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Expanded Sodalite-Type Metal–Organic Frameworks: Increased Stability and H_2 Adsorption through Ligand-Directed Catenation

Mircea Dincă,[†] **Anne Dailly,**[‡] **Charlene Tsay,**[†] **and Jeffrey R. Long***[,†]

Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, and
Chemical and Environmental Sciences Laboratory, General Motors Corporation,
Warren, Michigan 48090

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The torsion between the central benzene ring and the outer aromatic rings in 1,3,5-tri-*p*-(tetrazol-5-yl)phenylbenzene (H_3TPB-3tz) and the absence of such strain in 2,4,6-tri-*p*-(tetrazol-5-yl)-phenyl-*s*-triazine (H_3TPT-3tz) are shown to allow the selective synthesis of noncatenated and catenated versions of expanded sodalite-type metal–organic frameworks. The reaction of H_3TPB-3tz with $CuCl_2\cdot 2H_2O$ affords the noncatenated compound $Cu_3[(Cu_4Cl)_3(\text{TPB-3tz})_8]_2\cdot 11CuCl_2\cdot 8H_2O\cdot 120DMF$ (**2**), while the reaction of H_3TPT-3tz with $MnCl_2\cdot 4H_2O$ or $CuCl_2\cdot 2H_2O$ generates the catenated compounds $Mn_3[(Mn_4Cl)_3(\text{TPT-3tz})_8]_2\cdot 25H_2O\cdot 15CH_3OH\cdot 95DMF$ (**3**) and $Cu_3[(Cu_4Cl)_3(\text{TPT-3tz})_8]_2\cdot x$solvent (**4**). Significantly, catenation helps to stabilize the framework toward collapse upon desolvation, leading to an increase in the surface area from 1120 to 1580 m^2/g and an increase in the hydrogen storage capacity from 2.8 to 3.7 excess wt % at 77 K for **2** and **3**, respectively. The total hydrogen uptake in desolvated **3** reaches 4.5 wt % and 37 g/L at 80 bar and 77 K, demonstrating that control of catenation can be an important factor in the generation of hydrogen storage materials.

Metal−organic frameworks have achieved recent prominence because of their remarkable gas adsorption capabilities, which may ultimately find applications in gas storage[1] and separations.[2] In particular, reports of reversible hydrogen uptake have spurred interest in these materials as possible storage media for hydrogen fuel cell vehicles.[3] One strategy for varying the adsorption capacity in microporous frameworks involves the expansion of known structure types through the use of elongated, but geometrically equivalent, organic bridging ligands.[4] Prediction of the resulting pore size is complicated, however, because the use of such ligands can also lead to interpenetration, wherein two or more identical frameworks are mechanically intertwined.[5] Despite its obvious importance in influencing the stability and pore size, control over catenation has mainly been achieved through the use of templating guest molecules/solvent,[5,6] as, for example, recently demonstrated in the reaction of Cu^{2+} salts with 4,4′,4″-*s*-triazine-2,4,6-triyltribenzoate (TATB^{3-}).[7] To date, there are no examples of ligand-directed catenation, where modification of the bridging ligand alone has been shown to dictate whether the resulting material exhibits interpenetration. Herein, we demonstrate that the use of benzene- or triazine-centered versions of an elongated triangular ligand leads to exclusive formation of noncatenated or catenated forms of an expanded sodalite-type framework. Importantly, the greater structural stability associated with

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* To whom correspondence should be addressed: E-mail: jrlong@berkeley.edu.
[†] University of California, Berkeley.
[‡] General Motors Corp.

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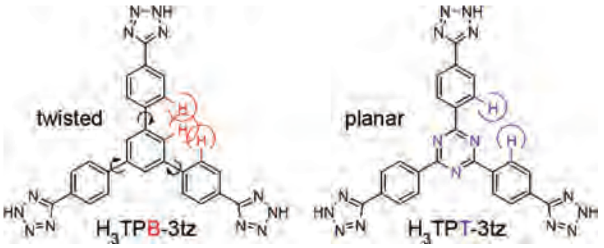
Scheme 1. Molecular Structures of the Extended Triangular Ligands H_3TPB-3tz and H_3TPT-3tz



the interpenetrated material results in an increased hydrogen adsorption capacity.

Recently, we reported the synthesis of $Mn_3[(Mn_4Cl)_3(BTT)_8(CH_3OH)_{10}]_2$ [**1**; BTT^{3-} = 1,3,5-benzenetris(tetrazolate)], a porous framework solid wherein exposed Mn^{2+} sites result in a high initial binding enthalpy of 10.1 kJ/mol and a volumetric storage density of 60 g/L at 77 K and 90 bar.[8] Through an increase in the number of unsaturated metal centers in a Cu^{2+}-containing analogue, it was further shown that stronger hydrogen binding at increased coverages could be attained.[9] In an effort to expand these sodalite-type framework structures, we synthesized two extended triangular ligands related to H_3BTT: 1,3,5-tri-*p*-(tetrazol-5-yl)phenylbenzene (H_3TPB-3tz) and 2,4,6-tri-*p*-(tetrazol-5-yl)phenyl-*s*-triazine (H_3TPT-3tz), as depicted in Scheme 1. Cyclotrimerization of 4-bromoacetophenone and 4-bromobenzonitrile provided the tribromo derivatives of the benzene- and triazine-centered ligand cores, respectively.[10] Copper-catalyzed halide exchange with cyanide afforded the respective trinitriles, which were then converted to tetrazoles via acid-catalyzed cycloaddition reactions with NaN_3. Note that the steric conflict between H atoms in H_3TPB-3tz causes a distortion away from planarity, which it was hypothesized might prohibit intraligand π-stacking interactions of the type observed in interpenetrated $TATB^{3-}$-bridged frameworks.[7,11]

Consistent with this hypothesis, a reaction between H_3TPB-3tz and $CuCl_2 \cdot 2H_2O$ at 80 °C in *N*,*N*-dimethylformamide (DMF) was found to yield green crystals of $Cu_3[(Cu_4Cl)_3(TPB\text{-}3tz)_8]_2 \cdot 11CuCl_2 \cdot 8H_2O \cdot 120DMF$ (**2**). X-ray analysis revealed an expanded, non-interpenetrated framework isotypic with that found in **1** (see Figure 1). Here, square-planar $[Cu_4Cl]^{7+}$ units are connected by TPB-$3tz^{3-}$ ligands to form a cubic 8,3-connected net resembling the structure of sodalite. The phenylene groups along each arm of the TPB-$3tz^{3-}$ ligands are indeed twisted at a mean angle of 31(3)° away from the plane of the central benzene ring. Significantly, the ensuing lack of catenation, together with the expanded structure, enables accommodation of 11 equiv of $CuCl_2$, which aggregate around the square-planar $[Cu_4Cl]^{7+}$ framework interfaces. The extraframework Cu^{2+} ions are each ligated by one chloride anion, N1 and N4 atoms of the tetrazolate rings, and two solvent molecules to give a trigonal-bipyramidal coordination environment. Removal of the bound solvent without framework collapse could therefore potentially create two open coordination sites for binding of hydrogen.

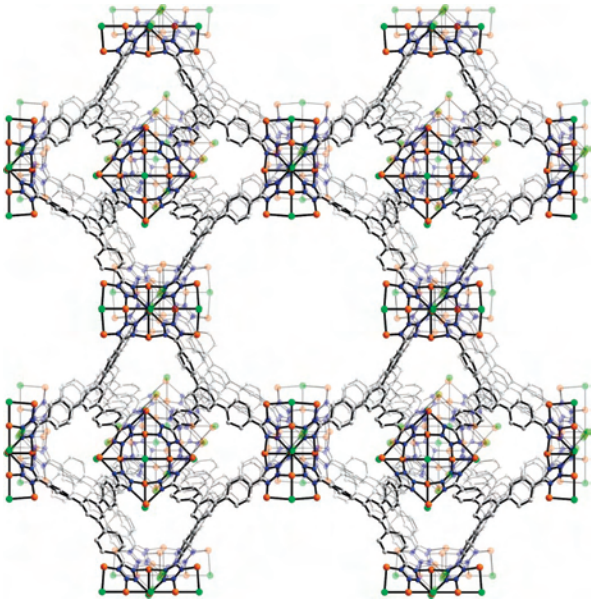


Figure 1. Portion of the non-interpenetrated structure of **2**, showing a cube formed by eight face-sharing sodalite-like cages, which together define 17-Å-wide pore openings. Orange, green, gray, and blue spheres represent Cu, Cl, C, and N atoms, respectively; solvent molecules and H atoms are omitted for clarity.

Similar reactions of H_3TPT-3tz with either $MnCl_2 \cdot 4H_2O$ or $CuCl_2 \cdot 2H_2O$ in mixtures of DMF and methanol produced colorless crystals of $Mn_3[(Mn_4Cl)_3(TPT\text{-}3tz)_8]_2 \cdot 25H_2O \cdot 15CH_3OH \cdot 95DMF$ (**3**) and green crystals of $Cu_3[(Cu_4Cl)_3(TPT\text{-}3tz)_8]_2 \cdot x$solvent (**4**).[12] X-ray analysis of **3** and **4** revealed unit cell parameters almost identical with those of **2**, while systematic absences indicated body-centered lattices indicative of catenated structures. Compounds **3** and **4** indeed exhibit two interpenetrating frameworks of the type observed in **2** displaced by a half unit cell diagonal along the [111] direction (see Figure S1 in the Supporting Information). As expected, the TPT-$3tz^{3-}$ ligands in **3** and **4** are planar, leading to π-stacking interactions with short interligand C···N distances of 3.30(1) and 3.23(5) Å, respectively.

To test the effect of catenation on stability and gas uptake, samples of **2** and **3** were subjected to evacuation and nitrogen sorption measurements. Initial attempts to desolvate **2** above 75 °C under reduced pressure produced an amorphous, nonporous solid, suggesting that the 17-Å-wide pores in **2** are more prone to collapse than the 11-Å-wide pores in **1**. A milder evacuation procedure involving heating at just 65 °C afforded **2d**, a material exhibiting a type I adsorption isotherm characteristic of a microporous solid. Compound **2d** adsorbs 300 cm^3/g of nitrogen at 77 K and 1 atm, corresponding to apparent Brunauer–Emmett–Teller (BET) and Langmuir surface areas of 1120 and 1200 m^2/g, respectively. In contrast, crystals of **3** are stable up to

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(12) Unlike **3**, compound **4** has thus far only been obtained in impure form, together with an amorphous yellow solid.

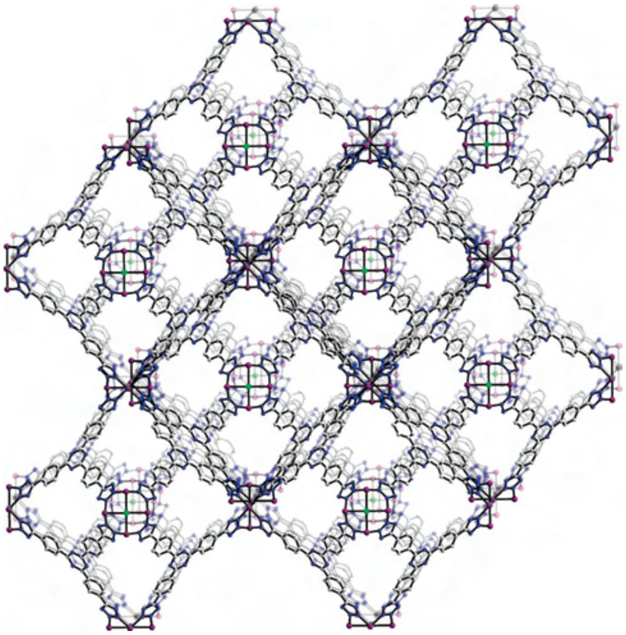

Figure 2. Portion of the interpenetrated structure of **3d**, showing two interpenetrated cubes, each formed by eight face-sharing sodalite-like cages. Purple, green, gray, and blue spheres represent Mn, Cl, C, and N atoms, respectively; solvent molecules and H atoms are omitted for clarity.

120 °C, and desolvation at this temperature affords $Mn_3[(Mn_4Cl)_3(TPT\text{-}3tz)_8(DMF)_{12}]_2$ (**3d**). Compound **3d**, shown in Figure 2, adsorbs 440 cm^3/g of nitrogen at 77 K and 1 atm and exhibits BET and Langmuir surface areas of 1580 and 1700 m^2/g, respectively. This substantial increase in surface area for the interpenetrated compound suggests that a certain degree of framework collapse occurs in **2d** even under mild desolvation conditions.

The effect of catenation on the hydrogen storage properties of the expanded sodalite framework materials was also investigated. As shown in Figure 3, hydrogen adsorption isotherms measured at 77 K reveal an excess uptake of 2.8 wt % at 30 bar for **2d**. In contrast, the more stable catenated frameworks of **3d** afford a significantly higher uptake of 3.7 wt % at 25 bar, with the total hydrogen uptake in **3d** reaching 4.5 wt % at 80 bar.[13] At 298 K, the two materials exhibit comparable excess hydrogen capacities of 0.5 wt % at 68 bar. Notably, X-ray analysis of a single crystal of **3d** showed that all of the framework Mn^{2+} sites retain a bound DMF molecule, just as was previously observed for the partially desolvated compound $Mn_3[(Mn_4Cl)_3(BTT)_8]_2{\cdot}42DMF$ (**1s**).[8] For **1s**, exchange of DMF with methanol prior to evacuation resulted in more complete desolvation and strong hydrogen binding associated with the exposed Mn^{2+} coordination sites of **1**.[8] Unfortunately, attempts to replace the bound DMF molecules in **3d** with more volatile coordinating solvents, such as methanol, acetonitrile, acetone, or THF, led to complete framework collapse, as evidenced by subsequent gas adsorption measurements.

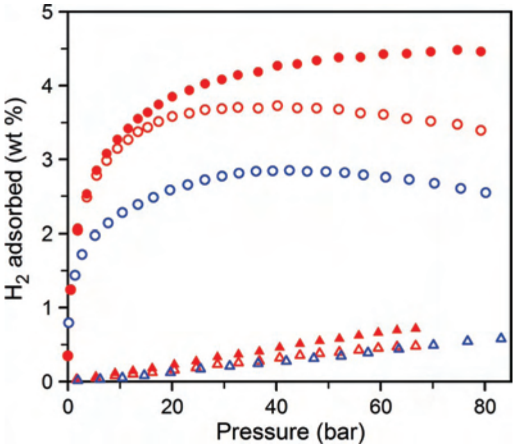

Figure 3. Isotherms for the adsorption of hydrogen within **2d** (blue) and **3d** (red) at 77 K (circles) and 298 K (triangles). Open and filled symbols represent excess and total adsorption, respectively. All isotherms were observed to be reversible, without hysteresis. Note that the downturn in the excess adsorption isotherms at higher pressures is a well-understood phenomenon.[14]

The affinity of hydrogen for the frameworks of **2d** and **3d** was probed by extracting isosteric adsorption enthalpies from hydrogen adsorption data measured at 77 and 87 K and pressures of up to 1.2 bar. The two compounds show initial adsorption enthalpies of 8.2 and 7.6 kJ/mol, respectively (see Figure S9 in the Supporting Information), with the latter value matching the 7.6 kJ/mol value observed for **1s**.[8] The slightly higher value attained by **2d** could potentially be a consequence of the exposed chloride anions associated with the additional $CuCl_2$. Note that neither compound achieves an initial binding enthalpy as high as the 10.1 kJ/mol value attributable to the exposed metal sites in **1**.[8] The lack of unsaturated metal centers is further reflected in the volumetric storage capacity of **3d**, which reaches 37 g/L at 80 bar and 77 K. This is lower than the record capacity of 60 g/L observed for **1** but is comparable to that observed in **1s** and other metal−organic frameworks with no open metal sites.[3e,8]

Our findings confirm that ligand-based control of catenation can help stabilize a porous metal−organic framework, thereby enhancing gas uptake. Future efforts will focus on developing nondestructive methods for exposing the metal sites within such materials as a means of increasing the hydrogen storage capacity and binding enthalpy. In particular, the photolysis of chilled samples under reduced pressure is being investigated for this purpose.

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Supporting Information Available: Experimental details, gas sorption, thermogravimetric analysis, and adsorption enthalpy data (PDF) and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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