Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
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Screening Metal-organic Frameworks for Selective Noble Gas Adsorption in Air: Effect of Pore Size and Framework Topology

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Supporting Information

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I. Lennard-Jones parameters

Table S1. Lennard-Jones parameters for each atom used in the GCMC simulations

	Atom	σ (Å)	ε/k_B (K)	Ref.
MOFs (UFF)	H	2.57	22.1	[1]
	C	3.43	52.8	[1]
	N	3.26	34.7	[1]
	O	3.12	30.2	[1]
	F	3.00	25.2	[1]
	Cl	3.52	114.2	[1]
	Cu	3.11	2.52	[1]
	Zn	2.46	62.4	[1]
	Br	3.73	126.3	[1]
	I	4.01	170.6	[1]
AlMIL-53 (TraPPE)	Al	0.000	0.0	[2]
	CHaa(aro)	3.695	50.5	[2]
	Caac(aro)	3.880	21.0	[2]
	Ccc=c(sp2)	3.850	20.0	[2]
	H	0.000	0.0	[2]
	Occ(sp3)	2.800	55.0	[2]
	Och(sp3)	3.020	93.0	[2]
Gases	N (N_2)	3.31	36.0	[3]
	Ar	3.45	120.0	[4]
	Kr	3.69	170.0	[4]
	Xe	4.10	211.0	[4]
	Rn	4.17	300.0	[5]

II. Snapshot of molecular model and atomic charges for each MOF

Figure S1: Model of IRMOF-1

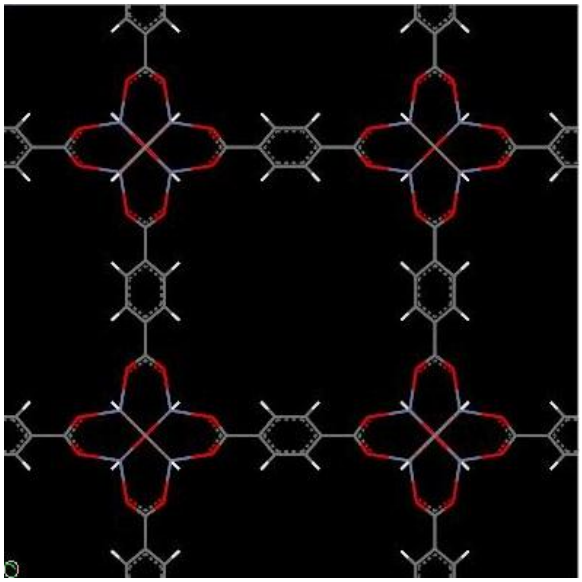

Table S2: Atomic charges used for IRMOF-1

element type	charge (*e*)
Zn(O,O,O,O)	1.624
O(Zn,Zn,Zn,Zn)	-1.882
O(C,Zn)	-0.780
C(C,O,O)	0.797
C(C,C,C)	0.042
C(C,C,H)	-0.136
H(C)	0.102

Figure S2: Model of IRMOF-2Br

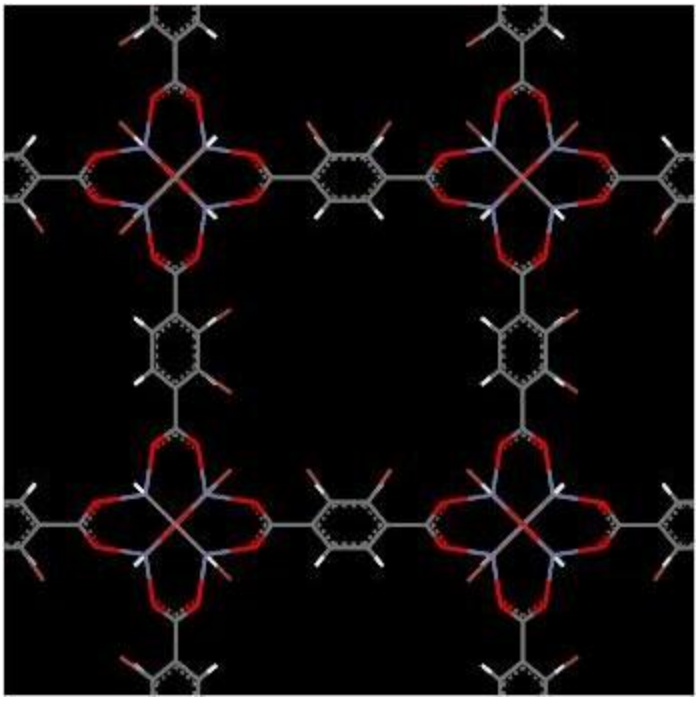

Table S3: Atomic charges used for IRMOF-2Br

element type	charge (*e*)
Zn(O,O,O,O)	1.622
O(Zn,Zn,Zn,Zn)	-1.880
O(C,Zn)	-0.781
C(C,O,O)	0.818
C(C,C,C)	0.042
C(C,C,H)	-0.135
C(C,C,Br)	0.004
H(C)	0.103
Br(C)	-0.040

Figure S3: Model of IRMOF-2F

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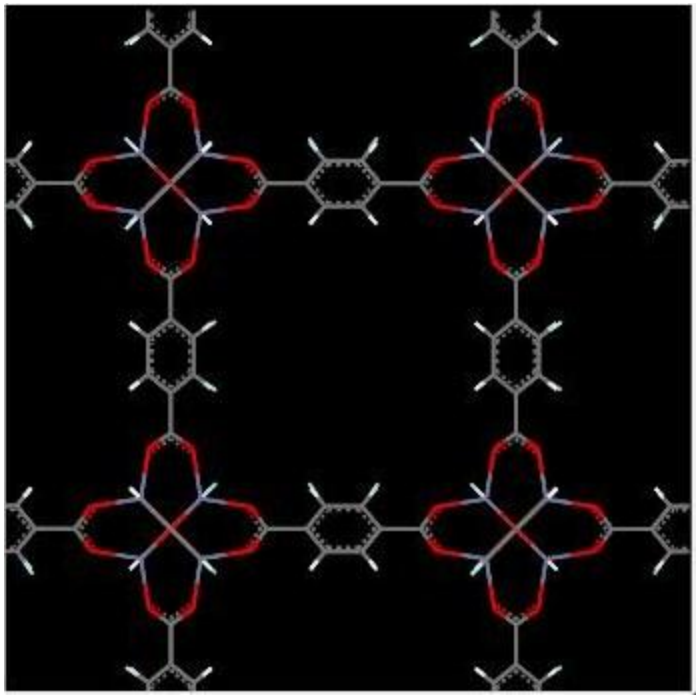

Table S4: Atomic charges used for IRMOF-2F

element type	charge (*e*)
Zn(O,O,O,O)	1.594
O(Zn,Zn,Zn,Zn)	-1.918
O(C,Zn)	-0.796
C(C,O,O)	0.803
C(C,C,C)	0.041
C(C,C,H)	-0.138
C(C,C,F)	0.304
H(C)	0.101
F(C)	-0.183

Figure S4: Model of IRMOF-2Cl

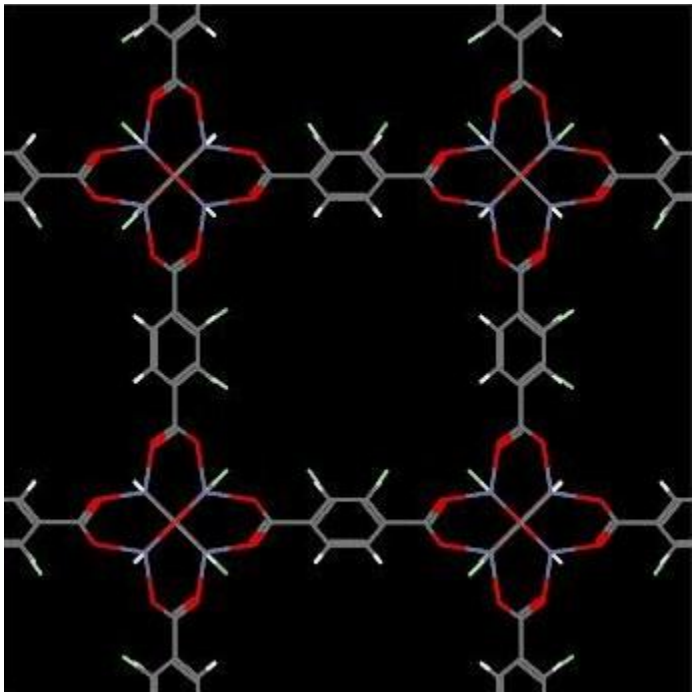

Table S5: Atomic charges used for IRMOF-2Cl

element type	charge (*e*)
Zn(O,O,O,O)	1.601
O(Zn,Zn,Zn,Zn)	-1.910
O(C,Zn)	-0.794
C(C,O,O)	0.805
C(C,C,C)	0.041
C(C,C,H)	-0.138
C(C,C,Cl)	0.394
H(C)	0.101
Cl(C)	-0.297

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Figure S5: Model of IRMOF-2I

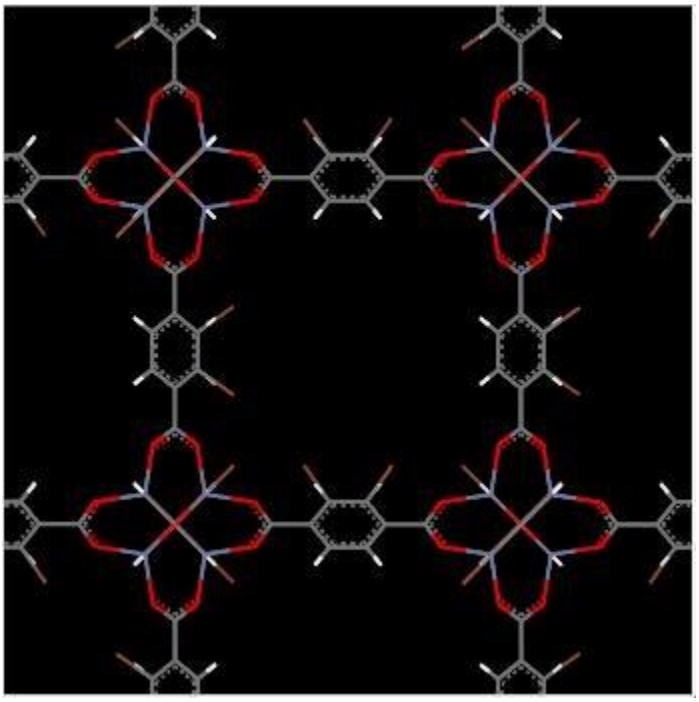

Table S6: Atomic charges used for IRMOF-2I

element type	charge (*e*)
Zn(O,O,O,O)	1.624
O(Zn,Zn,Zn,Zn)	-1.879
O(C,Zn)	-0.781
C(C,O,O)	0.818
C(C,C,C)	0.042
C(C,C,H)	-0.135
C(C,C,I)	-0.047
H(C)	0.103
I(C)	0.008

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Figure S6: Model of NOTT-100

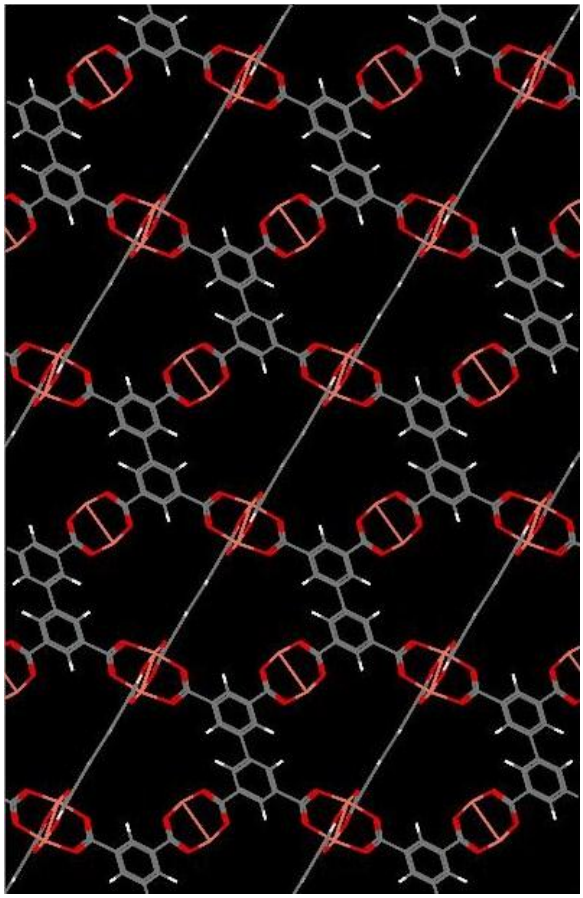

Table S7: Atomic charges used for NOTT-100

element type	charge (*e*)
Cu(O,O,O,O)	1.048
O(C,Cu)	-0.653
C(C,O,O)	0.785
C(C,C,C)	0.040
C(C,C,H)	-0.141
H(C)	0.099

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Figure S7: Model of NOTT-101

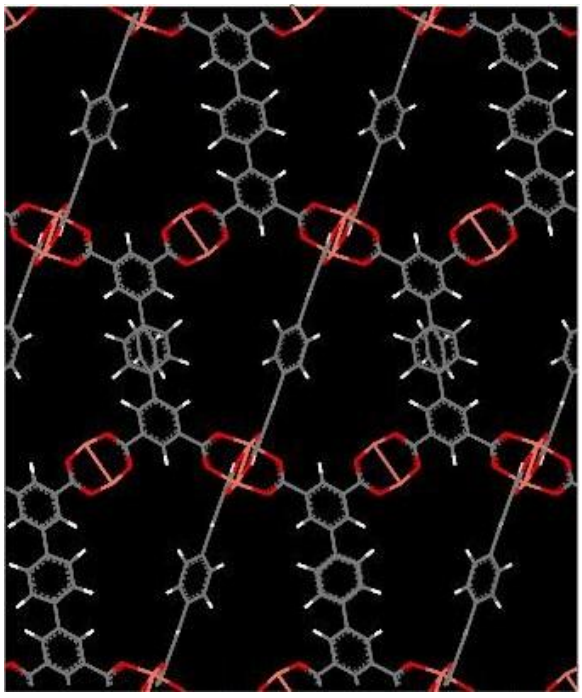

Table S8: Atomic charges used for NOTT-101

element type	charge (*e*)
Cu(O,O,O,O)	1.057
O(C,Cu)	-0.649
C(C,O,O)	0.790
C(C,C,C)	0.041
C(C,C,H)	-0.140
H(C)	0.099

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Figure S8: Model of NOTT-102

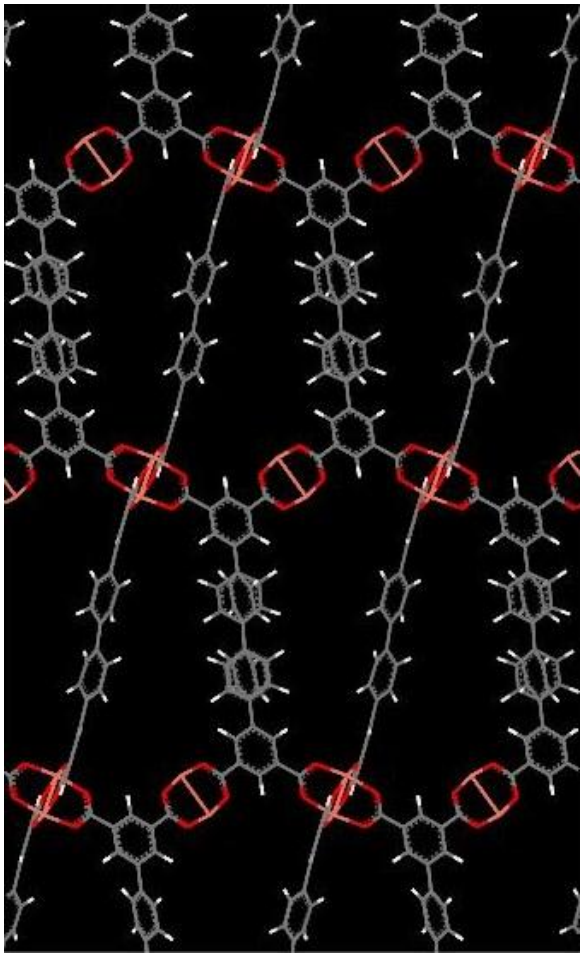

Table S9: Atomic charges used for NOTT-102

element type	charge (*e*)
Cu(O,O,O,O)	1.062
O(C,Cu)	-0.646
C(C,O,O)	0.795
C(C,C,C)	0.041
C(C,C,H)	-0.139
H(C)	0.100

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Figure S9: Model of NOTT-103

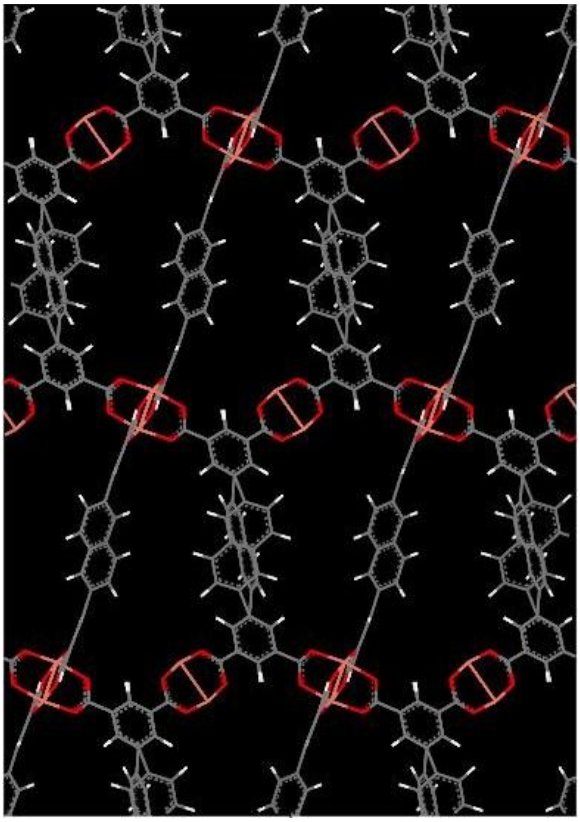

Table S10: Atomic charges used for NOTT-103

element type	charge (*e*)
Cu(O,O,O,O)	1.057
O(C,Cu)	-0.649
C(C,O,O)	0.790
C(C,C,C)	0.041
C(C,C,H)	-0.140
H(C)	0.099

Figure S10: Model of PCN-14

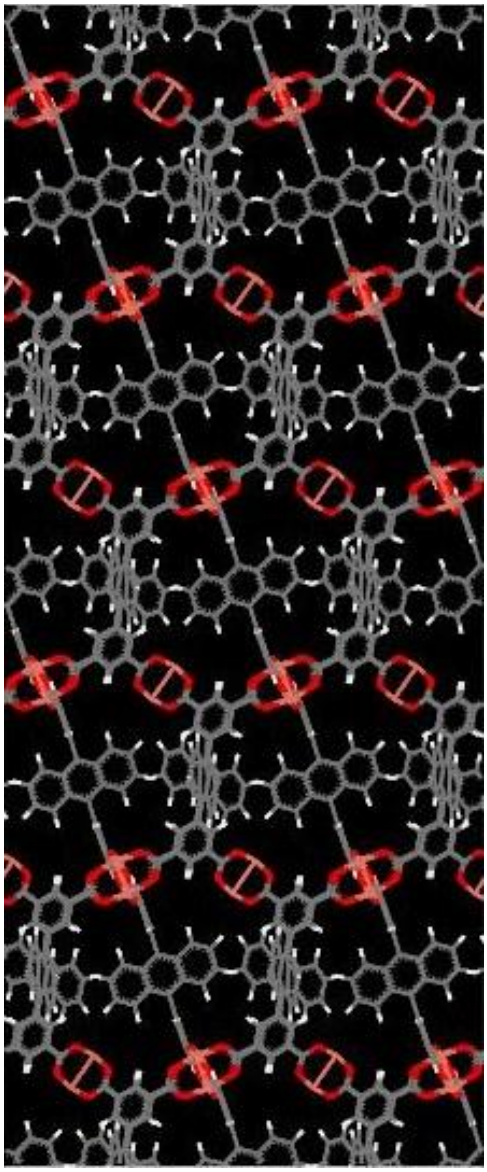

Table S11: Atomic charges used for PCN-14

element type	charge (*e*)
Cu(O,O,O,O)	1.057
O(C,Cu)	-0.649
C(C,O,O)	0.790
C(C,C,C)	0.041
C(C,C,H)	-0.140
H(C)	0.099

Figure S11: Model of PMOF-2

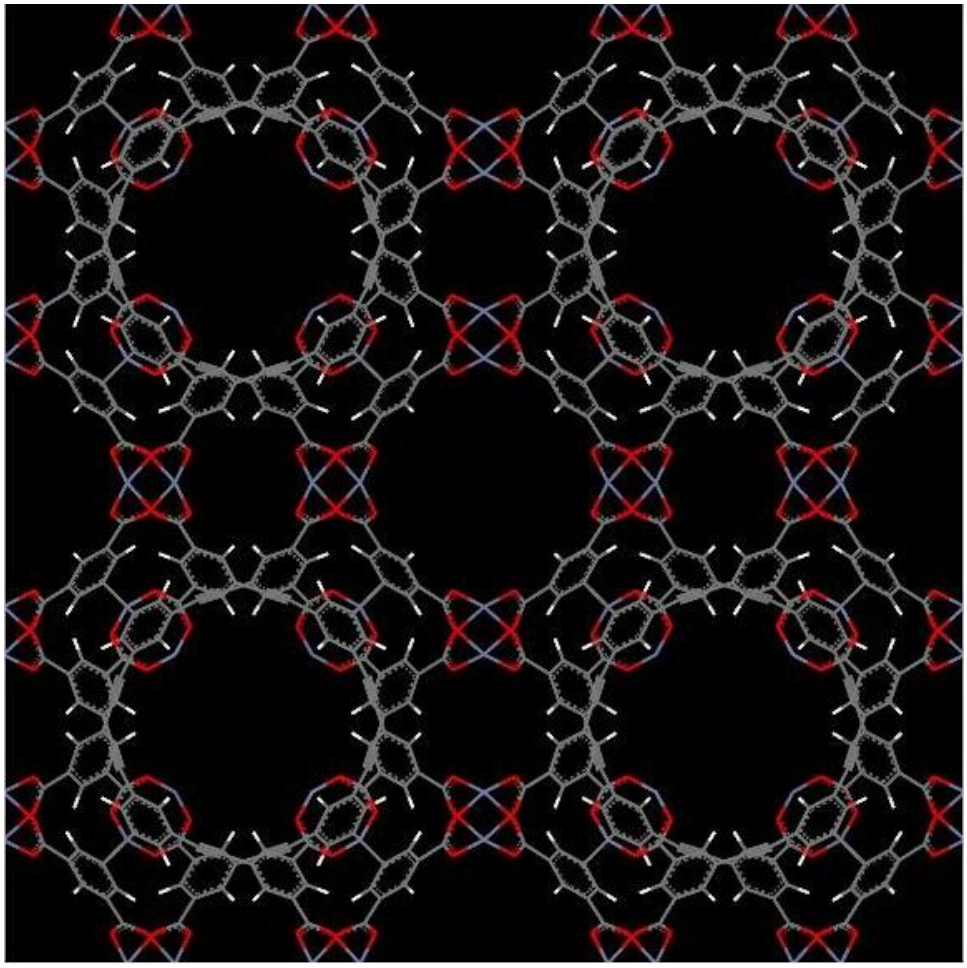

Table S12: Atomic charges used for PMOF-2

element type	charge (*e*)
Zn(O,O,O,O)	1.648
O(C,Zn)	-0.769
C(C,O,O)	0.830
C(C,C,C)	0.043
C(C,C,H)	-0.132
C(C,C)	-0.148
H(C)	0.105

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Figure S12: Model of NOTT-112

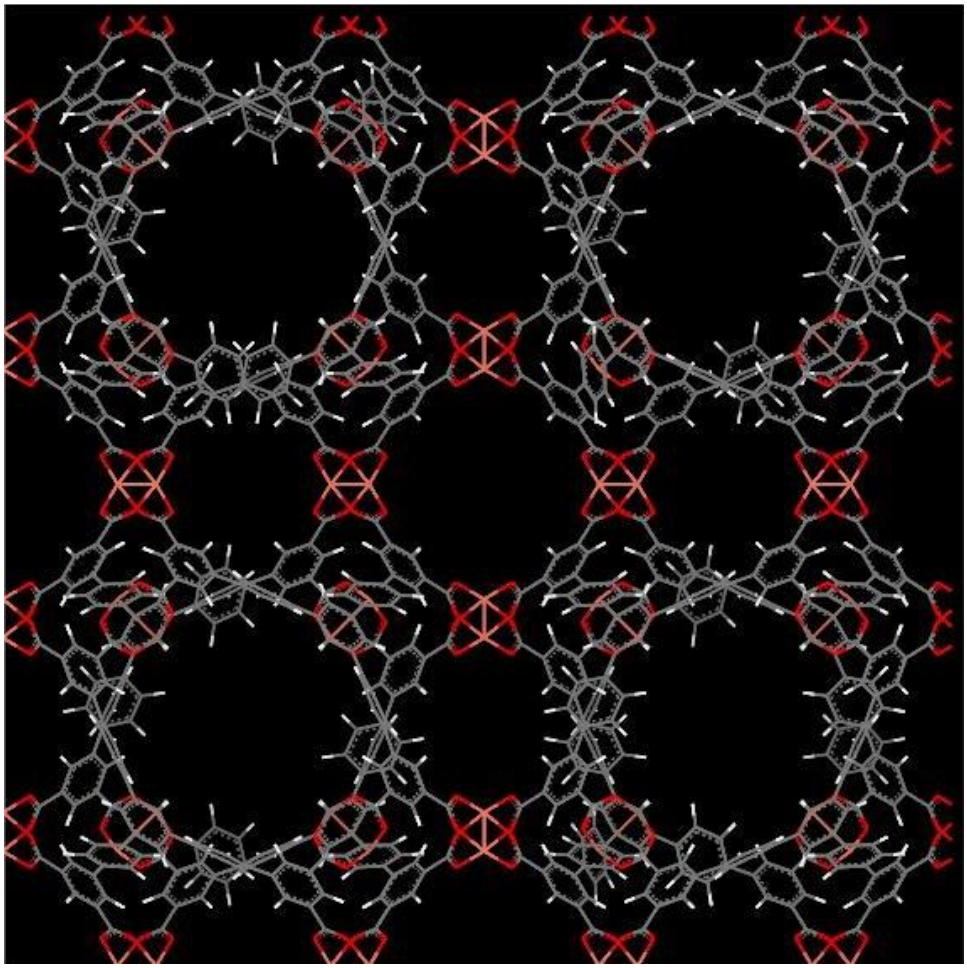

Table S13: Atomic charges used for NOTT-112

element type	charge (*e*)
Cu(O,O,O,O)	1.062
O(C,Cu)	-0.646
C(C,O,O)	0.794
C(C,C,C)	0.041
C(C,C,H)	-0.139
H(C)	0.100

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Figure S13: Model of NOTT-116

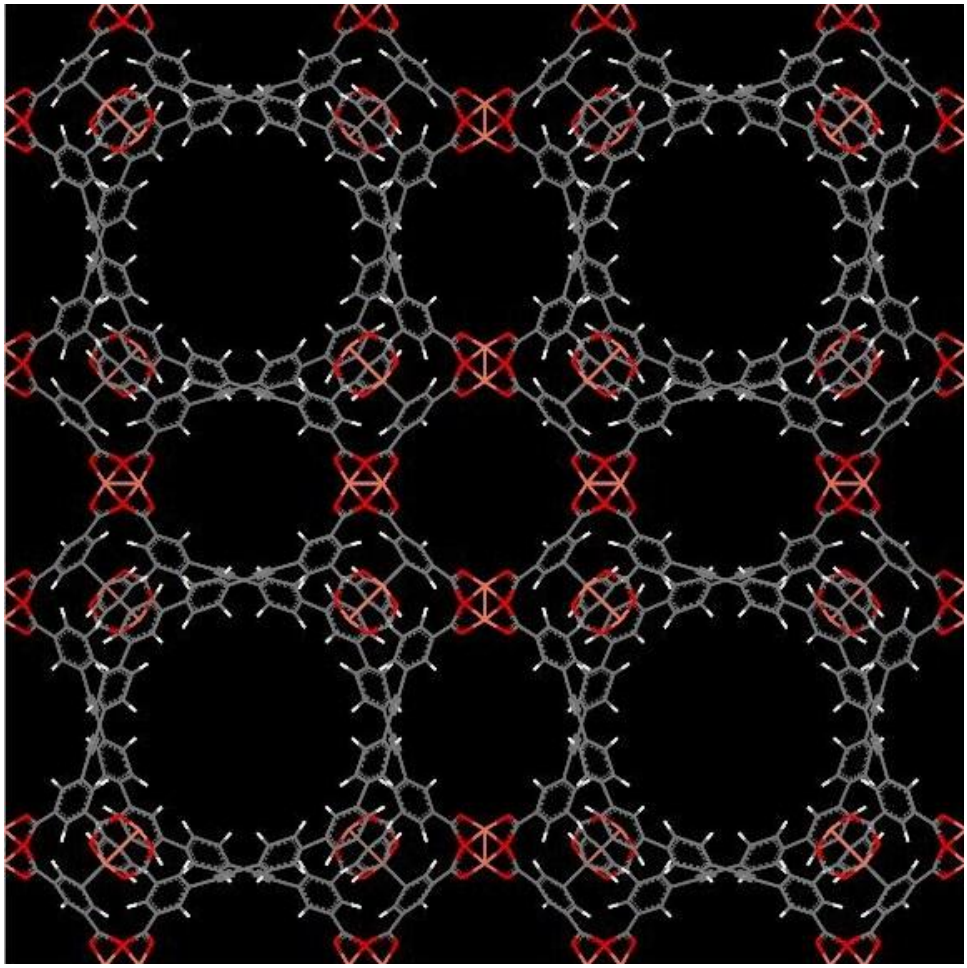

Table S14: Atomic charges used for NOTT-116

element type	charge (*e*)
Cu(O,O,O,O)	1.104
O(C,Cu)	-0.620
C(C,O,O)	0.826
C(C,C,C)	0.043
C(C,C,H)	-0.134
C(C,C)	-0.147
H(C)	0.104

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Figure S14: Model of HKUST-1

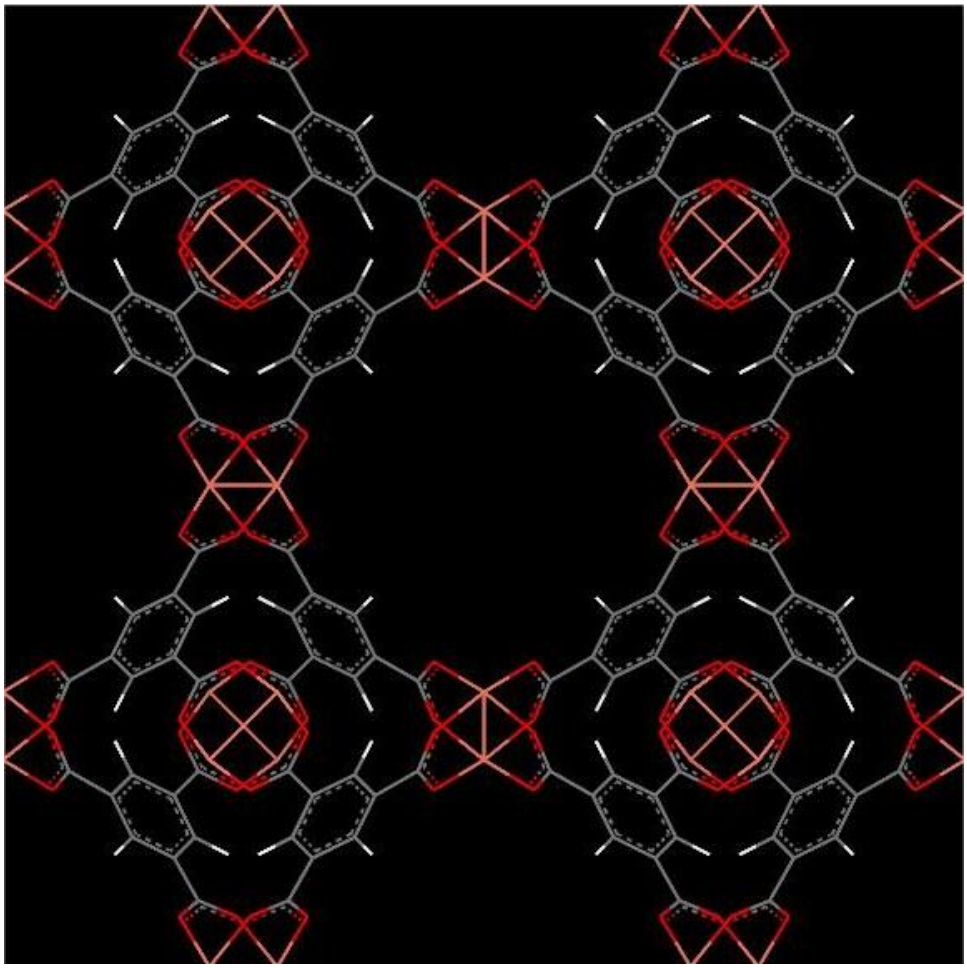

Table S15: Atomic charges used for HKUST-1

element type	charge (*e*)
Cu(O,O,O,O)	1.050
O(C,Cu)	-0.654
C(C,O,O)	0.786
C(C,C,C)	0.040
C(C,C,H)	-0.141
H(C)	0.098

Figure S15: Model of MIL-53(Al)

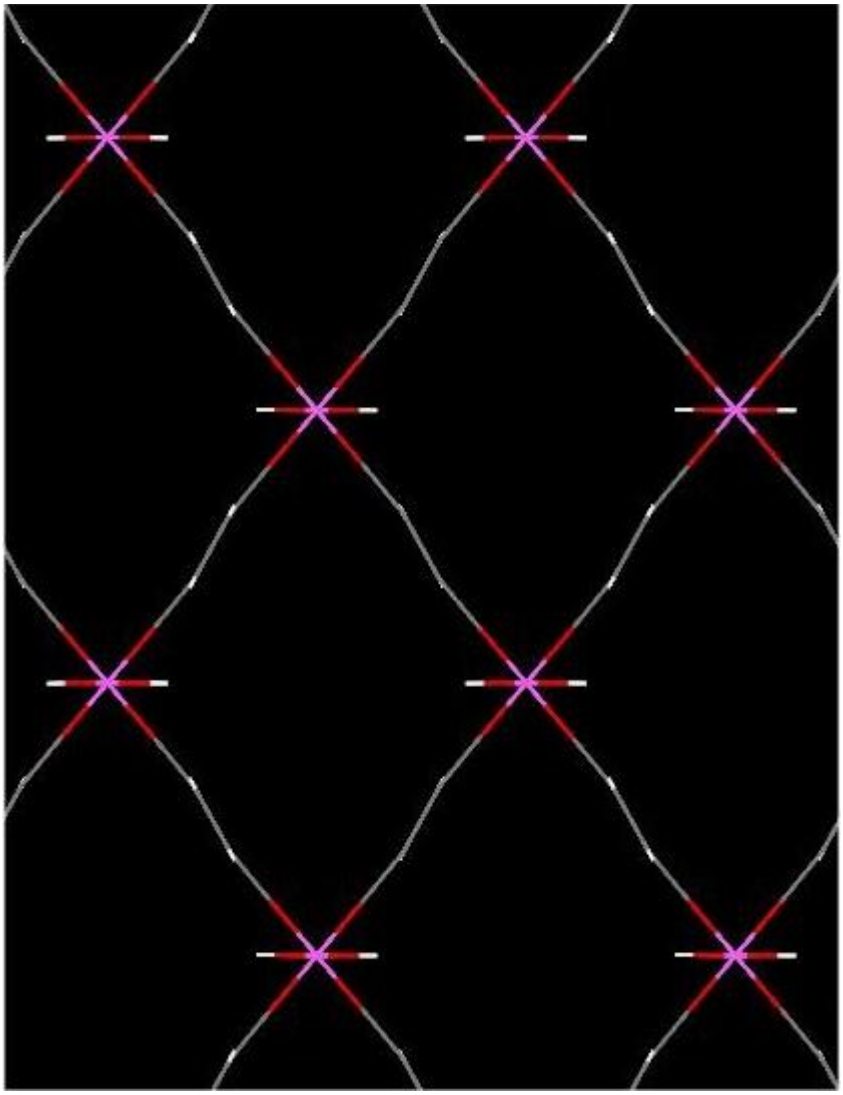

Table S16: Atomic charges used for MIL-53(Al)

element type	charge (*e*)
Al(O,O,O,O,O,O)	1.415
O(Al,Al,H)	-0.731
O(Al,C)	-0.567
C(C,O,O)	0.584
C(C,C,C)	-0.072
C(C,C,H)	-0.079
H(C)	0.144
H(O)	0.300

Figure S16: Model of ZIF-8

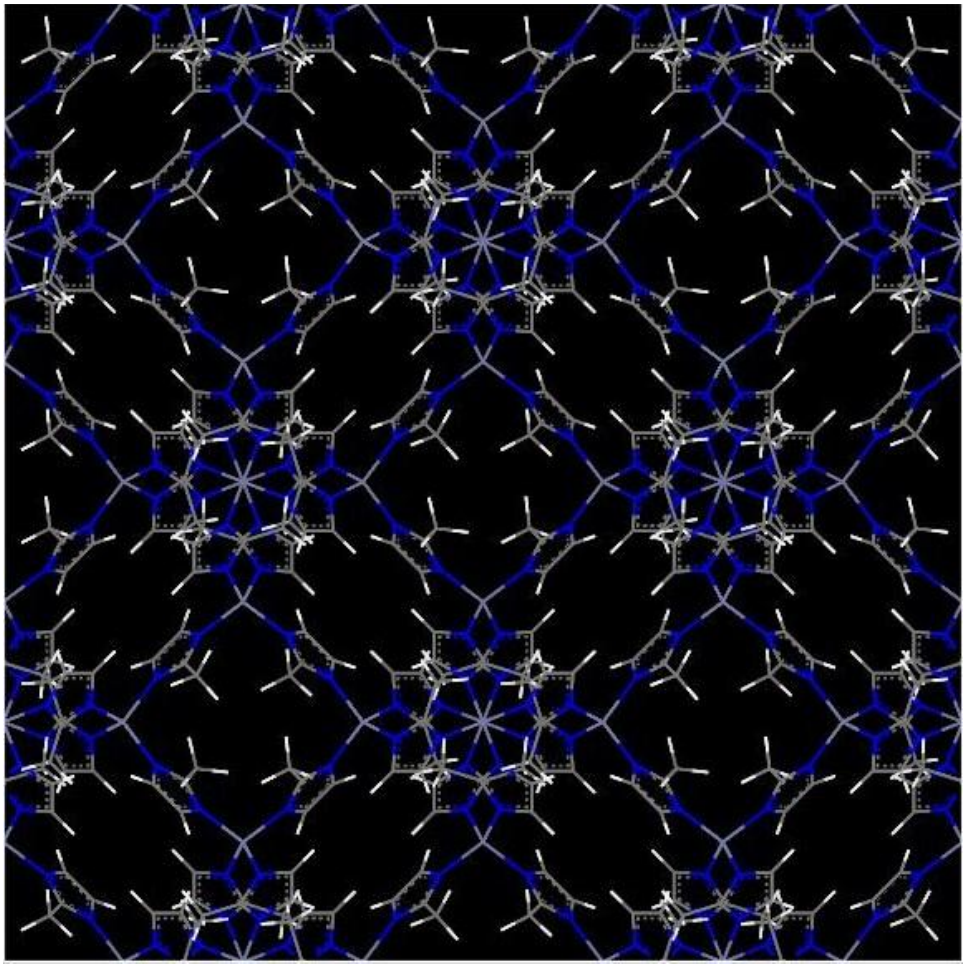

Table S17: Atomic charges used for ZIF-8

element type	charge (*e*)
Zn(N,N,N,N)	0.454
C(C,N,N)	0.423
C(C,H,H,H)	0.028
C(C,H,N)	0.016
N(C,C,Zn)	-0.500
H(C)	0.058

III. Simulated single-component adsorption isotherms for each gas

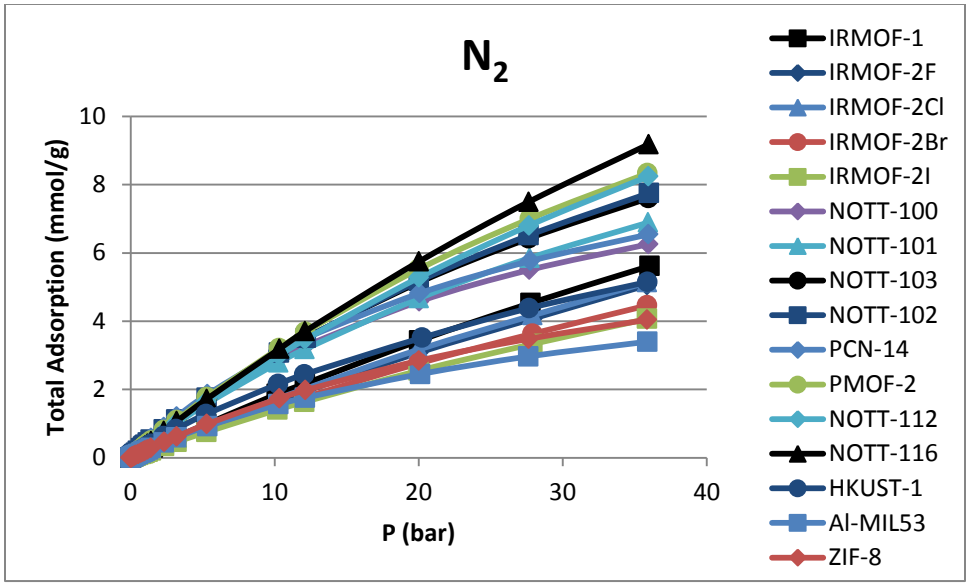

Figure S17: N_2 adsorption isotherms

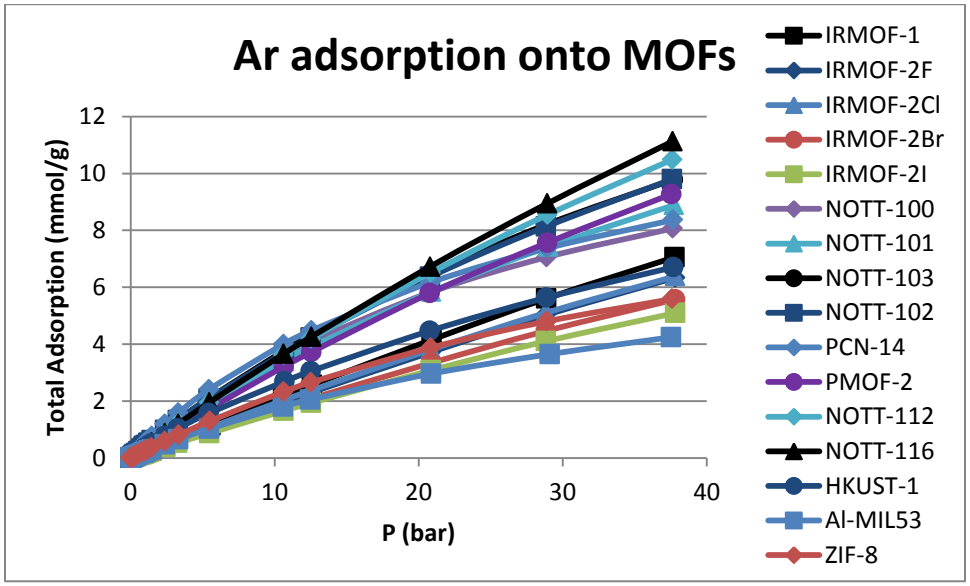

Figure S18: Ar adsorption isotherms

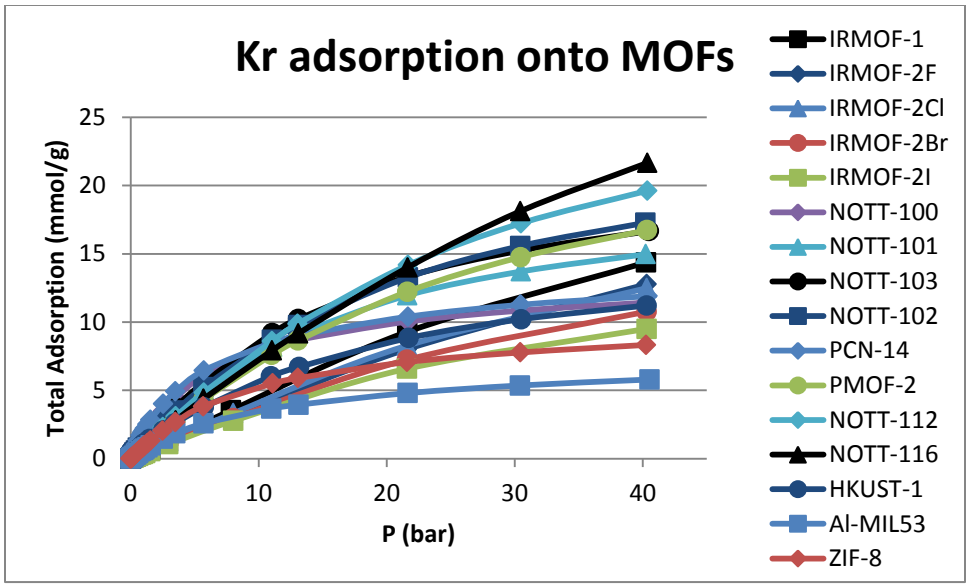

Figure S19: Kr adsorption isotherms

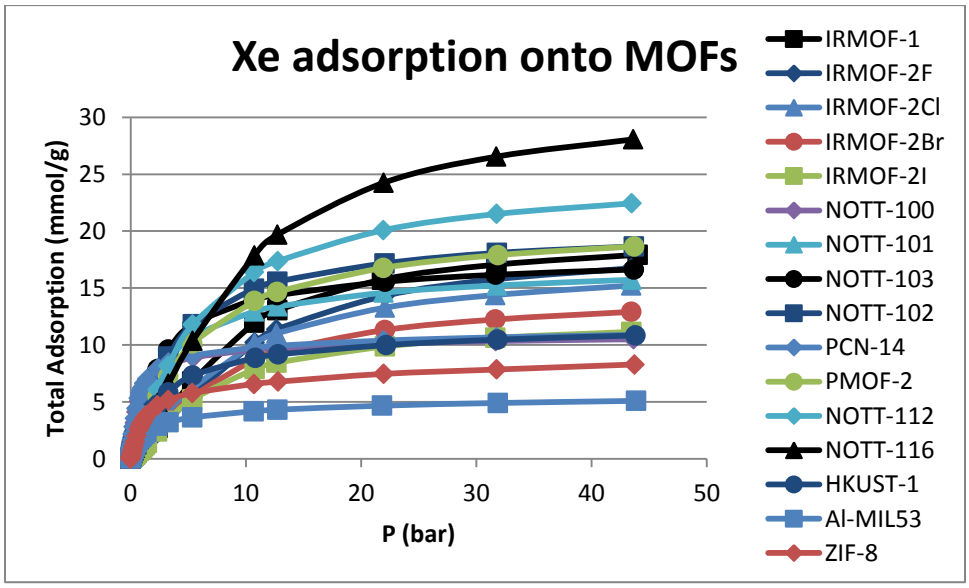

Figure S20: Xe adsorption isotherms

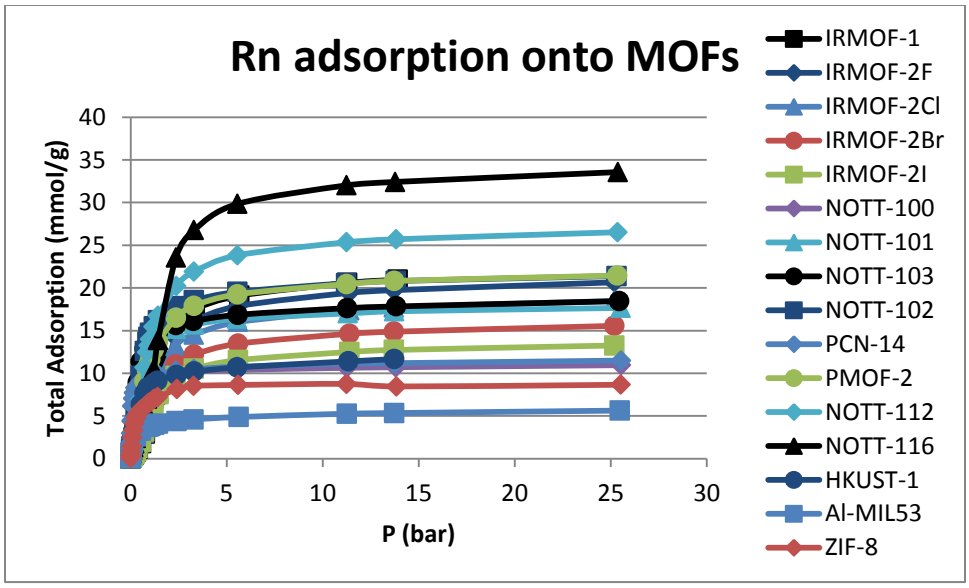

Figure S21: Rn adsorption isotherms

IV. Comparison of force field model on Kr and N_2 uptake from GCMC simulations with experiment for AlMIL-53.

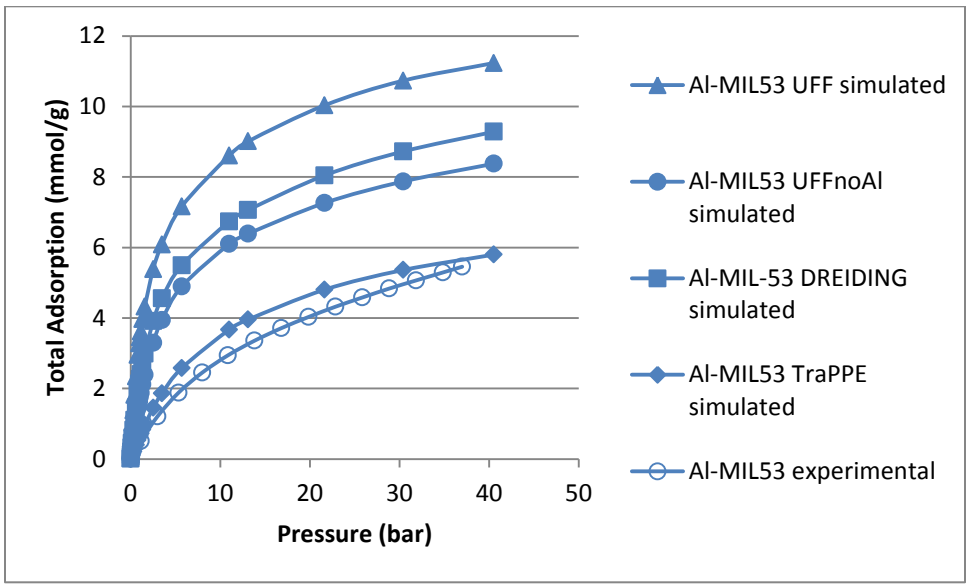

Figure S22: Experimental and simulated isotherms for adsorption of Kr using different force field models. For the results labeled "Al-MIL53 UFF no Al", the van der Waals parameters for Al atoms were set to zero.

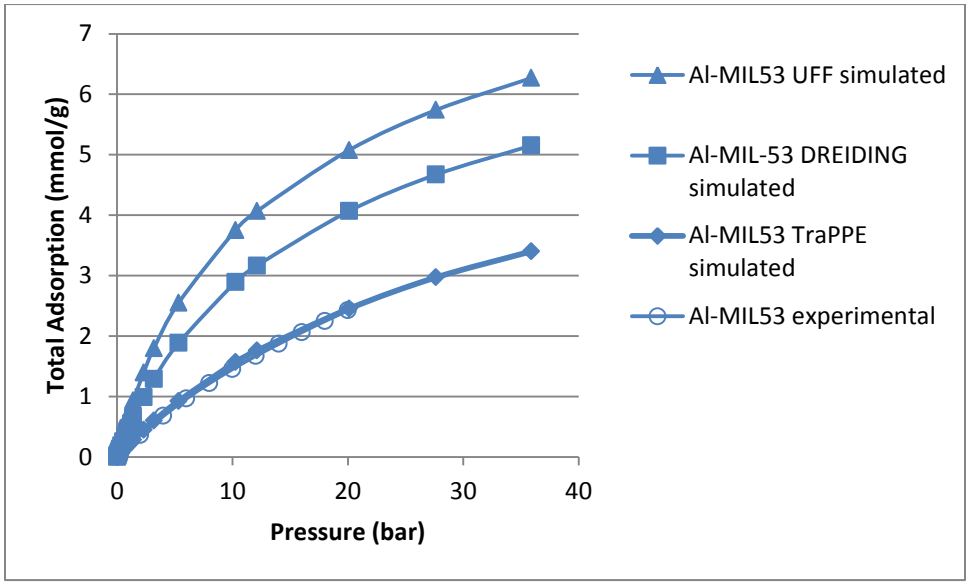

Figure S23: Experimental and simulated isotherms for adsorption of N_2 using different force field models.

V. Henry's constants and isosteric heats of adsorption

Table S18: Henry's Constants (k_H, mmol·cm^{-3}·atm^{-1}) and Isosteric Heats of Adsorption (Q_{st}, kJ·mol^{-1}) from GCMC Simulations

	N_2		Ar		Kr		Xe		Rn	
MOF	K_H	Q_{st}	K_H	Q_{st}	K_H	Q_{st}	K_H	Q_{st}	K_H	Q_{st}
NOTT-100	0.35	13.6	0.39	15.5	1.48	15.5	7.95	23.8	59.05	23.8
NOTT-101	0.24	9.1	0.27	15.0	0.93	15.0	3.50	23.3	11.62	31.7
NOTT-102	0.23	11.0	0.27	10.8	0.91	16.6	3.21	24.9	8.85	33.2
NOTT-103	0.24	10.9	0.30	13.9	0.96	16.8	3.63	22.2	12.29	30.5
PCN-14	0.35	13.4	0.48	13.3	2.18	22.9	9.14	31.2	48.37	38.2
PMOF-2	0.21	7.6	0.19	9.2	0.49	16.7	1.60	17.5	5.91	25.8
NOTT-112	0.17	13.2	0.19	12.3	0.52	14.4	1.70	22.7	5.67	26.0
NOTT-116	0.14	16.8	0.16	17.8	0.37	17.8	1.11	17.8	3.69	17.8
IRMOF-1	0.12	8.2	0.13	8.5	0.25	11.0	0.63	13.5	1.77	16.8
IRMOF-2F	0.11	8.2	0.12	8.2	0.24	10.2	0.56	13.4	1.43	16.2
IRMOF-2Cl	0.13	8.6	0.13	8.6	0.28	11.1	0.70	14.2	1.98	17.4
IRMOF-2Br	0.13	8.5	0.14	8.8	0.29	11.3	0.74	14.5	2.12	18.0
IRMOF-2I	0.14	8.9	0.15	9.2	0.31	11.7	0.84	15.0	2.55	18.3
HKUST-1	0.27	14.2	0.34	14.5	1.27	21.5	3.78	31.0	8.76	38.6
AlMIL-53	0.20	13.5	0.22	11.6	0.71	11.6	3.07	20.0	13.09	28.3
ZIF-8	0.21	12.	0.23	13.1	0.80	13.1	3.75	21.4	23.06	21.4

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VI. Gas Selectivities at Infinite Dilution

Table S19: Gas selectivities at infinite dilution from GCMC simulations

MOF	Ar/N_2	Kr/N_2	Xe/N_2	Rn/N_2
NOTT-100	1.1	4.2	22.7	168.3
NOTT-101	1.1	3.9	14.6	48.6
NOTT-102	1.2	4.0	14.2	39.2
NOTT-103	1.2	3.9	14.9	50.3
PCN-14	1.4	6.2	26.0	137.6
PMOF-2	0.9	2.4	7.6	28.2
NOTT-112	1.1	3.1	10.0	33.2
NOTT-116	1.1	2.6	7.8	25.9
IRMOF-1	1.1	2.1	5.2	14.6
IRMOF-2F	1.1	2.1	5.0	12.8
IRMOF-2Cl	1.1	2.2	5.6	15.8
IRMOF-2Br	1.1	2.3	5.8	16.7
IRMOF-2I	1.1	2.3	6.2	18.9
HKUST-1	1.3	4.7	14.0	32.5
AlMIL-53	1.1	3.6	15.3	65.4
ZIF-8	1.1	3.9	18.3	112.2

VII. MD trajectories of krypton atoms in ZIF-8, AlMIL-53, and PCN-14

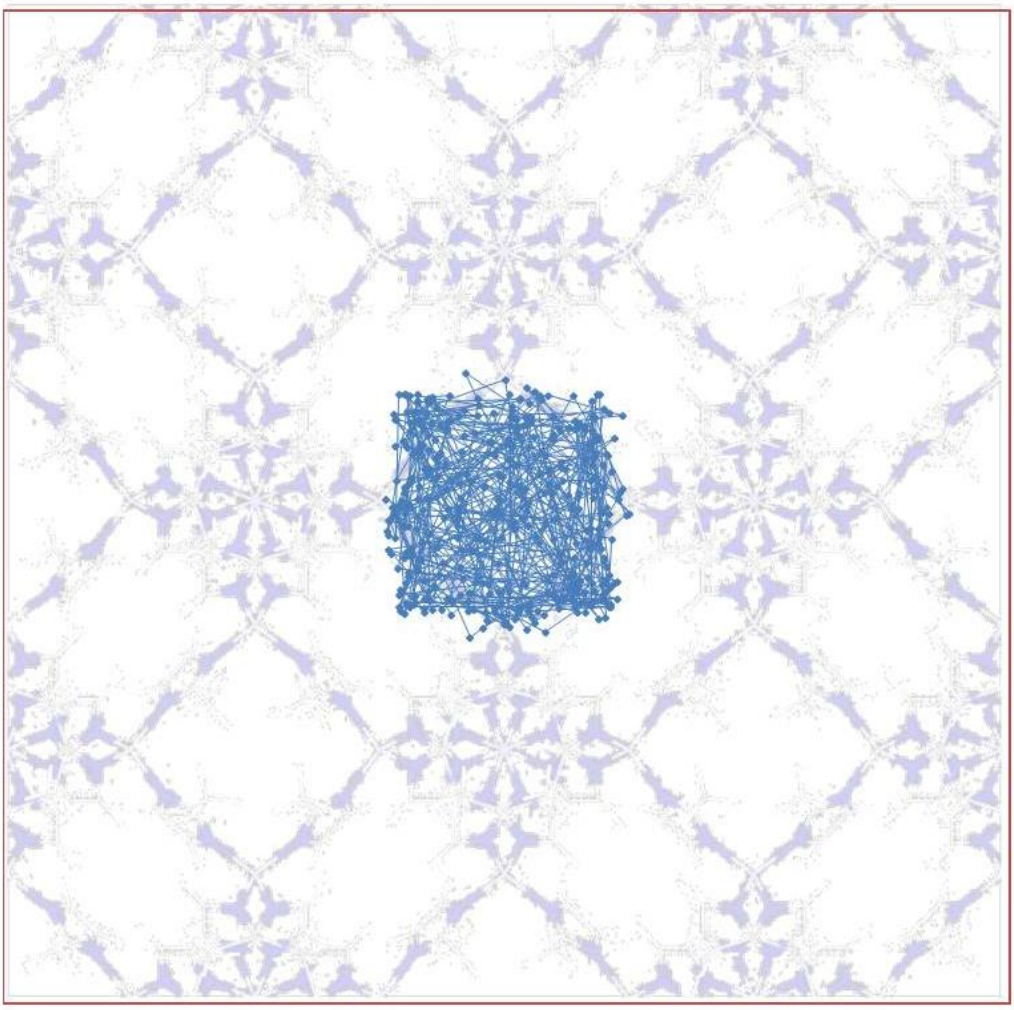

Figure S24: MD trajectories (x,y plane) of a representative krypton atom in ZIF-8 at 500 K, showing a single krypton atom confined to a single cage throughout the 2 ns simulation. Each point represents the krypton atom position every 400 fs throughout the simulation.

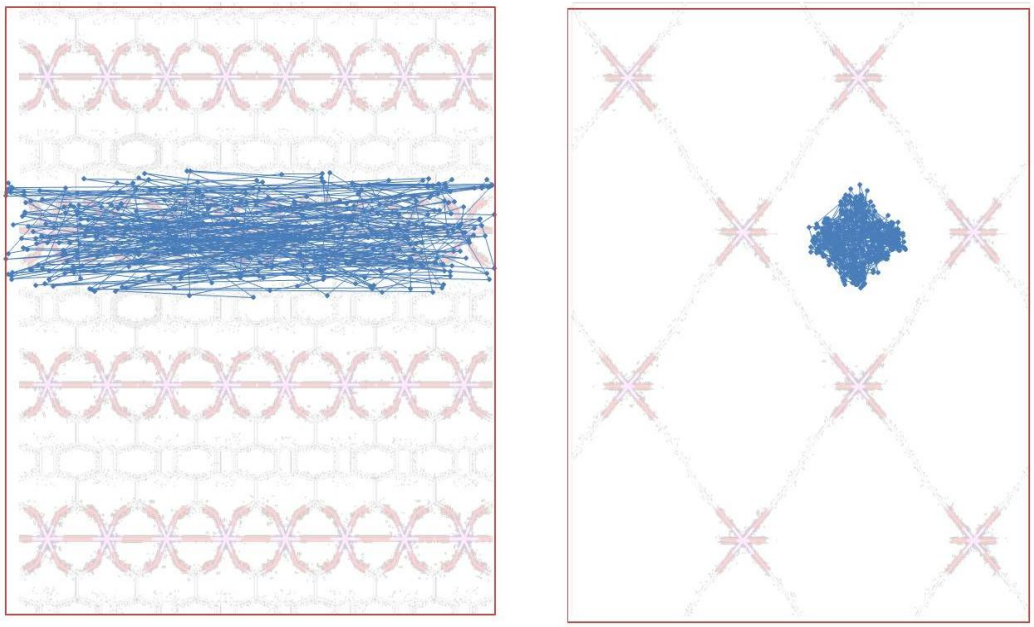

Figure S25: MD trajectories (left: x,y plane; right: y,z plane) of selected krypton atoms in AlMIL-53 at 500 K showing a single krypton atom confined to a single channel throughout the 2 ns simulation. Each point represents the krypton atom position every 400 fs throughout the simulation.

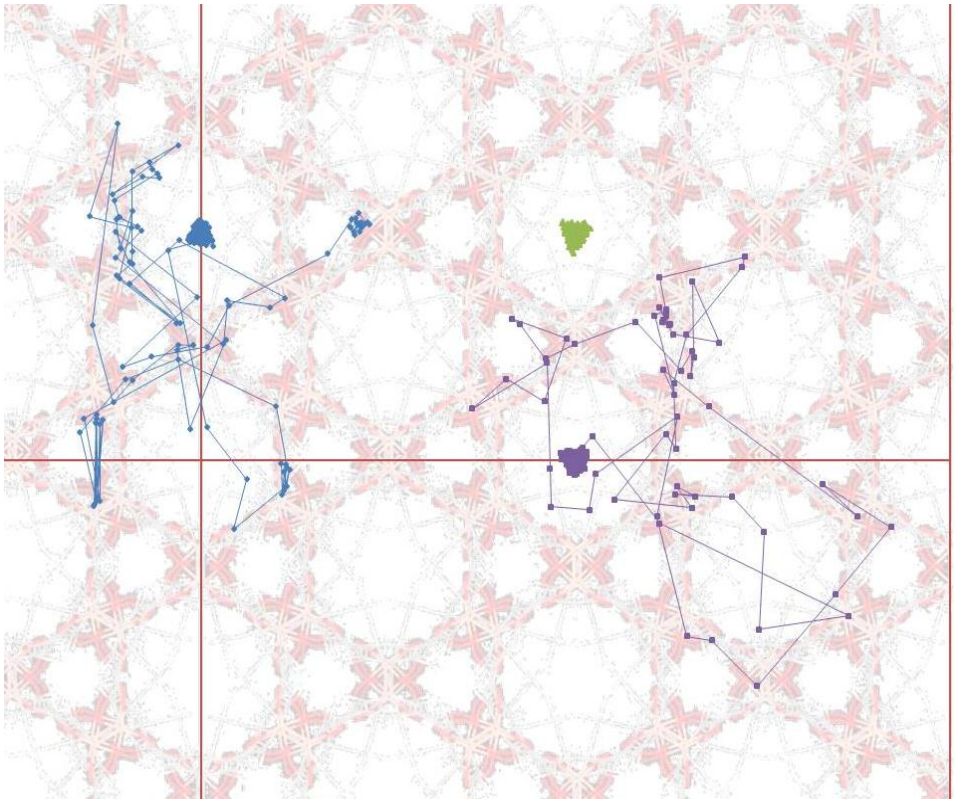

Figure S26: MD trajectories (x,y plane) of selected krypton atoms in PCN-14 at 250 K showing three krypton atoms: one (green) is confined to a single cage throughout the 2 ns simulation; one (blue) spends 1.54 ns confined to a cage and 0.46 ns outside the cage; and one (purple) spends 1.70 ns confined to a cage and 0.30 ns outside the cage. Each point represents the krypton atom position every 400 fs throughout the simulation.

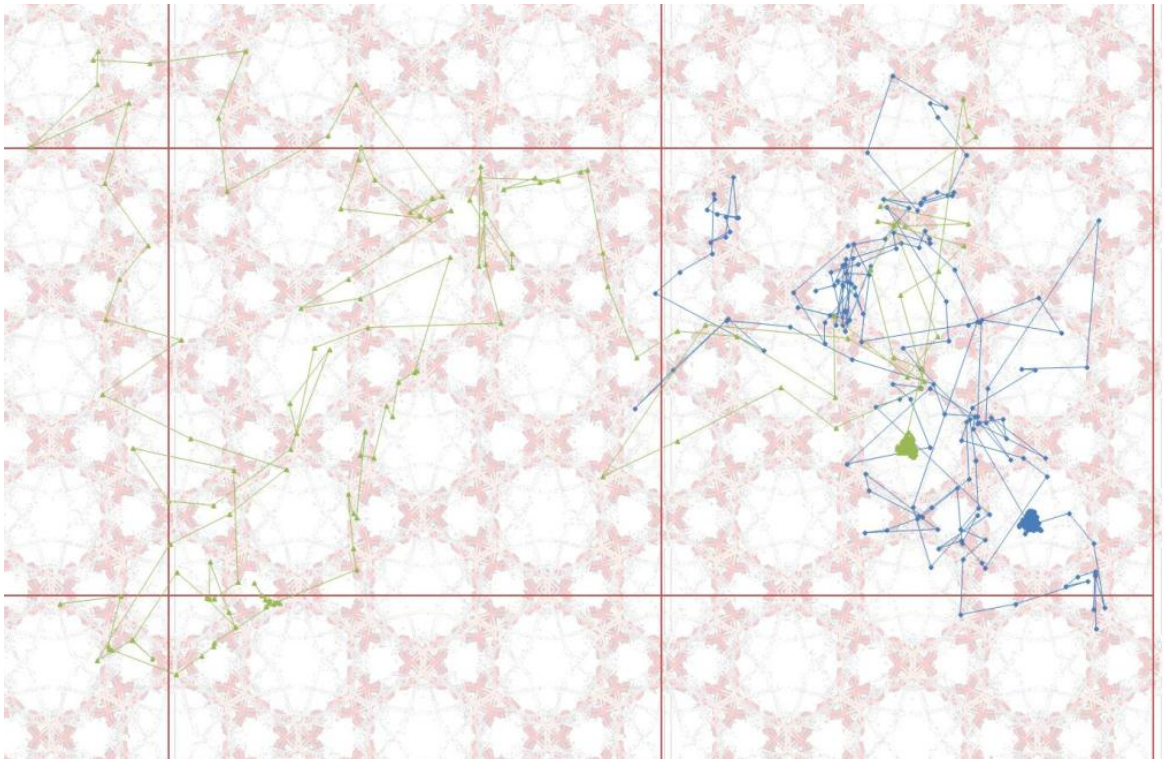

Figure S27: MD trajectories (x,y plane) of selected krypton atoms in PCN-14 at 400 K showing two krypton atoms: one (blue) spends 1.20 ns confined to a cage and 0.80 ns outside the cage; and one (green) spends 1.30 ns confined to a cage and 0.70 ns outside the cage. Each point represents the krypton atom position every 400 fs throughout the simulation.

Table S20: Fraction of simulation time krypton atoms spend trapped in a PCN-14 cage at different temperatures

Temperature	Fraction of time Kr spends trapped in a cage
250 K	0.74
300 K	0.56
350 K	0.43
400 K	0.38
450 K	0.13
500 K	0.15

VIII. Henry's constants as a function of percent free volume, for argon, xenon, radon, and nitrogen

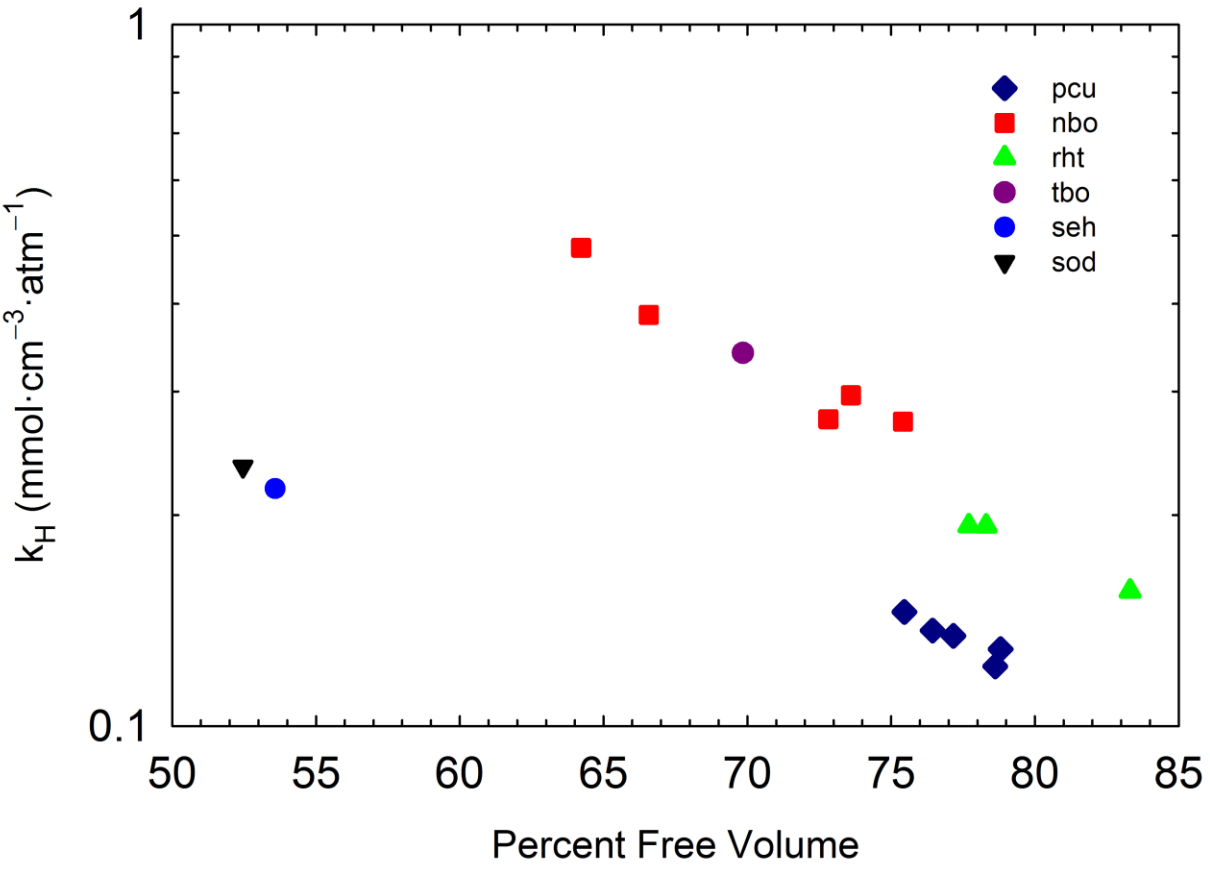

Figure S28: Henry's constants (k_H) for argon adsorption at infinite dilution plotted against percent free volume for each MOF, grouped by net topology.

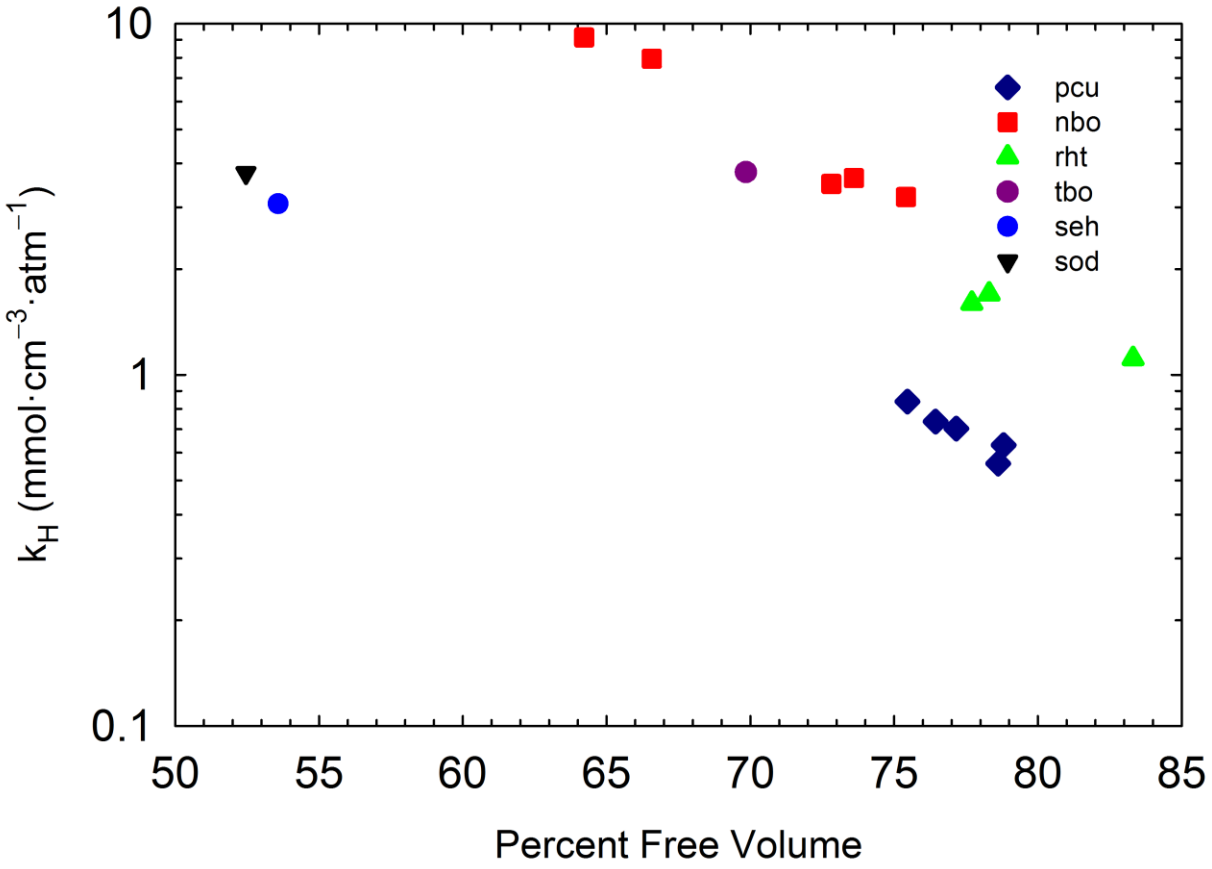

Figure S29: Henry's constants (k_H) for xenon adsorption at infinite dilution plotted against percent free volume for each MOF, grouped by net topology.

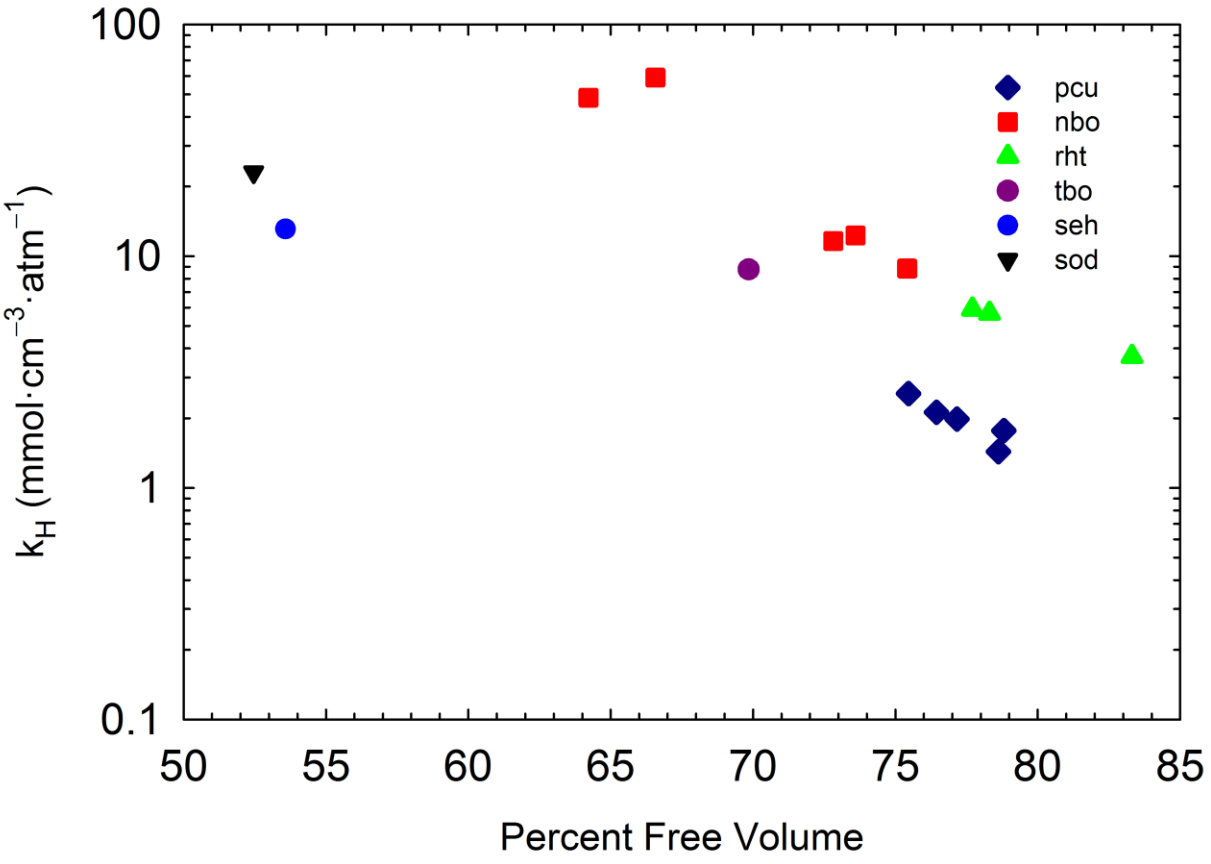

Figure S30: Henry's constants (k_H) for radon adsorption at infinite dilution plotted against percent free volume for each MOF, grouped by net topology.

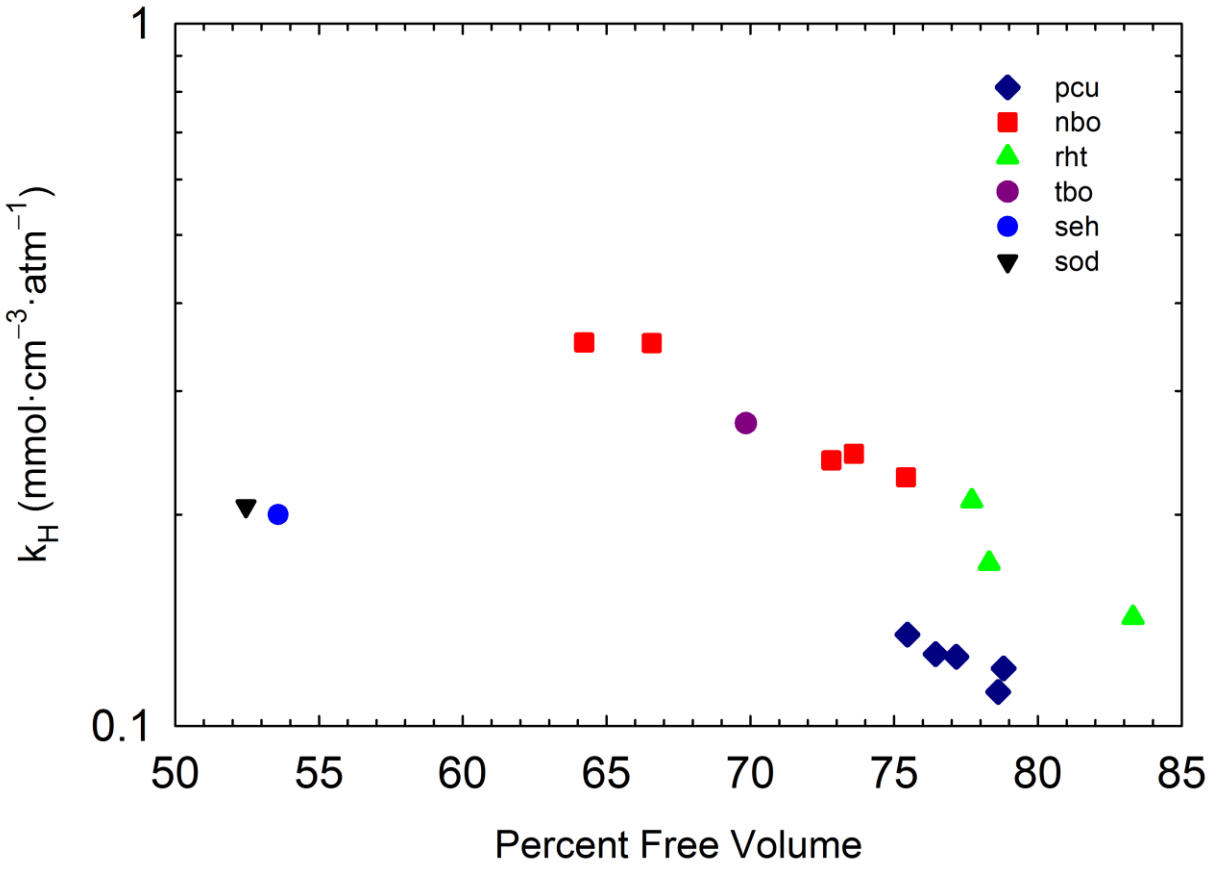

Figure S31: Henry's constants (k_H) for nitrogen adsorption at infinite dilution plotted against percent free volume for each MOF, grouped by net topology.

IX. References

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