Supporting Information

# Steric hindrance regulation in hydrogen-bonded organic

## frameworks: from nonporous to microporous

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## **Experimental Procedures**

#### Materials and instruments

All reagents were commercially available and used without further purification.

<sup>1</sup>H NMR spectrum was obtained on an Inova 500 MHz spectrometer. Single crystal X-ray diffraction experiments were carried out on a SuperNova diffractometer equipped with mirror Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å) and an Eos CCD detector. Powder X-ray diffraction (PXRD) was carried out on a Bruker D8-Focus Bragg-Brentano X-ray powder diffractometer equipped with a Cu sealed tube at 40 kV and 15 mA. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC1 instrument under a static N<sub>2</sub> atmosphere with a heating rate of 10 °C/min at the range of 40-900 °C. Infrared (IR) spectroscopy spectrum was collected on a Nicolet 330 FTIR Spectrometer within 4000-400 cm<sup>-1</sup> region. Gas sorption measurements were conducted on a Micrometritics ASAP 2020 surface area analyzer.

### Synthesis of ligands

2'-methyl-[1,1':3',1"-terphenyl]-4,4",5'-tricarboxylic acid (H<sub>3</sub>TTCA-CH<sub>3</sub>) and 2'methoxy-[1,1':3',1"-terphenyl]-4,4",5'-tricarboxylic acid (H<sub>3</sub>TTCA-OCH<sub>3</sub>) were synthesized according to previous literature.<sup>1</sup>



Scheme S1 Synthetic procedure of H<sub>3</sub>TTCA-CH<sub>3</sub> ligand.

#### 3,5-diiodo-4-methylbenzoic acid

According to literature, to finely powdered iodine (1.20 g, 4.73 mmol) suspended in  $H_2SO_4$  (95%, 30 mL, V/V) was added NaIO<sub>4</sub> (0.34 g, 1.59 mmol). The mixture was stirred at about 30 °C for 30 min. 4-methylbenzoic acid (2.04 g, 15.0 mmol) was added to the solution. The mixture was stirred at 30 °C for 2 h, then poured into ice/water, and filtered by a vacuum. The solid was washed with cool water and dried by vacuum at 50 °C. After recrystallization with ethanol, crude (3.43 g, 59%) as a white solid was used without further purification.

#### Methyl 3,5-diiodo-4-methylbenzoate

A sample of 3,5-diiodo-4-methylbenzoic acid (19.39 g, 50.0 mmol) was suspended in 200 mL of absolute methanol at room temperature. Concentrated H<sub>2</sub>SO<sub>4</sub> (9.5 mL) was slowly added with rapid stirring and then the reaction mixture was heated at reflux for 48 h. At the end of the reflux period, TLC (silica,  $CH_2Cl_2$ ) indicated the complete consumption of the starting material. The solution was initially cooled to room temperature, and then put in an ice bath to precipitate the product. Vacuum filtration afforded 19.08 g (95%) of a white solid.

#### Trimethyl 2'-methyl-[1,1':3',1''-terphenyl]-4,4'',5'-tricarboxylate

Methyl 3,5-diiodo-4-methylbenzoate (1.61 g, 4 mmol), methyl 4-boronobenzoate (1.57 g, 9.6 mmol),  $Pd(PPh_3)_4$  (0.15 g, 0.13 mmol) and  $K_3PO_4$  (3.82 g, 18.0 mmol) were placed in a 500 mL two-necked round bottom flask under a N<sub>2</sub> gas atmosphere. The flask was further charged with a 200 mL of dry 1,4-dioxane, and the contents were heated at reflux for 48 h. After the mixture was cooled to room temperature, the solvent

was removed, and water was added. The water phase was washed with  $CH_2Cl_2$ . The mixed organic phases were dried with  $MgSO_4$ . After the solvent was removed, the crude product was purified by column chromatography with  $CH_2Cl_2$  as the eluent.

## 2'-methyl-[1,1':3',1''-terphenyl]-4,4'',5'-tricarboxylic acid

Trimethyl 2'-methyl-[1,1':3',1"-terphenyl]-4,4",5'-tricarboxylate (2.0 g, 4.8 mmol) was dissolved in 50 mL MeOH, and 50 mL 2 M NaOH aqueous solution was added. The mixture was stirred at 50 °C overnight. The organic phase was removed, and the aqueous phase was acidified with diluted hydrochloric acid to give white precipitate, which was filtered and washed with water several times. <sup>1</sup>H NMR ( $d_6$ -DMSO):  $\delta = 3.36$  (s, 3H), 7.59 (d, 4H), 7.80 (s, 2H), 8.05 (d, 4H), 13.10 (s, 3H).



Scheme S1 Synthetic procedure of H<sub>3</sub>TTCA-OCH<sub>3</sub> ligand.

### 3,5-diiodo-4-methoxybenzoic acid

According to literature, to finely powdered iodine (1.20 g, 4.73 mmol) suspended in  $H_2SO_4$  (95%, 30 mL, V/V) was added NaIO<sub>4</sub> (0.34 g, 1.59 mmol). The mixture was stirred at about 30 °C for 30 min. 4-methoxybenzoic acid (2.28 g, 15.0 mmol) was added to the solution. The mixture was stirred at 30 °C for 2 h, then poured into ice/water, and filtered by a vacuum. The solid was washed with cool water and dried by vacuum at 50 °C. After recrystallization with ethanol, crude (3.82 g, 63%) as a white solid was used without further purification.

### Methyl 3,5-diiodo-4-methoxybenzoate

A sample of 3,5-diiodo-4-methoxybenzoic acid (20.19 g, 50.0 mmol) was suspended in 200 mL of absolute methanol at room temperature. Concentrated  $H_2SO_4$  (9.5 mL) was slowly added with rapid stirring and then the reaction mixture was heated at reflux for 48 h. At the end of the reflux period, TLC (silica,  $CH_2Cl_2$ ) indicated the complete consumption of the starting material. The solution was initially cooled to room temperature, and then put in an ice bath to precipitate the product. Vacuum filtration afforded 20.0 g (96%) of a white solid.

#### Trimethyl 2'-methoxy-[1,1':3',1''-terphenyl]-4,4'',5'-tricarboxylate

Methyl 3,5-diiodo-4-methoxybenzoate (1.67 g, 4 mmol), methyl 4-boronobenzoate (1.57 g, 9.6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.15 g, 0.13 mmol) and K<sub>3</sub>PO<sub>4</sub> (3.82 g, 18.0 mmol) were placed in a 500 mL two-necked round bottom flask under a N<sub>2</sub> gas atmosphere. The flask was further charged with a 200 mL of dry 1,4-dioxane, and the contents were heated at reflux for 48 h. After the mixture was cooled to room temperature, the solvent was removed, and water was added. The water phase was washed with  $CH_2Cl_2$ . The mixed organic phases were dried with MgSO<sub>4</sub>. After the solvent was removed, the crude product was purified by column chromatography with  $CH_2Cl_2$  as the eluent.

2'-methoxy-[1,1':3',1''-terphenyl]-4,4'',5'-tricarboxylic acid

Trimethyl 2'-methoxy-[1,1':3',1"-terphenyl]-4,4",5'-tricarboxylate (2.0 g, 4.6 mmol) was dissolved in 50 mL MeOH, and 50 mL 2 M NaOH aqueous solution was added. The mixture was stirred at 50 °C overnight. The organic phase was removed, and the aqueous phase was acidified with diluted hydrochloric acid to give white precipitate, which was filtered and washed with water several times. <sup>1</sup>H NMR ( $d_6$ -DMSO):  $\delta$  = 3.53 (s, 3H), 7.73 (d, 4H), 7.96 (s, 2H), 8.05 (d, 4H), 13.11 (s, 3H).

## Synthesis of UPC-HOFs

## Synthesis of UPC-HOF-15

 $H_3$ TTCA-CH<sub>3</sub> precursor (10 mg) dissolving in *N*,*N*'-dimethylformamide (1 mL) and dichloromethane (3 mL) was added to a 10 mL glass vial. After slow evaporation of solvents for 3-4 weeks, colourless block crystals of UPC-HOF-15 were obtained with a yield of 52%.

## Synthesis of UPC-HOF-16

 $H_3$ TTCA-OCH<sub>3</sub> precursor (10 mg) dissolving in *N*,*N'*-dimethylformamide (1 mL) and methanol (3 mL) was added to a 10 mL glass vial. After slow evaporation of solvents for 3-4 weeks, colourless needle crystals of UPC-HOF-16 were obtained with a yield of 55%.

#### Single-crystal X-ray diffraction

The as-synthesized crystals of UPC-HOF-15 and UPC-HOF-16 were taken from the mother liquid without further treatment, transferred to oil and mounted on to a loop for single crystal X-ray data collection. The crystal data of UPC-HOF-15 and UPC-HOF-16 were collected on an Agilent Technologies SuperNova diffractometer equipped with graphite monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å). With the help of Olex2, the structures of UPC-HOF-15 and UPC-HOF-16 were solved with the Superflip structure solution program using charge flipping and refined with the ShelXL refinement package using least squares minimization. The structures of UPC-HOF-15 and UPC-HOF-16 were placed in calculated ideal positions and refined as riding on their respective nonhydrogen atoms. PLATON and SQUEEZE<sup>2</sup> were used to calculate the diffraction contribution of the solvent molecules in UPC-HOF-15, and thereby produced a set of partly solvent-free diffraction intensities.

The crystal data of UPC-HOF-15 and UPC-HOF-16 have been deposited to Cambridge Crystallographic Data Center (CCDC) as 2444439 and 2444440, respectively.

#### Gas sorption measurements

The activated samples were prepared by immersing the as-synthesized UPC-HOF-15 and UPC-HOF-16 in acetone for solvent exchange followed by activation at 373 K under vacuum for 10 h. Gas adsorption experiments containing N<sub>2</sub> at 77 K, C<sub>2</sub>H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> at 273 and 298 K, were performed by using ASAP-2020 surface area analyzer. Liquid nitrogen bath was used to stabilize the temperature at 77 K, whereas other test temperatures were maintained via a circulating water bath. The Brunauer-Emmett-Teller (BET) surface area was calculated using multi-point BET equation with the P/P<sub>0</sub> range of 0.005-0.1. Pore volume was calculated with the maximal adsorption capacity. Pore size distribution was calculated with non-local density functional theory (NLDFT) and the experimental adsorption isotherm by solving the integral adsorption equation.

$$N_{exp}(P/P_0) = \int_{D_{min}}^{D_{max}} N_{NLDTF}(P/P_0,D)f(D)dD$$

Here,  $N_{exp}(P/P_0)$  is the experimental adsorption isotherm,  $D_{min}$  and  $D_{max}$  are the minimum and maximum pore sizes,  $N_{NLDFT}(P/P_0, D)$  is the theoretical adsorption isotherms, f(D) is the pore size distribution, D is the pore size.

#### **Computational methods**

### Isosteric heat of adsorption

A Virial equation comprising the temperature-independent parameters  $a_i$  and  $b_j$  was employed to calculate the enthalpies of adsorption for C<sub>2</sub>H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> in UPC-HOF-16, which were measured at 273 and 298 K.

$$\ln P = \ln N + \frac{1}{T} \sum_{i}^{m} a_i N_i + \sum_{j}^{n} b_j N_j$$

$$Q_{st} = -R \sum_{i=0}^{m} a_i N_i$$

Here, *P* is the pressure expressed in mmHg, *N* is the amount absorbed in mmol/g, *T* is the temperature in K,  $a_i$  and  $b_j$  are virial coefficients, and *m*, *n* represent the number of coefficients required to adequately describe the isotherms (herein, m = 5 and n = 2).  $Q_{st}$  is the coverage-dependent isosteric heat of adsorption and *R* is the universal gas constant.

#### Selectivity based on ideal adsorbed solution theory

Before estimating the selectivity for binary gas mixture, the single-component gas adsorption isotherms were first fitted to a dual-site Langmuir-Freundlich (DSLF) model:

$$q = q_{A,sat} \frac{b_A p^{n_1}}{1 + b_A p^{n_1}} + q_{B,sat} \frac{b_B p^{n_2}}{1 + b_B p^{n_2}}$$

where q is the amount of adsorbed gas (mmol/g), p is the bulk gas phase pressure (kPa),  $q_{sat}$  is the saturation amount (mmol/g), b is the Langmuir-Freundlich parameter (kPa<sup>-1</sup>), and n is the Langmuir-Freundlich exponent (dimensionless) for two adsorption sites A and B indicating the presence of weak and strong adsorption sites.  $b_A$  and  $b_B$  are both temperature-dependent.

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right); b_B = b_{B0} \exp\left(\frac{E_B}{RT}\right)$$

The adsorption selectivity  $S_{ads}$  was calculated by ideal adsorbed solution theory:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

where  $q_1$  and  $q_2$  are the molar loadings in the adsorbed phase in equilibrium with the bulk gas phase,  $p_1$  and  $p_2$  are partial pressure.

## **Grand canonical Monte Carlo simulations**

Grand canonical Monte Carlo (GCMC) simulations were carried out using the Sorption module of Materials Studio package. The Locate and Metropolis methods were used to predict the possible binding sites of  $C_2H_2$ ,  $CO_2$ , and  $CH_4$  onto the framework. During the simulation, the  $C_2H_2$ ,  $CO_2$ , and  $CH_4$  molecules including the frameworks were considered as rigid bodies. The optimal adsorption sites were simulated under 298 K and 100 kPa by the fixed loading task and Metropolis method. The atomic partial charges of the host HOF skeleton and all gas molecules were obtained from QEq method. The equilibration steps and the production steps were set to  $5.0 \times 10^6$  and  $1.0 \times 10^7$ , respectively. The gas-skeleton interaction and the gas-gas interaction were characterized by the standard universal force field (UFF). The cut-off radius used for the Lennard-Jones interactions is 15.5 Å and the long-range electrostatic interactions were considered by the Ewald summation method.

#### **Density functional theory calculations**

Density functional theory (DFT) calculations were performed using Dmol3 module embedded in the Materials Studio software. Since it is a vast task to do the DFT calculations using a whole HOF unit cell, we used fragmented cluster models cleaved from unit cells representing the actual situations as high as possible, and the cleaved bonds at cluster boundaries were saturated by protons. The generalized gradient approximation (GGA) with the Perdewe Burkee Ernzerh of (PBE) exchangecorrelation functional was employed for the spin-unrestricted DFT calculations. The electronic wave functions were expanded by the double numerical plus polarization (DNP) basis set. The van der Waals correction was considered by Grimme to precisely describe the adsorption/penetration of gas molecules on/through the g-GYN and g-GYH membranes. The convergence criterion was  $1 \times 10^5$  Ha for energies,  $2 \times 10^3$  Ha/ Å for forces, and  $5 \times 10^3$  Å for atomic displacements. The global cutoff radius was set as 6.0 Å. In all the DFT calculations, all the atoms were allowed to fully relax. The adsorption energy ( $\Delta E_{ads}$ ) is expressed as  $\Delta E_{ads} = E_{ads+fram} - E_{fram} - E_{ads}$ , where  $E_{ads+fram}$ ,  $E_{fram}$ , and  $E_{ads}$  are the total energy of the adsorbate-framework adsorption system, adsorbent framework, and adsorbate molecule, respectively. Figures S1-S18



Fig. S2 <sup>1</sup>H NMR spectrum of synthesized H<sub>3</sub>TTCA-OCH<sub>3</sub> ligand.



Fig. S3 Electron cloud density of UPC-HOF-15 and simulated methoxy-modified isomorphic framework.



Fig. S4 PXRD patterns of UPC-HOF-15.



Fig. S5 PXRD patterns of UPC-HOF-16.



Fig. S6 TGA curves of UPC-HOF-15 and UPC-HOF-16.



Fig. S7 IR spectra of UPC-HOF-15 and UPC-HOF-16.



Fig. S8 Experimental isotherms and NLDFT fitting theoretical isotherms.



**Fig. S9** Single-component C<sub>2</sub>H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> adsorption/desorption isotherms of UPC-HOF-15 at 273 K.



**Fig. S10** Single-component C<sub>2</sub>H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> adsorption/desorption isotherms of UPC-HOF-15 at 298 K.



Fig. S11 Virial fitting of  $C_2H_2$  adsorption isotherms for UPC-HOF-16.



Fig. S12 Virial fitting of CO<sub>2</sub> adsorption isotherms for UPC-HOF-16.



Fig. S13 Virial fitting of CH<sub>4</sub> adsorption isotherms for UPC-HOF-16.



Fig. S14 Langmuir-Freundlich fitting of C<sub>2</sub>H<sub>2</sub> adsorption isotherms for UPC-HOF-16 at 273 K.



Fig. S15 Langmuir-Freundlich fitting of CO<sub>2</sub> adsorption isotherms for UPC-HOF-16 at 273 K.



Fig. S16 Langmuir-Freundlich fitting of CH<sub>4</sub> adsorption isotherms for UPC-HOF-16 at 273 K.



Fig. S17 Langmuir-Freundlich fitting of C<sub>2</sub>H<sub>2</sub> adsorption isotherms for UPC-HOF-16 at 298 K.



Fig. S18 Langmuir-Freundlich fitting of CO<sub>2</sub> adsorption isotherms for UPC-HOF-16 at 298 K.



Fig. S19 Langmuir-Freundlich fitting of CH<sub>4</sub> adsorption isotherms for UPC-HOF-16 at 298 K.

# Tables S1-S5

Table S1. Crystal data of UPC-HOFs.	
Compound	I

Compound	UPC-HOF-15	UPC-HOF-16
CCDC	2444439	2444440
Formula	$C_{26.88}H_{27.38}N_{1.62}O_{7.62}$	C <sub>25</sub> H <sub>23</sub> NO <sub>8</sub>
Formula weight	495.04	465.44
Temperature/K	294.8(6)	294.0(5)
Crystal system	monoclinic	monoclinic
Space group	<i>I2/c</i>	$P2_{I}/c$
a/Å	24.5252(19)	12.0307(3)
b/Å	7.1491(5)	22.7887(5)
c/Å	30.553(2)	8.6147(2)
a/°	90	90
β/°	106.418(8)	100.092(3)
$\gamma^{ m o}$	90	90
Volume/Å <sup>3</sup>	5138.5(7)	2325.30(10)
Z	8	4
ρ g/cm <sup>3</sup>	1.280	1.330
$\mu/mm^{-1}$	0.783	0.837
F(000)	2088.0	976.0
$2\theta$ range for data collection	7.516 to 133.196	7.464 to 141.012
	$-23 \le h \le 29$	$-14 \le h \le 14$
Index ranges	$-4 \le k \le 8$	$-27 \le k \le 20$
	$-36 \le l \le 36$	$-10 \le l \le 10$
Reflections collected	9639	10232
R <sub>int</sub>	0.0287	0.0241
Data/restraints/parameters	4613/0/333	4403/0/313
Goodness-of-fit on F <sup>2</sup>	1.816	1.022
Einel D in dense $[I > 2 - \langle I \rangle]$	$R_1 = 0.1324$	$R_1 = 0.0465$
Final K indexes $[1 \ge 2\sigma(1)]$	$wR_2 = 0.4163$	$wR_2 = 0.1207$
Final D indexes [all data]	$R_1 = 0.1436$	$R_1 = 0.0665$
rinai K indexes [all data]	$wR_2 = 0.4338$	$wR_2 = 0.1364$
Largest diff. peak/hole /eÅ-3	0.68/-0.40	0.17/-0.19

 Table S2. Details of hydrogen-bonding in UPC-HOF-15.

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_	D–H…A	D–H (Å)	H···A (Å)	D…A (Å)	D–H···A (°)	symop-for-A	
	O1–H1…O7	0.82	1.80	2.590(3)	160	x, -1+y, z	
	O3–H3…O4	0.82	1.86	2.644(5)	160	1-x, y, 1/2-z	
	O5–H5…O6	0.82	1.83	2.628(5)	169	-x, y, -1/2-z	

**Table S3.** Details of hydrogen-bonding in UPC-HOF-16.

D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	D–H…A (°)	symop-for-A
01–H1…O4	0.82	1.85	2.665(8)	171	-x, 1/2+y, 1/2-z
O3–H3…O2	0.82	1.76	2.577(6)	171	-x, -1/2+y, 1/2-z
O5–H5…O8	0.82	1.77	2.571(5)	165	x, y, 2+z

Table S4. Comparison of adsorption performance in HOFs at room temperature.

Matariala	BET surface area	$Q_{s}$	$Q_{\rm st}$ (kJ/mol)		IAST selectivity		Dof
Materials	$(m^{2}/g)$	$C_2H_2$	$CO_2$	$\mathrm{CH}_4$	$C_2H_2/CH_4$	$\rm CO_2/\rm CH_4$	Kel.
UPC-HOF-16	218.6	16.8	15.3	6.9	14.2	6.7	This work
UPC-HOF-13	_	14.9	3.9	3.0	5.7	4.2	3
HOF-5a	1101	27.6	22.8	19.2	13.6ª	5.0ª	4
HOF-9a	286	_	23.5	14.4	—	2.9ª	5
HOF-11a	687	18.8	19.6	16.6	7.2	3.4	6
HOF-12	320	_	28.5	-	_	5.3	7
HOF-14	2573	_	-	-	3.7	—	8
HOF-16a	302	23.0	21.6	18.5	107	8.9	6
JLU-SOF1-R	460	_	34.3	18.9	—	3.9	9
BTBA-1a	285.6	_	25.1	-	—	14	10
PTBA-1a	202.6	_	33.7	-	—	6	10
HOF-BTB	955	24.3	-	-	9.3 <sup>b</sup>	—	11
SOF-1a	474	36.2	27.6	20.8	—	4.2	12
SOF-7a	900	_	21.6	_	_	9.1	13

<sup>a</sup> 296 K, <sup>b</sup> 295 K

 Table S5. Steric volumes of methyl and methoxy group.

Eurotional group	Van d	er Waals radi	Van der Waals volume	
Functional group	С	Н	0	(Å <sup>3</sup> )
Methyl	1.70	1.20	_	22-25
Methoxy	1.70	1.20	1.52	30-35

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