# **Supporting Information**

# Stepwise Adsorption in a Mesoporous Metal-Organic Framework: Experimental and Computational Analysis

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#### **Experimental General Information**

Commercially available reagents were used as received without further purification. Elemental analyses (C, H, and N) were obtained by Atlantic Microlab, Inc.. Nuclear magnetic resonance (NMR) data were collected on a Mercury 300 spectrometer. The powder X-ray diffraction patterns (PXRD) were recorded on a Bruker D8 Discover diffractometer equipped with a Cu sealed tube ( $\lambda = 1.54178$  Å) at a scan rate of 1 s deg<sup>-1</sup>. Powder samples were dispersed on low-background quartz discs (G. M. Associates, Inc., Oakland, California) for analyses. Simulation of the PXRD spectra was carried out by the single-crystal data and diffraction-crystal module of the Mercury program available free of charge via internet at http://www.ccdc.cam.ac.uk/free\_services/mercury/. Thermogravimetric analysis (TGA) was obtained under N<sub>2</sub> atmosphere on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 2 °C min<sup>-1</sup>. Mössbauer spectra were collected on a Model MS4 WRC spectrometer (SEE Co., Edina, MN) and were calibrated using an  $\alpha$ -Fe foil.

#### Synthesis of H<sub>3</sub>BTTC, Benzo-(1,2;3,4;5,6)-tris(thiophene-2'-carboxylic acid.

The H<sub>3</sub>BTTC ligand was synthesized following the literature method.<sup>[1,2]</sup>



Synthesis of PCN-53. A mixture of H<sub>3</sub>BTTC (5.0 mg, 0.013 mmol),  $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$  (15 mg, 0.038 mmol) in 0.2 ml DMF, 1.2 mL DMSO and 3 drop 40% HBF<sub>4</sub> was sealed in a Pyrex glass tube (ID 8 mm/OD 10 mm) and heated to 120 °C at a rate of 1 °C min<sup>-1</sup>. (*Caution! Extreme care should be exercised during the reaction because of high pressure developed in the reaction. The glass tubes should be put in a blast shield.*) After staying at 120 °C for 5 days, it was cooled to 25 °C at a rate of 0.1°C / min to produce red block crystals of PCN-53 (6.3 mg, 56 % yield based on H<sub>3</sub>BTTC) with a formula of Fe<sub>3</sub>O(H<sub>2</sub>O)<sub>3</sub>(BTTC)<sub>2</sub>·10(DMF). This formula was derived from crystallographic data, elemental analysis (calculated for C<sub>60</sub>H<sub>82</sub>Fe<sub>3</sub>N<sub>10</sub>O<sub>26</sub>S<sub>6</sub>: C, 41.92; H, 4.81; N, 8.15. Found: C, 42.01; H, 4.68; N, 8.32 %) and TGA.

#### X-ray Crystallography

Single crystal X-ray data of PCN-53 were collected on beamline 15ID-B at the Advanced Photon source in Argonne National Laboratory. Structures were solved by direct method and refined by full-matrix least-squares on  $F^2$  using *SHELXTL*.<sup>[3]</sup> Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to  $1.2 \times U_{eq}$  of the attached atom. The solvent molecules are highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. Contributions to scattering due to these solvent molecules were removed using the *SQUEEZE* routine of *PLATON*;<sup>[4]</sup> structures were then refined again using the data generated.

Crystal data for PCN-53:  $C_{30}H_{12}Fe_{3}O_{16}S_{6}$ , Mr = 988.31, red prism, 0.09 × 0.07 × 0.07 mm<sup>3</sup>, cubic, space group *Fd-3m*, *a* = 50.817(2) Å, *V* = 131227(9) Å<sup>3</sup>, *Z* = 48, *D*<sub>c</sub> = 0.600 g cm<sup>-3</sup>,  $F_{000}$  = 23712, synchrotron radiation,  $\lambda$ = 0.44280 Å, T = 163(2) K,  $2\theta_{max}$  = 33.9°, 356952 reflections collected, 7161 unique ( $R_{int}$  = 0.0871). Final *GooF* = 1.109,  $R_1$  = 0.0676,  $wR_2$  = 0.1818, *R* indices based on 5818 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 163 parameters, 12 restraints.  $\mu$  = 0.143 mm<sup>-1</sup>. CCDC 823155 contains the supplementary crystallographic data for this paper. These data can be

obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### **Low-Pressure Sorption Measurements**

Gas sorption isotherm measurements were performed on a Micromeritics ASAP 2020 Surface Area and Pore Size Analyzer. Before the measurements, the samples of PCN-53 were washed with  $CH_2Cl_2$  3 times. The wet sample was then evacuated at 120°C for 6 h to remove the included solvent molecules and yield an activated sample. UHP-grade N<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub> and Ar source was used in the sorption measurements. In the hydrogen sorption measurement, high purity hydrogen (99.9995%) was used. The temperature was maintained at 77 K with liquid nitrogen or 87 K with liquid argon or 195 K with dry ice / acetone throughout the entire measurement.

#### **High-Pressure Gas Sorption Measurements**

High pressure excess adsorption of H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> of PCN-53 were measured using an automated controlled Sieverts' apparatus (PCT-Pro 2000 from Setaram) at 77 K (liquid nitrogen bath) or 298 K (room temperature). About 800 mg of activated sample were loaded into a sample holder under an argon atmosphere. Before measurements, the sample was degassed at 100°C overnight. The free volume was determined by the expansion of low-pressure He (<5 bar) at room temperature. The temperature gradient between gas reservoir and sample holder was corrected by applying a correction factor to the raw data, which was obtained by replacing the sample with a polished stainless-steel rod and measuring the adsorption isotherm at the same temperature over the requisite pressure regime. The total gas uptake was calculated by:  $N_{\text{total}} = N_{\text{excess}} + Q_{\text{bulk}}V_{\text{pore}}$ , where  $Q_{\text{bulk}}$  equals to the density of compressed gases at the measured temperature and  $V_{\text{pore}}$  was obtained from the N<sub>2</sub> isotherm at 77 K.<sup>[5]</sup>

#### Bond Valence Analysis<sup>[6,7]</sup>

Bond-valence analysis were performed using *PLATON*;<sup>[4]</sup> bond-valence sum for Fe atom were listed.

Fe(1)	(II)	$V_{sum} = 2.33$	$D_{max} = 2.1810$	$N_{Sum} = 6$
Fe(2)	(III)	$V_{sum} = 2.71$	$D_{max} = 2.1260$	$N_{sum} = 6$

Bond Valence Analysis - Assume Valence = 2 -- Min. BondVal Contribution = 0.04 \* Cation Val.

Nr	Bond	Dist	R	В	$B_{\rm Val}$	Sum	Diff
1	Fe(1)-O(4)	2.0590	1.7340	0.37	0.415	0.415	1.585
2	Fe(1)-O(1)	2.0700	1.7340	0.37	0.403	0.819	1.181
3	Fe(1)-O(1)q	2.0700	1.7340	0.37	0.403	1.222	0.778
4	Fe(1)-O(1)*	2.0700	1.7340	0.37	0.403	1.625	0.375
5	Fe(1)-O(1)*	2.0700	1.7340	0.37	0.403	2.029	0.029
6	Fe(1)-O(5)	2.1810	1.7340	0.37	0.299	2.327	0.327

Bond Valence Analysis - Assume Valence = 3 -- Min. BondVal Contribution = 0.04 \* Cation Val.

Nr	Bond	Dist	R	В	$\mathbf{B}_{\mathrm{Val}}$	Sum	Diff
1	Fe(1)-O(4)	2.0590	1.7590	0.37	0.444	0.444	2.556
2	Fe(1)-O(1)	2.0700	1.7590	0.37	0.431	0.876	2.124
3	Fe(1)-O(1)q	2.0700	1.7590	0.37	0.431	1.307	1.693
4	Fe(1)-O(1)*	2.0700	1.7590	0.37	0.431	1.739	1.261
5	Fe(1)-O(1)*	2.0700	1.7590	0.37	0.431	2.170	0.830
6	Fe(1)-O(5)	2.1810	1.7590	0.37	0.320	2.490	0.510

Bond Valence Analysis - Assume Valence = 2 -- Min. BondVal Contribution = 0.04 \* Cation Val.

Nr	Bond	Dist	R	В	$\mathbf{B}_{\mathrm{Val}}$	Sum	Diff
1	Fe(2)-O(2)	2.0310	1.7340	0.37	0.448	0.448	1.552
2	Fe(2)-O(2)*	2.0310	1.7340	0.37	0.448	0.896	1.104
3	Fe(2)-O(4)	2.0420	1.7340	0.37	0.435	1.331	0.669
4	Fe(2)-O(3)*	2.0470	1.7340	0.37	0.429	1.760	0.240
5	Fe(2)-O(3)*	2.0470	1.7340	0.37	0.429	2.190	0.190
6	Fe(2)-O(6)	2.1260	1.7340	0.37	0.347	2.536	0.536

Nr	Bond	Dist	R	В	$\mathbf{B}_{\mathrm{Val}}$	Sum	Diff
1	Fe(2)-O(2)	2.0310	1.7590	0.37	0.479	0.479	2.521
2	Fe(2)-O(2)*	2.0310	1.7590	0.37	0.479	0.959	2.041
3	Fe(2)-O(4)	2.0420	1.7590	0.37	0.465	1.424	1.576
4	Fe(2)-O(3)*	2.0470	1.7590	0.37	0.459	1.883	1.117
5	Fe(2)-O(3)*	2.0470	1.7590	0.37	0.459	2.343	0.657
6	Fe(2)-O(6)	2.1260	1.7590	0.37	0.371	2.713	0.287

Bond Valence Analysis - Assume Valence = 3 -- Min. BondVal Contribution = 0.04 \* Cation Val.

#### **Topology analysis**

The analysis of local and global topology of PCN-53 was made with the program package *TOPOS* 4.0.<sup>[8]</sup>

Topology for node1 (N1)

## Node N2 links by bridge ligands and has

Comm	ion vertex w	ith			R(A-A)	f
N1	0.6250	0.8302	0.1250	(10-1)	7.391 A	1
N1	0.6698	0.8750	-0.1250	(0 1 -1)	8.194 A	1
N1	0.8750	0.8750	0.0802	(0 0 0)	8.194 A	1

Topology for node2 (N2)

Node N1 links by bridge ligands and has

Comr	non vertex w	ith			R(A-A)	f
N2	0.7773	0.7773	0.1257	(0 1-1)	7.391 A	1
N2	0.9727	0.9727	0.1257	(0 1-1)	7.391 A	1
N2	0.8743	1.0273	0.0273	(1 1 0)	8.194 A	1
N2	0.8757	0.7227	0.0273	(0 0 0)	8.194 A	1
N2	0.7227	0.8757	0.0273	(0 0 0)	8.194 A	1

N2	1.027	3 (	0.8743	0.02	273	(1 1 0)		8.194 A	1	
Structu	ıral grou	ıp analy	sis							
Coordi	ination s	sequence	es							
N2:	1	2	3	4	5	6	7	8	9	10
Num	3	13	14	44	34	97	73	185	118	283
Cum	4	17	31	75	109	206	279	464	582	865
N1:	1	2	3	4	5	6	7	8	9	10
Num	6	8	28	23	68	54	146	99	236	136
Cum	7	15	43	66	134	188	334	433	669	805
TD10=	=845									

Vertex symbols for selected sublattice

N2 Point symbol: {4^2.6}

Extended point symbol: [4.4.6(3)]

N1 Point symbol:{4^4.6^4.8^6.10}

Extended point symbol: [4.4.4.6.6.6(2).6(2).8(2).8(2).8(2).8(2).8(3).8(3).10(8)]

Point symbol for net: {4^2.6}2{4^4.6^4.8^6.10}

3,6-c net with stoichiometry (3-c)2(6-c); 2-nodal net

New topology (71801 types in 11 databases)



Fig. S1. <sup>57</sup>Fe-Mössbauer spectra of PCN-53.



Fig. S2. TGA of PCN-53.



Fig. S3. PXRD of PCN-53.



Fig. S4.  $N_2$  sorption isotherms of PCN-53 at 77 K



**Fig. S5.**  $V(P_0-P)$  vs.  $P/P_0$  for PCN-53 (N2 isotherm at 77 K). Only the range below  $P/P_0 = 0.2$  satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.



Fig. S6. Ar sorption isotherms of PCN-53 at 87 K



Fig. S7. CO<sub>2</sub> sorption isotherms of PCN-53 at 195 K



Fig. S8.  $H_2$  sorption isotherms of PCN-53 at 77 K and 87 K



Fig. S9. The virial fitting graph for H<sub>2</sub> uptake isotherms of PCN-53 at 77 K and 87 K.



**Fig. S10.** Coverage dependence of the isosteric heat of adsorption for H<sub>2</sub> in PCN-53 calculated from fits of its 77 and 87 K isotherms.



Fig. S11. Gravimetric and volumetric H<sub>2</sub> uptake in PCN-53 at 77 K



Fig. S12. Gravimetric and volume ratio CH<sub>4</sub> uptake in PCN-53 at 295 K



Fig. S13. Gravimetric and volume ratio CO<sub>2</sub> uptake in PCN-53 at 295 K

# **Computational Details**

#### Partial Charges on Sorbent Atoms

Electronic structure calculations were performed with the Gaussian 09 software.<sup>[9]</sup> We used the M06<sup>[10]</sup> density functional along with the 6-31G\* basis set to compute the electronic structures of two fragments of the PCN-53 structure (Fig. S14). All atoms were held fixed in their crystallographically determined positions. Dangling bonds on fragment atoms were capped with H atoms. Partial charges on framework atoms were derived from these calculations using the ChelpG method,<sup>[11]</sup> which is a grid based method that calculates nucleus-centered partial charges in order to reproduce the electrostatic potential outside of the van der Waals radii of all the atoms.

van der Waals radii were obtained from webelements.com and are given in Table S1. All electronic structure calculations were performed self-consistently, and electronic structures were considered to be converged when the change in the density matrix and change in electronic energy between subsequent iterations fell below  $10^{-6}$  Å<sup>-3</sup> and  $10^{-6}$  Ha, respectively. The partial charges used in adsorption simulations are given in Table S2.



Fig. S14. PCN-53 fragments used to obtain partial charges on framework atoms. Distinct carbon and oxygen atoms are labeled.

Element	van der Waals radius (Å)
Fe <sup>a</sup>	1.40
S	1.80
С	1.70
Н	1.20
0	1.52

Table S1. van der Waals radii from webelements.com.

<sup>a</sup>atomic radius (empirical) used due to lack of data for van der Waals radius

Framework atom	Partial charge
Fe	1.25
S	0.0
Ca	0.8
Cb	-0.2
Cc	0.0
C <sub>d</sub>	0.2
C <sub>e</sub>	-0.225
Н	0.15
Oa	-0.6
Ob	-0.9

 Table S2.
 Partial charges on framework atoms used in adsorption simulations.

#### Grand Canonical Monte Carlo Simulations

Adsorption simulations were performed with our in-house multipurpose code RASPA.<sup>[12]</sup> Positions of framework atoms were taken from crystallography and held fixed throughout the simulations. Sorbate/sorbate and sorbate/sorbent interactions were calculated with a Lennard-Jones (LJ) + Coulomb potential. Sorbate molecules were assumed to be rigid and modeled as follows:

- The N<sub>2</sub> molecule has a N-N bond length of 1.16 Å. It has LJ sites on both N nuclei and Coulomb sites on the N nuclei and at the center of mass.
- CO<sub>2</sub> is linear with C-O bond lengths of 1.10 Å. It has LJ and Coulomb sites on all three nuclei.
- Ar is a sphere with a LJ site at the center.
- The H<sub>2</sub> molecule is a sphere with a LJ site at the center of mass.

Lennard-Jones parameters for framework atoms were taken from the DREIDING force field<sup>[13]</sup> except for Fe, which were taken from the Universal Force Field<sup>[14]</sup> because they were unavailable in DREIDING. LJ parameters for sorbate atoms were

taken from the TraPPE force field<sup>[15]</sup> except for H<sub>2</sub>, which were taken from empirical data based on the second virial coefficient,<sup>[16]</sup> and cross-terms were obtained using Lorentz-Berthelot mixing rules.<sup>[17]</sup> All LJ parameters are provided in Table S3. Partial charges on sorbent molecules were computed with quantum chemistry, as discussed above. Partial charges on sorbate molecules were taken from the TraPPE force field where applicable. They are as follows: in  $CO_2$ , C = 0.7, O = -0.35; in  $N_2$ , N = -0.482, center of mass = 0.964.

Sorbate-Sorbate Interaction Parameters							
	<i>i</i> (sorbate atom)	$\sigma_{ij}$ (Å)	$\varepsilon_{ij}/k_B(\mathbf{K})$				
	N (N <sub>2</sub> )	3.31	36.0				
	C (CO <sub>2</sub> )	2.80	27.0				
	$O(CO_2)$	3.05	79.0				
	Ar	3.40	119.8				
	H <sub>2</sub>	2.958	36.7				
<i>i</i> (sorbate atom)	<i>j</i> (sorbate atom)	$\sigma_{ij}$ (Å)	$\varepsilon_{ij}/k_B(\mathbf{K})$				
C (CO <sub>2</sub> )	$O(CO_2)$	2.925	46.184				
	Sorbate-Sorbent Int	eraction Parameters					
<i>i</i> (sorbate atom)	<i>j</i> (framework atom)	$\sigma_{ij}$ (Å)	$\varepsilon_{ij}/k_B(\mathbf{K})$				
N (N <sub>2</sub> )	Fe	3.678	31.578				
	S	3.453	70.476				
	C	3.39	41.508				
	Н	3.08	16.595				
	0	3.17	45.651				
C (CO <sub>2</sub> )	Fe	3.423	27.348				
	S	3.198	61.034				
	С	3.135	35.947				
	Н	2.825	14.372				
	0	2.915	3.071				
$O(CO_2)$	Fe	3.548	46.779				
	S	3.323	104.401				
	С	3.26	61.489				
	Н	2.95	24.584				
	0	3.04	61.701				
Ar	Fe	3.723	57.606				
	S	3.498	128.564				
	С	3.435	75.721				
	Н	3.125	30.273				
	0	3.215	75.981				
$H_2$	Fe	3.502	31.884				
	S	3.277	71.158				
	С	3.214	41.910				
	Н	2.904	16.756				
	0	2.994	42.054				

 Table S3. Lennard-Jones parameters for adsorption simulations.

Prior research indicates that quantum diffraction effects contribute significantly to adsorption for  $H_2$  and other light molecules at cryogenic temperatures.<sup>[18,19]</sup> We included these effects using the Feynman-Hibbs (FH) effective potential.<sup>[19,20]</sup>

$$\mathcal{V}_{ij}^{\rm FH}(r_{ij}) = \mathcal{V}_{ij}^{\rm LJ}(r_{ij}) + \left(\frac{\hbar^2}{24\mu k_B T}\right) \nabla \mathcal{V}_{ij}^{\rm LJ}(r_{ij}) \qquad \text{Eq. S1}$$

Here  $\psi^{\text{LJ}}$  represents the Lennard-Jones potential,  $r_{ij}$  is the sorbate/sorbate or sorbate/sorbent atom distance,  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $\mu = m_i m_j / (m_i + m_j)$  is the reduced mass,  $k_B$  is Boltzmann's constant, and *T* is the adsorption temperature. Adsorbate loadings and heats of adsorption were computed using grand canonical Monte Carlo (GCMC). In each simulation, 100,000 cycles were performed for system equilibration, and an additional 100,000 cycles were performed to compute ensemble averages. In one cycle, an average of *N* moves was performed, where *N* is the number of molecules in the system (which fluctuates during a GCMC simulation). Monte Carlo moves used were translation, rotation, insertion, deletion, and random reinsertion at a new position in the framework.

### Calculation of $Q_{st}$

The isosteric heats of adsorption average over all sorbate molecules in the system and were calculated using grand canonical Monte Carlo (GCMC) simulations.

$$Q_{\rm st} = RT - \left(\frac{\partial \langle \psi \rangle \langle N \rangle}{\partial \langle N \rangle}\right)_{T,V}$$
 Eq. S2

where  $\mathcal{V}$  is the potential energy per sorbate molecule, *N* is the number of molecules, *R* is the ideal gas constant, *T* is the temperature, and *V* is the volume.<sup>[21]</sup> The brackets in Eq. S2 indicate ensemble averages.

# Surface Area Calculations

Surface areas were calculated geometrically from the crystal structures using a  $N_2$  probe in the same manner as described in Ref.<sup>[22]</sup> Framework atom diameters used in these calculations are given in Table S4.

	Diameter (Å)
Fe	3.68
С	3.39
0	3.17
S	3.45
Н	3.08

 Table S4.
 Framework atom diameters used in the surface area calculations.

#### **Computational Results**



Fig. S14. Experimental and simulated H<sub>2</sub> adsorption isotherms in PCN-53 at 77 K.



**Fig. S15.** Experimental and simulated H<sub>2</sub> adsorption isotherms in PCN-53 plotted on a logarithmic scale at 77 K.



Fig. S16. Snapshots of CO<sub>2</sub> adsorption along the isotherm taken in PCN-53 at 195 K.



Fig. S17. Snapshots of  $CO_2$  adsorption along the isotherm taken in PCN-53 at 195 K, plotted on a logarithmic scale. Black = simulated data, grey = experimental data.



**Fig. S18.** Snapshots of Ar adsorption along the isotherm taken in PCN-53 at 87 K. Black = simulated data, grey = experimental data.



**Fig. S19.** Snapshots of Ar adsorption along the isotherm taken in PCN-53 at 87 K, plotted on a logarithmic scale. Black = simulated data, grey = experimental data.



Fig. S20. Inflections in N<sub>2</sub> isotherms calculated at 77 K at low (left) and high pressure (right). Inflections correspond with increases in Q<sub>st</sub> due to favorable N<sub>2</sub>-N<sub>2</sub> interactions (see the main text.)



**Fig. S21.** Simulated (gray) and experimentally observed (black) isotherms for  $N_2$  adsorption at 77 K in PCN-53. Simulated isotherms were obtained using the methods described above, but with the Lennard-Jones  $\varepsilon$  values for interactions between N (in N<sub>2</sub>) and the framework atoms scaled by 0.75 of the values in Table S3.



**Fig. S21.** Three types of cavities in PCN-53 (diameter: blue 10 Å; red 12 Å; yellow 25 Å).

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