Metal–Organic Frameworks Incorporating Copper-Complexed Rotaxanes**

Ali Coskun, Mohamad Hmadeh, Gokhan Barin, Felipe Gándara, Qiaowei Li, Eunwoo Choi, Nathan L. Strutt, David B. Cordes, Alexandra M. Z. Slawin, J. Fraser Stoddart,* Jean-Pierre Sauvage,* and Omar M. Yaghi*

The incorporation of mechanically interlocked molecules (MIMs), such as rotaxanes and catenanes, into porous metal–organic frameworks (MOFs) has recently been recognized[1] as a strategy for introducing dynamics into otherwise rigid, robust frameworks. In this manner, the interlocked nature of these switchable components allows dynamics to be expressed independently of the MOF backbone and, therefore, without compromising the fidelity of the whole system. Accordingly, \( \pi \)-electron-rich crown ethers, capable of binding \( \pi \)-electron-deficient substrates,[2] and degenerate donor–acceptor[2]catenanes[3] have already been introduced into MOFs. In addition, [2]rotaxanes, wherein the dumbbell components function as struts in the frameworks, have also been incorporated[4] into MOFs. While this strategy has been applied[4a–f] to the preparation of a number of 2D and 3D frameworks from [2]pseudorotaxanate subunits, it remains a challenge to locate switchable rotaxanes and catenanes inside extended frameworks. Metal-containing MIMs—particularly those based on the well-known[5] copper(I)-templated systems—offer the opportunity to locate switches within MOFs. Herein, we

Scheme 1. Synthesis of the [2]pseudorotaxanate [1·Cu]·PF\(_6\) and MOF-1040. The synthesis of the [2]pseudorotaxanate was achieved using metal-templated protocols; the copper-complexed ring 3 was added to a solution of 2 in CH\(_2\)Cl\(_2\) to form the [2]pseudorotaxanate [1·Cu]·PF\(_6\). Red cubic crystals, suitable for X-ray crystallographic analysis, were obtained by mixing [1·Cu]·PF\(_6\) and Zn(NO\(_3\))\(_2\)·6 H\(_2\)O in \( \text{N,N-diethylformamide} \) in a sealed tube at 100°C for 2 days.
report the successful incorporation (Scheme 1) of copper(I)-complexed [2]pseudorotaxanate struts into a MOF (MOF-1040). Each of the struts is composed of a rigid rod-like fragment containing a 1,10-phenanthroline unit which is encircled by a coordinating 30-membered ring. We present 1) the synthesis and solid-state structure of the strut in the form of a [2]pseudorotaxanate, 2) the preparation of MOF-1040 and its single crystal structure, along with 3) data supporting the oxidation of copper(I) in the struts to copper(II), as well as 4) the demetalation of the strut, creating rotaxanes with free coordination sites within the solid-state structure of MOF-1040.

The synthesis of the copper-coordinated pseudorotaxanate [1-Cu]PF$_6$ and the subsequent preparation of MOF-1040 employing this strut are summarized in Scheme 1. The [2]pseudorotaxanate [1-Cu]PF$_6$ was prepared through the effective “gathering-and-threading” approach$^{[a,b]}$ of a copper(I) catenate by 1) mixing of 2HCl$^{[c]}$ with Et$_3$N, thus generating the dicarboxylate of 2, followed by 2) the addition of the copper complex$^{[3]}$ of 3, which was prepared by 3) the reaction of the coordinating ring with [Cu(CH$_3$CN)$_4$]PF$_6$ in stoichiometric amounts, followed by 4) reprotonation of the dicarboxylate and counterion exchange with saturated aqueous NH$_4$PF$_6$ solution, resulting in the production of [1-Cu]PF$_6$ in 87% yield.

Dark red single crystals of the copper-coordinated [2]pseudorotaxanate were grown by diffusing Et$_2$O into a solution of [1-Cu]PF$_6$ in CH$_2$Cl$_2$. The solid-state superstructure$^{[8]}$ (Figure 1), which occupies the triclinic space group $P1$, comprises three independent [2]pseudorotaxanes, in addition to disordered PF$_6^-$ ions and CH$_2$Cl$_2$ solvent molecules. The Cu–N bond lengths are typical (2.014 to 2.080 Å) of such complexes, and, while the N-Cu-N angles are in some cases distorted significantly from ideal tetrahedral geometry (81 to 139°), this occurrence is in agreement with previously reported examples.$^{[9]}$ It would appear that these distortions occur to enable more efficient packing, as well as stabilizing intramolecular interactions, e.g., one of the phenoxy moieties of the ring component participates in [π-π] stacking interactions with the phenanthroline ring system of the rod component. The three independent [2]pseudorotaxanes found in the unit cell arise primarily from the changes in the arrangement of the two phenanthroline ring systems and the intramolecular interactions they seek to satisfy.

Mixing [1-Cu]PF$_6$ and Zn(NO$_3$)$_2$·6H$_2$O in diethylformamide (DEF) at 100°C in a sealed tube for 48 h resulted (see Experimental Section) in the formation of red cubic crystals of MOF-1040. The single-crystal X-ray diffraction study was performed using synchrotron radiation in the beamline 24-ID-C at NECAT, in the Advanced Photon Source (APS) at Argonne National Laboratory. The crystal structure was solved in the monoclinic space group $P2_1/c$,$^{[10]}$ revealing a structure (Figure 2) consisting of threefold interpenetrated networks. The inorganic Zn$_4$O secondary building units (SBUs) are linked by the [1-Cu] complex struts, producing a framework with pea$^{[11]}$ topology. The inorganic SBUs, the Cu complexes and the rest of the aromatic rings in the organic strut were unambiguously determined from the single-crystal structural analysis of MOF-1040. In common with other crown-ether containing MOFs$^{[2]}$ the polyether part of the

![Figure 1. Solid-state (super)structure of the copper-complexed [2]pseudorotaxanate [1-Cu]PF$_6$ in a) ball-and-stick and b) space-filling representations. The copper(I) complex is distorted significantly from ideal tetrahedral geometry on account of the [π-π] stacking interactions between one of the phenoxy moieties of the ring and the phenanthroline ring system in the thread component. The hydrogen atoms and counterions have been omitted for clarity.](image)

![Figure 2. a) Ball-and-stick representation of the crystal structure of MOF-1040 which has threefold interpenetrated networks shown in red, yellow and black, respectively, with coordinating rings represented in red balls and wires, the copper atoms are represented in gold. b) Space-filling representations of the threefold interpenetrated networks of MOF-1040 shown in blue, yellow and black, respectively, with coordinating rings represented in red. The polyether parts of coordinating ring in the structure were modeled by using Material Studio software.$^{[7]}$](image)
... coordinating ring were found to be highly disordered in the structure (see Supporting Information for details). In addition, the interstitial spaces of MOF-1040 are not only occupied by disordered solvent molecules, but also by disordered PF$_6^-$ ions. The polyether loops of the coordinating rings in the structure were modeled by using Material Studio software. Nonetheless, the crystal structure of MOF-1040 confirms that the integrity of the copper(I)-complexed [2]pseudorotaxane is maintained after the formation of the MOF.

The stable Cu$^{II}$N$_4$ complex of MOF-1040 with four-coordinate d$^{10}$ metal (pseudo-tetrahedral) is oxidized (Figure 3a) by the addition of oxone solution in CH$_3$CN (0.05 M) at room temperature, forming the paramagnetic copper(II) complex, Cu$^{II}$N$_4$$^{2+}$ (d$^2$ configuration), in the oxidized MOF-1040 (referred to as MOF-1041). The oxidation of Cu$^I$ to Cu$^{II}$ has been monitored (Figure 3b) by EPR spectroscopy. While it is important to note that the EPR experiment does not allow us to quantify the degree of change in the redox state of copper ions, those Cu$^I$ ions which happen to be oxidized to Cu$^{II}$ can be regarded as local electronic switches which will undoubtedly be accompanied by significant alterations in the coordination geometries surrounding these copper ions located inside MOF-1040/1041. The resulting spectrum displays characteristic features of a d$^2$ Cu$^{II}$N$_4$ complex with g-factors of $g_1 = 2.290$, $g_2 = 2.064$ and $A_z = 11.1$ mT, values expected for four-coordinate Cu$^{II}$ in a distorted tetrahedral arrangement. These values are in perfect agreement with those obtained in the solution studies of related complexes consisting of the same chelating units, namely 2,9-diphenyl-1,10-phenanthroline. Additionally, we have performed inductively coupled plasma mass spectrometry (ICP-MS) in order to quantify the amount of copper within the framework.

![Figure 3](image)

**Figure 3.** a) Graphical representation of the oxidation of Cu$^I$ to Cu$^{II}$ by using oxone solution (0.05 M) in CH$_3$CN resulting in the formation of MOF-1041 with the Cu$^{II}$N$_4$ complex, and of the demetallation of MOF-1040 by using KCN (5 g/148 mL) in anhydrous CH$_3$OH affording MOF-1042 in which 60% of rotaxanes are demetalated.

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**Experimental Section**

[1-Cu]$^+$PF$_6^-$ : [Cu(CH$_3$CN)$_4$]$^+$PF$_6^-$ (37 mg, 0.1 mmol) dissolved in anhydrous CH$_3$CN (5 mL) under a N$_2$ atmosphere and added, using a cannula, to a solution of 3 (58 mg, 0.1 mmol) in CH$_2$Cl$_2$ (2.5 mL), affording a dark orange solution, which was stirred at room temperature for 10 min. This solution, when added to a solution of 2 (50 mg, 0.1 mmol) in CH$_2$Cl$_2$ (5 mL) containing Et$_3$N (0.3 mmol, 45 µL), formed a dark red solution, which was stirred for 12 h. It was then concentrated under vacuum, before being dissolved in the minimum amount of CH$_3$CN (3 mL) and added to H$_2$O (200 mL) at pH 3.5. Countercurrent exchange with a saturated aqueous NH$_4$PF$_6$ solution afforded analytically pure [1-Cu]$^+$PF$_6^-$ as a red solid (106 mg, 87%).
mechanostereochemistry · metal–organic frameworks · taxanate were grown by diffusing Et₂O in to a solution of crystals were collected and rinsed with fresh DEF (3°C148 2 mL). from the oven and allowed to cool to room temperature. Red cubic

Published online: January 20, 2012
Received: November 8, 2011

Keywords: interpenetrated networks · mechanostereochemistry · metal–organic frameworks · reticular chemistry · rotaxanes


[10] Single-crystal data for [I-Cu]PF₆–Cu₂[H₂O]₃CF₆₃N₄O₉P₂, red crystals, Mₘ = 3575.73, crystal size 0.15 x 0.15 x 10 mm, triclinic, space group P1, a = 20.5328(8), b = 22.1408(8), c = 24.8729(9), α = 91.721(2), β = 101.310(2), γ = 117.2740(10), V = 9761.5(6) Å³, Z = 2, Pca₂₁ = 1.278 g cm⁻³; T = 173(2) K, R₁ (F > 2σ(F)) = 0.1532, wR₂ = 0.4433. CCDC 852836 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


[12] Generally speaking, copper(II) complexes are strongly distorted in a four-coordinate tetrahedral environment in contrast with their copper(I) analogues. In addition, the Cu II in a tetrahedral environment in contrast with their copper(I) analogues. In addition, the Cu II in a four-coordinate tetrahedral environment in contrast with the same bonds in the corresponding monovalent complexes (G. Murphy, C. O’ Sullivan, B. Murphy, B. Hathaway, Inorg. Chem. 1998, 37, 240 – 248). As a consequence, oxidation of copper(I) to copper(II) is very likely to trigger a shrinking and flattening of the entire metal coordination sphere.


[15] All our attempts to date to increase the degree of demetalation from MOF-1040 have been unsuccessful. Prolonged demetalation reaction times and high temperatures result in the partial degradation of the framework. We hypothesize, however, that the threefold interpenetrated structure of the framework provides additional stabilization to the copper complexes and renders them inaccessible. We believe that decreasing the interpenetration of framework could increase the demetalation ratio.

