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An Example of Node-Based Postassembly Elaboration of a Hydrogen-Sorbing, Metal−Organic Framework Material

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A robust, noncatenated, and permanently microporous metal−organic framework (MOF) material has been synthesized by combining a new nonplanar ligand, 4,4′,4″,4‴-benzene-1,2,4,5-tetrayltetrabenzoic acid, with a zinc(II) source under solvothermal conditions. The new material features cavities that are readily modified via activation and functionalization of framework *nodes* (as opposed to struts). A preliminary investigation of the "empty cavity" version of the material and six cavity-modified versions reveals that modification can substantially modulate the MOF's internal surface area, pore volume, and ability to sorb molecular hydrogen.

Crystalline metal−organic frameworks (MOFs) comprise a rapidly growing class of permanently microporous materials.[1] They are characterized by low densities, high internal surface areas, and uniformly sized pores and channels. These properties point to a broad range of potential applications, including chemical separations,[2] catalysis,[3] gas storage and release,[4] biological imaging,[5] and drug delivery.[6] Optimal performance in applications depends upon the ability to obtain MOFs having (a) cavities and pores of optimal size, shape, and/or chirality and (b) interior and/or exterior surfaces of suitable chemical composition. Systematic (i.e., predictable) tunability of the pore size, and, to some extent, the surface chemical composition, has indeed been nicely demonstrated for certain families of MOFs.[7] For others, however, even minor changes in the synthesis conditions or strut composition can lead, seemingly unpredictably, to significant differences in cavity-defining metal-node/organic-strut coordination and/or degree of framework catenation.[8] Additionally, certain desirable functional groups may be difficult to incorporate directly into MOFs, either because of thermal instability under material synthesis conditions[9] or because of competitive reaction with intended framework components. Together, these complications can make the direct assembly of MOFs that are optimal for specific applications particularly challenging.

An emerging alternative design strategy is to construct robust *precursor* MOFs and then chemically elaborate their internal and/or external surfaces to impart desired properties. While only a handful of examples has thus far been reported,[3f,4e,10] it is clear that the strategy is a powerful one. For example, Wu and co-workers added highly catalytic titanium(IV) sites to the chiral dinapthol-based struts of a preformed MOF and subsequently used the MOF to facilitate the enantioselective addition of $ZnEt_2$ to aromatic aldehydes.[3f] Kaye and Long[10e] photochemically attached $Cr(CO)_3$ to a benzenedicarboxylate strut in an η^6 fashion. Wang and Cohen[10a] were able to modify IRMOF-3 postsynthetically by reacting pendant amines with anhydrides; they subsequently demonstrated that modification could alter the affinities of a simple cubic MOF for various guest molecules.[10c] Our group has reported (a) the introduction of charge-compensating alkali-metal cations (potential H_2 binding sites[11]) via strut reduction,[4e,10g] (b) surface tailoring of *non*porous metallosalen MOFs via reversible coordination of salen

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(9) For example, compound **8** (below) degrades under solvothermal conditions (likely by polymerization), preventing MOF formation.

10.1021/ic8018452 CCC: $40.75

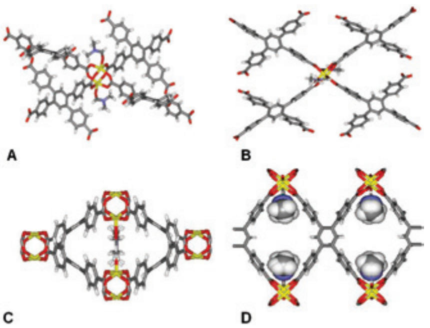


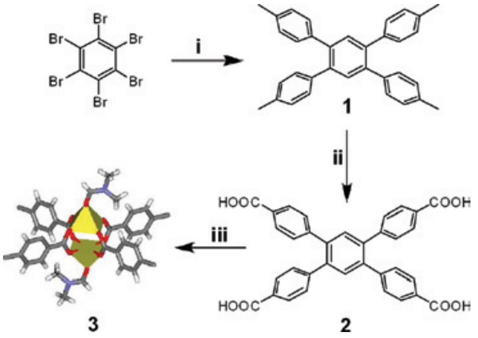
Figure 1. Crystallographically derived (A) structure of **3**, (B) topology and connectivity of **3**, (C) *ac* plane, looking down *b* channels, and (D) *ab* plane, looking down *c* channels. In image D, coordinated DMF molecules are shown in a space-filling fashion. Noncoordinated solvent molecules (disordered) are omitted from the structure representations.

metal sites with chiral ligands and subsequent use of the modified MOFs to accomplish partial separation of the *R* and *S* forms of 2-phenylethyl alcohol,[12] and (c) "click"-based modification[13] of alkyne-bearing struts to impart hydrophilicity.[10f]

Nearly all examples to date have entailed elaboration of *struts* of intact framework compounds[14] (however, see the recent report by Hwang et al.[15]). Here we report on MOF cavity modification via the activation[4f,16] and elaboration of framework *nodes*. We then examine how cavity modification affects the material's ability to sorb molecular hydrogen.

To motivate the investigation, a new tetracarboxylic acid species (4,4′,4″,4‴-benzene-1,2,4,5-tetrayltetrabenzoic acid, **2**) was synthesized as shown in Scheme 1. We envisioned that deprotonated **2** would, as (a) an unusually shaped molecule, resist the formation of catenated MOFs, (b) a tetratopic building block, produce robust frameworks, and (c) a nonplanar moiety, potentially produce a 3D framework. These three characteristics should favor the formation of comparatively large cavities, a desirable feature for postassembly functionalization.

Scheme 1. Added Reagents: (i) *p*-Tolylmagnesium Bromide/THF, (ii) HNO_3/H_2O, (iii) $Zn(NO_3)_2{\cdot}6H_2O$/DMF



A solvothermal reaction of **2** and $Zn(NO_3)_2{\cdot}6H_2O$ in DMF at 80 °C for 24 h afforded in high yield a MOF (**3**) having the *framework* formula $[Zn_2(\mathbf{2})(DMF)_2]_n$ (DMF = dimethylformamide; Scheme 1 and Figures 1 and 2). X-ray analysis of a single crystal of **3** revealed a noncatenated structure in which the framework nodes consist of Zn^{II}_2 units coordinated by the carboxylates of **2** in a paddlewheel fashion. Notably, the strut twists sufficiently to create a true 3D rather than a layered 2D framework. Importantly, the axial sites of the Zn^{II}_2 units are ligated by solvent molecules.

Thermogravimetric analysis (TGA) of **3** revealed mass losses at about 100 and 175 °C, assigned to free and coordinated DMF, respectively; no further mass loss occurs until 425 °C (Figure 2A). Heating **3** under vacuum at 100 °C allows for selective removal of noncoordinated DMF, while heating under vacuum at 150 °C removes all solvent molecules. The partially and fully evacuated MOFs are designated respectively as **3′** and **4**. Void volumes from *PLATON*[17] for **3′** and **4** are 53 and 65%, respectively. Followup TGA experiments (Figure 2A) show that

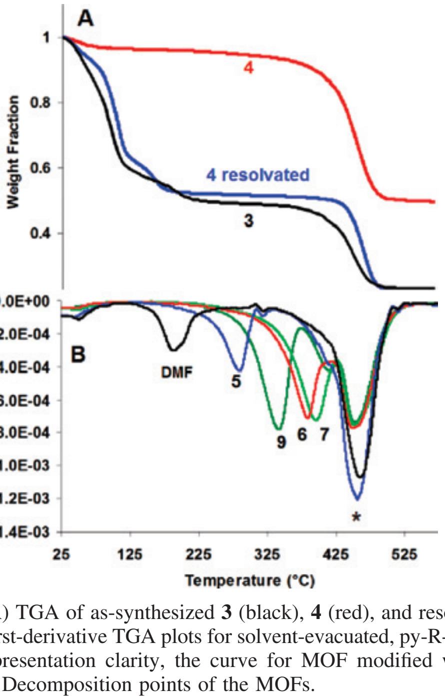


Figure 2. (A) TGA of as-synthesized **3** (black), **4** (red), and resolvated **4** (blue). (B) First-derivative TGA plots for solvent-evacuated, py-R-modified MOFs. For presentation clarity, the curve for MOF modified with **8** is omitted. * = Decomposition points of the MOFs.

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(14) An exception is the early work of Chui and co-workers (ref 10h). They report that $[Cu_3(\text{benzene-1,3,5-carboxylate})_3(H_2O)_3]_n$ (also known as "HKUST-1") can be derivatized with pyridine via displacement of water. While likely correct, the evidence for derivatization is limited, consisting of elemental analysis data showing the incorporation of 1.5 pyridines per Cu and interpreted as uptake of both coordinated and noncoordinated pyridine. Selective removal of noncoordinated pyridine was not reported possibly because of the relatively low temperature for decomposition of the parent compound (240 °C). Properties of the putative modified cavity (e.g., surface area, micropore volume, sorbate uptake) were not explored.

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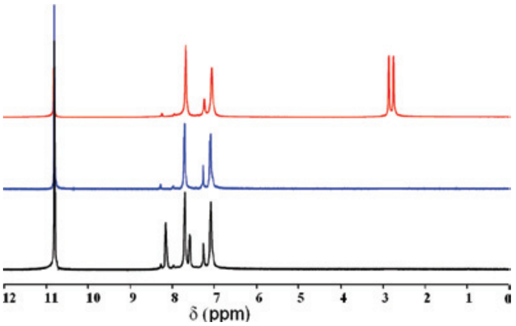


Figure 3. ^{1}H NMR of dissolved **3′** (top), **4** (middle), and **4** + **5** (bottom).

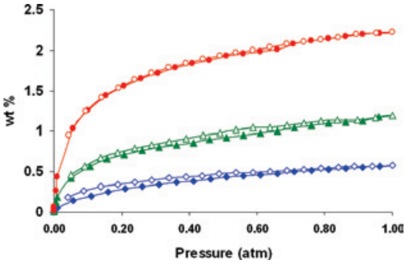
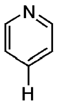


Figure 4. Isotherms for the uptake of H_2 at 77 K and 1 atm by **4** + **9** (bottom), **3′** (middle), and **4** (top). Closed symbols: adsorption. Open symbols: desorption. See the SI for additional data (**4** + **5**, **4** + **6**, **4** + **7**, and **4** + **8**).

4 can be fully resolvated, while powder X-ray diffraction (PXRD) shows that the resolvated form retains crystallinity.

We reasoned that the thermal lability of coordinated DMF should permit its replacement by other ligands. Samples of **3** were converted to **4** and immersed for 24 h in CH_2Cl_2 solutions of each of several candidate pyridine ligands (py-R, **5**−**9**). Following an extensive washing, soaking, and drying protocol designed to remove solvent and free ligands (see the Supporting Information, SI), each of the putative py-R-modified MOFs was dissolved in D_2SO_4/D_2O. ^{1}H NMR measurements established the retention of py-R ligands (see the examples in Figures 3 and 4).

In each case, proton peak integrations were consistent with complete the derivatization of Zn^{II} nodes and the formation of the desired cavity-modified species, $[Zn_2(\mathbf{2})(\text{py-R})_2]_n$. TGA measurements of rinsed and dried samples provided compelling support for coordinative (as opposed to sorptive) binding of the various py-R. As shown in Figure 2B, the pyridines bind to the zinc sites more strongly than does DMF, with temperatures for dissociation ranging from ~260 to ~375 °C. Finally, TGA measurements with resolvated samples established that the modified MOFs retain high porosities (see the SI).



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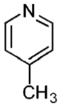

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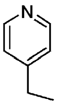

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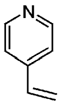

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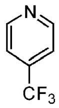

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CO_2 adsorption (T = 273 K) was used to determine the accessible surface areas and pore volumes of the original and cavity-modified MOFs (see the SI for data and details). The areas range from 310 to 1370 m^2/g; the volumes range from 0.106 to 0.404 cm^3/g, with the volume for the "empty cavity" MOF (**4**) being the largest. With these results in hand, the sorption measurements were extended to molecular hydrogen. At 77 K and 1 atm, **4** displays reasonably high H_2 uptake:[18] 2.2% at 1 atm, roughly double the uptake by **3′**. The difference can be attributed to the greater surface area for **4**, as well as greater heats of adsorption (presumably due to open metal sites; see the SI for ΔH data and for isotherms for additional **4** + py-R compounds).

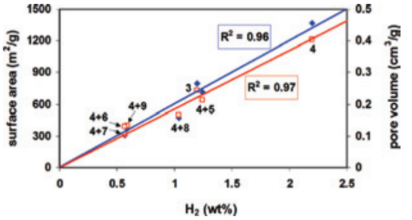

Figure 5. H_2 uptake versus pore volume (red, open squares) and surface area (blue, diamonds).

Figure 5 summarizes the H_2 uptake data for the "empty cavity" MOF and the six cavity-tailored variants. At 77 K and 1 atm, the range of gravimetric loadings for these otherwise identical compounds spans a rather remarkable factor of 4. Consistent with expectations from recent computational studies,[19] the variations correlate well with both surface area and pore volume. In an illustration of a relatively simple case (cryogenic H_2 uptake), the correlations clearly point to the potential for node-based, postassembly modification for systematic altering of the sorption properties. Equally compelling would be tuning of the selectivity for pairs of sorbents. Work in progress shows that cavity modification of **4** can indeed substantially alter the selectivity of the MOF for CO_2 versus methane. The details of this new work will be reported elsewhere.

To summarize, we have synthesized a noncatenated, 3D MOF featuring solvent-capped metal nodes. The coordinated solvent molecules, which are directed toward the cavity interiors, can be readily removed and/or replaced with various cavity modifiers, including delicate modifiers such as **8** that degrade under standard solvothermal synthesis conditions. The resulting tailored cavities show differing degrees of uptake of molecular hydrogen under cryogenic conditions, an observation that may foreshadow a range of other applications, including cavity tuning of chemical catalysis and chemical separations. More generally, the reported results comprise the experimental realization of a promising approach to MOF property modulation/optimization.

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Supporting Information Available: Experimental procedures for the synthesis of **2**, **3**, **3′**, **4**, **4** + **5**, **4** + **6**, **4** + **7**, **4** + **8**, and **4** + **9**, PXRD, TGA, and sorption isotherm data, and an X-ray crystallographic file for **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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