Construction of a Porous Homochiral Coordination Polymer with Two Types of Cu_nI_n Alternating Units Linked by Quinine: A Solvothermal and a Mechanochemical Approach
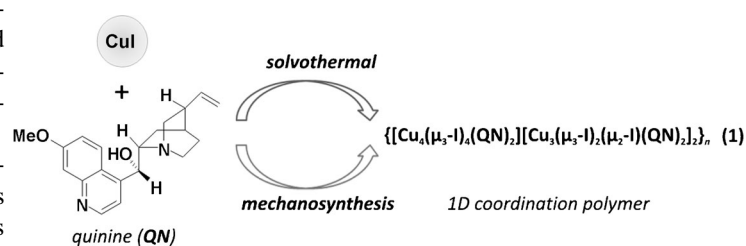
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The construction of inorganic–organic hybrid materials based on copper(I) halides, especially copper(I) iodide, has been extensively investigated due to their intriguing topology and interesting physical and chemical properties.[1] Reactions of CuI with bidentate (ditopic) or polydentate ligands may generate 0D macrocycles[2] or 1D,[3] 2D and 3D metal–organic frameworks with various $[Cu_nI_n]$ structural motifs, such as Cu_2I_2 rhomboid dimers,[4] triangular Cu_3I_3 clusters,[5] cubanelike or chairlike $[Cu_4I_4]$ tetramers,[6] hexagonal Cu_6I_6 clusters,[7] ladderlike or ribbonlike $[Cu_2I_2]_n$ chains,[8] zigzag $[CuI]_n$ or $[Cu_3I_4]_n^{n-}$ chains,[4c, 9] and 2D $[CuI]_n$ layers.[4e, 10] Among the various clusters acting as connecting nodes, dimeric and tetrameric units have been seen to be the most common, whereas triangular Cu_3I_3 clusters are comparatively very rare. $[Cu_nI_n]$ 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_nI_n cluster as connecting nodes and to the best of our knowledge there are only two examples of coordination polymers with different Cu_nI_n alternating units incorporating two types of Cu_nI_n cluster as connecting nodes.[7a, 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 up to now.[6b, 10b, d, 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.[13] 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 CuI/quinine system. Herein, we describe the formation and characterization of a novel homochiral 1D coordination polymer of alternating Cu_3I_3 and Cu_4I_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 $\{[Cu_4(\mu_3\text{-}I)_4(QN)_2][Cu_3(\mu_3\text{-}I)_2(\mu_2\text{-}I)(QN)_2]_2\}_n$ (**1**) irrespective of the molar ratio of the reactants used (Scheme 1). Single-crystal X-ray crystallo-

Scheme 1.

graphic analysis revealed that **1** crystallizes in the chiral noncentrosymmetric trigonal space group $P3_12_1$. It has a unique ladderlike framework constructed from cubanelike $[Cu_4(\mu_3\text{-}I)_4]$ and triangular $[Cu_3(\mu_3\text{-}I)_2(\mu_2\text{-}I)]$ 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_4I_4 unit

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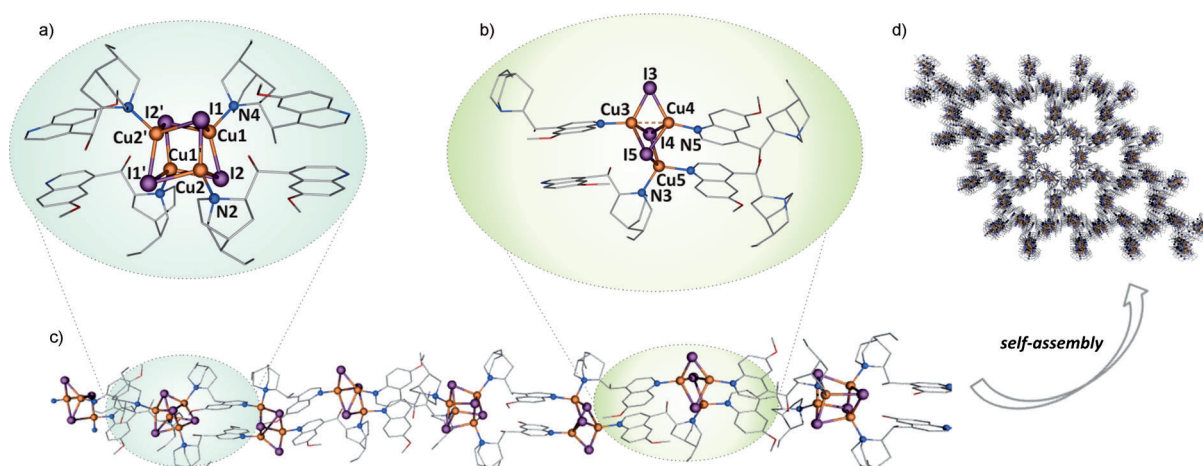Supporting information for this article is available on the WWW
under http://dx.doi.org/10.1002/chem.201200236.

Figure 1. The molecular and crystal structure of **1**; a) and b) show the local coordination environment in $[Cu_4(\mu_3-I)_4]$ and $[Cu_3(\mu_3-I)_2(\mu_2-I)]$ cluster units, respectively, c) shows the overall view of **1** along the *b* axis, and d) shows the crystal structure of **1** along the *c* axis. The orange and purple dots represent the Cu and I atoms, respectively; all hydrogen atoms were omitted for clarity.

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 Cu_4I_4 complexes with N ligands).[6] The discrete Cu_3I_3 cluster may be described as a Cu_2I_2 dimeric aggregate assembled with one monomeric CuI unit (Figure 1b). In the resulting cluster two distinct sets of both Cu^I centers and bridging iodides are present. Two Cu atoms are linked through two μ_3- and one μ_2-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 μ_3-iodine atoms and has a significantly larger Cu···Cu separation of 3.217(2)–3.431(5) Å. From a topological perspective view, each Cu_3I_3 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,[6a,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_1-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 Å^3) of the structure. Thermogravimetric
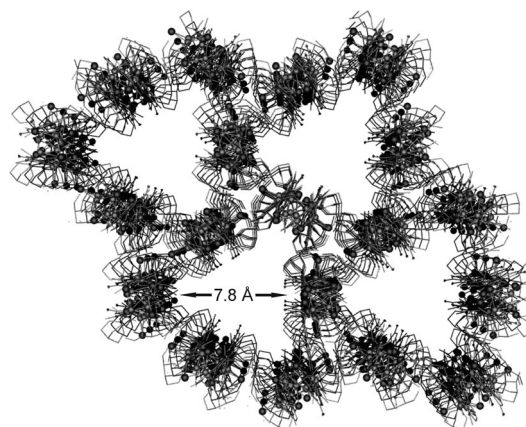

Figure 2. The supramolecular 3D network in **1**, with an extended view of the 1D tubular channels along the *c* axis.

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 N_2 (3.54 Å) is much smaller than that of the effective pore window of **1**, the N_2 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 m^{2}g^{-1}; see Figure S3 in the Supporting Information).[15] However, **1** adsorbs moderate amounts of CO_2 at 195 K (38 cm^{3}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 cm^{3}g^{-1}), estimated from the Dubinin–Raduskhvich equation for CO_2 adsorption data, is significantly lower than the value of 0.283 cm^{3}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 CO_2 is a favored adsorptive by **1** under low pressures due to the high quadrupole

moment interacting with polar regions of the framework. However, in the case of N_2, it is likely that a few strongly adsorbed molecules at the pore entrance block further diffusion and adsorption inside the 1D channels because of overlapping potentials from opposite walls.[17]

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 Cu_nI_n 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−I cluster-centered (CC) excited state with the excitation localized on the Cu_3I_3 core, indicating the aforementioned cuprophilic interaction.[18c,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 dry, free-flowing yellow 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,
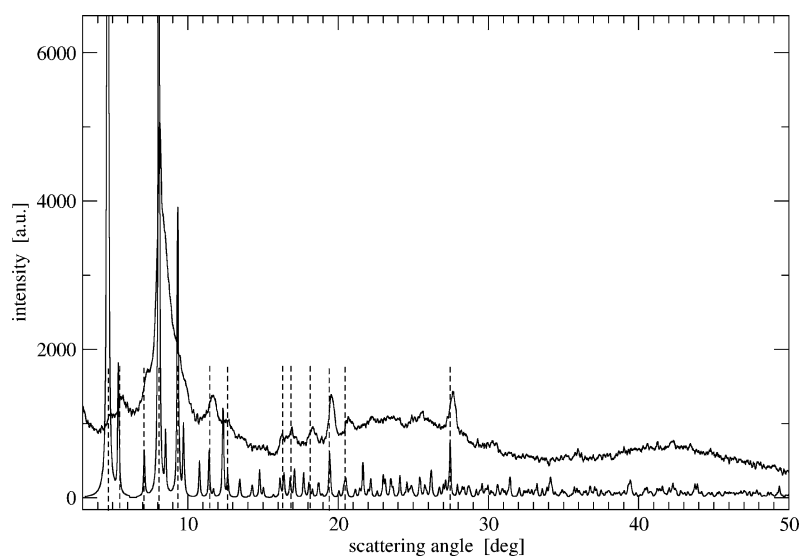

Figure 3. PXRD patterns of **1** calculated from single-crystal data (lower curve) and measured for the ground sample (upper curve).

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 mechanochromic 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 Cu_nI_n 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

Acknowledgements

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