



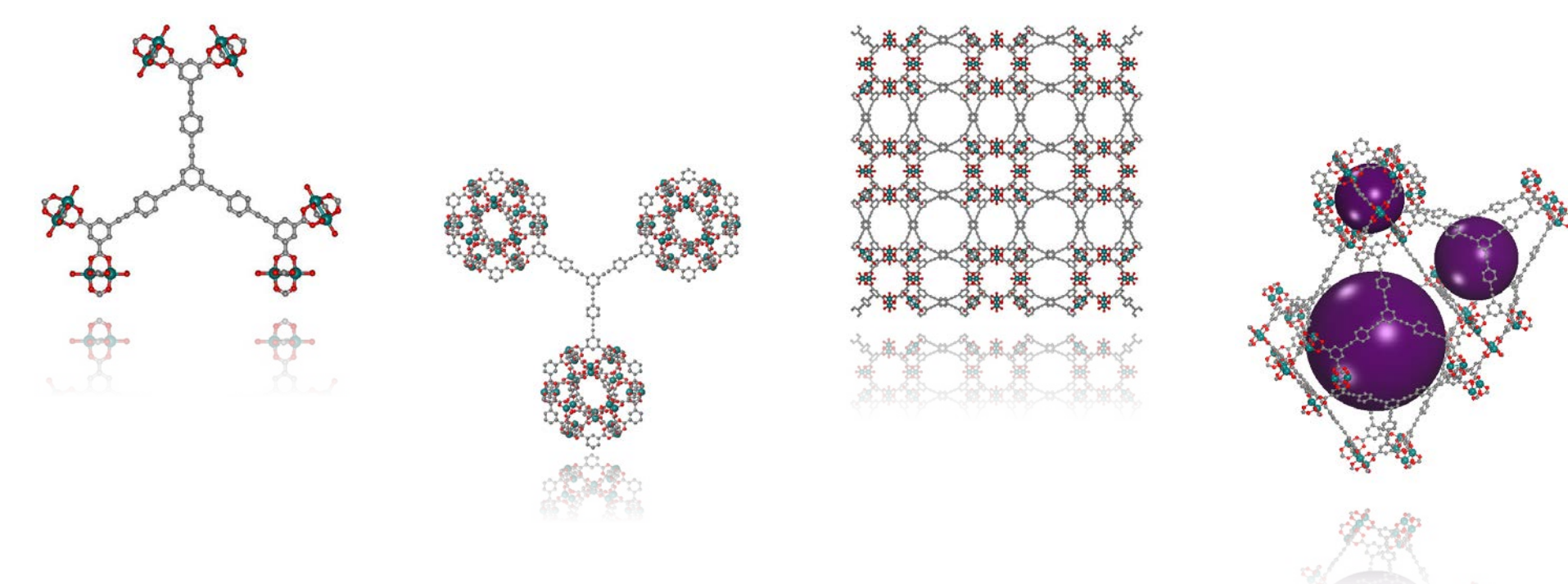
Metal- and Cluster-Modified Ultrahigh-Area Diamond Network Materials for the Ambient Temperature Storage of Molecular H₂

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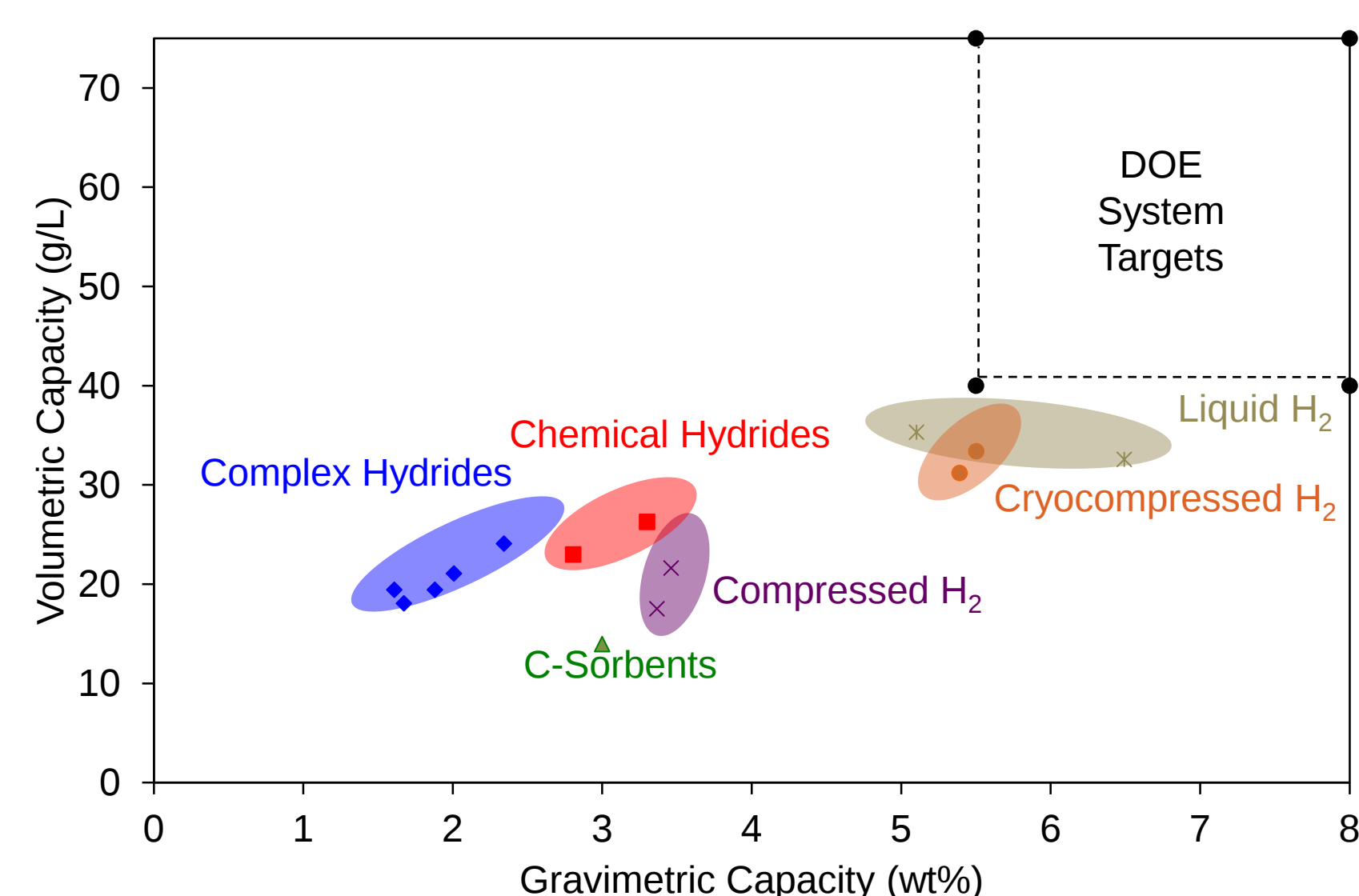
Background and Introduction

- Molecular hydrogen (H₂) is an attractive alternative energy source that can potentially replace hydrocarbon technology.¹
- A crucial challenge to enable H₂ as an energy carrier is the development of suitable storage materials.
- Both chemical (typically dissociative) and physical (non-dissociative physisorption) sorption-based strategies are being actively pursued to overcome this challenge.²

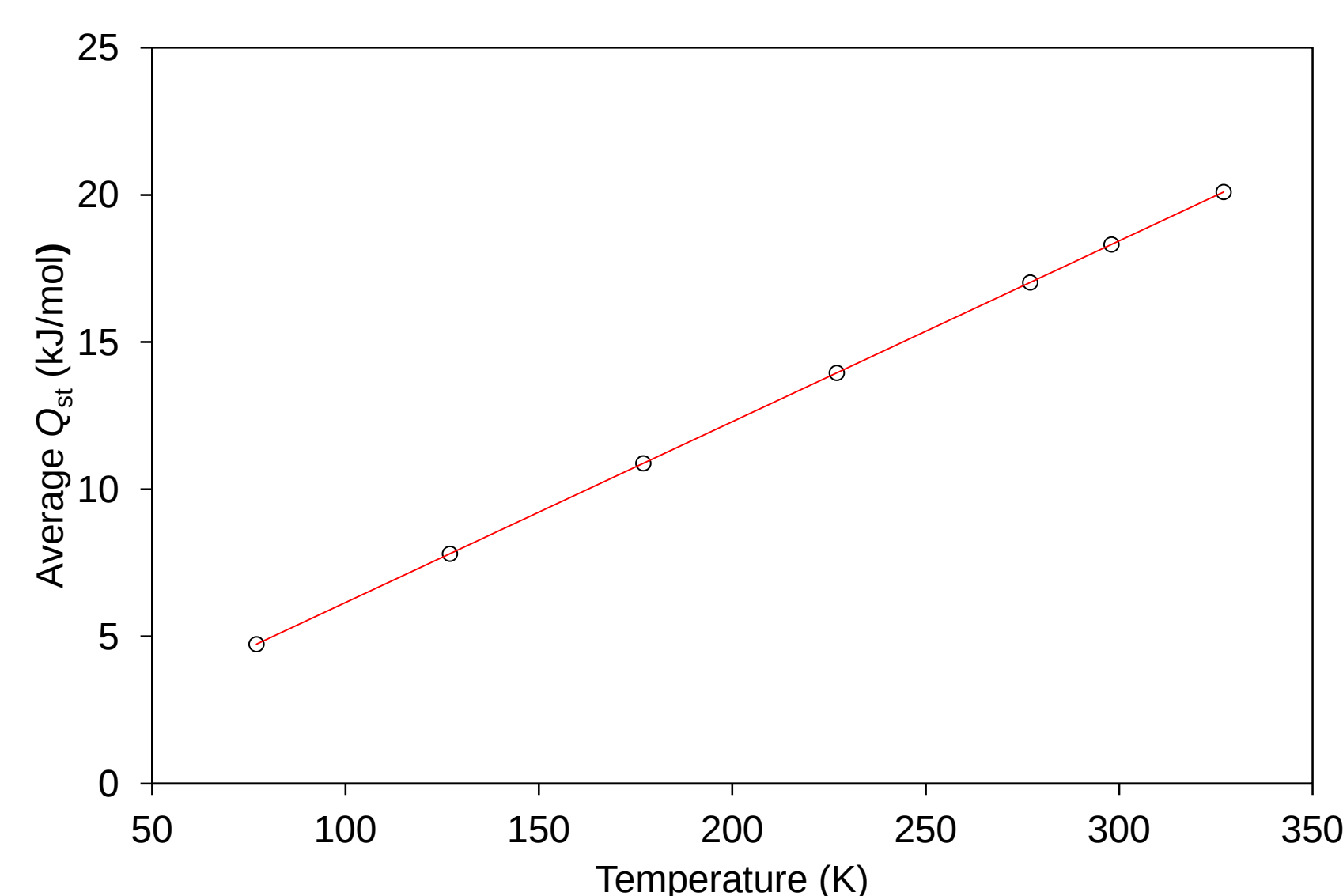


- However, their typically low isosteric heats of adsorption (Q_{st}) require that H₂ be stored at cryogenic temperatures (e.g., 77 K).⁴
- A key experimental challenge to implement ambient temperature H₂ storage (in physisorption-based sorbents) is to increase their Q_{st} .⁵
- **One very promising strategy to achieve the desired Q_{st} is to incorporate stable, but coordinately unsaturated, divalent metal cations into ultrahigh-area sorbents!**

¹ Schlapbach, L.; Züttel, A. *Nature* **2001**, 414, 353. ² Reproduced from: http://www1.eere.energy.gov/hydrogenandfuelcells/storage/tech_status.html. ³ Farha, O.K.; Yazaydin, A.O.; Eryazici, I.; Malliakas, C.D.; Hauser, B.G.; Kanatzidis, M.G.; Nguyen, S.T.; Snurr, R.Q.; Hupp, J.T. *Nature Chem.* **2010**, 2, 944.

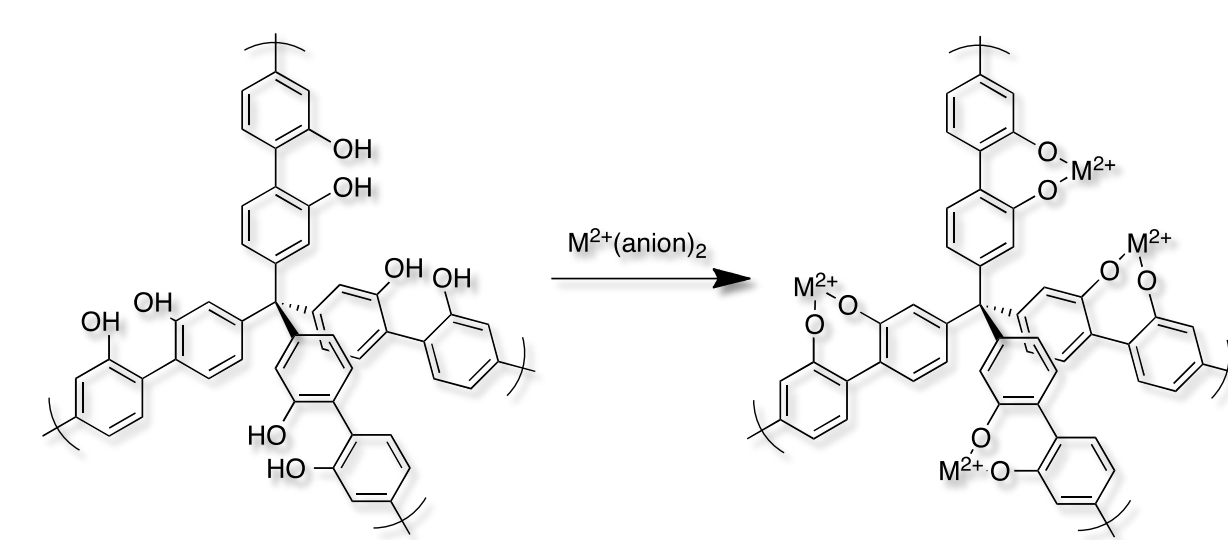


- Ultrahigh-area (> 3,000 m² g⁻¹) physisorption-based sorbents approaching the DOE's gravimetric and volumetric system targets have been developed (e.g., NU-100).³

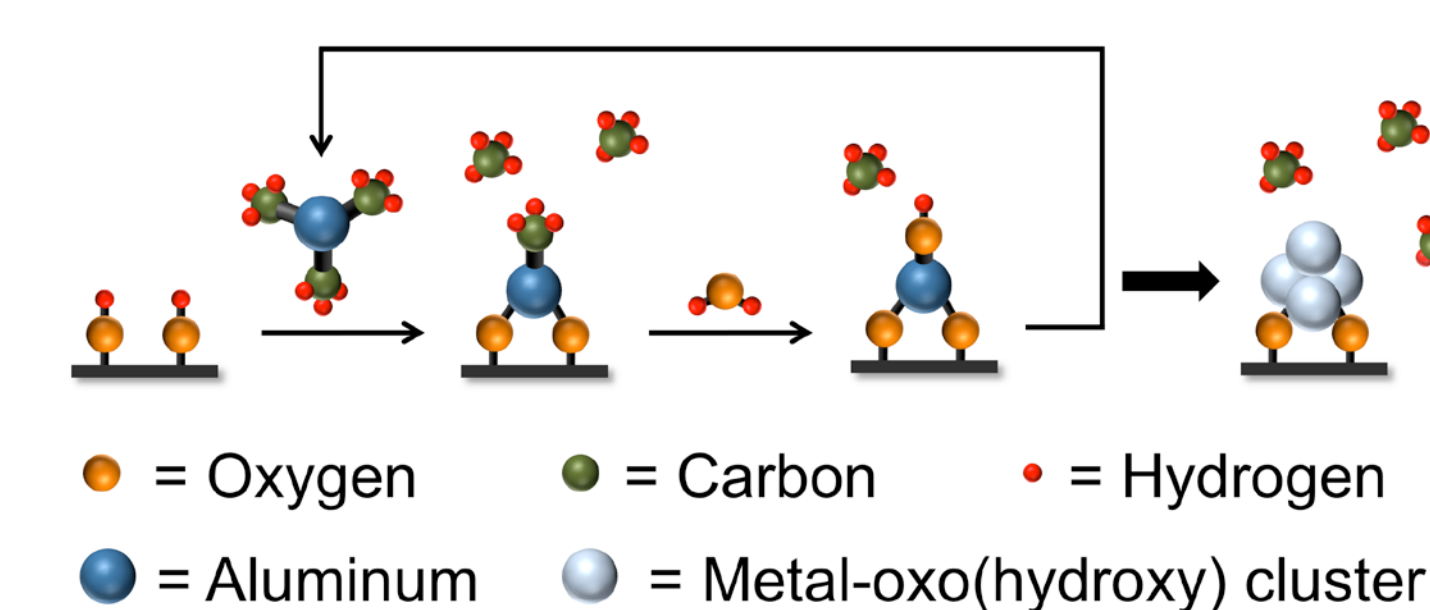


Approach

- An ultrahigh-area diamond network material (PAF-1 @ 5,600 m² g⁻¹) was recently reported by Ben et al.⁶
- PAF-1 will be functionalized with a varying number of –OH or –NH₂ groups per cavity and subsequently divalent metal cations.

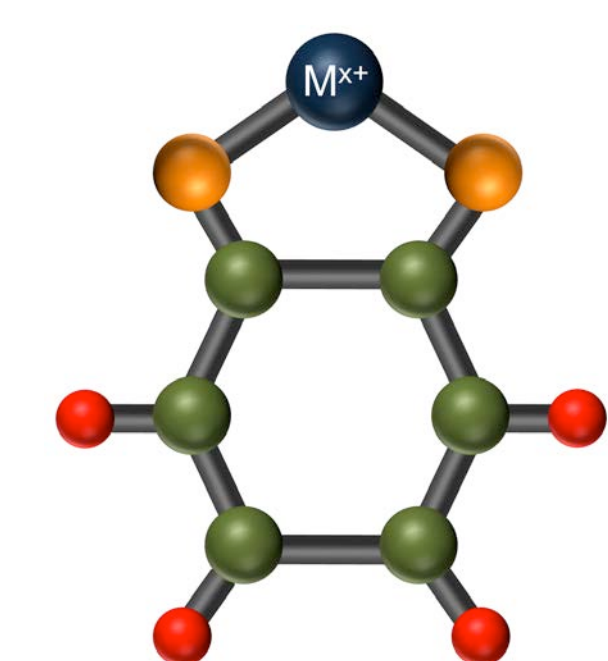


- Small metal-oxo(hydroxy) clusters will be deposited onto functionalized PAF-1 derivatives via atomic layer deposition.



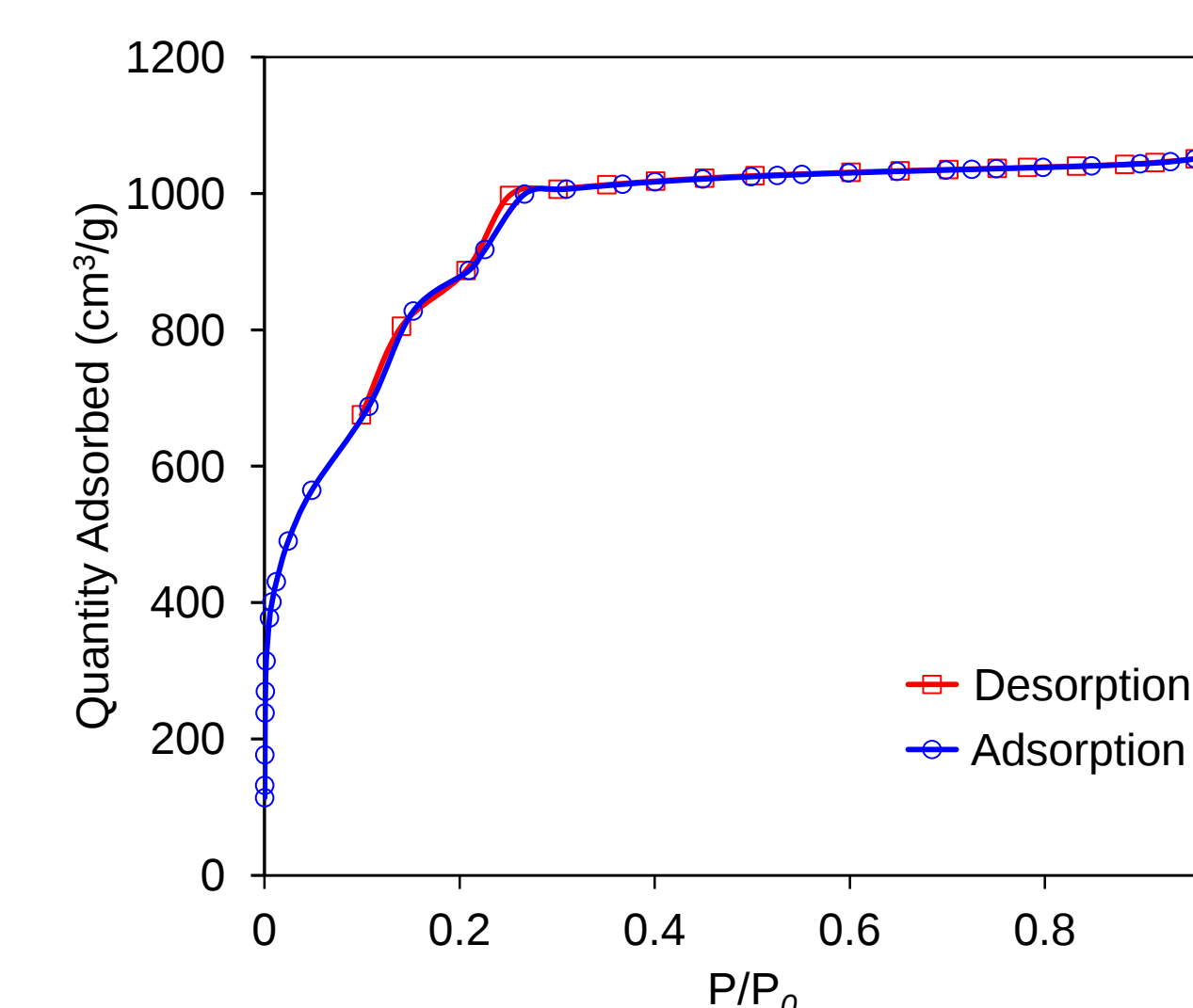
⁴ Bhatia, S.K.; Myers, A.L. *Langmuir*, 2006, 22, 1688. ⁵ Simpson, L. "U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Program Hydrogen Sorption Center of Excellence: Materials Go/No-Go Recommendation Document" **2009**, 1-41. ⁶ Ben, T.; Ren, H.; Ma, S.; Cao, D.; Lan, J.; Jing, X.; Wang, W.; Xu, J.; Deng, F.; Simmons, J.M.; Qiu, S.; Zhu, G. *Angew. Chem. Int. Ed.* **2009**, 48, 9457. ⁷ Getman, R.B.; Miller, J.H.; Wang, K.; Snurr, R.Q. *J. Phys. Chem. C* **2011**, 115, 2066.

- Given the large number of potential materials, we will utilize computational guidance from Prof. Randall Q. Snurr to target the most promising Q_{st} .⁷

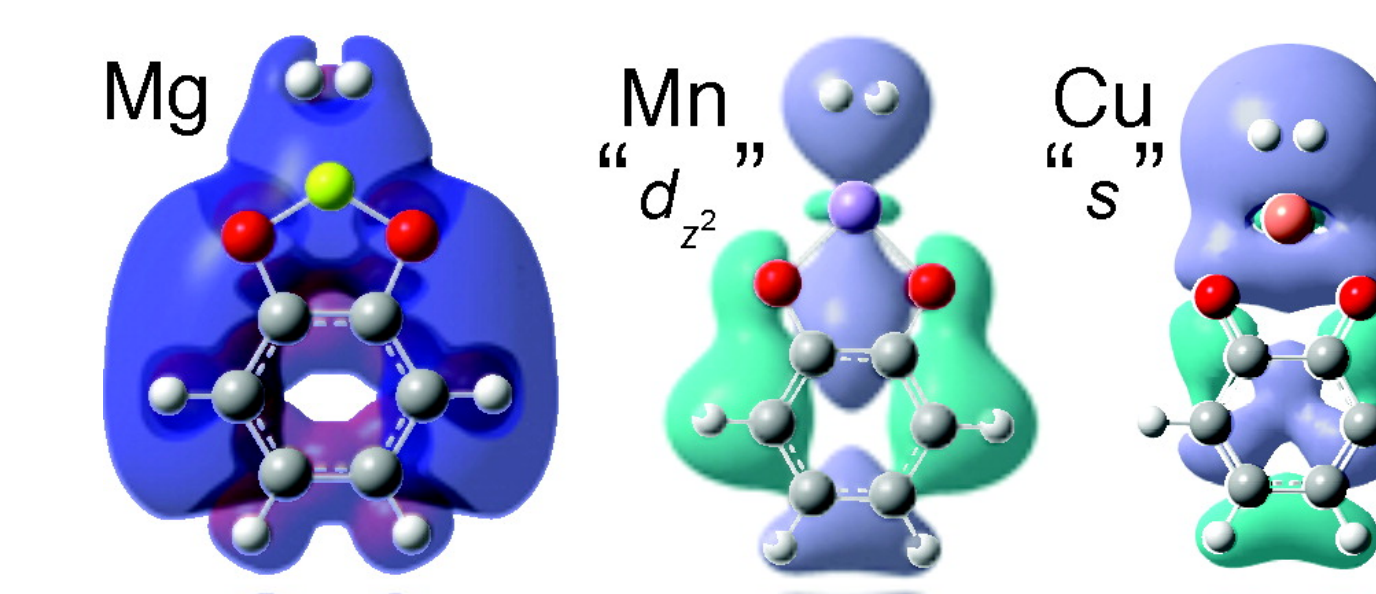


Metal	Q_{st} (kJ/mol)
Li ⁺	-10
Mn ²⁺	-20
Mg ²⁺	-22
Ni ²⁺	-78
Cu ²⁺	-84

- Metalated PAF-1 derivatives will be characterized by ICP-OES, gas sorption measurements and XAFS (among others).



- Despite ambitious computational efforts,⁷ little experimental data exists regarding the detailed mechanism(s) of enhanced H₂ sorption.



- In collaboration with Dr. Jeff Miller at the DOE's ANL and APS, we will utilize XAFS to probe the local atomic structure of the metal- and cluster-modified PAF-1 derivatives under dynamic conditions.



Impact

This project aims to synthesize, characterize and evaluate a new class of materials, namely metal- and cluster-modified ultra-high area diamond network materials. If fully successful, these materials are potentially capable of satisfying, and even exceeding, the U.S. DOE's 2015 excess gravimetric and volumetric H₂ storage requirements at ambient temperature (to start, on a "materials only" basis). In addition, by utilizing *in operando* XAFS measurements, we aim to obtain a predictive understanding of the mechanism(s) by which enhanced H₂ sorption is realized. Such insights promise to help guide the next generation syntheses of improved sorbent materials.

Acknowledgments

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