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Robust Non-Interpenetrating Coordination Frameworks from New Shape-Persistent Building Blocks

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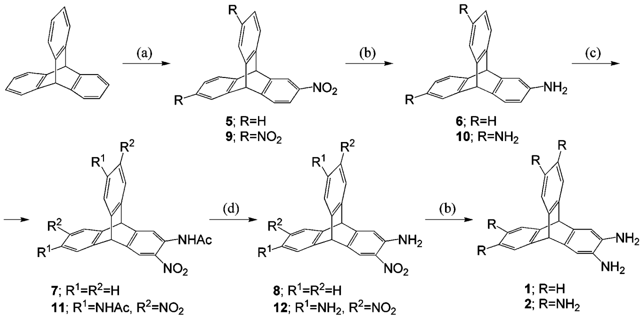
New shape-persistent ligands derived from triptycene were synthesized, and reaction with copper iodide results in the assembly of non-interpenetrating coordination frameworks with hydrophobic void spaces. These structures are thermally stable and display reversible solvent adsorption, and ^{1}H NMR experiments show that they can be used to remove benzene from water.

Metal–organic coordination frameworks are promising candidates for developing new sorbent, catalytic, or electronic materials.[1] Variation of synthetic conditions and precursors enables tuning of the pore sizes, pore geometries, and magnetic/optical properties. Unfortunately, most coordination frameworks either are subject to interpenetration that renders them nonporous, or are unstable to solvent removal, preventing their use in applications requiring accessible pores. Using secondary building units or molecules that do not pack well together (e.g., 9,9′-spirobifluorenes, rotaxanes, etc.) to assemble structures can prevent interpenetration.[2]

Environmental remediation has been proposed as an application of metal–organic frameworks but has not been demonstrated. With the goal of developing porous, hydrophobic framework materials, we targeted a new class of ligands based on triptycene, a molecule with a large built-in free volume. Triptycene and its derivatives have been used to inhibit aggregation in conjugated polymers and to align liquid crystals.[3] However, their use to develop porous networks has not been adequately explored.[4] Here we report the first of a new class of ligands based on triptycene quinoxalines. These ligands form two-dimensional coordination networks with CuI that are thermally stable, water-stable, hydrophobic and remain crystalline after guest removal. Moreover, we demonstrate that one of the structures, **Cu-3**, can be used to remove benzene from contaminated water.

Scheme 1. Synthesis of Polyaminotriptycenes **1** and **2**[a]



[a] (a) HNO_3, CH_3COOH. (b) H_2NNH_2, catalyst Raney Ni catalyst, THF. (c) Ac_2O, then KNO_3, HTos. (d) NaOH, H_2O, EtOH.

Polyaminotriptycenes **1** and **2** were prepared by sequential nitration and reduction of triptycene (Scheme 1). Subsequent condensation with 2,3-dihydroxy-1,4-dioxane afforded the new triptycenylquinoxaline ligands **3** and **4** (Scheme 2). ^{1}H NMR spectra of these compounds were consistent with their structures and showed the bridgehead protons at 5.64 and 6.13 ppm for **3** and **4**, respectively.

Shape-persistent ligands **3** and **4** possess rigid “wings” that should prevent them from packing together well in extended coordination networks, thus creating pores. To explore their use to generate porous structures, we reacted the ligands with CuI in acetonitrile (MeCN), affording red crystalline solids

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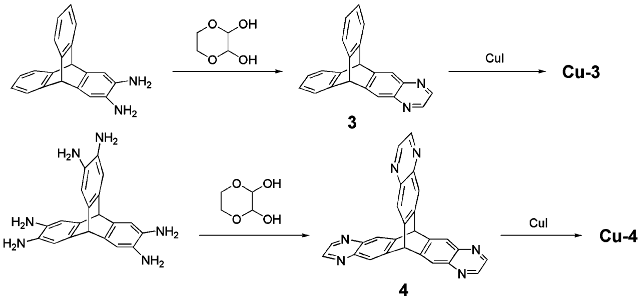
Scheme 2. Synthesis of Triptycenylquinoxaline Ligands **3** and **4** and Their CuI Complexes



of **Cu-3**·MeCN and **Cu-4**·2MeCN, respectively (Scheme 2). The structures of the products were determined by single-crystal X-ray diffraction (SCXRD; Figure 1).[5]

In **Cu-3**, the Cu atoms are each tetrahedrally coordinated to one quinoxaline and three I^- ligands. The CuI extends in a polymeric ladder structure along the *c* axis, and a chain of alternating Cu^I and quinoxaline ligands along the *a* axis. These motifs have been observed in other quinoxaline/copper systems with similar topologies,[6] but the free volume of the shape-persistent ligand **3** generates a channel structure in the lattice. Rectangular channels measuring ca. 12 × 5 Å run parallel to the direction of the Cu^I/I^- chains along the *c* axis and contain four guest MeCN molecules per unit cell. If the presence of the guest MeCN is ignored, this framework has a void space of 44%.[7]

In **Cu-4**, the Cu^I ions are also tetrahedral, coordinated to both quinoxaline and I^- ligands. Only two of three quinoxalines on each ligand **4** coordinate to Cu^I; the other ring does not coordinate. As in **Cu-3**, **Cu-4** has chains of alternating Cu^I/quinoxaline ligands in one direction (*a* axis). However, the Cu^I/I^- chains running perpendicular are present as Cu_8I_8 oligomers with terminal MeCN ligands. The topology of **Cu-4** is not obvious but appears to have an undulating layered motif. This layered framework has three types of small channels that run parallel to the *a* axis and two of these are occupied by eight noncoordinated guest MeCN molecules per unit cell. Without any MeCN molecules, the structure would have a void space of 44%, and with coordinated MeCN molecules, the amount of void space decreases to 39%.[7]

Figure 2a shows the predicted powder XRD (PXRD) pattern of **Cu-3**·MeCN based on the SCXRD data. The

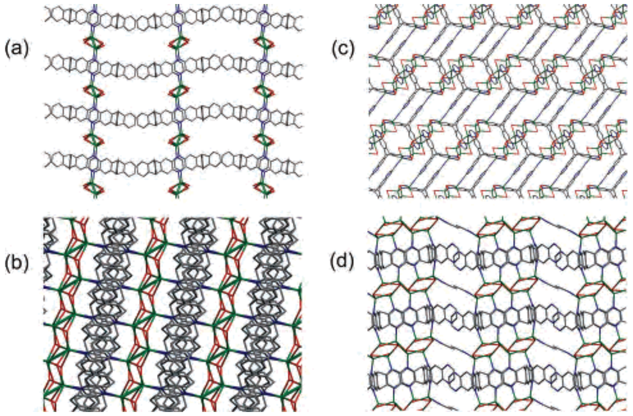


Figure 1. Structures of quinoxaline/copper frameworks as determined by SCXRD. View of **Cu-3** (a) along the *c* axis and (b) along the *b* axis. View of **Cu-4** (c) along the *a* axis and (d) along the *b* axis. Colors: red, I; green, Cu; gray, C. H atoms and solvent molecules have been removed for clarity.

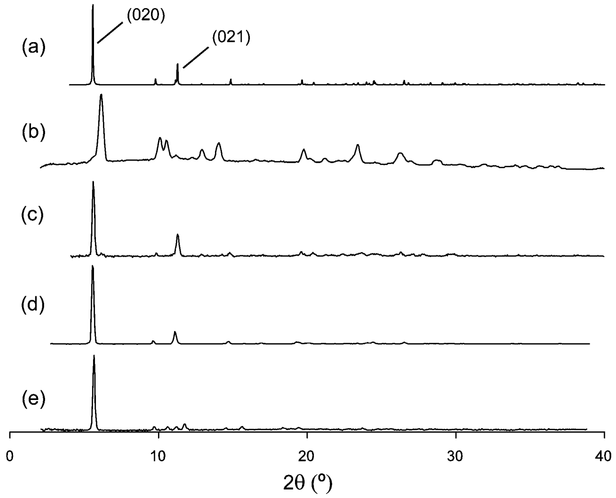


Figure 2. PXRD of **Cu-3** evacuated and with various guests: (a) predicted spectrum with MeCN from the SCXRD structure; (b) empty framework; (c) adsorption of MeCN; (d) adsorption of *n*-pentane; (e) adsorption of benzene.

PXRD pattern of **Cu-3**, after standing in the atmosphere at room temperature (Figure 2b), indicates that the solid is still crystalline but has a different pattern. Thermogravimetric analysis of **Cu-3** shows that it contains no adsorbed solvent (MeCN or water) and is stable to ∼350 °C.

In the case of **Cu-4**, the physisorbed MeCN is desorbed upon standing at room temperature and the coordinated MeCN is removed above 50 °C. This material also remains crystalline after all MeCN is removed from the lattice (Figure 3). Thermogravimetric analysis (TGA) indicated that **Cu-4** was stable to over 380 °C.

Upon solvent loss, the lattice of **Cu-3** undergoes a small compression but retains crystallinity, as indicated by a shift of the (020) peak from 5.60° to 6.20° (2θ). This shift results from a framework contraction that reduces porosity, confirmed by gas adsorption studies that showed no N_2 uptake by solvent-evacuated **Cu-3**. However, the pores could still be accessed by organic solvents. Upon exposure to MeCN vapor, the structure reverted to that predicted for the lattice impregnated with MeCN (Figure 2c). Pentane and benzene were also adsorbed into the hydrophobic channels of **Cu-3**,

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(5) (a) Crystallographic data for **Cu-3**: monoclinic, space group $P2_1/c$, $a = 9.1569(11)$ Å, $b = 31.760(4)$ Å, $c = 8.2462(9)$ Å, $\alpha = 90°$, $\beta = 99.380(3)°$, $\gamma = 90°$, $V = 2366.1(5)$ Å^3, $Z = 4$, mol wt = 728.29, $T = -100(1)$ °C, μ(Mo Kα) = 4.423 cm^{-1}, 19 632 observed (4612 unique) reflections, 270 variables, R1 = 0.0526 ($I > 2\sigma(I)$), wR2 = 0.1023 ($I > 2\sigma(I)$), R1 = 0.0741 (all data), wR2 = 0.1138 (all data), GOF = 1.143. (b) Crystallographic data for **Cu-4**: triclinic, space group $P\bar{1}$, $a = 9.8372(5)$ Å, $b = 11.9700(6)$ Å, $c = 15.8616(8)$ Å, $\alpha = 75.471(2)°$, $\beta = 86.569(2)°$, $\gamma = 67.827(2)°$, $V = 1673.03(15)$ Å^3, $Z = 4$, mol wt = 627.15, $T = -100(1)$ °C, μ(Mo Kα) = 6.235 cm^{-1}, 21 643 observed (5093 unique) reflections, 445 variables, R1 = 0.0260 ($I > 2\sigma(I)$), wR2 = 0.0583 ($I > 2\sigma(I)$), R1 = 0.0450 (all data), wR2 = 0.0635 (all data), GOF = 0.983.

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(7) The void space of each structure was calculated using PLATON (Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7).

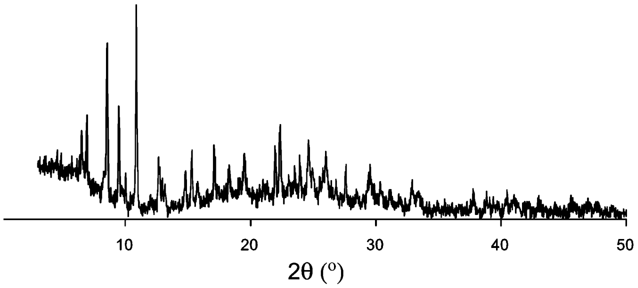

Figure 3. PXRD of **Cu-4** after heating to 100 °C to remove coordinated MeCN.

resulting in crystalline structures similar to those of the MeCN-saturated lattice (Figure 2d,e). Although the channels are inaccessible to N_2, the lattice was expanded by organic vapors, indicating adsorption of these molecules.

The structures of **Cu-3** and **Cu-4** appear to be very hydrophobic because there is no evidence from TGA that they absorb water from solvents or the atmosphere. Furthermore, **Cu-3** is water-stable, without any noticeable decomposition after refluxing overnight in D_2O. Unlike most other microporous solids, which either are unstable in water or have hydrophilic channels that adsorb water (e.g., zeolites), the properties of **Cu-3** present an opportunity to observe guest uptake in water. Framework **Cu-3** was effective at removing benzene from D_2O as monitored by ^1H NMR spectroscopy. A short treatment of the polluted water reduced the dissolved benzene concentration from 0.8 to <0.01 mg mL^{-1} (Figure 4). After the sample was allowed to equilibrate with **Cu-3** for 2 days, the level of benzene present was undetectable by ^1H NMR spectroscopy.[8] **Cu-3** does not uptake MeCN from water, indicating a selective uptake for nonpolar organics. Importantly, **Cu-3** can be regenerated under vacuum and even recycled (by recrystallization from MeCN).

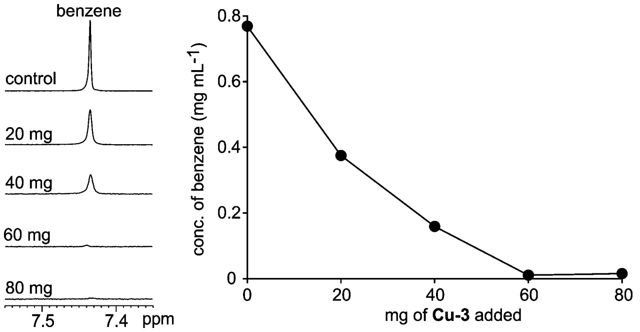

Figure 4. ^1H NMR measurement of benzene adsorption by **Cu-3** after 20, 40, 60, or 80 mg of **Cu-3** was added to 1.5 mL of D_2O containing 0.01 M benzene. Sucrose was used as the internal standard.

In summary, we have presented a new class of shape-persistent ligands derived from triptycene and shown that when coordinated to transition metals, they can assemble into non-interpenetrating coordination frameworks with hydrophobic void spaces. These robust structures are thermally stable and display reversible solvent adsorption. **Cu-3** and related frameworks may be good sorbents for the removal of organic pollutants from contaminated water. Future work will involve extension of this class of frameworks and exploitation of their porosity.

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Supporting Information Available: Experimental conditions, compound characterization, X-ray data, and TGA data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) In the treatment with 40 mg of **Cu-3**, the lattice removes about 0.83 benzene molecules per unit cell, or about 0.1 benzene molecules per Cu atom.