

Chemical Reduction of Metal–Organic Framework Materials as a Method to Enhance Gas Uptake and Binding

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Permanently porous metal–organic framework (MOF) materials are of tremendous current interest because of both their well-defined, low-density structures and their enormous potential in applications such as gas storage,^{1–4} catalysis,^{5,6} and small molecule sensing.⁷ We are particularly interested in hydrogen storage. Impressive advances have been made here in a surprisingly small amount of time.^{8,9} Nevertheless, there have been no reports of MOF-based H₂ storage that meet the published DOE target levels at noncryogenic temperatures.^{10,11} Clearly there is a need for further enhancement. Rather than attempting to effect slight structural changes, such as choice of ligand or metal which may lead to incremental enhancements in H₂ uptake, we have chosen to examine framework reduction as a method to dramatically enhance hydrogen uptake as well as the heat of adsorption. We reasoned that framework reduction might well boost adsorption by (a) increasing the polarizability of organic struts, thereby strengthening adsorbate/framework van der Waals interactions, (b) introducing charge-compensating cations capable of binding gas molecules via charge/quadrupole or more specific interactions, and/or (c) coulombically displacing interwoven frameworks, thereby enhancing accessible surface area.

We, and others, have developed a family of mixed-ligand MOFs that exhibit permanent microporosity and, by changing either or both struts, have interchangeable functionality.^{12–14} We have purposely targeted redox-active ligands as struts in a number of these structures. In this report we present a method by which to exploit the ligand redox activity within a mixed-ligand MOF to dope the framework with alkali metal cations, specifically Li⁺. We find that reductive doping does indeed very substantially enhance both nitrogen and hydrogen gas uptake.

As a starting point, we chose a material whose synthesis and structure has already been reported, Zn₂(NDC)₂(diPyNI), **1** (NDC = 2,6-naphthalenedicarboxylate, diPyNI = *N,N'*-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide) (Figure 1). This compound features 2-fold interpenetration, yet retains 54% solvent-accessible void volume. Extensive experimental work has demonstrated that **1** is robust and permanently porous. Most interestingly, **1** contains the redox active ligand diPyNI which is reversibly reducible at –0.79 and –1.30 V versus the ferrocene couple.¹⁵

Several methods of framework reduction were examined, including employing a redox shuttle and interaction with the solvated electron in liquid ammonia. Surprisingly, the most effective approach turned out to be direct reduction with lithium metal in dimethylformamide (DMF) as solvent (Scheme 1). Immediately upon exposure to Li in DMF, **1** changed color from bright yellow to brown. The change mimics the color change observed in solutions of the diPyNI ligand alone. Powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) confirm the structural integrity

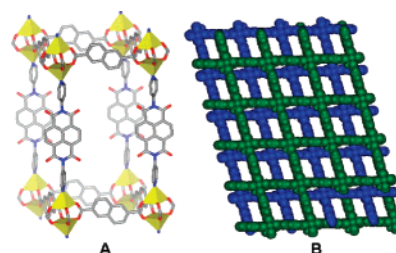


Figure 1. (A) Crystal structure of **1** omitting interwoven second network. The yellow polyhedra represent the zinc ions: carbon, gray; oxygen, red; nitrogen, blue. (B) Packing diagram of **1** down diPyNI axis showing 2-fold interpenetration.

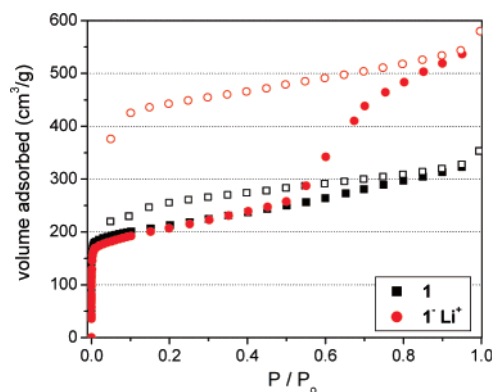


Figure 2. Nitrogen isotherms of **1** and **1**–Li⁺: closed symbols, adsorption; open symbols, desorption.

of **1** through reduction and subsequent oxidation by exposure to air (Figure S2). Inductively coupled plasma (ICP) methods were used to measure the Li⁺ loading within the reduced MOF, designated **1**–Li⁺. Preliminary results indicate that substoichiometric amounts of lithium, ~5 mol %, are optimal for improving gas adsorption.¹⁶

N₂ adsorption isotherms for **1** and **1**–Li⁺ are presented in Figure 2. The nitrogen-accessible BET surface area and Dubinin–Radushkevich (DR) micropore volumes of the two samples are nearly identical (see Supporting Information). But, the isotherm of **1**–Li⁺ exhibits a large step at $P/P_0 \approx 0.5$, and the capacity at 1 atm is almost double that of **1**. (Notably, the hysteresis behavior is repeatable (Figure S3).) Moreover, the desorption curve has a distinct hysteresis loop that does not rejoin the adsorption curve until $P/P_0 \approx 0.01$. This particular type of hysteresis is generally not indicative of mesoporosity, but rather of dynamic framework behavior,^{4,17–20} for example, shifting of interwoven frameworks with respect to each other. Here the introduction of lithium has apparently rendered the interpenetrated networks mobile in the solid state, particularly at high nitrogen loading, and therefore able to accommodate more guests. PXRD measurements confirm that any

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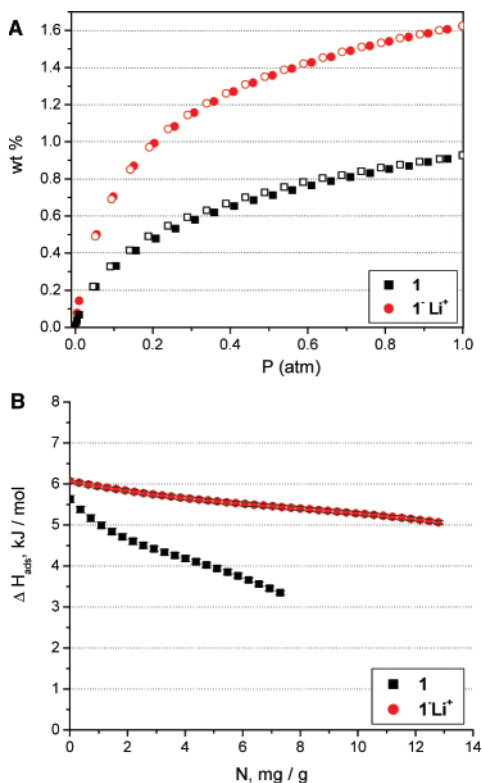
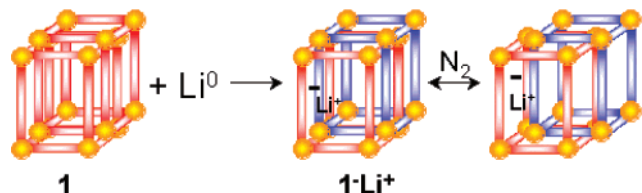


Figure 3. (A) H₂ adsorption isotherms of **1** and **1-Li⁺** at 77 K; (B) isosteric H₂ heat of adsorption of **1** and **1-Li⁺**.

Scheme 1. Reduction of **1** in DMF to Form **1-Li⁺**^a



^a N₂ adsorption measurements suggest a reversible structural change, represented speculatively here as framework displacement.

structural changes are reversed upon reoxidation (see Supporting Information). It has not yet been possible, however, to monitor structural changes as a function of N₂ pressure.

Remarkable enhancements are also seen for H₂ sorption (Figure 3A). At 77 K and 1 atm the H₂ capacity of **1** is 0.93 wt %, but for **1-Li⁺** it is nearly double (1.63 wt %). Additionally, the isosteric heat of adsorption, a measure of the interaction strength between H₂ and the adsorbent, is substantially greater for **1-Li⁺** than **1** over the entire loading range (Figure 3B). This is notable as the inclusion of unsaturated metal sites in MOFs is recognized as an approach to create stronger H₂ binding.^{21,22} Rather than introducing metal unsaturation through desolvation at the MOF nodes, framework reduction provides such sites in the form of cations that balance negative charge of the reduced ligands. At 1 atm, the enhancement in H₂ uptake is 60 H₂ molecules per added Li⁺. This cannot be explained solely by direct H₂/cation binding and instead points to

other factors such as framework displacement (Scheme 1) and/or enhanced strut polarizability.

While comparatively high, the hydrogen uptake levels reported here do not meet the DOE targets or even match those reported for the very best existing MOFs. Nevertheless, chemical reduction represents a unique approach to enhancing sorption. We are currently pursuing studies with other MOFs (including non-interpenetrating MOFs) and with other cations to elucidate further the mechanisms by which framework reduction enhances gas uptake.

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Supporting Information Available: Synthesis of **1** and **1-Li⁺**, structural characterization (PXRD, TGA, EA, ICP), gas adsorption measurement details, nitrogen isotherm cycling, and H₂ heat of adsorption isotherm fitting and calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304–1315.
- (2) Latroche, M.; Surble, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J. H.; Chang, J. S.; Jhung, S. H.; Ferey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8227–8231.
- (3) Ma, S. Q.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 11734–11735.
- (4) Zhao, X. B.; Xiao, B.; Fletcher, A. J.; Thomas, K. M.; Bradshaw, D.; Rosseinsky, M. J. *Science* **2004**, *306*, 1012–1015.
- (5) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982–986.
- (6) Cho, S. H.; Ma, B. Q.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, 2563–2565.
- (7) Zhao, B.; Chen, X. Y.; Cheng, P.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H. *J. Am. Chem. Soc.* **2004**, *126*, 15394–15395.
- (8) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 3494–3495.
- (9) Dinca, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876–16883.
- (10) Schlögl, L.; Züttel, A. *Nature* **2001**, *414*, 353–358.
- (11) Hydrogen, Fuel Cells & Infrastructure Technologies Program: Multiyear Research, Development, and Demonstration Plan. U.S. Department of Energy. <http://www.eere.energy.gov/hydrogenandfuelcells/mypp/>, 2005.
- (12) Ma, B. Q.; Mulfort, K. L.; Hupp, J. T. *Inorg. Chem.* **2005**, *44*, 4912–4914.
- (13) Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. *Chem. Eur. J.* **2005**, *11*, 3521–3529.
- (14) Chen, B. L.; Ma, S. Q.; Zapata, F.; Fronczek, F. R.; Lobkovsky, E. B.; Zhou, H. C. *Inorg. Chem.* **2007**, *46*, 1233–1236.
- (15) Dinolfo, P. H.; Williams, M. E.; Stern, C. L.; Hupp, J. T. *J. Am. Chem. Soc.* **2004**, *126*, 12989–13001.
- (16) The optimal cation loading found in this study was ~5 mol% based on one-electron diPyNI strut reduction; presumably this will differ for other MOFs and other cations.
- (17) Seki, K. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1968–1971.
- (18) Maji, T. K.; Matsuda, R.; Kitagawa, S. *Nat. Mater.* **2007**, *6*, 142–148.
- (19) Uemura, K.; Matsuda, R.; Kitagawa, S. *J. Solid State Chem.* **2005**, *178*, 2420–2429.
- (20) Chen, B. L.; Ma, S. Q.; Zapata, F.; Lobkovsky, E. B.; Yang, J. *Inorg. Chem.* **2006**, *45*, 5718–5720.
- (21) Dinca, M.; Han, W. S.; Liu, Y.; Dailly, A.; Brown, C. M.; Long, J. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 1419–1422.
- (22) Forster, P. M.; Eckert, J.; Heiken, B. D.; Parise, J. B.; Yoon, J. W.; Jhung, S. H.; Chang, J. S.; Cheetham, A. K. *J. Am. Chem. Soc.* **2006**, *128*, 16846–16850.

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