Construction of a Porous Homochiral Coordination Polymer with Two Types of Cu$_n$I$_n$ Alternating Units Linked by Quinine: A Solvothermal and a Mechanochemical Approach

Daniel Prochowicz,[a] Iwona Justyniak,[b] Arkadiusz Kornowicz,[a] Tomasz Kaczorowski,[b] Zbigniew Kaszkur,[b] and Janusz Lewiński*[a, b]

The construction of inorganic–organic hybrid materials based on copper(I) halides, especially copper(I) iodide, has been extensively investigated due to their intriguing topology and interesting physical and chemical properties.[1] Reactions of CuI with bidentate (ditopic) or polydentate ligands may generate 0D macrocycles[2] or 1D,[3] 2D and 3D metal–organic frameworks with various [Cu$_n$I$_n$] structural motifs, such as Cu$_2$I$_2$ rhomboid dimers,[4] triangular Cu$_3$I$_3$ clusters,[5] cubanelike or chairlike [Cu$_4$I$_4$] tetrasmers,[6] hexagonal Cu$_6$I$_6$ clusters,[7] ladderlike or ribbonlike [Cu$_4$I$_4$]$_m$ chains,[8] zigzag [Cu$_n$I$_n$] or [Cu$_n$I$_n$]$_m$ chains,[9, 10] and 2D [Cu$_n$I$_n$]$_m$ layers.[11] Among the various clusters acting as connecting nodes, dimeric and tetrameric units have been seen to be the most common, whereas triangular Cu$_3$I$_3$ clusters are comparatively very rare. [Cu$_4$I$_4$] clusters not only show structural variety, but also exhibit emission behavior that can often vary markedly with the adopted structure. Another potential level of tailoring in the construction of coordination polymers can be achieved by use of two types of Cu$_n$I$_n$ cluster as connecting nodes and to the best of our knowledge there are only two examples of coordination polymers with different Cu$_n$I$_n$ alternating units incorporating two types of Cu$_n$I$_n$ cluster as connecting nodes.[15, 11] Furthermore, homochiral coordination polymers based on copper(I) halides can potentially have the advantage of offering applications in heterogeneous asymmetric catalysis, enantioselective separation and second-order nonlinear optical materials. However, this research area remains a great challenge and is largely unexplored to now.[16, 10, 4, 12]

Recently, we focused our attention on metal alkoxides derived from cinchona alkaloids, exploring their utility as chiral building blocks for the construction of microporous homochiral networks, including coordination- and noncovalent-interaction-driven assemblies, prone to enantioselective sorption and having unique gas-separation properties.[11] The continuing interest in this area and the relatively little research on cinchona alkaloid/copper(I) coordination chemistry (the two known examples are limited to homochiral Cu I chloride (or bromide)–olefin coordination polymers)[12a, b] prompted us to investigate the possibility of fabricating new structures based on the Cu/quinine system. Herein, we describe the formation and characterization of a novel homochiral 1D coordination polymer of alternating Cu$_3$I$_3$ and Cu$_4$I$_4$ units linked by a quinine molecule (not deprotonated). Remarkably, van der Waals interactions between adjacent 1D polymer chains lead to an extended quasi-honeycomb homochiral pillared 3D network with solvent-free 1D channels. Another intriguing result is the formation of the inorganic–organic porous material under both conventional solvothermal and mechanochemical conditions.

The reaction between quinine (QN) and CuI under solvothermal conditions in a sealed tube yielded yellow block crystals of coordination polymer [([Cu$_3$(μ$_3$-I)$_3$](QN)$_2$)][Cu$_4$(μ$_4$-I)$_3$](μ$_4$-I)(QN)$_2$]$_{1}$ (1) irrespective of the molar ratio of the reactants used (Scheme 1). Single-crystal X-ray crystallographic analysis revealed that 1 crystallizes in the chiral non-centrosymmetric trigonal space group $P3_12_1$. It has a unique ladderlike framework constructed from cubanelike [Cu$_4$(μ$_4$-I)$_3$] and triangular [Cu$_3$(μ$_3$-I)$_3$](μ$_4$-I) clusters acting as alternating rings in a 1:2 ratio and with the QN ligands acting as $N,N$-ditopic spacers; the quinine OH group is not involved in the coordination to the metal center and acts as a spectator moiety (Figure 1). As shown in Figure 1a, the Cu$_4$I$_4$ unit...
acts as a classical tetrahedral node with the quinuclidine N atoms completing the tetrahedral coordination sphere of each copper(I) atom (with Cu–I and Cu–N separations of 2.637(8)–2.770(7) Å and 2.127(5)–2.132(5) Å, respectively, and Cu–Cu separations of 2.989(1)–3.022(1) Å, which is longer than those found in related Cu4I4 complexes with N ligands). The discrete Cu3I3 cluster may be described as a Cu2I2 dimeric aggregate assembled with one monomeric CuI unit (Figure 1b). In the resulting cluster two distinct sets of both Cu2 centers and bridging iodides are present. Two Cu atoms are linked through two μ3- and one μ2-iodine atoms with a relatively short Cu···Cu separation of 2.480(1) Å (the Cu3···Cu4 separation is shorter than the van der Waals radii (2.80 Å), indicating a cuprophilic interaction), and one Cu center is bound to two μ3-iodine atoms and has a significantly larger Cu···Cu separation of 3.217(2)–3.431(5) Å. From a topological perspective view, each Cu3I3 core acts as a rare nonsymmetrical four-connecting node; the Cu5 atom is coordinated to quinoline and quinuclidine N atoms, whereas each of the other two copper atoms, Cu3 and Cu4, is bound to one quinoline N atom. It should be noted that 1 represents a very rare example of a copper(I) coordination polymer incorporating two different types of inorganic cluster acting as nodes,[9a,10] and a particularly exciting feature is their alternating 1:2 sequence.

A more detailed analysis of the supramolecular structure of 1 shows that stacking along the second dimension is dictated by weak van der Waals interactions. Interestingly, the remaining OH group is not involved in either intra- or intermolecular noncovalent interactions. Each polymeric chain is related by a 3,3-screw axis and stacked in an extended quasi-honeycomb homochiral 3D network with solvent-free 1D tubular channels (Figure 1d). The average inner diameter of the channels is approximately 7.8 Å, without guest molecules in the pores (Figure 2). On the basis of PLATON calculations,[14] the open channels constitute about 39.3% (5428.1 of 13811.6 Å3) of the structure. Thermogravimetric analysis (TGA) studies show that 1 is stable up to approximately 150°C (Figure S2 in the Supporting Information).

The permanent porosity of the solvent-free structure of 1 was further verified by gas sorption measurements. Surprisingly, although the kinetic diameter of N2 (3.54 Å) is much smaller than that of the effective pore window of 1, the N2 adsorption isotherm at 77 K revealed no significant uptake up to 1 bar of pressure and has a very low BET surface area (1.74 m2 g−1; see Figure S3 in the Supporting Information).[15] However, 1 adsorbs moderate amounts of CO2 at 195 K (38 cm3 g−1 at STP) with a type I isotherm typical for microporous materials (Figure S4 in the Supporting Information). The micropore volume for 1 (0.076 cm3 g−1), estimated from the Dubinin–Radushkevich equation for CO2 adsorption data, is significantly lower than the value of 0.283 cm3 g−1 derived from PLATON calculations. The difference in the observed gas-sorption data can likely be explained as an effect of the framework polarity and kinetic aspects of the sorption measurements.[16] We reason that CO2 is a favored adsorbative by 1 under low pressures due to the high quadrupole
Copper(I) iodide clusters are well-known for their rich luminescence properties,[18] which is the reason that we were also curious about the photoluminescence behavior of the novel coordination polymer 1, composed of two distinct CuIₙ units. The luminescence spectrum of 1 in the solid state at room temperature was recorded by excitation at 510 nm, leading to one very broad yellow emission band at 625 nm (Figure S5 in the Supporting Information). This broad emission band can be attributed to halide-to-metal charge transfer (XMCT) and a triplet Cu⁻¹ cluster-centered (CC) excited state with the excitation localized on the CuIₙ core, indicating the aforementioned cuprophilic interaction.[18,c-e]

Most syntheses of copper(I) halide aggregates require energy-consuming solvothermal conditions for homogeneity of reaction mixtures, whereas the use of mechanochemical methods is still limited.[19] Since solvent-free synthesis is becoming an increasingly important strategy in materials synthesis,[20,21] we exploited this approach for the CuI/QN system. In our investigation of the CuI/QN system in a number of control experiments under mechanochemical conditions, we first attempted the synthesis of 1 by grinding CuI and quinine in the desired stoichiometry, that is, a CuI/QN ratio of 5:3.[22] As revealed by PXRD, neat grinding even for a prolonged time provided only the CuI salt. Guided by the observation that small amounts of a liquid phase can significantly enhance the scope and rate of mechanosynthesis, we turned to liquid-assisted grinding.[20h–j] Addition of a small amount of acetonitrile to the preformed reaction mixture, followed by grinding for 30 min provided a yellow, free-flowing powder quantitatively. The measured PXRD spectrum confirmed that the mechanochemical synthesis produced a material with no detectable amounts of the starting materials present and showing a high background (porous glass support and amorphous contents scattering) with broadened peaks due to the presence of small crystallites and possible microstrain (Figure 3). Broad nanocrystalline peaks may easily show slight shifts of their position, for example, due to surface relaxation and/or a solvent concentration gradient, the peaks may overlap and the powder pattern carries more complex and indirect structural information than just the elementary cell composition. Thus, profile fitting tools like Rietveld refinement are of less use. Nevertheless, the observed set of reflections agrees well with a set of principal peaks of the calculated pattern of 1, confirming the purity of the powdered sample. The material obtained in such a way showed similar gas sorption behavior to that derived from the solvothermal method. Moreover, the measured luminescence properties of the ground material at room temperature revealed an identical spectrum, with an emission maximum at 625 nm. Thus, in this case mechanical treatments did not affect the luminescence of 1 in contrast to the recent well-documented reports showing mecha-nochroimic behavior of copper(I) iodide clusters that originate from local distortions in the crystal packing.[19b]

In conclusion, we have demonstrated that cinchona alkaloids in combination with copper(I) iodide can effectively act as molecular building blocks for the construction of novel chiral nanotubular architectures through noncovalent-interaction-driven self-assembly, as well as new 1D coordination polymers with various types of CuIₙ alternating units under both solvothermal and liquid-assisted grinding conditions. The results open new routes for the rational design and preparation of homochiral metal–organic materials based on CuI clusters and further investigations in this direction are in progress.

**Experimental Section**

**Synthesis of 1:** A mixture of CuI (0.38 g, 2.0 mmol) and quinine (0.324 g, 1.0 mmol) in a mixed solution of MeCN/EtOH (2:1) was sealed in a Teflon-lined stainless-steel reactor and heated at 80°C for 20 h. After cooling to room temperature, block-yellow crystals of 1 were obtained (78% based on quinine). Compound 1 can also be formed in a similar procedure by using a 1:1 molar ratio of reactants (58% based on quinine). Elemental analysis calc’d (%) for C₆₀H₇₁Cu₅I₅N₆O₆: C 37.41, H 3.69, N 4.36; found: C 37.63, H 3.73, N 4.32.
Crystal data for 1: Ca$_2$H$_5$Cu$_4$In$_4$O$_{24}$; $M = 1924.48$, trigonal space group $P3_2$ (no. 152), $a = 21.9950(2)$, $b = 21.9950(2)$, $c = 32.9660(4)$ Å. $U = 13811.6(3)$ Å$^3$. $Z = 6$, $F(000) = 5586$. $\rho_{\text{cal}} = 1.388$ g cm$^{-3}$, $\rho_{\text{exp}} = 1.383$ g cm$^{-3}$. $R_1 = 0.0423$ and $wR_2$ (all data) = 0.0120. CCDC-862204 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. Diffraction data were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) and equipped with an Oxford Cryostream low-temperature device.

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[22] Reactions were performed on a 1 mmol scale. In the liquid-assisted grinding experiment, 50 µL of a liquid was added to a 5:3 mixture of CuI and QN. The mixture was ground in a steel jar by using a Retsch MM400 mill operating at 30 Hz.

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