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Supplementary Information

Balancing gravimetric and volumetric hydrogen density in MOFs

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1. EXPERIMENTAL DETAILS

1.1 General considerations. All reagents were obtained from commercial sources and used as received unless otherwise noted. $Zn(NO_3)_2$ •6H₂O (Fisher), 1,4-benzenedicarboxylic acid (Acros), N,N-diethylformamide (DEF, TCI), anhydrous N,N-dimethylformamide (DMF, Sigma-Aldrich) was used as received. CH_2Cl_2 was dried over activated alumina under nitrogen. Crystal structures were characterized by powdered X-ray diffraction (PXRD), using a Bruker D8 advance diffractometer equipped with a 60 mm sealed Göbel mirror and a LynxEye linear position sensitive detector. The Cu-K α X-ray source was operated at 40 kV and 40 mA. Samples were deposited on Fisherfinest Premium microscopic slides and were measured while still in solvent. BET surface areas and pore volumes were measured by nitrogen adsorption and desorption at 77 K from 0.005 to 1 bar using a NOVA e-series 4200 surface area analyzer from Quantachrome Instruments (Boynton Beach, Florida, USA).

1.2 Synthesis of MOF-5. MOF-5 was prepared according to literature procedure.¹ To four 120 mL wide mouth jars with Teflon-lined lids were added $Zn(NO_3)_2 \cdot 6H_2O$ (1.80 g, 6.05 mmol) and 1,4-benzenedicarboxylic acid (0.33 g, 2.0 mmol), followed by DEF (50 mL). The mixtures were allowed to fully dissolve, then placed in a prethermostated oven at 80 °C. Crystals were not observed after 18 h in the oven in any of the vessels. Heating was continued until the bottom and sides of the jars were covered by a layer of clear cubic-shaped crystals (additional 14 h). The reactions were removed from the oven and allowed to cool to room temperature. The crystals were then consolidated as quickly as possible into a single jar keeping the crystals fully submerged in the reaction. Using a modified Teflon-lined lid to allow for Schlenk-type techniques to be used, all subsequent manipulations were carried out with anhydrous solvents under a nitrogen atmosphere. The reaction solvent was removed via syringe under a counter flow of nitrogen. The remaining crystals were then washed with anhydrous DMF (6 x 50 mL) under nitrogen using syringe techniques over 48 h. Next the sample was washed with CH₂Cl₂ (6 x 50 mL) under nitrogen using syringe techniques over 48 h. The sample was then transferred into an oven dried gas sorption tube outfitted with a vacuum adaptor and a Teflon metering valve. Using the metering valve, all solvent was then slowly removed under high vacuum at room temperature (~ 1 x 10⁻⁴ torr) to yield clear colorless crystals. At this point the valve was opened fully and the sample was left under vacuum overnight to yield 0.294 g (average yield = 14.5 %). All subsequent manipulations were carried out in a nitrogen filled glovebox.

1.3 Synthesis of IRMOF-20. IRMOF-20 was prepared according to literature procedure.² To a 500 mL wide mouth jar were added $Zn(NO_3)_2 \cdot 4H_2O$ (6.0 g, 23 mmol) and thieno[3,2-b]thiophene-2,5-dicarboxylic acid (1.50 g, 6.57 mmol), followed by DEF (200 mL). The jar was sealed and the mixture was allowed to fully dissolve before placing in a prethermostated oven at 100 °C for approximately 18 h. The reaction was allowed to cool to room temperature prior to decanting the mother liquor away from the crystals that formed. The crystals were then washed with DMF and soaked in CHCl₃ for at least 3 days to activate them. Each day the solvent was decanted and replaced with fresh CHCl₃. The contents were then transferred to a large glass tube outfitted with a vacuum adaptor and all solvent was removed under vacuum at room to yield clear cubic crystals. The tube was then flamed sealed under vacuum for storage. All subsequent manipulations were handled in a nitrogen filled glovebox.

1.4 Synthesis of SUKYON. SUKYON was prepared according to literature procedure.³ To a 25 mL round-bottom flask was added methanetetra(bi-phenyl-*p*-carboxylic acid) (40 mg, 0.05 mmol), $Cu(NO_3)_2 \cdot 2.5H_2O$ (80 mg, 0.34 mmol), and DMF/H₂O (18 mL/2 mL). The mixture was sonicated to a light blue cloudy solution. Eight drops of 3N HCl was added, and the solution turned yellowish green. The solution was heated gently to almost clear, then allowed to cool to room temperature. The solution was taken up in a syringe and filtered through PTFE microfilters into two 20 mL vials (10 mL in each). After the vials were heated in an oven at 85 °C for 51 h and cooled to room temperature, the light greenish blue crystals were combined, washed with fresh DMF (10 mL x 2), and activated by flowing supercritical CO_2 to provide deep blue crystals (32 mg).

1.5 Synthesis of EPOTAF (SNU-21). EPOTAF was prepared according to literature procedure.⁴ In a 60 mL jar, tetrakis[(4-carboxyphenyl)oxamethyl]methane (165 mg, 0.27 mmol) was dissolved in DMF/1,4-dioxane (15 mL/15 mL), and the mixture was sonicated for 2 min to a clear solution. A solution of $Cu(NO_3)_2$ •2.5H₂O (125 mg, 0.55 mmol) in MeOH (5 mL) was added to give a light blue solution. Five drops of concentrated HCl (37%) were added, and the solution immediately turned greenish yellow. This solution was distributed into five 20 mL scintillation vials, 7 mL in each. After the vials were heated in an oven at 85 °C for 24 h and cooled to room temperature, the light blue crystals from the first three vials were combined, washed with fresh DMF (10 mL x 3), and activated by flowing supercritical CO₂ to provide a light blue opaque powder (25 mg).

1.6 Synthesis of DIDDOK. DIDDOK was prepared according to literature procedure.⁵ $Zn(OAc)_2 \cdot 2H_2O$ (88 mg, 0.8 mmol) was dissolved in DMF (8 mL). 4,4'-oxybis(benzoic acid) (208 mg, 0.8 mmol) and bis(4-pyridyl)ethylene (144 mg, 0.8 mmol) were dissolved in DMF (8 mL). The linker solution was carefully layered on top of the metal salt solution. White solids immediately appeared. The mixture was stored at room temperature for 7 days. Then the solids were washed with fresh DMF (10 mL x 3) and activated by flowing supercritical CO₂ to provide a white powder (169 mg).

2. NITROGEN ADSORPTION ISOTHERM OF MOF-5



Figure S1. N₂ Isotherm of MOF-5 synthesized in this work (before heating to 150 °C for 48h). There was no difference in the isotherm collected after heating to 150 °C for 48 h.

3. COMPARISON OF PORE GEOMETRIES OF MOFs STUDIED HERE

Figure S2 shows a comparison between the porous structures of MOFs where the dotted lines separate "small" (<10 Å) micropore (SMP), "large" (>10 Å and <20 Å) micropore (LMP), and mesopore (MSP) (\geq 20Å) regions using the classification proposed by Gómez-Gualdrón et al.⁶ Both EPOTAF and DIDDOK consists of only SMPs. MOF-5 and IRMOF-20 consist of two types of LMPs "large" micropores (> 10 Å) but smaller than mesopores (i.e., <20 Å) Only SUKYON consists of both SMP and LMP. The maximum pore diameters of the MOFs are compiled in Table S1. The pore diameters of MOF-5 are 12 and 15 Å, which depends on the orientation of the benzene rings of the linker being parallel or perpendicular to the pore surface, as suggested earlier.^{7,8}

MOF channel analysis performed using Zeo++9 and a nitrogen molecule probe with radius of 1.86 Å revealed that all

MOFs studied here only a single 3D This analysis predicts IRMOF-20, 5. EPOTAF, and will allow particles of 9.3, 8.2, 6.6 and 7.3 Å,respectively, to move through the Therefore, channels of IRMOF-20, and are amenable to N₂ formation. while formation is the only option for the rest of MOFs.



Figure S2. Pore size distribution of synthesized MOFs.

	Pore Diameter [Å]	Pore Aperture [Å]	Porosity	
MOF			Helium Void Fraction	Geometric Void Fraction
MOF-5	15.1	7.9	0.82	0.81
IRMOF-20	17.3	9.3	0.88	0.84
SUKYON	10.8	7.3	0.81	0.77
EPOTAF	7.6	6.6	0.79	0.77
DIDDOK	9.6	8.2	0.79	0.78

Table S1. Comparison of the calculated pore geometry of MOFs studied here.

4. POWDER X-RAY DIFFRACTION PATTERNS OF MOF-5



Figure S3. PXRD pattern of activated MOF-5 (blue is the experimental pattern, black is the simulated pattern derived from the single crystal x-ray structure).



Figure S4. PXRD pattern of activated HSECoE MOF-5 (blue is the experimental pattern, black is the simulated pattern derived from the single crystal x-ray structure).

5. POWDER X-RAY DIFFRACTION OF MOFs PREDICTED BY GOLDSMITH et al.¹⁰



Figure S5. PXRD pattern of DIDDOK (blue is the experimental pattern, black is the simulated pattern derived from the single crystal x-ray structure).



Figure S6. PXRD pattern of SUKYON (blue is the experimental pattern, black is the simulated pattern derived from the single crystal x-ray structure).



Figure S7. PXRD pattern of EPOTAF (blue is the experimental pattern, black is the simulated pattern derived from the single crystal x-ray structure).



NITROGEN ADSORPTION ISOTHERMS OF MOFs PREDICTED BY GOLDSMITH et al.¹⁰ 6.

Figure S8. N₂ Isotherm of DIDDOK.



Figure S9. N₂ Isotherm of SUKYON



Figure S10. N₂ Isotherm of EPOTAF.

7. PERFORMANCE EVALUATION OF MOF-5 SYTHESIZED IN THIS WORK

Pressure (bar)	Total Gravimetric (wt.%)	Total Volumetric (g H ₂ /L)	Usable Gravimetric (wt.%)	Usable Volumetric (g H ₂ /L)
5	3.5	22.2	N/A	N/A
35	6.8	44.4	3.3	22.2
50	7.3	47.8	3.8	25.6
100	8.0	53.3	4.5	31.1

Table S2. Measured total and usable H_2 capacity of MOF-5 as a function of pressure at 77K. Usable capacities were calculated from the difference of total uptakes assuming pressure swing between 5 bar and the other high pressures listed.

8. CORRELATIONS BETWEEN THE PERFORMANCES OF HYDROGEN MODELS

Table S3. Comparison between Chahine rule and GCMC H_2 total capacity predictions at 77 K and 35 bar for selected high-performing MOFs compiled in Ref 10. In general, the Chahine rule predicts higher capacities compared to the GCMC, regardless of the interatomic potential used. On average the Chahine rule overestimates gravimetric capacities by 0.6 and 2 wt.% compared to the MGS and p-FH values, respectively. Similarly, volumetric capacities, are overpredicted by 4.1 g/L and 13.7 g/L.

	Total Gr	av. (wt.	%)	Total Vol. (g H_2/L)				
MOF	Chahine Rule	P-FH	MGS	Chahine Rule	P-FH	MGS		
POTAF	11.0	7.6	8.9	71.4	47.6	56.4		
ENITAX	9.3	7.7	9.3	58.7	47.7	59.0		
DIDDOK	10.3	8.1	9.7	60.5	46.6	56.6		
URGEL	9.7	7.6	9.0	57.4	43.5	52.9		
ANUGUM	7.9	6.6	7.7	58.2	47.7	56.1		
SUKYIH	8.8	7.2	8.9	57.7	46.4	58.8		
SUKYON	10.8	8.3	9.9	63.4	48.2	57.8		
MOF-5	8.3	7.0	8.4	54.7	44.5	55.3		



Figure S11. Correlations between total (a) gravimetric and (b) volumetric performances of MGS and p-FH H_2 models at 77K and 35bar. These data show that the MGS model over-predicts hydrogen adsorption in those MOFs having high gravimetric hydrogen capacities.

Table S4. Correlations between different methods for predicting H_2 uptake in 2800 MOFs. Three methods are considered: the Chahine rule, GCMC calculations using the MGS interatomic potential, and GCMC calculations using the p-FH interatomic potential. Rows 1-3 report correlations for total capacity at 77 K and 35 bar. The last row reports correlations for usable H2 capacities assuming an isothermal pressure swing between 5 and 100 bar at 77 K.

	Pearson Correlation	on Coefficient (r)	Kendall's Tau Correlation (τ)					
Methods	Gravimetric Capacity	Volumetric Capacity	Gravimetric Capacity	Volumetric Capacity				
Total Capacity								
Chahine Rule & GCMC-MGS	0.98	0.91	0.88	0.74				
Chahine Rule & GCMC-p-FH	0.98	0.89	0.87	0.71				
GCMC-MGS & GCMC-p-FH	0.99	0.99	0.97	0.91				
Usable Capacity								
GCMC-MGS & GCMC-p-FH	0.99	0.99	0.92	0.89				

9. DATABASE SCREENING RESULTS

Table S5. High capacity compounds in the non-hypothetical MOF database of 5,309 MOFs studied here with *total* capacities greater than MOF-5 (total gravimetric = 6.8 wt. %, total volumetric = 44.4 g H_2/L) at 77 K and 35 bar.

CSD REF. CODE	Metal Type	Density [g/cm3]	Pore Diameter [Å]	Volumetric Surface Area [m ² /cm ³]	Gravimetric Surface Area [m²/g]	Void Fraction	Pore Volume [cm³/g]	Total Gravimetric [wt. %]	Total Volumetric [g/L]
SUKYON	Cu	0.53	10.8	2701	5130	0.85	1.47	8.3	48.2
ODIXEG	Si, Zn	0.55	10.36	2259	4090	0.84	1.42	8.0	48.0
ENITAX	Cu, Si	0.57	10.08	2304	4021	0.83	1.36	7.7	47.7
EPOTAF	Cu	0.58	7.63	2988	5194	0.82	1.34	7.6	47.6
ANUGIA	Cu	0.57	13.85	2137	3762	0.86	1.38	7.7	47.5
TOHSAL	Cu	0.58	9.79	2485	4312	0.8	1.3	7.5	47.3
RAYMIP	In	0.5	13.47	2062	4101	0.9	1.61	8.6	47.2
ADASOP	Zn	0.63	18.07	2122	3359	0.84	1.22	6.9	46.7
CEKHIL	Со	0.61	8.91	2618	4266	0.82	1.24	7.1	46.7
ANUGOG	Cu	0.58	11.39	2364	4043	0.84	1.33	7.4	46.7
DIDDOK	Zn	0.53	9.6	2440	4640	0.83	1.49	8.1	46.6
ALUKOI	Sm	0.58	8.55	2918	5032	0.83	1.36	7.4	46.6
QUSBIP	Zn	0.57	10.67	2357	4172	0.82	1.38	7.5	46.5
SUKYIH	Cu	0.6	9.65	2271	3789	0.82	1.28	7.2	46.3
MUDTAH	Zn	0.56	18.89	2077	3694	0.85	1.41	7.6	46.3
ΜΑΥΚΟΟ	Cu	0.6	12.58	1904	3156	0.81	1.26	7.2	46.2
VUJBEI	Zn	0.56	18.45	2092	3718	0.85	1.41	7.6	46.2
SETTAO	Cr, Zn	0.53	13.88	2034	3808	0.86	1.48	8.0	46.0
JEJWEB	Zn	0.54	11.27	2203	4046	0.84	1.46	7.8	45.9
AMODUC	Tb	0.58	8.56	2896	5030	0.85	1.37	7.3	45.9

Table S6. High capacity MOFs in the non-hypothetical database of 5,309 MOFs studied here with *usable* capacities greater than MOF-5 (usable gravimetric = 4.5 wt. %, usable volumetric = 31.1 g H_2/L) at 77K assuming a pressure swing between 5 bar and 100 bar.

CSD REF. CODE	Common Name	Metal Type	Density [g/cm ³]	Pore Diameter [Å]	Volumetric Surface Area [m ² /cm ³]	Gravimetric Surface Area [m²/g]	Void Fraction	Pore Volume [cm ³ /g]	Usable Gravimetric [wt. %]	Usable Volumetric [g/L]
ECOLEP	-	Со	0.41	11.6	1836	4510	0.89	2.09	8.2	39.0
XUKYEI	-	Cu	0.29	13.2	1817	6327	0.88	3.02	10.7	37.4
VEBHUG	IRMOF-20	Zn	0.51	17.3	1936	4302	0.87	1.89	7.2	37.4
BAZFUF	MOF-143	Cu	0.34	20.2	1860	5470	0.91	2.54	9.1	37.1
HABQUY	PCN-610	Cu	0.29	25.7	1664	5750	0.91	3.04	10.5	37.1
GAGZEV	NU-100	Cu	0.28	28.7	1613	5777	0.92	3.17	10.8	37.0
ZELROZ	-	Zn	0.36	16.9	1790	4947	0.88	2.4	8.7	36.8
XAFFIV	DUT-10(Co)	Со	0.36	14.2	1910	5329	0.89	2.36	8.5	36.6
VAGMAT	SNU-30	Zn	0.36	14.9	1898	5203	0.89	2.33	8.5	36.5
XAFFAN	DUT-10(Zn)	Zn	0.37	14.9	1892	5181	0.89	2.33	8.3	36.5
XAFFOB	DUT-10(Cu)	Cu	0.37	14.8	1907	5195	0.89	2.32	8.3	36.4
XAFFER	DUT-11	Zn	0.36	14.2	1861	5171	0.89	2.37	8.5	36.3
VAGMEX	SNU-30SC	Zn	0.35	15.3	1815	5152	0.90	2.43	8.7	36.3
NIBHOW	PCN-6'	Cu	0.28	27.5	1427	5103	0.92	3.19	10.6	36.2
ADATIK	rht-MOF	Cu	0.38	24.6	1724	4566	0.89	2.3	8.1	36.0
ADATAC	rht-MOF	Zn	0.34	26.3	1735	5145	0.90	2.57	8.9	35.9
VETMIS	-	Cu	0.31	17.2	1782	5713	0.90	2.77	9.5	35.7
XAHPON	CMOF-1a	Cu	0.28	17.3	1498	5268	0.92	3.10	10.4	35.5
FEBXIV	CMOF-2	Cu	0.29	17.3	1517	5166	0.91	3.00	10.1	35.5
LEJCIO	_	Zn	0.33	18.5	1722	5275	0.91	2.66	8.9	35.4

Continued

CSD REF. CODE	Common Name	Metal Type	Density [g/cm ³]	Pore Diameter [Å]	Volumetric Surface Area [m ² /cm ³]	Gravimetric Surface Area [m²/g]	Void Fraction	Pore Volume [cm ³ /g]	Usable Gravimetric [wt. %]	Usable Volumetric [g/L]
RUTNOK	-	Zn	0.24	24.6	1493	6200	0.9	3.73	12.1	35.4
MEHMET	-	Cu	0.41	21.8	1878	4594	0.89	2.06	7.3	35.2
LEJCEK	-	Zn	0.33	17.2	1929	5776	0.88	2.58	8.9	35.0
EHIJAH	-	Zn	0.39	18.5	1734	4503	0.88	2.21	7.6	35.0
EDUVOO	-	Zn	0.37	20.9	1814	4857	0.91	2.31	8.0	35.0
XAHPIH	-	Cu	0.36	14.3	1668	4683	0.89	2.42	8.2	35.0
HABRAF	-	Cu	0.38	24.3	1854	4850	0.89	2.21	7.8	35.0
LURRIA	-	Cu	0.41	22.4	1864	4586	0.92	2.08	7.2	34.9
XAHQAA	-	Cu	0.17	23.0	1065	6250	0.95	5.44	15.7	34.9
WIYMOG	-	Tb	0.41	12.1	2788	6833	0.81	2.05	7.3	34.8
XAFFUH	-	Cu	0.33	23.7	1696	5152	0.9	2.63	8.8	34.8
XAHPUT	-	Cu	0.18	21.8	1126	6301	0.94	5.15	14.9	34.7
ADASEF	-	Cu	0.44	21.6	1816	4168	0.89	1.96	6.8	34.5
HOMXIR	-	Zn	0.39	23.7	1731	4388	0.88	2.16	7.6	34.5
ECOKAJ	-	Zn	0.33	19.0	1163	3575	0.89	2.69	8.9	34.5
BIBXOB	-	Ni	0.41	19.7	2017	4924	0.87	2.04	7.2	34.2
HOHMEX	-	Cu	0.32	18.8	1575	4986	0.88	2.74	9.0	34.1
PIBPIA	-	Cd	0.46	15.5	1368	2982	0.85	1.83	6.6	34.1
XAHPED	-	Cu	0.37	12.4	1921	5131	0.87	2.26	7.8	34.0
PIBNUK	-	Zn	0.42	15.4	1391	3289	0.85	1.98	7.1	34.0

10. POWDER X-RAY DIFFRACTION PATTERN OF IRMOF-20



Figure S12. PXRD pattern of activated IRMOF-20 (blue is the experimental pattern, black is the simulated pattern derived from the single crystal x-ray structure).

11. NITROGEN ADSORPTION ISOTHERM OF IRMOF-20



Figure S13. N₂ Isotherm of IRMOF-20.

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