

Metal–Organic Frameworks Incorporating Copper-Complexed Rotaxanes**

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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, π -electron-rich crown ethers, capable of binding π -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

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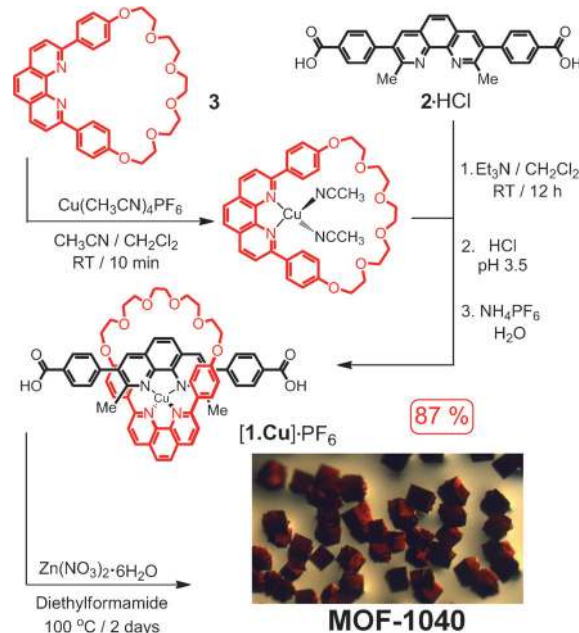
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Scheme 1. Synthesis of the [2]pseudorotaxanate [1·Cu]·PF₆ and MOF-1040. The synthesis of the [2]pseudorotaxanate was achieved using metal-templated protocols; the copper-complexed ring **3** was added to a solution of **2** in CH₂Cl₂ to form the [2]pseudorotaxanate [1·Cu]·PF₆. Red cubic crystals, suitable for X-ray crystallographic analysis, were obtained by mixing [1·Cu]·PF₆ and Zn(NO₃)₂·6H₂O in *N,N*-diethylformamide in a sealed tube at 100 °C for 2 days.

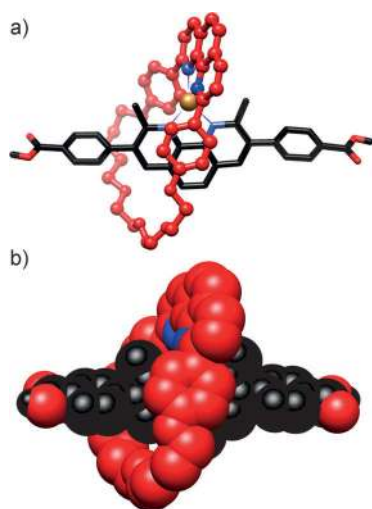


Figure 1. Solid-state (super)structure of the copper-complexed [2]pseudorotaxanate [1-Cu]·PF₆ in a) ball-and-stick and b) space-filling representations. The copper(I) complex is distorted significantly from ideal tetrahedral geometry on account of the $[\pi\cdots\pi]$ stacking interactions between one 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.

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]·PF₆ and the subsequent preparation of MOF-1040 employing this strut are summarized in Scheme 1. The [2]pseudorotaxanate [1-Cu]·PF₆ was prepared through the effective Cu^I-templated “gathering-and-threading” approach^[5a,b] of a copper(I) catenate by 1) mixing of 2·HCl^[6] with Et₃N, thus generating the dicarboxylate of 2, followed by 2) the addition of the copper complex^[7] of 3, which was prepared by 3) the reaction of the coordinating ring with [Cu(CH₃CN)₄]PF₆ in stoichiometric amounts, followed by 4) reprotonation of the dicarboxylate and counterion exchange with saturated aqueous NH₄PF₆ solution, resulting in the production of [1-Cu]·PF₆ in 87% yield.

Dark red single crystals of the copper-coordinated [2]pseudorotaxanate were grown by diffusing Et₂O into a solution of [1-Cu]·PF₆ in CH₂Cl₂. The solid-state superstructure^[8] (Figure 1), which occupies the triclinic space group *P* $\bar{1}$, comprises three independent [2]pseudorotaxanates, in addition to disordered PF₆⁻ ions and CH₂Cl₂ 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 $[\pi\cdots\pi]$ stacking interactions with the phenanthroline ring system of the rod component. The three independent [2]pseudorotaxanates 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]·PF₆ and Zn(NO₃)₂·6H₂O 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 *P*2₁/*c*,^[10] revealing a structure (Figure 2) consisting of threefold interpenetrated networks. The inorganic Zn₄O secondary building units (SBUs) are linked by the [1-Cu] complex struts, producing a framework with **pcu** topology.^[11] 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

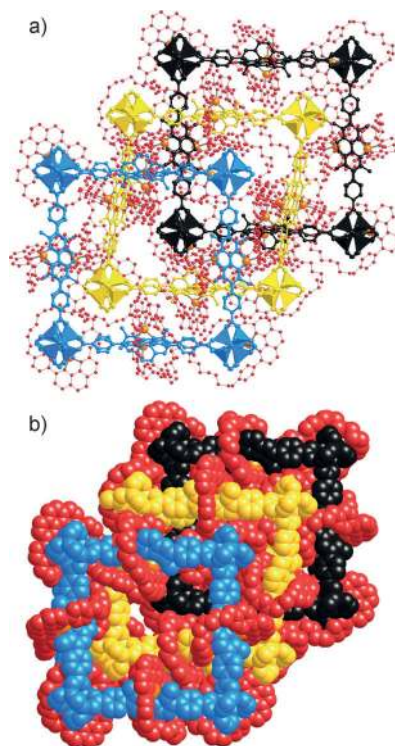


Figure 2. a) Ball-and-stick representation of the crystal structure of MOF-1040 which has threefold interpenetrated networks shown in blue, yellow, and black, respectively, with coordinating rings represented by red balls and wires, the copper atoms are represented in gold. b) Space-filling representations 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.^[10]

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.^[10] Nonetheless, the crystal structure of MOF-1040 confirms that the integrity of the copper(I)-complexed [2]pseudorotaxanate is maintained after the formation of the MOF.

The stable $\text{Cu}^{\text{I}}\text{N}_4^+$ complex of MOF-1040 with four-coordinate d^{10} metal (pseudo-tetrahedral) is oxidized (Figure 3a) by the addition of oxone solution in CH_3CN (0.05 M) at room temperature, forming the paramagnetic copper(II) complex, $\text{Cu}^{\text{II}}\text{N}_4^{2+}$ (d^9 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^[12] alterations in the coordination geometries surrounding these copper ions located inside MOF-1040/1041. The resulting spectrum displays characteristic features of a d^9 $\text{Cu}^{\text{II}}\text{N}_4^+$ complex with $g_{\parallel} = 2.290$, $g_{\perp} = 2.064$ and $A_{\parallel} = 11.1$ mT, values expected for four-coordinate Cu^{II} in a distorted tetrahedral arrangement. These values are in perfect agreement with those obtained^[13] 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.

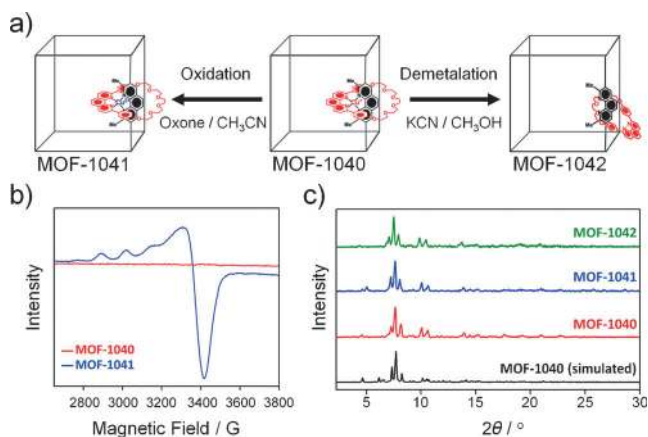


Figure 3. a) Graphical representation of the oxidation of Cu^{I} to Cu^{II} by using oxone solution (0.05 M) in CH_3CN resulting in the formation of MOF-1041 with the $\text{Cu}^{\text{II}}\text{N}_4^{2+}$ rotaxane complexes, and of the demetalation of MOF-1040 by using KCN (5×10^{-3} M in anhydrous CH_3OH) affording MOF-1042 in which 60% of rotaxanes are demetalated. b) Solid-state EPR spectra of MOF-1040 (red line) and its oxidized form (MOF-1041) (blue line) recorded at room temperature at 9.78 GHz. c) PXRD patterns of as-synthesized MOF-1040 (red), after oxidation reaction (MOF-1041) (blue) and after demetalation (MOF-1042) (green) compared with calculated pattern (black) derived from the crystal structure, reveal that MOF-1040 maintained its structural topology throughout the oxidation and the demetalation.

MOF-1041 revealed a decrease in the amount of copper with the calculated molar ratios $[\text{Zn}]/[\text{Cu}]$ of 1.33 and 1.50, before and after oxidation, respectively. These numbers support the fact that the complex of the copper(II) ion in a four-coordinate environment is a thermodynamically unstable species and can be dissociated easily.^[13b,14] Furthermore, the powder X-ray diffraction (PXRD) pattern (Figure 3c) of MOF-1041 proves conclusively that the structure of the framework is maintained after oxidation has occurred.

In addition to the switching experiments, we have carried out demetalation (Figure 3) by following well-established literature procedures already developed for the molecular strut,^[14] wherein Cu^{I} -complexed rotaxanes and catenanes can be demetalated by reaction with CN^- ion under mild reaction conditions, leading to rotaxanes and catenanes with free coordination sites. In order to demetalate the rotaxane in MOF-1040, a reaction between MOF-1040 crystals and KCN (5×10^{-3} M) in CH_3OH has been performed (see Supporting Information for details). After the reaction, a sample analyzed by ICP-MS revealed a 60% decrease in the amount of Cu^{I} , compared with the original sample, indicating that not all of the Cu^{I} -complexing sites within the framework are accessible.^[15] The partially demetalated MOF-1040 (termed MOF-1042) maintains (Figure 3c) its structural topology throughout the reaction as evidenced by PXRD measurements.

We have demonstrated that metal-templated [2]pseudorotaxanates bearing carboxyl groups can be incorporated into metal-organic frameworks. The structural characterization of MOF-1040, based on X-ray structural analysis, shows that these struts form threefold interpenetrated **pcu** networks. While both the oxidation and demetalation experiments have been demonstrated to occur without disrupting the crystallinity of the frameworks, the fact that at least some of the copper ions can be oxidized to their dicationic states indicates the presence of electronic switches which are presumably accompanied by geometrical changes involving shrinking and flattening in the coordination sphere of the copper ions in question. These observations allow us to contemplate incorporating molecular switches into the metal-organic frameworks, thus uniting the concepts of mechanostereochemistry,^[16] chemical topology^[17] and reticular chemistry^[18] to create robust, yet dynamic systems.^[14] They mark a significant step towards transferring the solution-state chemistry of mechanically interlocked molecules into the solid-state in the form of a porous extended structure.

Experimental Section

[1-Cu]- PF_6 : $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (37 mg, 0.1 mmol) was dissolved in anhydrous CH_3CN (5 mL) under a N_2 atmosphere and added, using a cannula, to a solution of **3** (58 mg, 0.1 mmol) in CH_2Cl_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_2Cl_2 (5 mL) containing Et_3N (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_3CN (3 mL) and added to H_2O (200 mL) at pH 3.5. Counterion exchange with a saturated aqueous NH_4PF_6 solution afforded analytically pure [1-Cu]- PF_6 as a red solid (106 mg, 87%).

FT-IR (KBr, $\bar{\nu}$ = 3500–400 cm^{-1}): 2920(w), 2870(w), 1715(s), 1605(s), 1481(m), 1390(br), 1250(s), 1173(m), 1111(m), 941(w), 840(s), 648(w). ^1H NMR (500 MHz, CD_3CN , 298 K): δ = 2.13 (s, 6H, Me), 3.38–3.69 (m, 20H), 6.05 (d, J = 8.5 Hz, 4H), 7.55 (d, J = 8.5 Hz, 4H), 7.60 (d, J = 8.0 Hz, 4H), 8.17 (d, J = 8 Hz, 4H), 8.20–8.23 (m, 6H), 8.51 (s, 2H), 8.78 ppm (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, CD_3CN , 298 K): δ = 24.1, 66.5, 67.9, 69.9, 70.0, 70.3, 112.6, 123.9, 126.0, 126.5, 127.3, 127.7, 129.1, 129.2, 129.5, 133.1, 136.9, 137.0, 137.2, 141.0, 143.2, 143.3, 154.0, 157.4, 158.7, 166.1 ppm. ESI-HRMS m/z calcd for $\text{C}_{62}\text{H}_{54}\text{CuN}_4\text{O}_{10}$: 1077.3136 ($[\text{M}-\text{PF}_6]^+$); found: 1077.3171 ($[\text{M}-\text{PF}_6]^+$). Single crystals of the copper(I)-complexed pseudoro-taxanate were grown by diffusing Et_2O in to a solution of $[\text{1-Cu}]\cdot\text{PF}_6$ in CH_2Cl_2 at room temperature.

MOF-1040: Strut $[\text{1-Cu}]\cdot\text{PF}_6$ (6.50 mg, 5.22×10^{-6} mol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10.00 mg, 3.36×10^{-5} mol) were dissolved in diethylformamide (1.0 mL) in a sealed tube which was placed in an isothermal oven at 100 °C for 48 h, after which time it was removed from the oven and allowed to cool to room temperature. Red cubic crystals were collected and rinsed with fresh DEF (3×2 mL). Elemental analysis: calcd (%): C 56.15, N 3.97, H 5.71, $[\text{Zn}]/[\text{Cu}]$ = 1.33; found: C 56.36, N 3.88, H 5.70, $[\text{Zn}]/[\text{Cu}]$ = 1.37. FT-IR (KBr, $\bar{\nu}$ = 3500–400 cm^{-1}): 2916(w), 2870(w), 1615(s), 1550(s), 1388(br), 1250(s), 1179(m), 1110(m), 946(w), 843(s), 671(w).

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