Supplementary Information

Fine-Tuning Pore Structure of Metal–Organic Frameworks by Linker Substitution for Enhanced Hydrogen Storage and Gas Separation

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Structure Simulation

All simulated structures are based on the given crystallographic topology of UiO-66 to be built. By modifying benzene rings of the organic linkers (terephthalic acid) in Materials Studio,[1] substituents (dihydroxy, dimethoxy and diethoxy groups) are introduced to the crystallographic topology. The geometry of the output MOFs is optimized using a molecular mechanics (MM) simulation in which the system energy is minimized as a function of the atomic coordinates. The system energy is derived by a force-field which describes the energetics of MOF intramolecular interactions. Here, we used the "Geometry Optimization" to describe the energetics of MOF intramolecular interactions with Materials Studio to perform the MM simulation. We optimized the atom positions and unit cell parameters together to obtain the structures. Finally, we refined the structures by conducting Pawley refinement of the experimental powder X-ray diffraction patterns with the Reflex Module of Materials Studio.
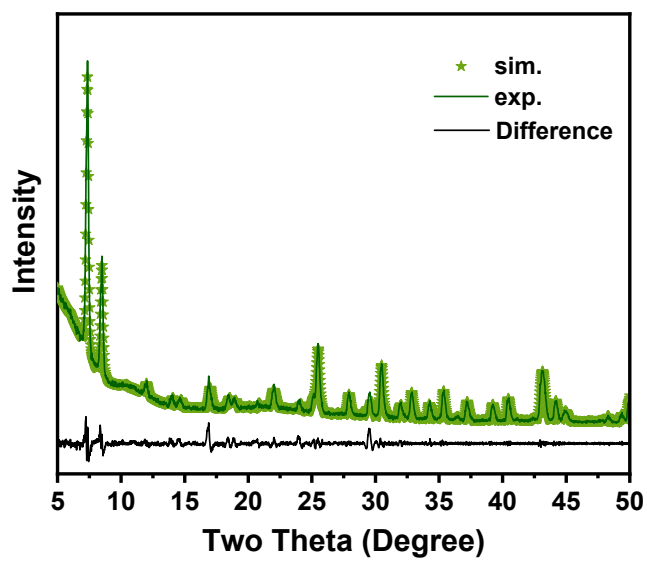
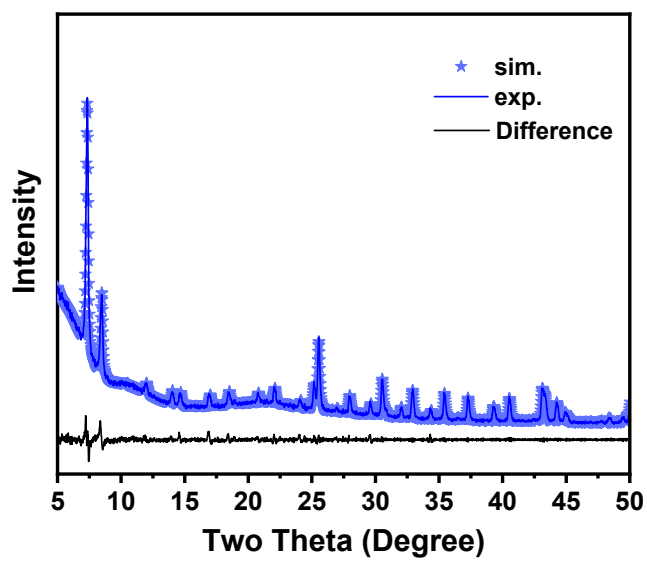**Fig. S1.** Pawley refinement result of UiO-66-(OH)$_2$.

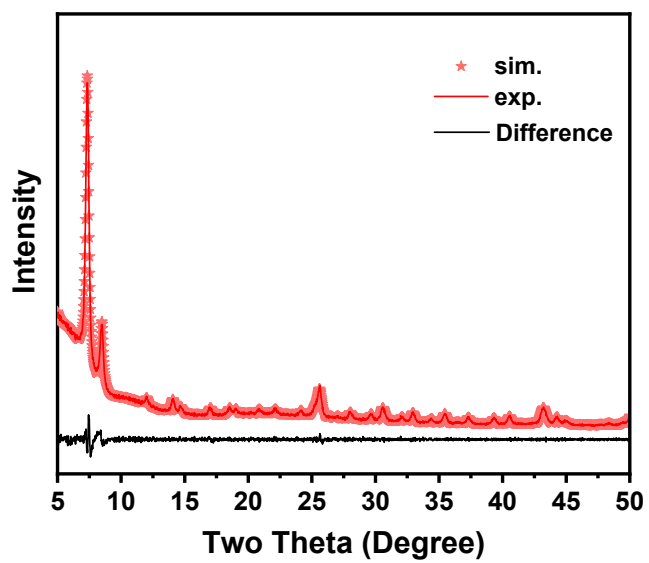**Fig. S2.** Pawley refinement result of UiO-66-(OCH$_3$)$_2$.

Fig. S3. Pawley refinement result of UiO-66-$(OCH_2CH_3)_2$.

Table S1. Summary of Pawley refinement results of the MOFs.

MOFs	Cell Volume (Å^3)	Pore Volume (cm^3/g)	BET Surface Area (m^2/g)	Octahedral Channel (Å)	Tetrahedral Channel (Å)	Window (Å)	*Rwp* (%)
UiO-66-$(OH)_2$	9057	0.35	795	12.5	10.0	7.3	4.48
UiO-66-$(OCH_3)_2$	9137	0.23	492	9.5	7.5	4.4	4.93
UiO-66-$(OCH_2CH_3)_2$	9091	0.06	202	7.5	7.0	3.8	3.78

Table S2. Textual properties of UiO-66, UiO-66-$(OH)_2$, UiO-66-$(OCH_3)_2$ and UiO-66-$(OCH_2CH_3)_2$.

MOFs	S_{BET}($\text{m}^2\cdot\text{g}^{-1}$)	V_{Tot}($\text{cm}^3\cdot\text{g}^{-1}$)	V_{Micro}($\text{cm}^3\cdot\text{g}^{-1}$)	Dav(nm)
UiO-66	1564	1.00	0.62	1.63
UiO-66-$(OH)_2$	945	0.69	0.46	0.78
UiO-66-$(OCH_3)_2$	901	1.10	0.37	0.74
UiO-66-$(OCH_2CH_3)_2$	982	0.96	0.31	1.43

Table S3. Parameters by fitting the isotherms with Langmuir model.

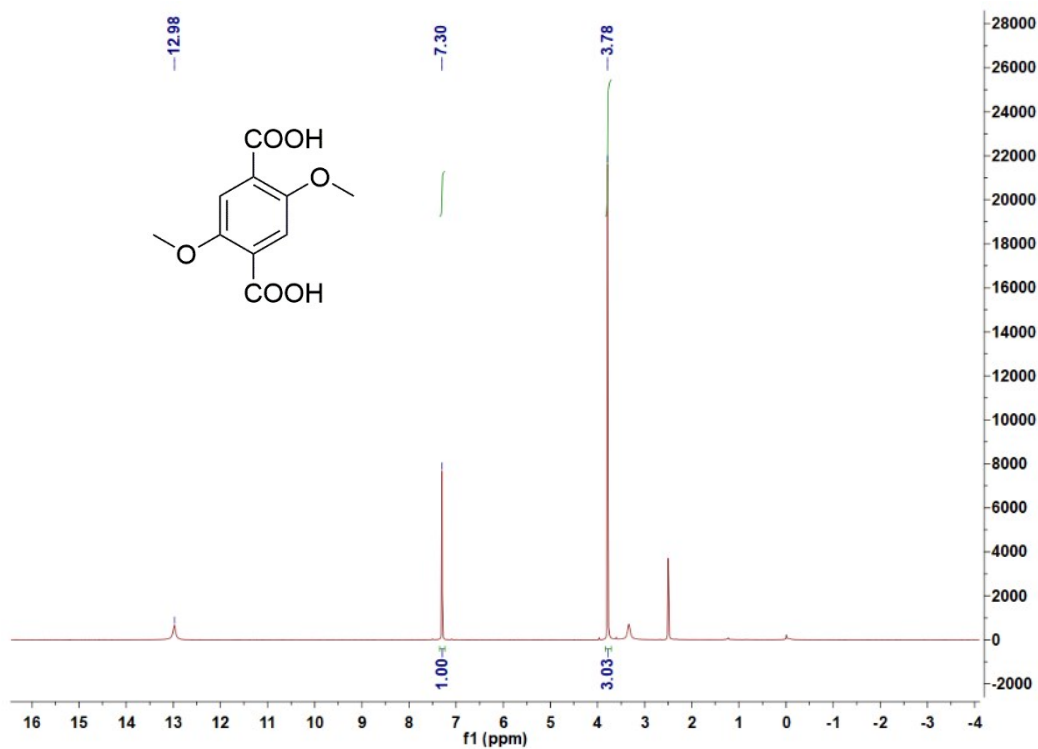| MOFs	CO_2			CH_4			N_2			H_2		
	K	Q_m (mol/kg)	R^2	*K*	Q_m (mol/kg)	R^2	*K*	Q_m (mol/kg)	R^2	*K*	Q_m (mol/kg)	R^2
UiO-66	13.11	1.06	0.999	7.69	0.52	0.999	4.43	0.36	0.999	2.49	0.08	0.994
UiO-66-$(OH)_2$	5.74	3.66	0.980	3.84	0.86	0.996	3.32	0.26	0.999	1.19	0.22	0.998
UiO-66-$(OCH_3)_2$	6.49	2.21	0.992	3.90	0.61	0.998	3.01	0.22	0.999	1.73	0.32	0.974
UiO-66-$(OCH_2CH_3)_2$	5.58	1.62	0.992	4.27	0.32	0.999	4.43	0.09	0.999	1.85	0.38	0.974

Fig. S4. Proton NMR (400 MHz, DMSO-*d6*) spectrum of 2,5-dimethoxy terephthalic acid (L1).
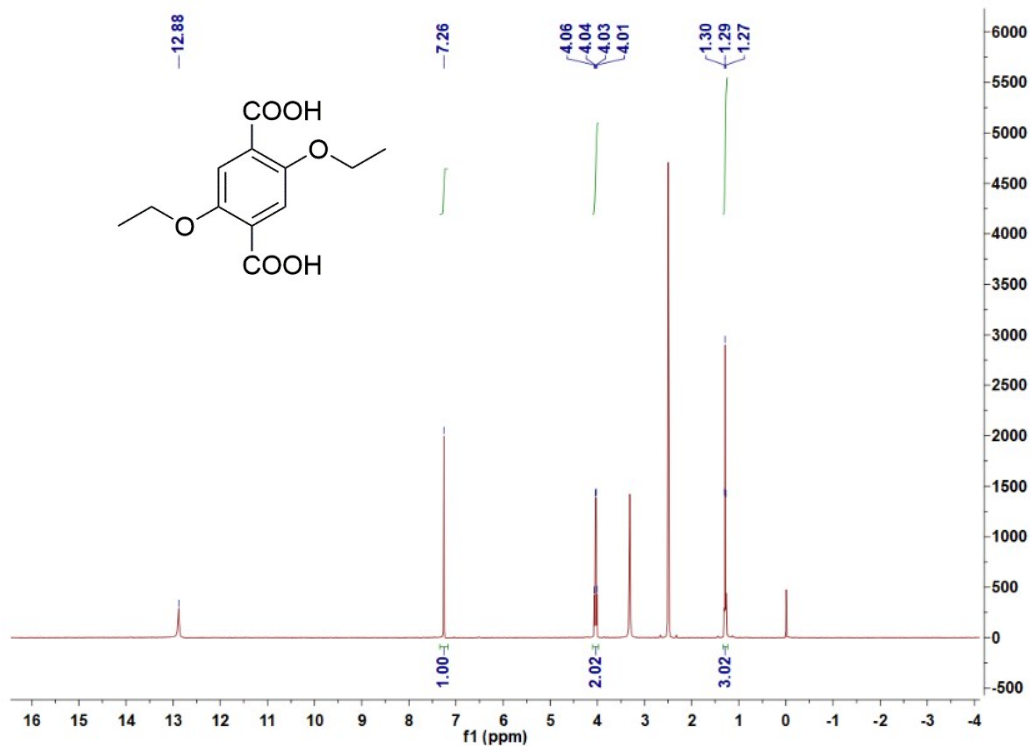

Fig. S5. Proton NMR (400 MHz, DMSO-*d6*) spectrum of 2,5-diethoxy terephthalic acid (L2).

Table S4. The hydrogen adsorption capacities of previously reported MOF materials.

Material	H$_2$ uptake (wt. %)	Temperature (K)	Pressure (bar)	Ref.
CAU-1	4.0	77	30	[2]
BUT-22	12	77	100	[3]
HKUST-1	3.6	77	50	[4]
MOF-5	11.5	77	170	[5]
NU-1500-Al	8.6	77	100	[6]
NU-1501-Al	14.5	77	100	[6]
NU-1501-Fe	13.2	77	100	[6]
MOF-177	7.5	77	70	[7]
IRMOF-6	4.6	77	45	[7]
IRMOF-8	3.4	77	33.7	[7]
SNU-4	3.7	77	50	[8]
SNU-5	5.2	77	50	[8]
SNU-6	10.0	77	70	[9]
Mn-BTT	6.9	77	90	[10]
Cu-BTT	3.7	77	90	[11]
Fe-BTT	4.1	77	95	[12]
Ni-MOF-74	2.95	77	10	[13]
Co-MOF-74	3.15	77	10	[13]
PCN-6	1.9	77	1	[14]
PCN-6′	1.1	77	1	[15]
PCN-10	6.84	30	3.5	[16]
PCN-12	3.05	77	1	[17]
PCN-12′	2.4	77	1	[17]
PCN-20	6	77	35	[18]
PCN-46	7.2	77	60	[18]
PCN-66	6.65	77	45	[19]
NOTT-140	6	77	20	[20]
UiO-67	4.6	77	38	[21]
UiO-66	2.4	77	38	[21]

Table S5. The adsorption selectivity for CO_2/N_2, CO_2/CH_4, CH_4/N_2 and CO_2/H_2 on previously reported MOF materials.

Material	Selectivity				Temperature (K)	Pressure (bar)	Ref.
	CO_2/N_2[a]	CO_2/CH_4[a]	CH_4/N_2[a]	CO_2/H_2[a]			
UiO-66	28				298	3	[22]
UiO-66−NH$_2$	68				298	3	[22]
UiO-66−1,4-Naphyl	32				298	3	[22]
UiO-66−2,5-(OMe)$_2$	68				298	3	[22]
UiO-66−NO$_2$	40				298	3	[22]
[Mn(CIP⁻)$_2$]	117	8			273	1	[23]
ATC-Cu			9.7		298	1	[24]
ZnZSM-5-pIM			8.44		298	1	[25]
InOF-18	37.83	10.44			273	1	[26]
UPC-99	150[b]	12.6			273	1	[27]
NKU-521a	170	36			273	1	[28]
Mg–MOF-74		~175			300	<1	[29]
Zn–MOF-74	35[c]	10			300	<1	[29]
IITKGP-8	106	17.7			273	1	[30]
IITKGP-5	435.5	151.6			273	1	[31]
UTSA-16	314.7	29.8			296	1	[32]
SIFSIX-2-Cu-i	140	33			298	1	[33]
467-MOF	<6	<6[d]		45	273 or 293	1	[34]
[Cu(tba)$_2$]$_n$	45	45[d]		51	293	1	[35]
Cu–MOF[e]				80	298	10	[36]
$^3_\infty$[Cu(Me-4py-trz-ia)]			4.0–4.4		298	5	[37]
UMCM-1[e]	5.4[f]	2.9	2.0	16.4[g]	298	40	[38]
UMCM-2[e]	7.8[f]	4.7	2.0	26.9[g]	298	40	[38]

[a] If not specially noted the selectivity is obtained from IAST calculations and the CO_2/N_2, CO_2/CH_4, CH_4/N_2, CO_2/H_2 mixtures are 15/85, 50/50, 50/50 and 15/85 binary gas mixtures, respectively.
[b] 10/90 CO_2/N_2 gas mixture.
[c] 20/80 CO_2/N_2 gas mixture.
[d] 15/85 CO_2/CH_4 gas mixture.
[e] Obtained from GCMC simulations.
[f] 50/50 CO_2/N_2 gas mixture.
[g] 50/50 CO_2/H_2 gas mixture.

Bnn-1-Ca				10^4 [g]			[39]
Bnn-1-Ca-H_2O	10^6	10^5			298	1	[39]
MCM-41	15 [c]	7		65 [h]	298	45	[40]
N-WAPC		3.19	7.62		298	1	[41]
Lignite Coal Liquefaction	35 [f]	11	38		273	1	[42]
CAU-21-BPDC			11.9		298	1	[43]
[$Co_3(C_4O_4)_2(OH)_2$]			12.5		298	1	[44]
UiO-66(Hf)-$(OH)_2$	93	30	3.6	>1700 [i]	298	1	[45]

[h] 20/80 CO_2/H_2 gas mixture.
[i] 30/70 CO_2/H_2 gas mixture.

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