Inelastic Neutron Scattering and Theoretical Studies of H_2 Sorption in a Dy(III)-Based Phosphine Coordination Material

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PCM-16 System Cell

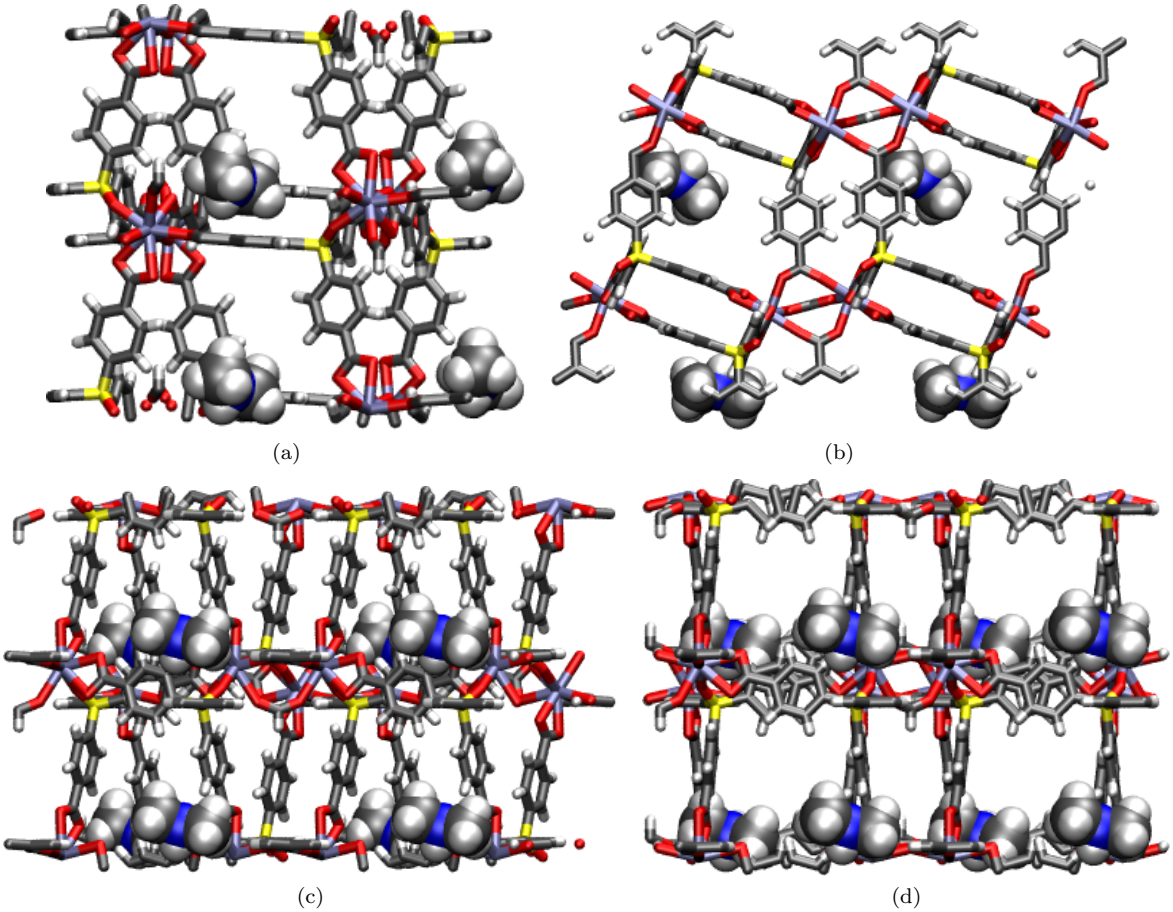


Figure S1. (a) The *a*-axis view, **(b)** *b*-axis view, **(c)** *c*-axis view, and **(d)** shifted *c*-axis view of the 2 × 2 × 1 system cell of PCM-16. The $(CH_3)_2NH_2^+$ counterions are shown in van der Waals representation in their equilibrium positions. All views are orthographic projections. Atom colors: C = grey, H = white, N = blue, O = red, P = yellow, Dy = lavender.

PCM-16 Partial Charges

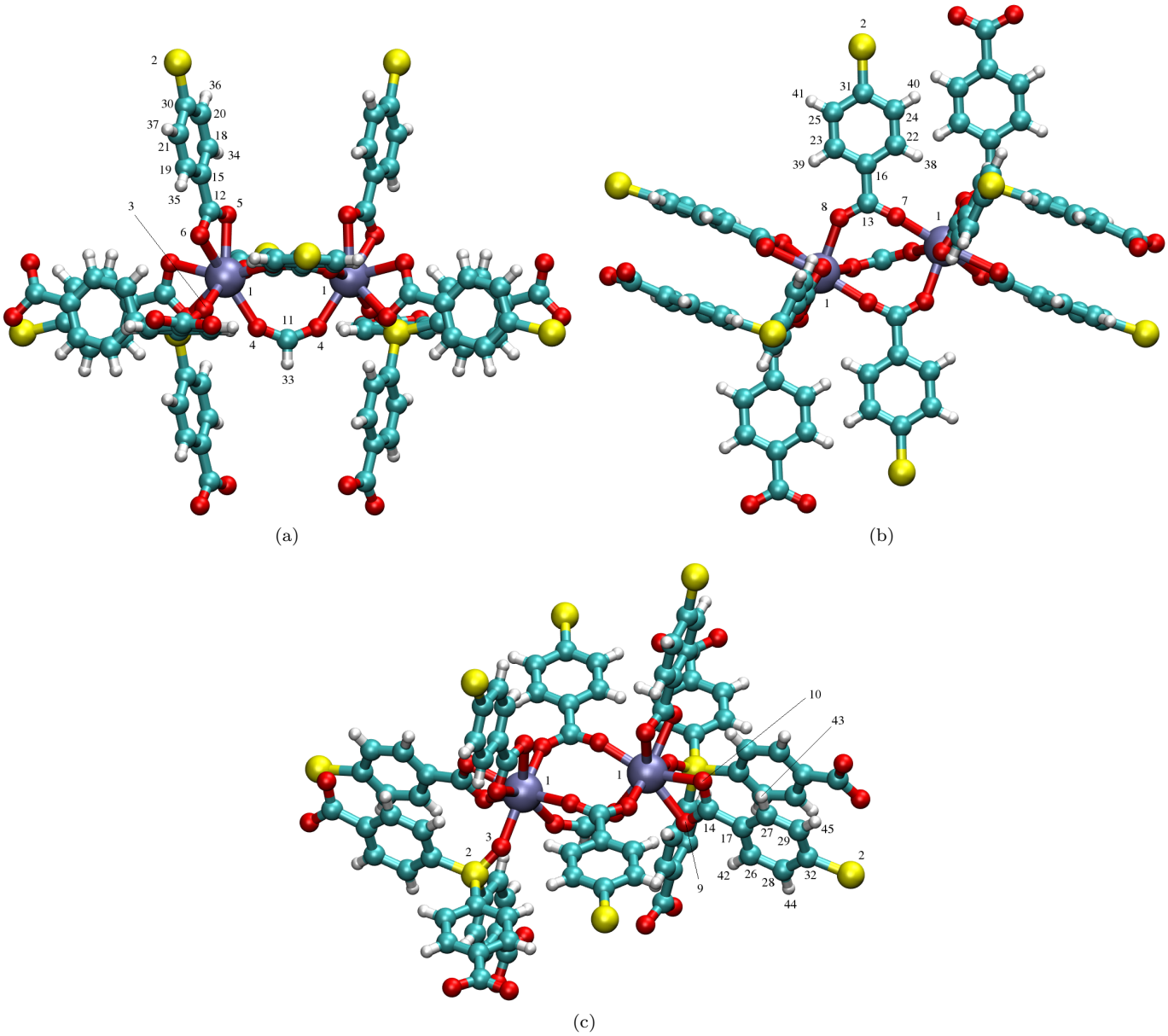


Figure S2. The numbering of the chemically distinct atoms in PCM-16 as referred to in Tables S1 and S2: **(a)** view 1; **(b)** view 2; **(c)** view 3. Atom colors: C = cyan, H = white, N = blue, O = red, P = yellow, Dy = lavender.

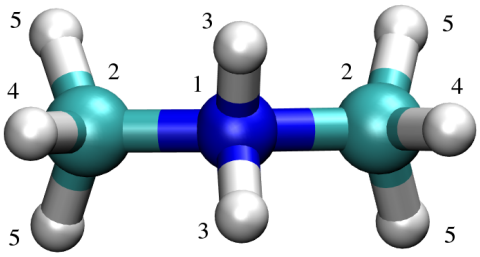


Figure S3. The numbering of the chemically distinct atoms on the $(CH_3)_2NH_2^+$ counterion as referred to in Table S3. Atom colors: C = cyan, H = white, N = blue.

Table S1. The crystallographic distances (Å) between various atoms in PCM-16. Label of atoms correspond to Figure S2.

Atom Pair	Distance (Å)
1–3	2.30413
1–4	2.33033
1–5	2.41892
1–6	2.45286
1–7	2.25342
1–8	2.29757
1–9	2.42732
1–10	2.42081
2–3	1.49599
2–30	1.77375
2–31	1.80162
2–32	1.81337
5–12	1.26946
6–12	1.23885
7–13	1.23672
8–13	1.25550
9–14	1.27686
10–14	1.26012

Table S2. The partial charges (e^-) for the chemically distinct atoms in PCM-16. Label of atoms correspond to Figure S2. These partial charges were determined using the extended charge equilibration (EQ_{eq}) method.[1]

Atom	Label	q (e^-)
Dy	1	2.12080
P	2	0.22070
O	3	-0.42430
O	4	-0.47760
O	5	-0.41440
O	6	-0.42310
O	7	-0.55750
O	8	-0.52310
O	9	-0.41490
O	10	-0.43480
C	11	0.41170
C	12	0.29600
C	13	0.48830
C	14	0.28470
C	15	-0.07170
C	16	-0.16920
C	17	-0.07090
C	18	-0.02040
C	19	-0.03260
C	20	-0.06690
C	21	-0.06320
C	22	0.06180
C	23	0.05570
C	24	-0.10500
C	25	-0.11400
C	26	-0.02240
C	27	0.00180
C	28	-0.06920
C	29	-0.08240
C	30	-0.03460
C	31	0.01050
C	32	-0.02590
H	33	-0.08260
H	34	0.04520
H	35	0.03870
H	36	0.06650
H	37	0.03040
H	38	0.01560
H	39	0.00850
H	40	0.07480
H	41	0.04970
H	42	0.01580
H	43	0.01360
H	44	0.00800
H	45	0.05370

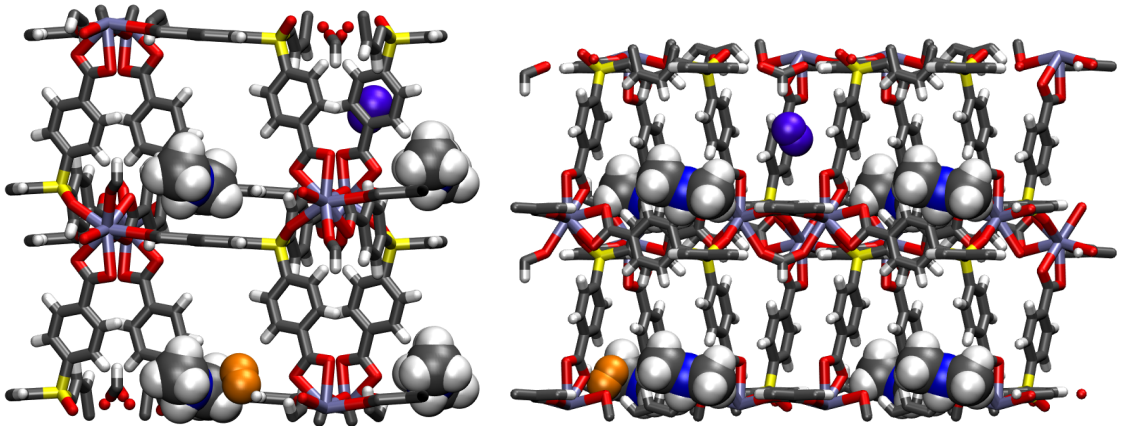
Table S3. The partial charges (e^-) for the chemically distinct atoms on the $(CH_3)_2NH_2^+$ counterion. Label of atoms corresponds to Figure S3. These partial charges were determined in previous work.[2]

Atom	Label	q (e^-)
N	1	0.20260
C	2	-0.19430
H	3	0.22290
H	4	0.12150
H	5	0.12430

Two-Dimensional Rotational Levels

Table S4. The calculated two-dimensional quantum rotational levels for a H_2 molecule sorbed at the two sites in PCM-16. Sites 1 and 2 are depicted in Figure S4. Relative energies are given in meV.

n	j	Site 1 ΔE (meV)	Site 2 ΔE (meV)
1	0	0.00	0.00
2		7.63	12.30
3	1	18.38	15.65
4		24.24	16.57
5		40.65	42.60
6		41.49	43.02
7	2	44.92	43.70
8		53.18	46.12
9		54.41	46.15



(a) (b)

Figure S4. **(a)** The *a*-axis view and **(b)** *c*-axis view of the 2 × 2 × 1 system cell of PCM-16 showing the singular locations of sites 1 (orange) and 2 (violet) that were used for the two-dimensional quantum rotation calculations in this work. Site 1 corresponds to sorption about the $(CH_3)_2NH_2^+$ counterions, whereas site 2 corresponds to sorption within the small pores of the framework. The $(CH_3)_2NH_2^+$ counterions are shown in van der Waals representation in their equilibrium positions. All views are orthographic projections. Atom colors: C = grey, H = white, N = blue, O = red, P = yellow, Dy = lavender.

Isosteric Heat of Adsorption

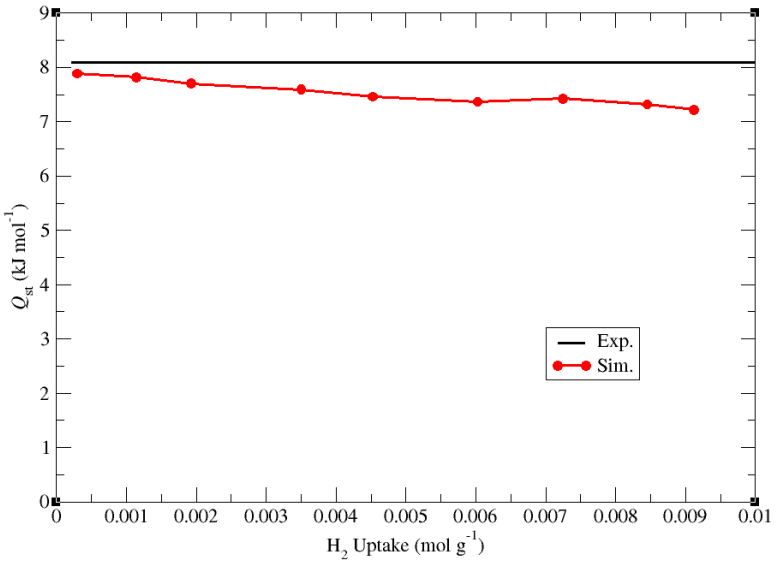


Figure S5. Isosteric heats of adsorption (Q_{st}) for H_2 in PCM-16 plotted against H_2 uptakes for experiment (black) and simulation (red). The simulated Q_{st} values were determined through fluctuations of the particle number and total potential energy within the PCM-16–H_2 system in grand canonical Monte Carlo (GCMC) simulations.[3] The experimental data was estimated from reference 4.

[1] Wilmer, C. E.; Kim, K. C.; Snurr, R. Q. An Extended Charge Equilibration Method. *J. Phys. Chem. Lett.* **2012**, *3*, 2506–2511.
[2] Pham, T.; Forrest, K. A.; Georgiev, P. A.; Lohstroh, W.; Xue, D.-X.; Hogan, A.; Eddaoudi, M.; Space, B.; Eckert, J. A high rotational barrier for physisorbed hydrogen in an fcu-metal–organic framework. *Chem. Commun.* **2014**, *50*, 14109–14112.
[3] Nicholson, D.; Parsonage, N. G. *Computer Simulation and the Statistical Mechanics of Adsorption*; Academic Press: London, 1982; pp. 97.
[4] Ibarra, I. A.; Yoon, J. W.; Chang, J.-S.; Lee, S. K.; Lynch, V. M.; Humphrey, S. M. Organic Vapor Sorption in a High Surface Area Dysprosium(III)–Phosphine Oxide Coordination Material. *Inorg. Chem.* **2012**, *51*, 12242–12247, PMID: 23116537.