Electronic Supplementary Information

A pillared-layer Framework with High Uptake and Selective Sorption of Light Hydrocarbons

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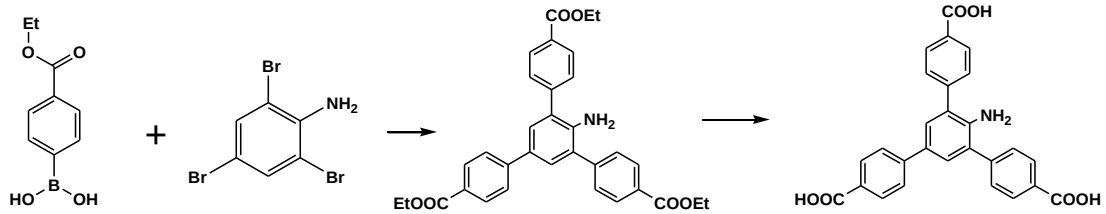
General methods.

Commercially available reagents were purchased used without further purification. 1,3,5-(tri-benzoic acid)aniline and 1,3,5-(tri-benzoic acid) phenol) were synthesized via suzuki reaction.[1]



A mixture of 2,4,6-Tribromoaniline (2.5 g, 7.5 mmol), p-ethoxycarbonylphenyl boronic acid (6 g, 30.0 mmol), Na_2CO_3 (4.0 g, 40 mmol), and $Pd(PPh_3)_4$ (0.7 g, 0.5 mmol) was added into degassed toluene–methanol–water (80/40/40 mL) under an argon atmosphere. The resulting reaction mixture was stirred for 24 h under reflux. After removal of the solvent, the residue was extracted with dichloromethane (80×3 mL), washed with brine (80 mL), dried over anhydrous $MgSO_4$ and concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleumether/dichloromethane¼1/5) to give 1,3,5-tri(p-methoxycarbonyl-phenyl)aniline (2.56 g, 73%), which was hydrolyzed with 6 M NaOH to afford the title compound. 1H NMR (DMSO-d 6 , 400 MHz) d (ppm): 13.04 (s, 3H), 8.10 (s, 3H), 8.0 6 (s, 12H); 13 C NMR (DMSO-d6 , 150 MHz) d (ppm): 167.11, 143.81, 140.72, 130.02, 129.88, 127.39, 125.54; FT-IR (KBr, cm 1): 3382, 3014, 2660, 2538, 1697, 1608, 1569, 1512, 14 47, 1416, 1393, 1317, 1286, 1241, 1181, 1016, 847, 76 4; MS (ESI) (m/z) calcd for C27N1H20O6 : 451.1, found: 451.6.

Adsorption Characterization.

Virial Equation Analysis. The virial equation can be written[2] as follows:

$$\ln(\frac{n}{p}) = A_0 + A_1 n + A_2 n^2 + \ldots \qquad \text{(S1)}$$

where n is the amount adsorbed (mol g^{-1}) at pressure p (Pa). At low surface coverage, the A_2 and higher terms can be neglected and the equation becomes

$$\ln(\frac{n}{p}) = A_0 + A_1 n \qquad \text{(S2)}$$

A linear graph of $\ln(n/p)$ versus n is obtained at low surface coverage and this is consistent with neglecting higher terms in equation (S2). A_0 quantifies the adsorbate-adsorbent interactions while A_1 is related to adsorbate-adsorbate interactions. This equation has been used extensively in probe molecule studies of adsorption on porous carbons and MOFs.

Table. S1 The crystallgraphy data of compound **1**.

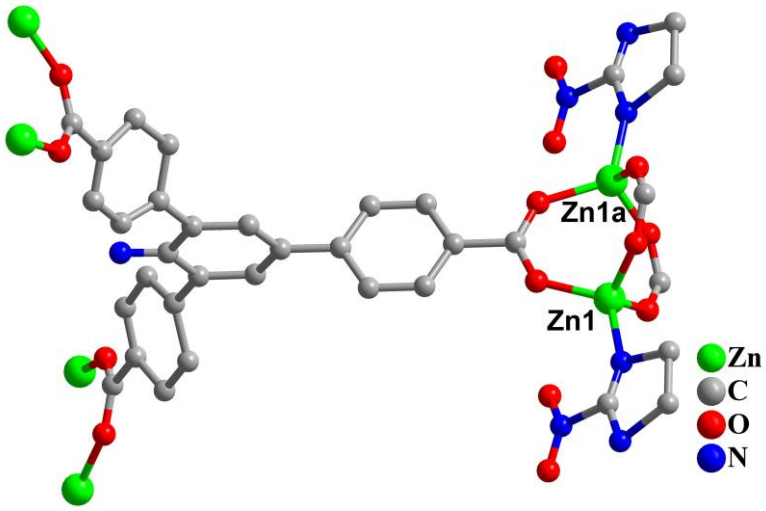
Compound	**1**
formula	$[Zn_2(NH_2\text{-BTB})][2\text{-nim}]\cdot DMF\cdot 6H_2O$
formula weight	874.27
crystal system	Monoclinic
space group	*P21/m*
***a* (Å)**	16.8524(8)
***b* (Å)**	9.365(5)
***c* (Å)**	16.264(8)
***α* (^{o})**	90
***β* (^{o})**	116.786(7)
***γ* (^{o})**	90
***V* (Å^3)**	2207.4
Z	2
Absorption coefficient (mm^{-1})	1.121
***μ*(Mo/Cu K*α*) (mm^{-1})**	0.71073
***F*(000)**	670
temperature (K)	100
Theta min, max(deg)	2.51, 27.58
T_{min} **and** T_{max}	0.799, 0.799
***R*(int)**	0.2460
N_{ref}, N_{par}	17739, 5381
R_1,wR [$I \geq 2\sigma(I)$]	0.1079, 0.3371
S	1.077
R_1, wR_2 **(all data)**	0.1515, 0.3859

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$

Table. S2 Comparison of hydrocarbons uptakes and isosteric heats of adsorption (Qst) for a series of MOFs.

	Uptake (mmol g^{-1})					Qst (kJ mol^{-1})					
Compounds	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_8	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_8	Ref.
1[a]	0.58	3.54	2.63	3.38	4.27	16.22	19.72	19.81	21.52	28.16	This
1[b]	0.97	6.79	4.92	5.18	5.9						work
FIR-51[c]	0.91	6.33	4.82	4.78	5.00	12.7	24.48	21.36	21.98	25.99	3
Fe_2(dobdc)[d]	0.77	6.89	6.02	5.00	5.67	20	47	45	25	33	4
CuTDPAT[e]	1.26	7.93	7.34	6.89	-	21	43	50	30	-	5
PAF-40[f]	0.54	-	1.80	1.95	2.39	18	-	25	36	-	6
PAF-40-Fe[f]	0.62	-	2.31	1.85	2.58	23	-	30	48		6
PAF-40-Mn[f]	0.49	-	2.18	2.05	2.51	16	-	25	35	-	6
MFM-300[g]	0.29	6.34	4.28	0.85	-	-	32	16	11	-	7
UTSA-35a[h]	0.43	2.90	2.16	2.43	2.97	18	29	28	30	42	8

[a] Data was measured and processed at 297 K and 1 bar; [b] Data was measured and processed at 297 K and 1 bar; [c] Data was measured and processed at 294K and 1 bar; [d] Data was measured and processed at 318 K and 1 bar; [e] Data was measured and processed at 298 K and 1 bar; [f] Data was measured and processed at 298 K and 1.1 bar; [g] Data was measured and processed at 293 K and 1 bar; [h] Data was measured and processed at 296 K and 1atm.



Figrue. S1 The coordination environment in compound **1**.

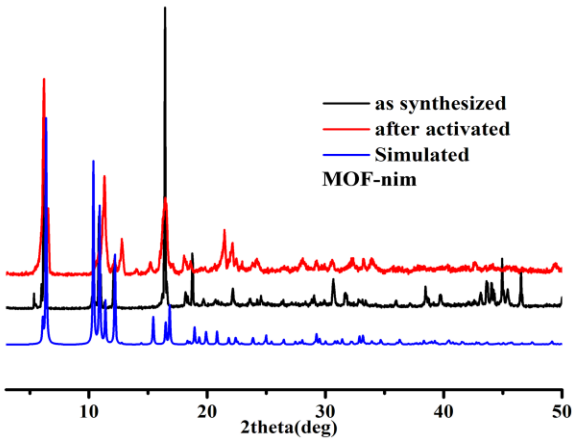


Figure. S2 The Powder XRD patterns of comound **1**.

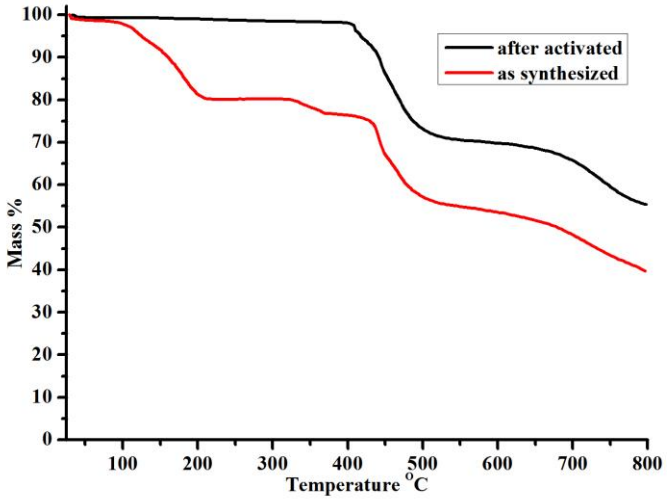


Figure. S3 The TGA plots of compound **1**.

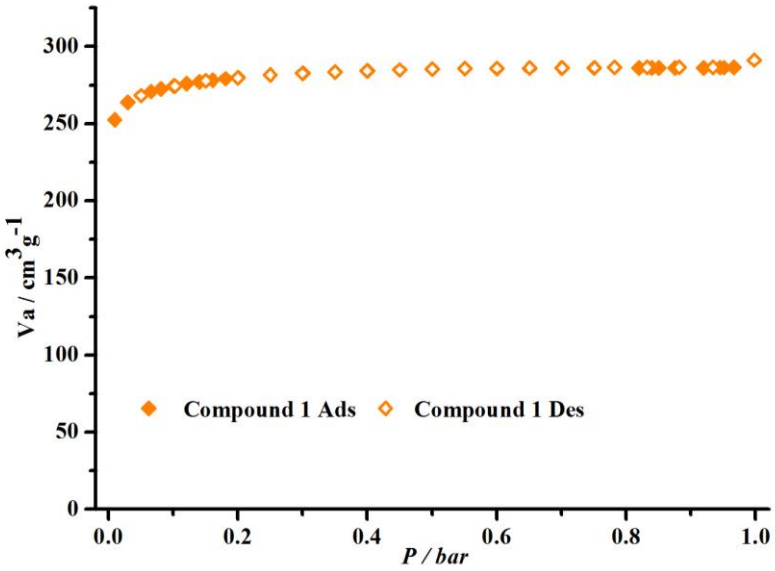


Figure. S4 N_2 sorption isotherms of **1** at 77 K.

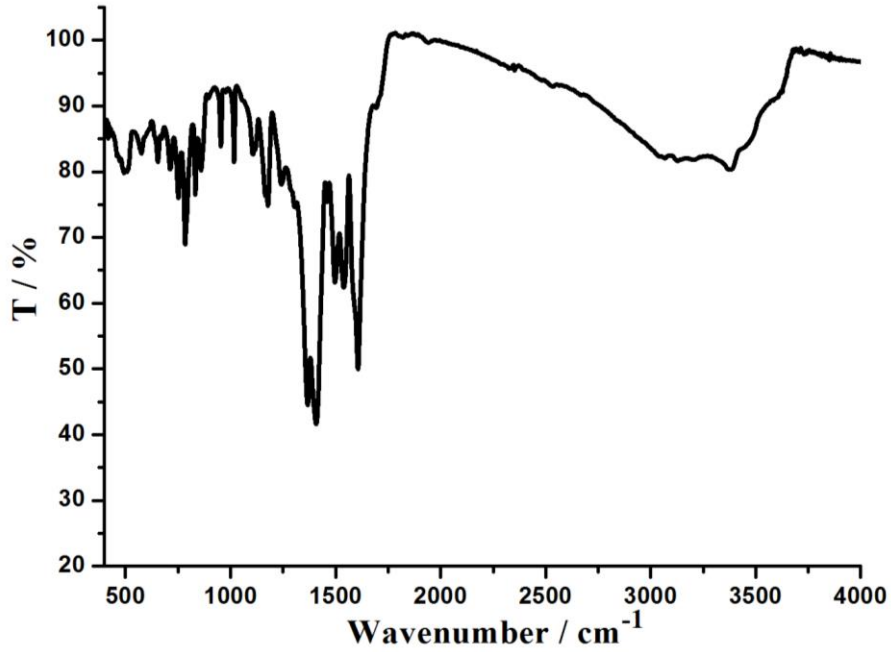


Figure. S5 The IR spectra of **1**.

By referring to the literature, the characteristic absorption bands in the frequency range 1360-1670 cm^{-1} corresponding to ν_{as}(C-O) and ν_{sym}(C-O) of the carboxylate groups[9]. The following are some primary IR peaks for compound **1**: 3054 cm^{-1} (w) is aromatic C–H stretch. 1620 cm^{-1} (s) is characteristic peak of N-O stretch of NO_2 groups. 1515 cm^{-1} (m) ascribes aromatic C=C stretch. The strong and sharp band at 1442 cm^{-1} can be assigned to the stretching vibrations of C–O stretch of the carboxylate groups. 870 cm^{-1} (m), 790 cm^{-1} (m) are characteristic peaks of ligand aromatic ring C–H bending vibration outside the plane. 727 cm^{-1}(m) is C–N stretch in

DMF molecules.

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