Electronic supplementary information

CO_2 capture in rht metal–organic frameworks: multiscale modeling from molecular simulation to breakthrough prediction

Kang Zhang, Anjaiah Nalaparaju and Jianwen Jiang*

Department of Chemical and Biomolecular Engineering, National University of Singapore, 117576, Singapore

1. Structures, atomic charges and potential parameters

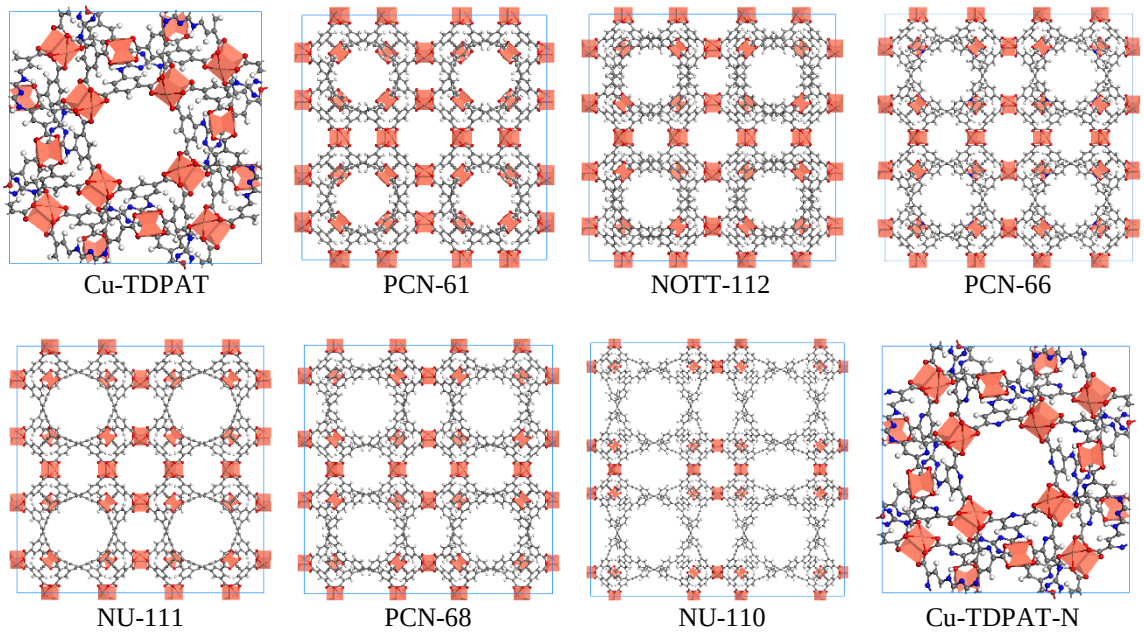


Fig. S1 Structures of **rht**-MOFs. Cu: orange polyhedron, C: grey, O: red, N: blue, and H: white. The sizes are not in the same scale.

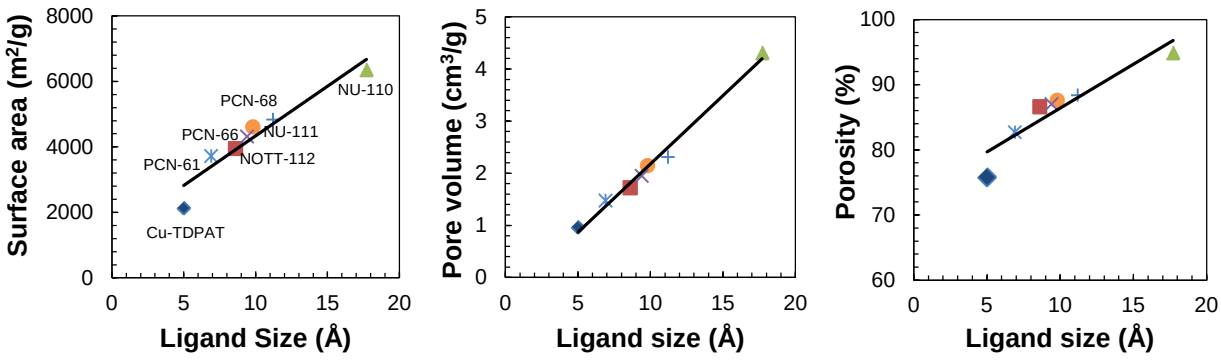
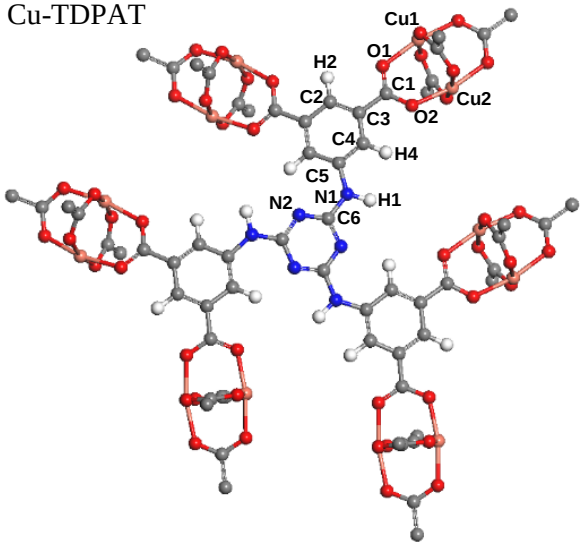
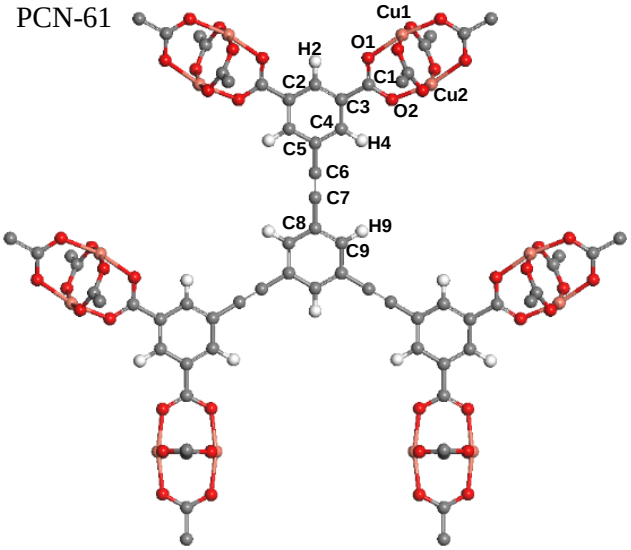


Fig. S2 Surface area, pore volume and porosity versus ligand size.

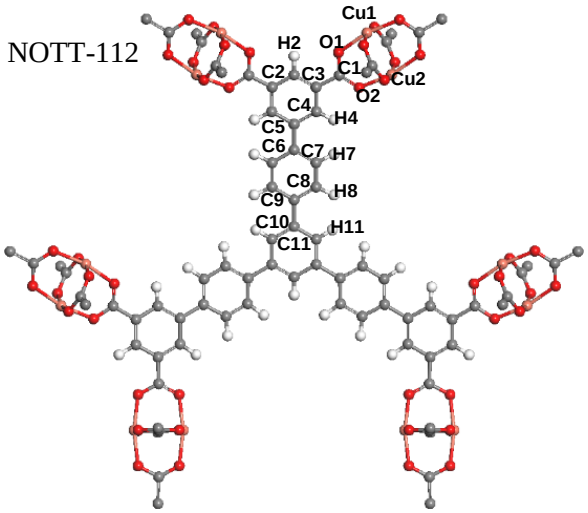
Cu-TDPAT



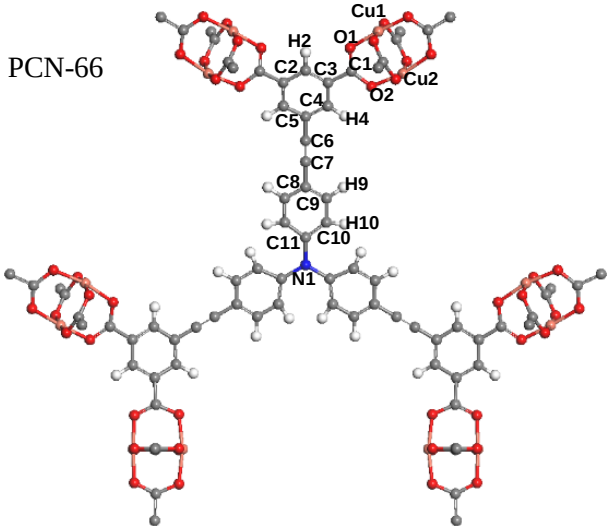
PCN-61



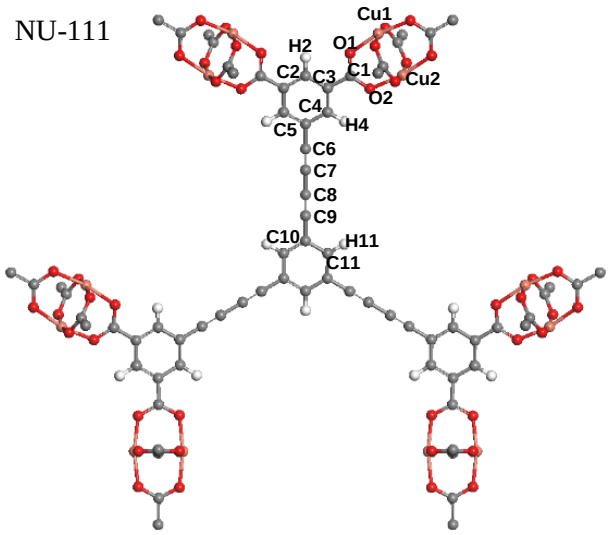
NOTT-112



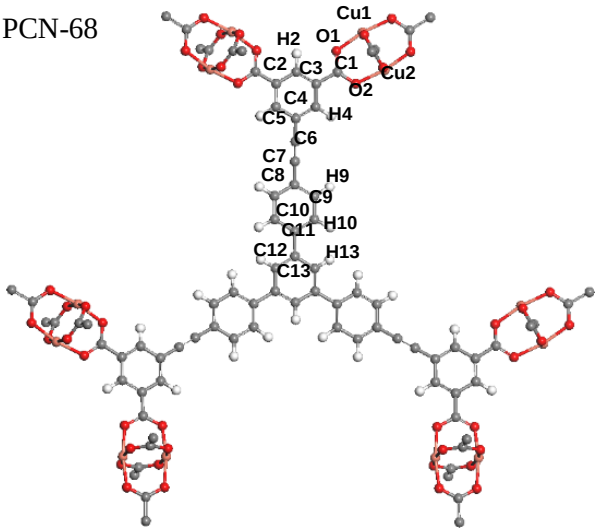
PCN-66



NU-111



PCN-68



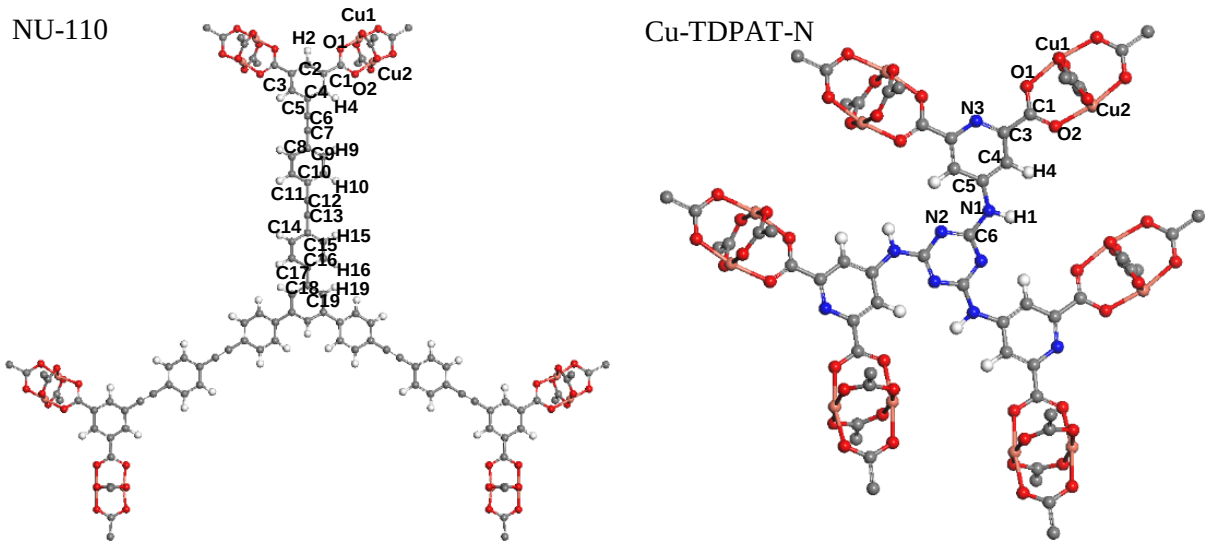


Fig. S3 Fragmental clusters used in DFT calculations. The cleaved bonds were terminated by methyl groups.

Table S1 Atomic charges of **rht**-MOFs.

Cu-TDPAT		Cu-TDPAT-N		PCN-61	
Atom	Charge (*e*)	Atom	Charge (*e*)	Atom	Charge (*e*)
Cu1	1.073	Cu1	1.091	Cu1	1.096
Cu2	1.081	Cu2	1.084	Cu2	1.067
O1	–0.657	O1	–0.653	O1	–0.657
O2	–0.672	O2	–0.683	O2	–0.667
C1	0.773	C1	0.727	C1	0.764
C2	–0.130	C3	0.370	C2	–0.089
C3	–0.016	C4	–0.421	C3	–0.025
C4	–0.231	C5	0.624	C4	–0.148
C5	0.440	C6	1.014	C5	0.221
C6	1.024	N1	–0.768	C6	–0.138
N1	–0.749	N2	–0.839	C7	–0.117
N2	–0.864	N3	–0.546	C8	0.248
H1	0.378	H1	0.389	C9	–0.264
H2	0.127	H4	0.179	H2	0.117
H4	0.152			H4	0.129
				H9	0.147

NOTT-112		NU-111		PCN-66		PCN-68	
Atom	Charge (*e*)	Atom	Charge (*e*)	Atom	Charge (*e*)	Atom	Charge (*e*)
Cu1	1.078	Cu1	1.073	Cu1	1.017	Cu1	1.055
Cu2	1.060	Cu2	1.048	Cu2	1.032	Cu2	1.090
O1	–0.644	O1	–0.645	O1	–0.568	O1	–0.631
O2	–0.646	O2	–0.645	O2	–0.602	O2	–0.655
C1	0.736	C1	0.744	C1	0.588	C1	0.717
C2	–0.076	C2	–0.083	C2	–0.155	C2	–0.121
C3	–0.036	C3	–0.028	C3	0.045	C3	0.002
C4	–0.099	C4	–0.153	C4	–0.170	C4	–0.171
C5	0.017	C5	0.251	C5	0.232	C5	0.245
C6	0.120	C6	–0.162	C6	–0.110	C6	–0.153
C7	–0.161	C7	0.006	C7	–0.212	C7	–0.135
C8	–0.148	C8	–0.004	C8	0.332	C8	0.235
C9	0.111	C9	–0.140	C9	–0.203	C9	–0.155
C10	0.042	C10	0.269	C10	–0.223	C10	–0.176
C11	–0.146	C11	–0.265	C11	0.357	C11	0.135
H2	0.111	H2	0.118	N1	–0.494	C12	0.017
H4	0.101	H4	0.130	H2	0.141	C13	–0.112
H7	0.115	H11	0.143	H4	0.138	H2	0.130
H8	0.125			H9	0.130	H4	0.135
H11	0.064			H10	0.143	H9	0.115
						H10	0.138
						H13	0.051

NU-110					
Atom	Charge (*e*)	Atom	Charge (*e*)	Atom	Charge (*e*)
Cu1	1.103	C7	–0.117	C17	0.054
Cu2	1.250	C8	0.220	C18	0.079
O1	–0.622	C9	–0.160	C19	–0.172
O2	–0.639	C10	–0.162	H2	0.114
C1	0.644	C11	0.233	H4	0.137
C2	–0.081	C12	–0.151	H9	0.123
C3	–0.025	C13	–0.144	H10	0.118
C4	–0.166	C14	0.261	H15	0.116
C5	0.262	C15	–0.183	H16	0.111
C6	–0.167	C16	–0.120	H19	0.084

Table S2 Universal force field parameters of **rht**-MOFs.

Atom	σ (Å)	ε/k_B
Cu	3.114	2.5138
O	3.118	30.166
N	3.261	34.691
C	3.431	52.790
H	2.571	22.122

Table S3 Potential parameters of CO_2, N_2, H_2 and CH_4.

Adsorbate	Site	σ (Å)	ε/k_B (K)	q (e)
CO_2	C	2.8	27	0.7
	O	3.05	79	–0.35
N_2	N	3.32	36.4	-
H_2	H	2.96	34.2	-
CH_4	CH_4	3.75	148	-

2. Breakthrough prediction

D_L, D_m and k_f in equations (5) and (7) were calculated using the Edwards-Richardson correlation,[1] the Chapman-Enskog equation,[2] and the Wakao-Funazkri correlation,[3] respectively. The parameters used are listed in Tables S4-S5.

Table S4 Parameters and constants.[4,5]

	CO_2	N_2	CH_4	H_2
Molar mass (g/mol)	44.009	28.014	16.043	2.016
Density (kg/m^3)	1.776	1.131	0.648	0.0814
Viscosity (10^{-5} kg/m/s)	1.503	1.769	1.114	0.885

Table S5 Fixed-bed properties and feed conditions.

Notation	Meaning	Value
T	temperature (K)	298
P	pressure (bar)	1
L_b	bed length (m)	0.2
ε_b	bed voidage	0.4
v	interstitial feed velocity (m/s)	0.07
R_p	particle radius (cm)	0.15
ε_p/τ_p	porosity/tortuosity	0.1

3. Comparison of experimental and simulated adsorption isotherms

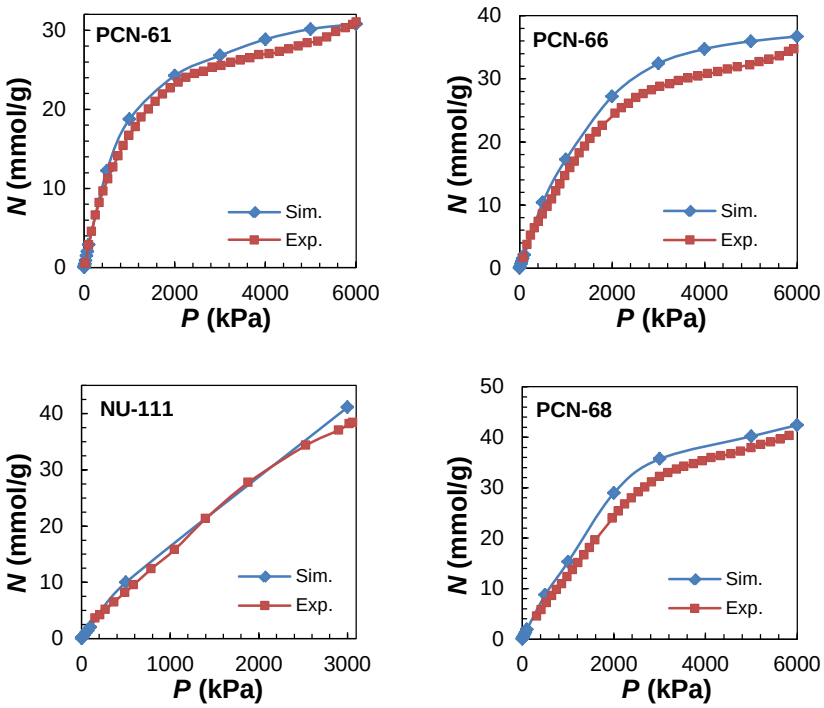


Fig. S4 CO_2 adsorption isotherms at 298 K. Experimental data in PCN-61, -66, and -68 are from ref. 6, in NU-111 from ref. 7.

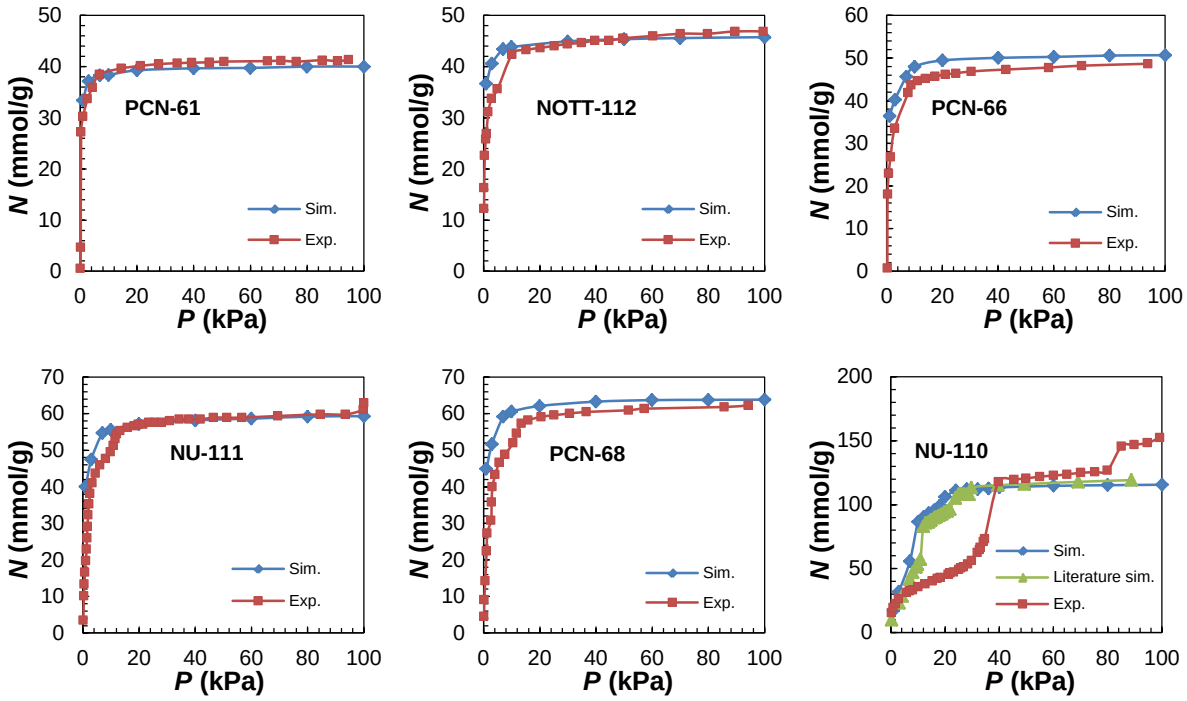


Fig. S5 N_2 adsorption isotherms at 77 K. Experimental data in PCN-61, -66, and -68 are from ref. 6, in NOTT-112 from ref. 8, in NU-111 from ref. 7. Experimental and literature simulation data in NU-110 are from ref. 9.

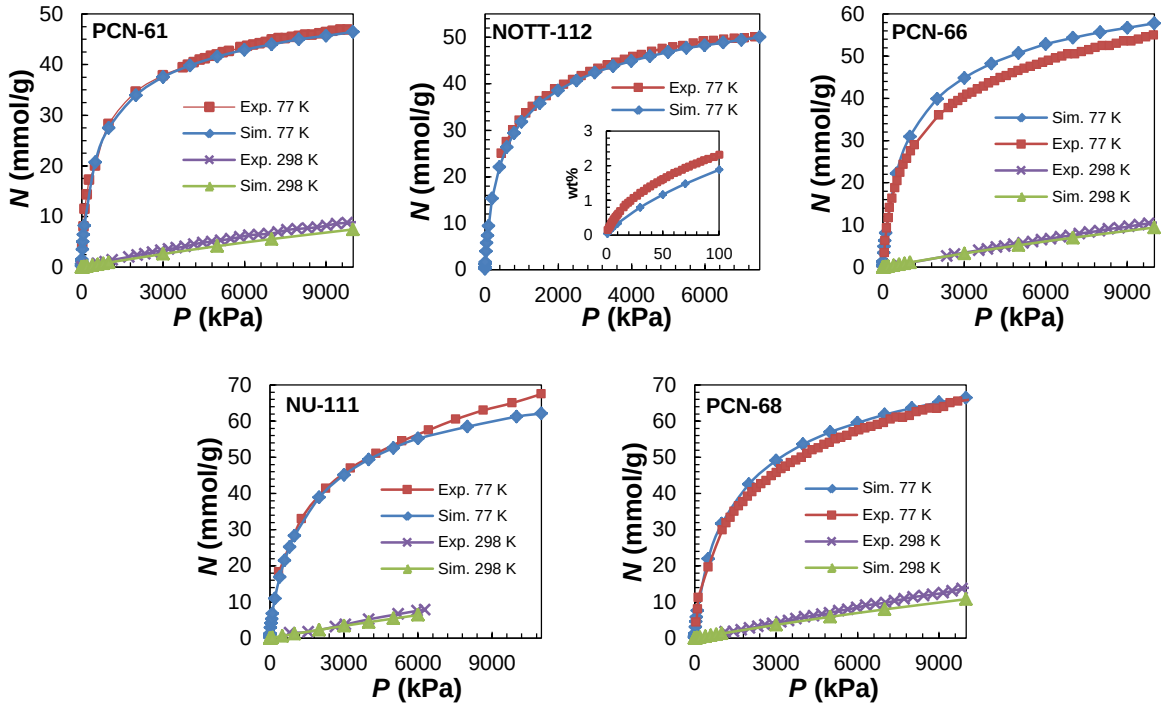


Fig. S6 H_2 adsorption isotherms. Experimental data in PCN-61, -66, and -68 are from ref. 6, in NOTT-112 from ref. 8, in NU-111 from ref. 7 for 298 K and from ref. 10 for 77 K.

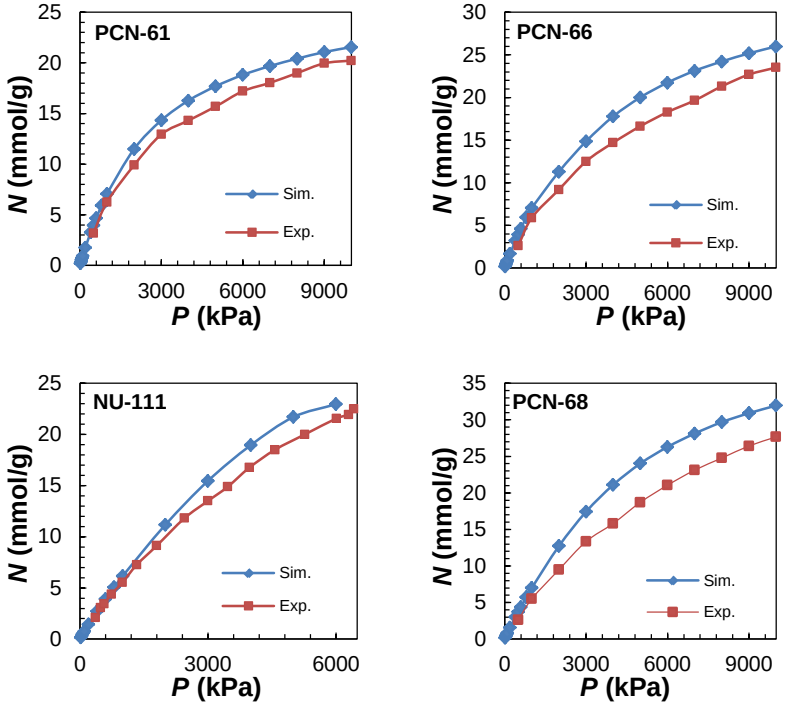


Fig. S7 CH_4 adsorption isotherms at 298 K. Experimental data in PCN-61, -66, and -68 are from ref. 6, in NU-111 from ref. 7.

References

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