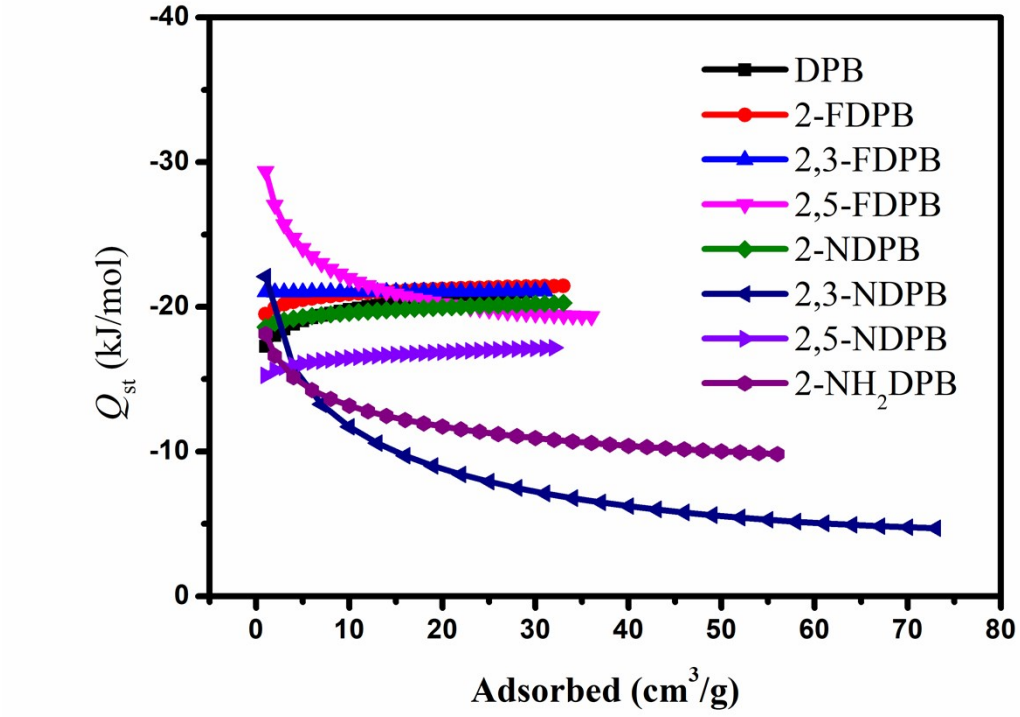


Figure S7. The isosteric heats (Q_{st}) of CO_2 adsorption which are calculated from the CO_2 adsorption isotherms at 273K and 298K by using the Clausius–Clapeyron equation in compounds **1-8.**

Table S4 The parameters and the CO_2 adsorption capacities of compounds **1** – **8** in CO_2 adsorption tests

	CO_2 adsorption capacities at 273K and 850 mmHg ($cm^3 \cdot g^{-1}$)		CO_2 adsorption capacities at 298K and 800 mmHg ($cm^3 \cdot g^{-1}$)	Q_{st} ($kJ \cdot mmol^{-1}$)	Disordered structure	Solvent-accessible volume[a]	Residual solvent (%)	The dihedral angles between the phenyl rings and the pyridyl rings (°)	Active site
	Test 1	Test 2							
1	70.0	70.4	29.2	-17.3 — -21.0	No	39.1%	—	16.19 and 17.75 22.16 and 31.72	No
2	74.9	75.2	34.0	-19.5 — -21.4	Yes	31.2%	—	27.86 and 36.35 29.51 and 34.53	No
3	70.8	71.9	31.7	-21.0— -21.1	Yes	30.7%	—	30.62 and 41.46 31.10 and 37.29	No
4	72.5	73.1	37.0	-29.5 — -19.3	Yes	29.4%	—	31.67 and 38.84 32.13 and 40.18	No
5	75.2	73.8	33.1	-18.6 — -20.3	No	40.3%	—	7.89 and 10.62 9.04 and 12.53	No
6	91.6	92.0	75.6	-22.1 — -4.7	Yes	31.9%	9.6%	3.30 and 22.37 13.28 and 23.49 18.44 and 19.90	No
7	65.9	67.2	32.5	-15.3 — -17.2	No	39.8%	—	4.74 and 7.48 5.15 and 5.77	No
8	81.7	80.5	56.8	-18.1 — -9.8	Yes	30.0%	6.2%	33.66 and 40.67 33.99 and 40.14	Yes ($-NH_2$)

[a]This is calculated by the SOLV program of PLATON.

Table S5 Adsorption capacities of different MOFs for CO_2.

MOFs	Pressure (mmHg)	Temperature (K)	Capacity ($mmol \cdot g^{-1}$)	Ref.
HKUST-1	760	298	4.1	1
IRMOF-11	836	298	1.8	
MOF-2	760	298	0.6	
MOF-505	836	298	3.3	
Mg-MOF-74	760	296	8.0	2
Zn-MOF-74	760	296	5.5	
Ni-MOF-74	760	296	5.8	
Co-MOF-74	760	296	7.0	
Mg_2(dobpdc)	760	298	6.4	3
NH2-MIL-125	760	273	4.0	4
TMOF-1	760	200	6.8	5
		273	2.2	
		298	1.4	
		308	1.2	
MAF-23	760	273	4.1	6
		298	2.7	
USTC-253	760	273	3.7	7
		298	2.1	
USTC-253-TFA	760	273	6.1	
		298	2.9	
LIFM-29	760	273	2.5	8
LIFM-30			2.6	
LIFM-31			2.6	
LIFM-32			2.7	
LIFM-33			3.6	
ZIF-20	760	273	3.1	9
Compound **1**	850	273	3.5	This work
	800	298	1.5	
Compound **2**	850	273	3.7	
	800	298	1.7	
Compound **3**	850	273	3.6	
	800	298	1.6	
Compound **4**	850	273	3.6	
	800	298	1.9	
Compound **5**	850	273	3.7	
	800	298	1.7	
Compound **6**	850	273	4.6	
	800	298	3.8	
Compound **7**	850	273	3.3	
	800	298	1.6	
Compound **8**	850	273	4.0	
	800	298	2.9	

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