# Supporting Information

# Triptycene-Based Porous Hydrogen-Bonded Organic Framework for Guest Incorporation with Tailored Fitting

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#### 1. Synthesis and Methods.

2,6,12-Trihydrotripty[2,3-d':6,7-d:12,13-d'']triimidazole (H<sub>3</sub>TBI) was synthesized according to the reported literature.<sup>1</sup> Triptycene (**1**) was dissolved in fuming nitric acid and heated at 80–85 °C for 4 hours to give a yellow solid of hexanitrotriptycene (**2**) followed by recrystallization from hot *N*,*N*-dimethylformamide (DMF). Tin(II) chloride was added to aqueous hydrochloride/ethanol solution of **2** to give the pale-yellow ammonium salt of **3** as a heptahydrate. Then **3** was suspended in DMF/dichloromethane solution with triethyl orthoformate and refluxed for 22 hours at room temperature to form H<sub>3</sub>TBI (Scheme S1).

Caution! Although we never experienced any serious accidents with hexanitrotriptycene on scales described within the reported literature, we cannot exclude a spontaneous combustion of hexanitrotriptycene on larger scales, e.g., by friction or shock, and therefore, the compound has to be treated as a potential safety hazard. We strongly recommend that adequate safety precautions be taken into account done when experiments are performed!



#### Scheme S1. Three-step synthesis of H<sub>3</sub>TBI.

 $H_3$ TBI (4.0 mg, 0.011 mmol) was dissolved in a 1:1 (v/v) mixture (2 mL) of *N*,*N*-diethylformamide (DEF) and methanol to form a saturated solution in an open jar. The reaction jar was heated in an oil bath at 60 °C until bright yellow rod-shaped crystals started to grow. These crystals were collected by removing mother liquor after cooling to room temperature.

For the removal of solvent inside the pores while retaining its framework to the maximum extent, we tried different solvent exchange methods like supercritical  $CO_2$  and several nonpolar or weak polar low boiling–point solvents (n-hexane, n-pentane,  $CH_2Cl_2$ ), respectively. These  $N_2$  adsorption isotherms showed that  $CH_2Cl_2$  exhibited the best performance. In a typical activated procedure, we exchanged the solvent with  $CH_2Cl_2$  for nine times over three days. The crystals were further activated under vacuum at room temperature for 24 h.  $N_2$  adsorption and desorption measurement was performed on a Quantachrome Autosorb-iQ gas adsorption and pore size analyzer at 77 K. Ultra-high purity  $N_2$  was purchased and used as received.

# 2. Single Crystal Structure Determination.

Structure	FDM-15				
Empirical formula based on atoms located	C38 H47 N9 O3				
by single X-ray diffraction					
Formula weight	677.85				
Temperature	170(2) K				
Wavelength	1.54178 Å				
Crystal system	Trigonal				
Space group	<i>P</i> 3 <sub>1</sub> <i>c</i>				
Unit cell dimensions	a = b = 18.5004(4)  Å; c = 9.6325(5)				
	$\alpha = \beta = 90.00^{\circ}; \gamma = 120.00^{\circ}$				
Volume	2855.17(17) Å <sup>3</sup>				
Z	2				
Density (calculated)	0.788 Mg/m <sup>3</sup>				
Absorption coefficient	0.414 mm <sup>-1</sup>				
F(000)	724				
Crystal size	10.2 x 2.2 x 2.1 mm <sup>3</sup>				
Theta range for data collection	2.76 to 68.32°				
Index ranges	-22<=h<=22				
	-22<=k<=21				
	-11<=l<=11				
Reflections collected	27233				
Independent reflections	3479 [R(int) = 0.0370]				
Completeness	99.8%				
Absorption correction	none				
Refinement method	Full-matrix least-squares on $F^2$				
Data / restraints / parameters	3479/29/152				
Goodness-of-fit on $F^2$	1.069				
Final R indices [I>2sigma(I)]	R1 = 0.0630, wR2 = 0.1758				
R indices (all data)	R1 = 0.0645, wR2 = 0.1790				
Largest diff. peak and hole	0.477 and -0.251 e.Å <sup>-3</sup>				

**Table S1.** Crystal data and refinement structure for FDM-15.

Crystal of FDM-15 coated with Paratone oil on a Cryoloop pin at 170 K was mounted on a Bruker SMART Apex II single-crystal X-ray diffractometer equipped with a CCD area detector and operated at 50 kV, 30 mA to generate Cu  $K\alpha$  radiation ( $\lambda = 1.54178$  Å). The crystal structure was solved by Direct Methods and refined on  $F^2$  by full-matrix least-squares using the Shelxtl-97 program<sup>2</sup> systems. Details of crystal data, data collection, structure solution, and refinement are given in Table S1. The density of 0.436 g cm<sup>-3</sup> was calculated based on the formula of desolvated FDM-15 while that of 0.788 g cm<sup>-3</sup> in Table S1 was calculated based on the formula from single crystal data which includes three DEF molecules per formula. CCDC 1522062 contains the crystallographic data for these structures. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>https://summary.ccdc.cam.ac.uk/structure-summary-form</u>.

# 3. Powder X-ray Diffraction.

Powder X-ray diffraction (XRD) was conducted by using a Bruker AXS D8 Advance diffractometer operated at 1,600 W power (40 kV, 40 mA) using Cu Kα radiation. Simulated powder XRD pattern was calculated using Mercury 3.0 from the corresponding single-crystal structural data.



Fig. S1. Powder X-ray diffraction (XRD) patterns of as-synthesized and simulated FDM-15.



Fig. S2. Powder X-ray diffraction (XRD) patterns of as-synthesized and activated FDM-15.

# 4. Comparison of Gas Adsorption Results of Extrinsic Porous HOF Materials.

Numerous HOFs have been reported recent years and only a few of them showed impressive surface area and pore size. Table S2 lists the comparison of gas adsorptions of these selective HOF materials.

Assembl	HOF	BET	Density	Pore size	V(N <sub>2</sub> )	V <sub>MP</sub> (cm <sup>3</sup>	References
y force		surface	(g cm <sup>-3</sup> )	(Å)	$(cm^3 g^{-1})$	g-1)	
		area (m <sup>2</sup>					
		g <sup>-1</sup> )					
Hydroge	TTEB	278	0.830	4×11	98	0.16	3a
n	HOF-1a <sup>b</sup>	359	0.834	8.2	/ <sup>c</sup>	/ <sup>c</sup>	3b
bonding	TTBI	2796	0.755	14.5	754	1.02	3c
only	HOF-3a <sup>b</sup>	165	0.430	7.0	/ <i>c</i>	/c	3d
	HOF-5a	1101	0.955	3.9×6.8	/ <sup>c</sup>	0.43	3e
	$HOP-1^{b}$	275	/ <sup>c</sup>	7.0	36	0.05	3f
	FDM-15	749	0.436	11.5	430	0.65	This work
Hydroge	$HOF-4^b$	312	0.899	3.8×8.1	/ <i>c</i>	/ <i>c</i>	4a
n	SOF-1a <sup>d</sup>	474	0.930	7.4	143	0.23	4b
bonding	HOF-8	/ <i>c</i>	1.132	6.8×3.4	/ <sup>c</sup>	/ <sup>c</sup>	4c
and $\pi$ – $\pi$	$HOF-2^d$	238	0.883	4.8	/ <i>c</i>	0.13	4d
stacking	$BTI^{e}$	/ <i>c</i>	1.545	3.8	/ <sup>c</sup>	/ <sup>c</sup>	4e
	BTI-F <sup>b,e</sup>	131	1.713	4.6×4.2	/ <sup>c</sup>	/ <sup>c</sup>	4e

Table S2. Comparison of gas adsorption results of extrinsic porous HOF materials.<sup>a</sup>

<sup>*a*</sup> The surface area and pore size were calculated by N<sub>2</sub> adsorption isotherms, and interpreted by the BET theory and the NLDFT method. The density reported were based on solvent-free frameworks. <sup>*b*</sup> Determined by CO<sub>2</sub> adsorption at 196 K. <sup>*c*</sup> Not reported. <sup>*d*</sup> Calculated from N<sub>2</sub> adsorption at 125 K and 1 bar. <sup>*e*</sup> BTI: benzo-trisimidazole; BTI-F: benzo-tris((trisfluoromethyl)- imidazole).

### 5. <sup>1</sup>H NMR Analysis of Aromatic Molecules Adsorption.

<sup>1</sup>H NMR spectra were obtained at 400 MHz with an AVANCE III HD spectrometer at 298 K. FDM-15 crystals were soaked in benzene, toluene, *p*-xylene, *o*-xylene, *m*-xylene, ethylbenzene, and styrene, respectively. After three days, these crystals were collected by filtering and then evacuated under vacuum at room temperature for 24 h. These crystals adsorbing different guest molecules were then dissolved in DMSO-*d*<sub>6</sub> and tested by <sup>1</sup>H-NMR spectroscopy, respectively (Table S3 lists the comparison of gas adsorptions of selective HOF materials).

As for the mixtures adsorption, FDM-15 crystals were soaked in the mixtures of p-

xylene/toluene, *p*-xylene/o-xylene, and *p*-xylene/ethylbenzene at the molar ratios of 1:1, respectively. After three days, these crystals were collected by filtering and then evacuated under vacuum at room temperature for 24 h. These crystals adsorbing different guest molecules were then dissolved in DMSO- $d_6$  and tested by <sup>1</sup>H-NMR spectroscopy, respectively.



**Fig. S3.** <sup>1</sup>H-NMR spectrum of FDM-15 adsorbing benzene after dissolution in DMSO- $d_6$ . Peak at 7.37 ppm corresponds to benzene, and peaks at 12.29, 8.07, 7.61, and 5.73 ppm correspond to H<sub>3</sub>TBI. The molar ratio (0.86:1.00) of benzene adsorbed by FDM-15 to H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.



**Fig. S4.** <sup>1</sup>H-NMR spectrum of FDM-15 adsorbing toluene after dissolution in DMSO- $d_6$ . Peaks at 7.20 and 2.30 ppm correspond to toluene, and peaks at 12.27, 8.06, 7.61, and 5.72 ppm correspond to H<sub>3</sub>TBI. The molar ratio (0.74:1.00) of toluene adsorbed by FDM-15 to H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.



**Fig. S5.** <sup>1</sup>H-NMR spectrum of FDM-15 adsorbing *p*-xylene after dissolution in DMSO-*d*<sub>6</sub>. Peaks at 7.05 and 2.27 ppm correspond to *p*-xylene, and peaks at 12.25, 8.06, 7.60, and 5.72 ppm correspond to H<sub>3</sub>TBI. The molar ratio (1.30:1.00) of *p*-xylene adsorbed by FDM-15 to H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.



**Fig. S6.** <sup>1</sup>H-NMR spectrum of FDM-15 adsorbing *o*-xylene after dissolution in DMSO-*d*<sub>6</sub>. Peaks at 7.09 and 2.21 ppm correspond to *o*-xylene, and peaks at 12.27, 8.06, 7.61, and 5.72 ppm correspond to H<sub>3</sub>TBI. The molar ratio (0.92:1.00) of *o*-xylene adsorbed by FDM-15 to H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.



**Fig. S7.** <sup>1</sup>H-NMR spectrum of FDM-15 adsorbing *m*-xylene after dissolution in DMSO- $d_6$ . Peaks at 7.13, 6.99, 6.96, and 2.26 ppm correspond to *m*-xylene, and peaks at 12.29, 8.07, 7.61, and 5.73 ppm correspond to H<sub>3</sub>TBI. The molar ratio (0.96:1.00) of *m*-xylene adsorbed by FDM-15 to H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.



**Fig. S8.** <sup>1</sup>H-NMR spectrum of FDM-15 adsorbing ethylbenzene after dissolution in DMSO- $d_6$ . Peaks at 7.23, 2.59, and 1.17 ppm correspond to ethylbenzene, and peaks at 8.15, 7.63, and 5.76 ppm correspond to H<sub>3</sub>TBI. The molar ratio (0.80:1.00) of ethylbenzene adsorbed by FDM-15 to H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.



**Fig. S9.** <sup>1</sup>H-NMR spectrum of FDM-15 adsorbing styrene after dissolution in DMSO- $d_6$ . Peaks at 7.47, 7.35, 7.28, 6.73, 5.83, and 5.26 ppm correspond to styrene, and peaks at 12.27, 8.06, 7.61, and 5.72 ppm correspond to H<sub>3</sub>TBI. The molar ratio (1.02:1.00) of styrene adsorbed by FDM-15 to H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.

Table S3. Molecular ratios of the aromatic compounds with H<sub>3</sub>TBI in FDM-15 after incorporation.<sup>a</sup>

Guest	Benzene	Toluene	Styrene	p-Xylene	o-Xylene	<i>m</i> -Xylene	Ethylbenzene
Molar							
ratio	0.96.1.00	0 74.1 00	1.02.1.00	1 20.1 00	0.02.1.00	0.06.1.00	0.90.1.00
VS	0.86:1.00 0	0.74:1.00	1.02:1.00	1.50:1.00	0.92:1.00	0.96:1.00	0.80:1.00
H <sub>3</sub> TBI							

<sup>*a*</sup> The molar ratios of adsorbates with H<sub>3</sub>TBI were determined by <sup>1</sup>H-NMR spectroscopy.



**Fig. S10.** <sup>1</sup>H NMR spectrum of FDM-15 soaked in the mixture of *p*-xylene/toluene after dissolution in DMSO- $d_6$ . Peaks at 7.05 and 2.24 ppm correspond to *p*-xylene, and peaks at 12.34, 8.09, 7.61, and 5.74 ppm correspond to H<sub>3</sub>TBI. The molar ratio (0.80:0.00:1.00) of *p*-xylene and toluene adsorbed by FDM-15 with H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy. No toluene molecules were adsorbed by FDM-15.



**Fig. S11.** <sup>1</sup>H NMR spectrum of FDM-15 soaked in the mixture of *p*-xylene/*o*-xylene after dissolution in DMSO- $d_6$ . Peaks at 7.07 and 2.24 ppm correspond to *p*-xylene, peaks at 7.07 and 2.21 ppm correspond to *o*-xylene, and peaks at 12.25, 8.06, 7.60, and 5.72 ppm correspond to H<sub>3</sub>TBI. The molar ratio (0.73:0.39:1.00) of *p*-xylene and *o*-xylene adsorbed by FDM-15 with H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.



**Fig. S12.** <sup>1</sup>H NMR spectrum of FDM-15 soaked in the mixture of *p*-xylene/ethylbenzene after dissolution in DMSO-*d*<sub>6</sub>. Peaks at 7.05 and 2.24 ppm correspond to *p*-xylene, peaks at 7.23, 2.59, and 1.17 ppm correspond to ethylbenzene, and peaks at 12.30, 8.07, 7.61, and 5.73 ppm correspond to H<sub>3</sub>TBI. The molar ratio (0.55:0.39:1.00) of *p*-xylene and ethylbenzene adsorbed by FDM-15 with H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.

#### 6. Studies on Fullerene Adsorption.

UV/Vis spectra were acquired on a UV-2550 UV-Visible Spectrophotometer in the 310 to 450 nm region using toluene as blank control trial. Elemental analysis was carried out by Shanghai Institute of Organic Chemistry, Chinese Academy of Science. UV/Vis diffuse reflectance adsorption spectra were collected on a Lambd50 UV-Visible Spectrophotometer in the 250 to 800 nm region using BaSO<sub>4</sub> as blank control trial. At least three parallel experiments have been carried out to confirm the amounts of fullerene and H<sub>3</sub>TBI.

For a typical adsorption procedure, ~ 25 mg FDM-15 crystals were added to a 25 mL capped jar with a solution of 20 mg  $C_{60}$  in 15 mL toluene. After three days, clear solution on the top was sampled twice for testing in order to calculate the amount of residual  $C_{60}$  in toluene. According to the standard plot in Fig. S13, 3.58 mg of  $C_{60}$  was adsorbed by FDM-15. After that, FDM-15 crystals were washed extensively with pure toluene and collected by filtration. Finally, they were evacuated under vacuum at room temperature for 24 h, which was weighed for further calculation. On the other hand, elemental analysis was performed twice to calculate the amount of  $H_3TBI$  in the sample. According to all these parallel experiments data mentioned above, the molecular ratio of  $H_3TBI$ /toluene/C<sub>60</sub> was 1:1.065:0.088.

In order to remove the toluene molecules within the channels, we tried different activated temperatures under vacuum. The <sup>1</sup>H-NMR spectroscopy showed no obvious decrease in the amount of toluene after being heated at 120 °C under vacuum for 24 h compared to room temperature, while nearly half of toluene was removed when the heating temperature was increased to 200 °C (Fig. S14 and S15). UV/Vis diffuse reflectance adsorption of C60@FDM-15 showed a significant enhancement of absorbance in the visible region, which agrees with our observation on the darker color of the crystals after adsorption (Fig. S16).



Fig. S13. UV/Vis adsorption spectrum of C<sub>60</sub> in toluene.



Fig. S14. The standard plot of absorbance of C<sub>60</sub> in toluene versus concentration.



**Fig. S15.** <sup>1</sup>H NMR spectrum of FDM-15 adsorbing  $C_{60}$  from toluene solution after being heated at 120 °C under vacuum for 24h and then dissolution in DMSO-*d*<sub>6</sub>. Peaks at 7.00 and 2.30 ppm correspond to toluene, and peaks at 12.25, 8.05, 7.60 and 5.72 ppm correspond to H<sub>3</sub>TBI. The molar ratio (0.73:1.00) of toluene adsorbed by FDM-15 to H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.



**Fig. S16.** <sup>1</sup>H NMR spectrum of FDM-15 adsorbing  $C_{60}$  from toluene solution after being heated at 200 °C under vacuum for 24h and then dissolution in DMSO-*d*<sub>6</sub>. Peaks at 7.18 and 2.30 ppm correspond to toluene, and peaks at 12.31, 8.09, 7.61 and 5.74 ppm correspond to H<sub>3</sub>TBI. The molar ratio (0.48:1.00) of toluene adsorbed by FDM-15 to H<sub>3</sub>TBI was calculated by <sup>1</sup>H-NMR spectroscopy.



Fig. S17. UV/Vis diffuse reflectance adsorption spectra of C<sub>60</sub>, FDM-15, and C<sub>60</sub>@FDM-15.

### 7. Studies on Thermal Stability.

The thermogravimetric analysis (TGA) was performed on a TGA8000 Thermogravimetric Analyzer with a heating rate of 10 °C/min from 25 to 800 °C in the air atmosphere. TGA curve of activated FDM-15 showed no obvious weight loss until 460 °C, which represented the beginning of the complete decomposition of FDM-15.



Fig. S18. Thermogravimetric Analyses (TGA) curve of activated FDM-15.



**Fig. S19.** 77 K low pressure  $N_2$  adsorption isotherm of FDM-15 activated by heating at 473 K under vacuum (solid symbols represent adsorption, while open symbols represent desorption).

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