Supplementary Material for PCCP

Electronic Supplementary Information

Computational Screening of Metal-Organic Frameworks for Large-Molecule Chemical Sensing

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1. Molecular Models of MOFs

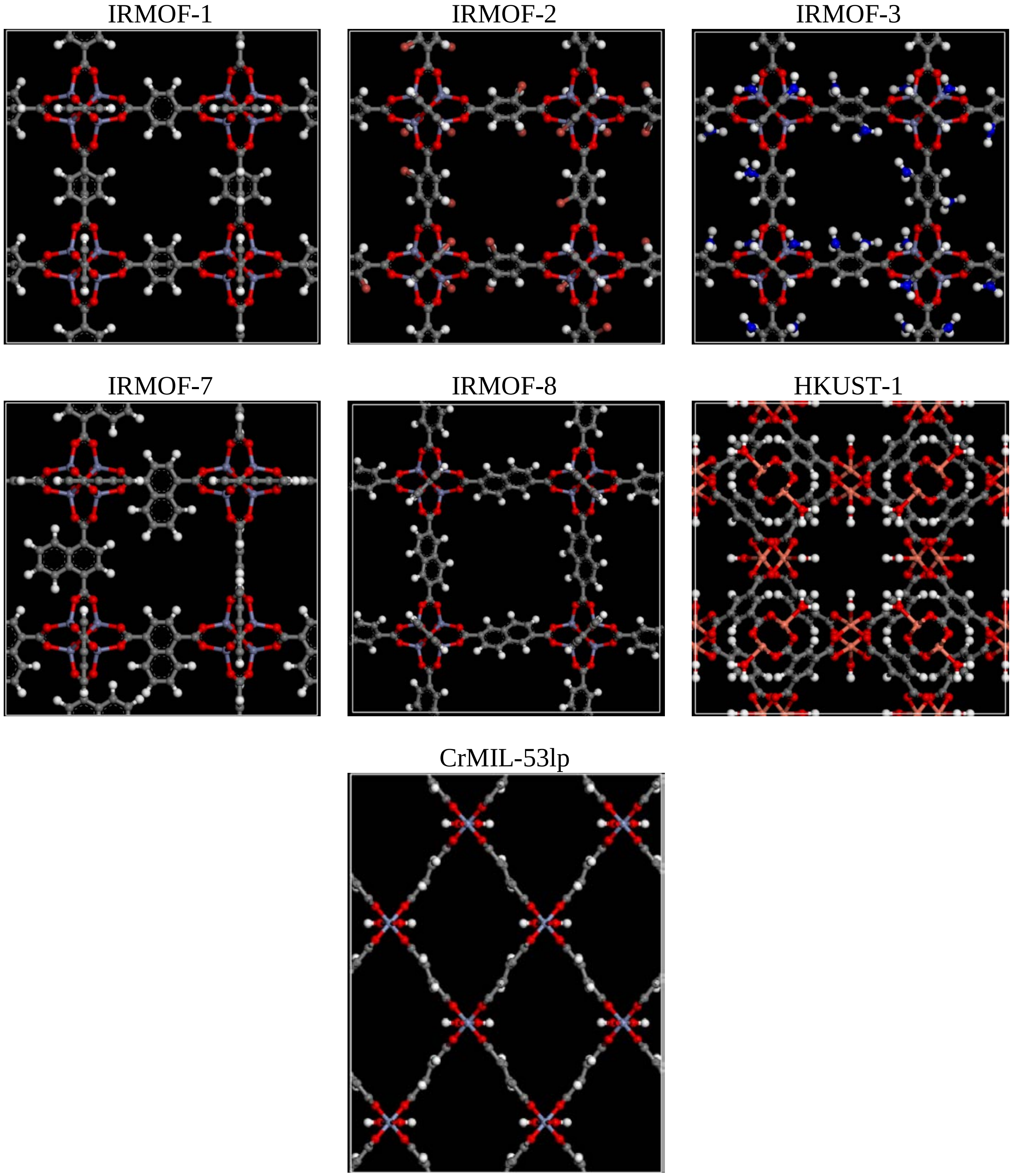
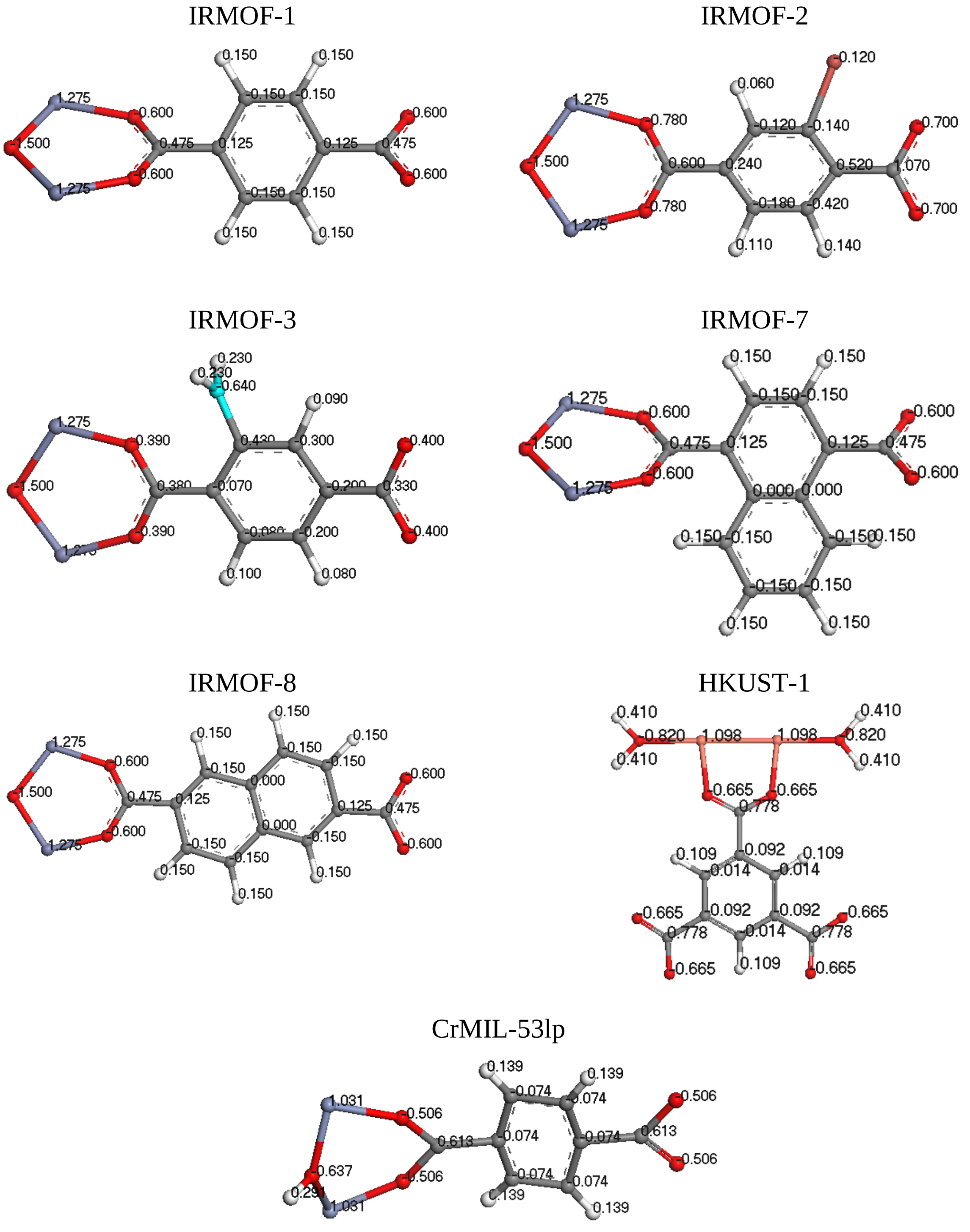


Figure S1. Molecular models of the MOFs used in this study.

2. ab initio Methods

Charges were calculated using the same approach as Dubbleldam et al.[1] Using the program, Gaussian (Gaussian, Inc.), *ab initio* cluster calculations were performed on experimental crystal structures to determine the charge distribution among atoms. Single point direct self-consistent field (SCF) calculations with normal tight convergence were used to calculate the energy of each MOF structure. These single point calculations were performed using the PBEPBE[2] for exchange and correlation and 6-31+g* basis set which includes one polarization (*) and one diffuse (+) function on all atoms except hydrogen. The POP = (readradii, chelpg) option was used. This option produces charges that fit an electrostatic potential at points selected according to the CHelpeG scheme developed by Breneman and Wiberg.[3] This method requires input atomic radii. The radii used for Br, C, N, O, Zn, and H are 1.85, 1.70, 1.55, 1.52, 1.39, and 1.09 Å respectively.[4]

3. Atomic Charges


IRMOF-1

IRMOF-2

IRMOF-3

IRMOF-7

IRMOF-8

HKUST-1

CrMIL-53lp

Figure S2. Atomic charges for MOFs used in this study.

4. Adsorption Isotherms

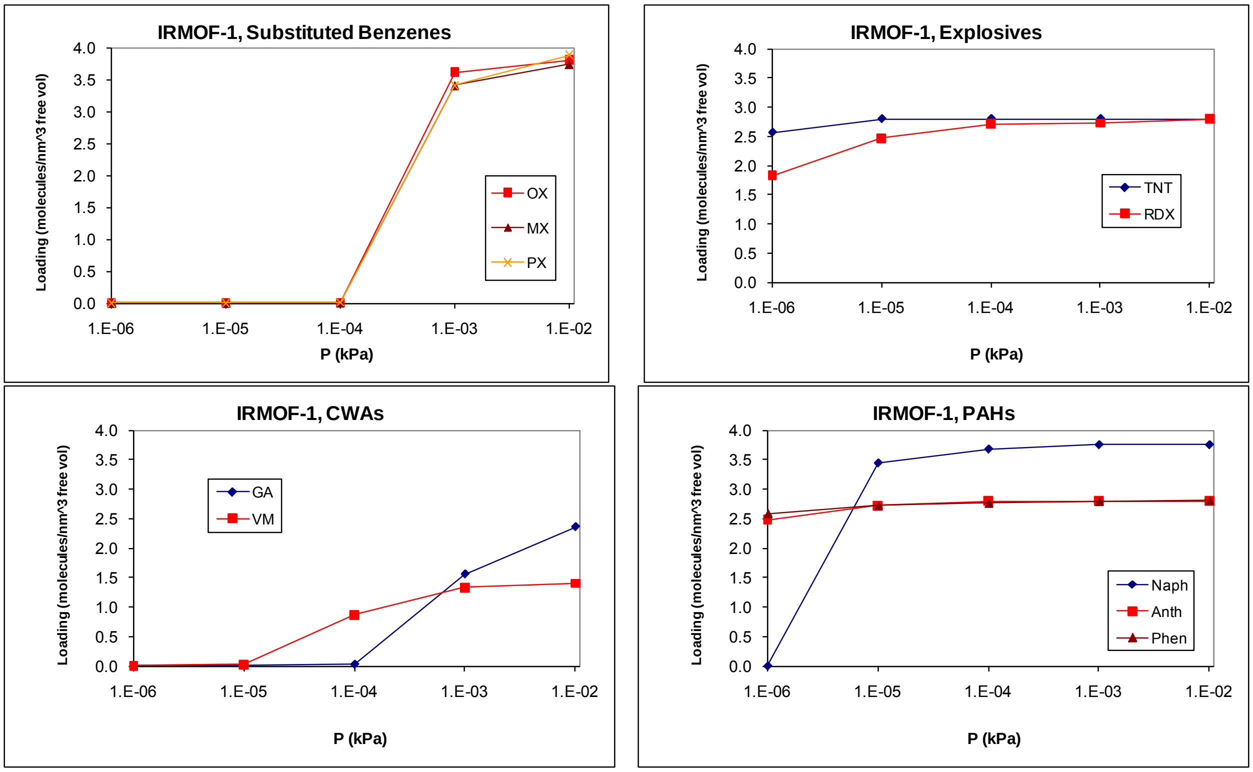


Figure S3. Adsorption isotherms for IRMOF-1 at 298 K.

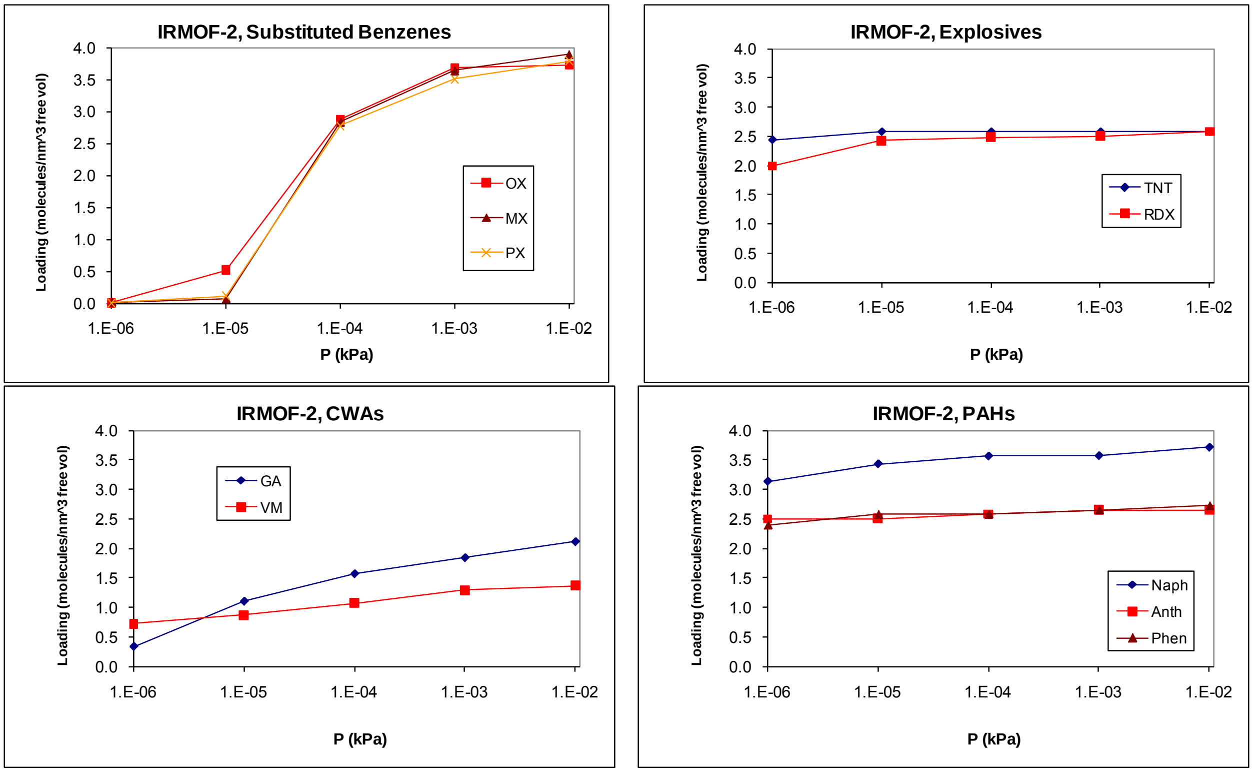


Figure S4. Adsorption isotherms for IRMOF-2 at 298 K.

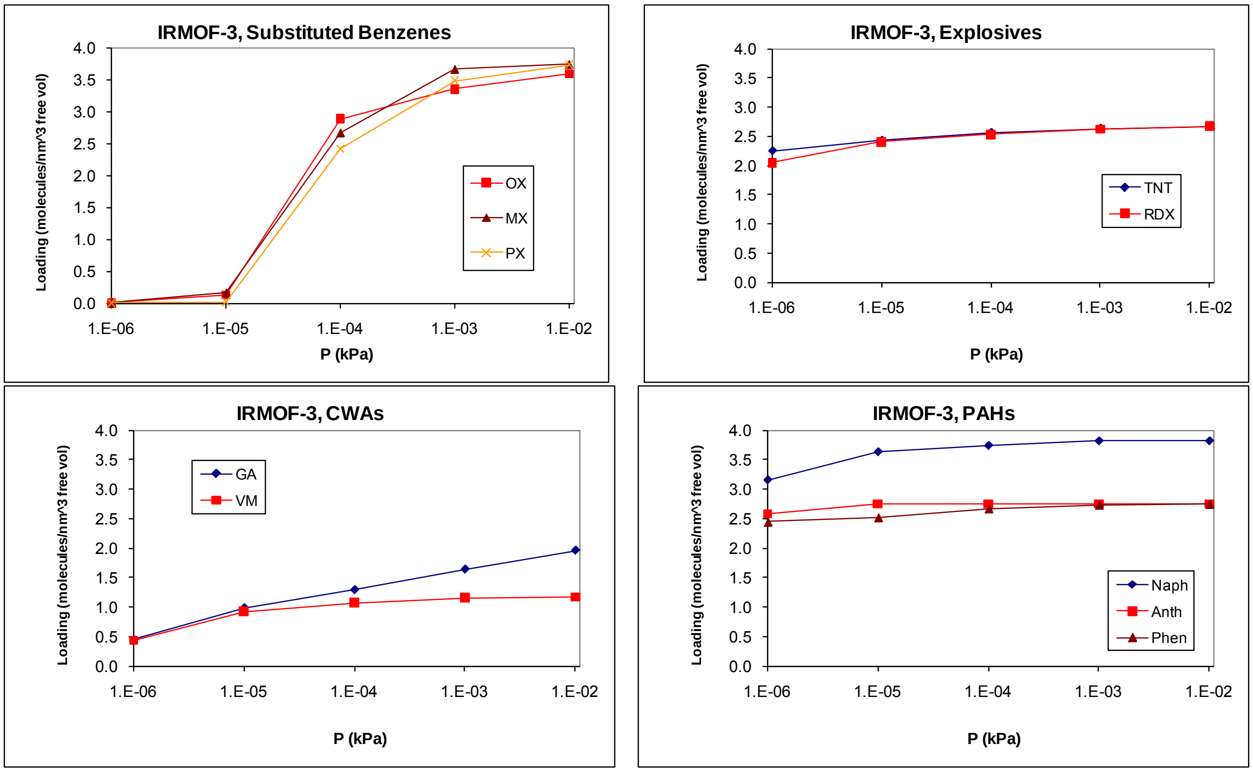


Figure S5. Adsorption isotherms for IRMOF-3 at 298 K.

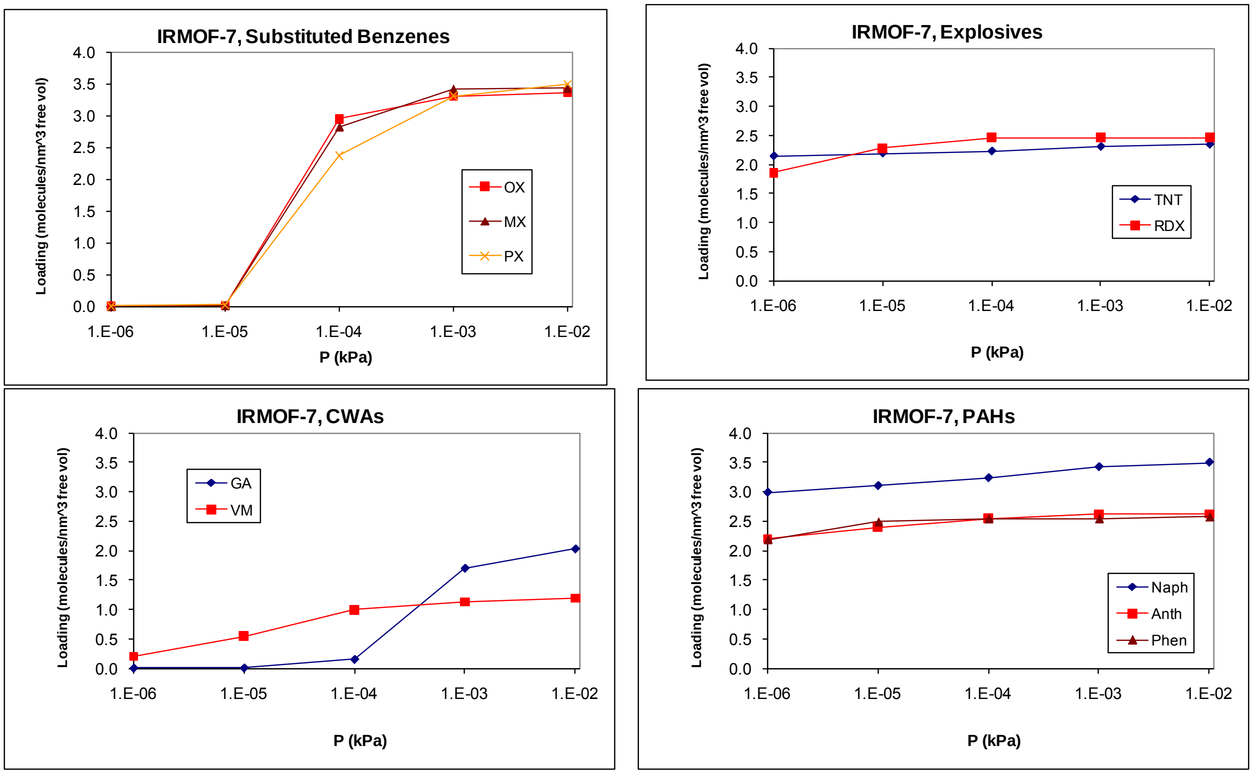


Figure S6. Adsorption isotherms for IRMOF-7 at 298 K.

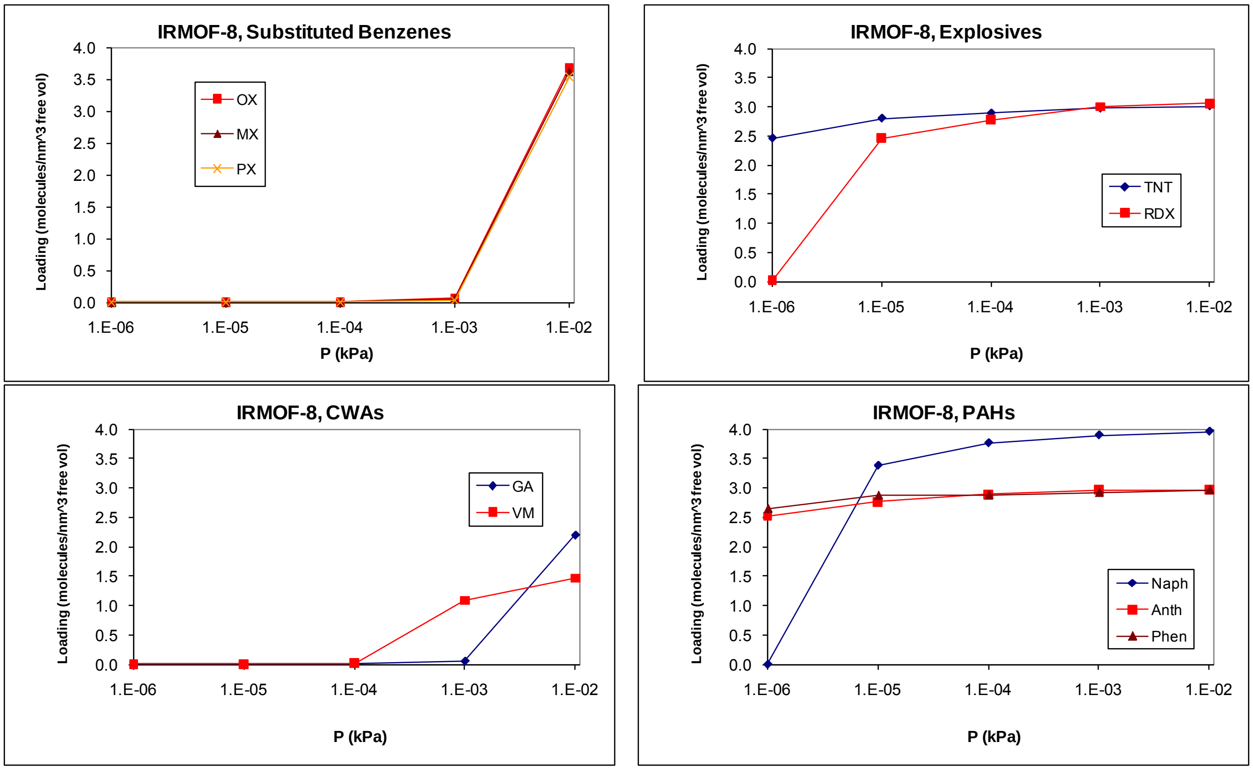


Figure S7. Adsorption isotherms for IRMOF-8 at 298 K.

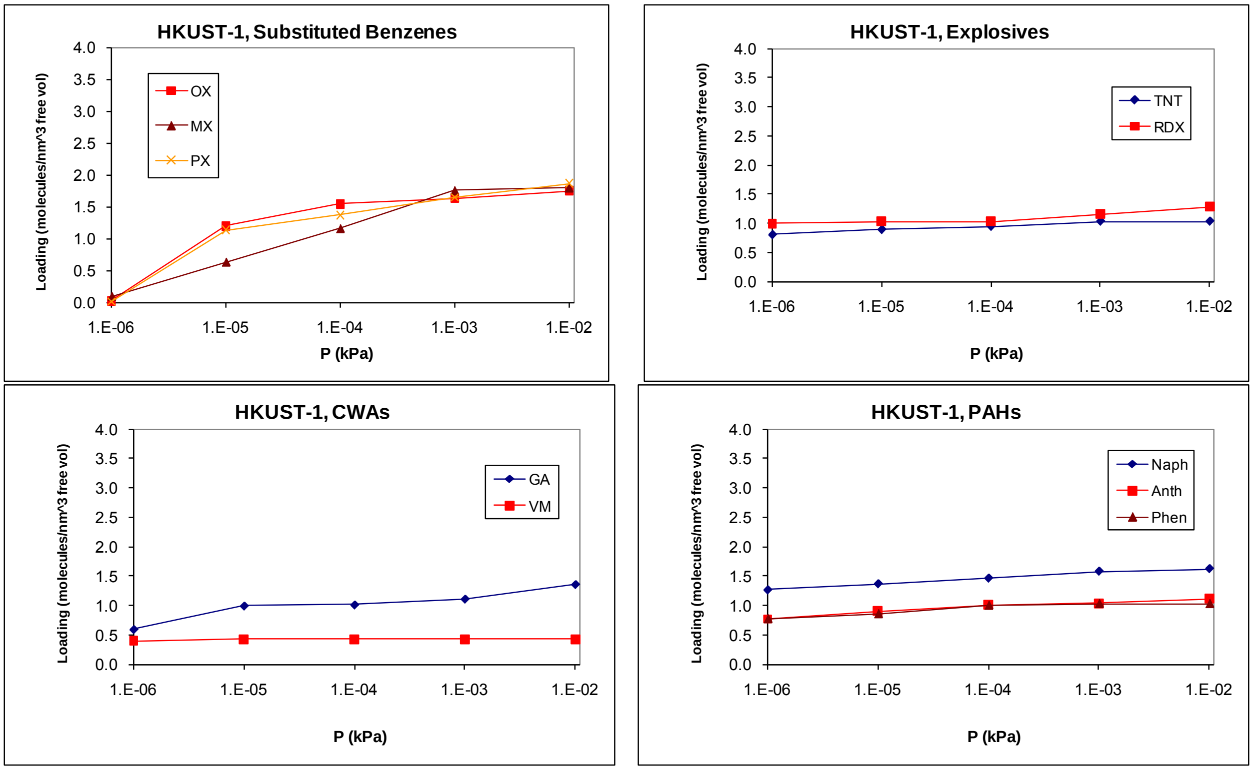


Figure S8. Adsorption isotherms for HKUST-1 at 298 K.

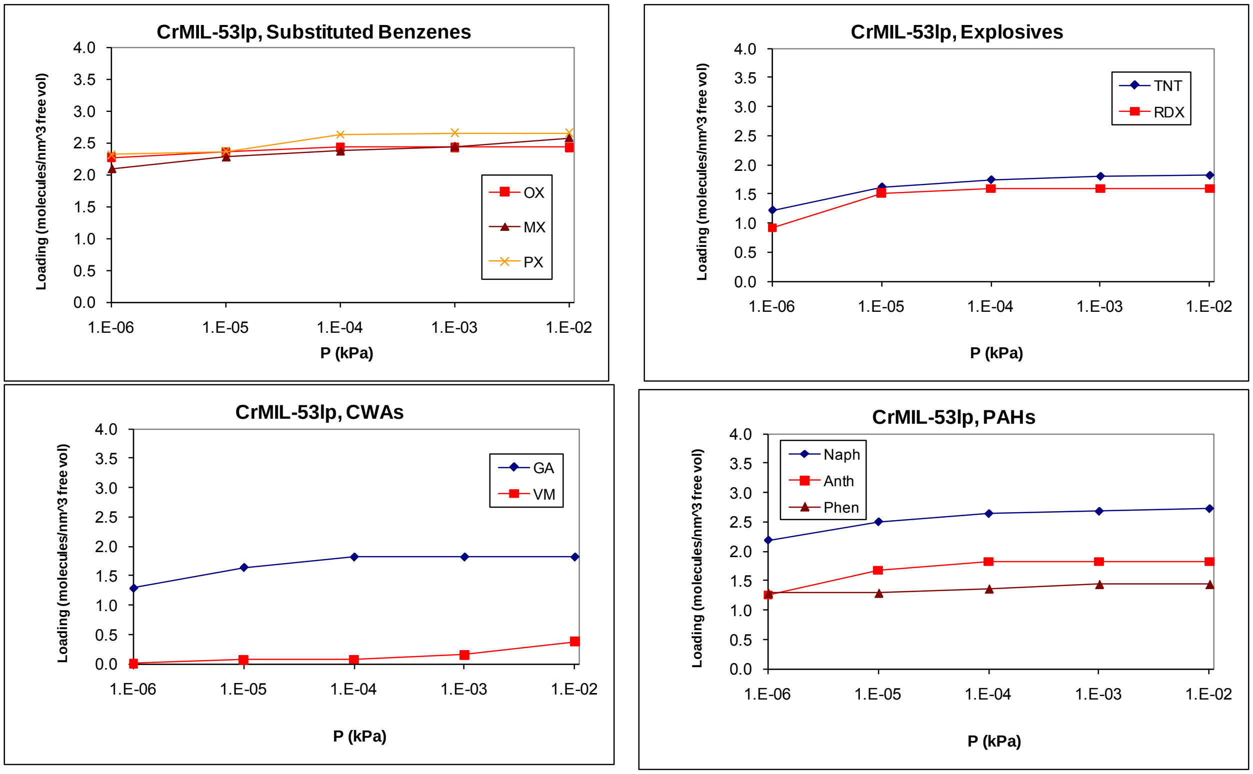


Figure S9. Adsorption isotherms for CrMIL-53lp at 298 K.

5. Dependence on Simulation Length

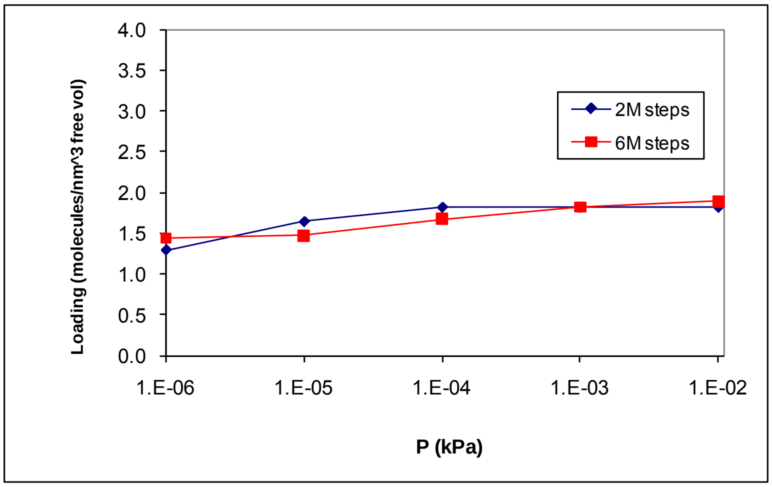


Figure S10. Adsorption isotherms for GA adsorption in CrMIL-53lp at 2 x 10^6 steps and 6 x 10^6 steps. Data were averaged over the final 1 x 10^6 steps and 3 x 10^6 steps, respectively.

6. Dependence on Analyte Flexibility

Table S1. Comparison of Isosteric Heats of Adsorption (kcal·mol^{-1}) at 298 K for Rigid Analyte (GCMC) and Flexible Analyte (Molecular Dynamics) at Infinite Dilution.

MOF	analyte	Q_{st}	
		GCMC (rigid)	MD (flexible)[a]
IRMOF-1	NAPH	15.3	11.8
IRMOF-7	NAPH	20.3	17.2
IRMOF-1	VM	15.3	15.8
IRMOF-3	VM	24.4	29.2

[a] Results for molecular dynamics (MD) simulation were obtained using the Forcite module of Materials Studio. Simulations were 2.0 ns long with a timestep of 1.0 fs, and data from the final 1.0 ns were used according to $Q_{st} = \langle E_{gh} \rangle - \langle E_g \rangle - RT$, where E_{gh} is the average potential energy of the adsorbed guest, E_g is the average potential energy of the analyte in an ideal gas reference state (1 molecule in a box with no framework), and RT is the thermal energy.

References

1. D. Dubbeldam, K. S. Walton, D. E. Ellis and R. Q. Snurr, *Angew. Chem. Int. Ed.*, 2007, **46**, 4496-4499.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
3. C. M. Breneman and K. B. Wiberg, *J. Comput. Chem.*, 1990, **11**, 361-373.
4. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451.