

# The First Highly Stable Homochiral Olefin–Copper(I) 2D Coordination Polymer Grid Based on Quinine as a Building Block

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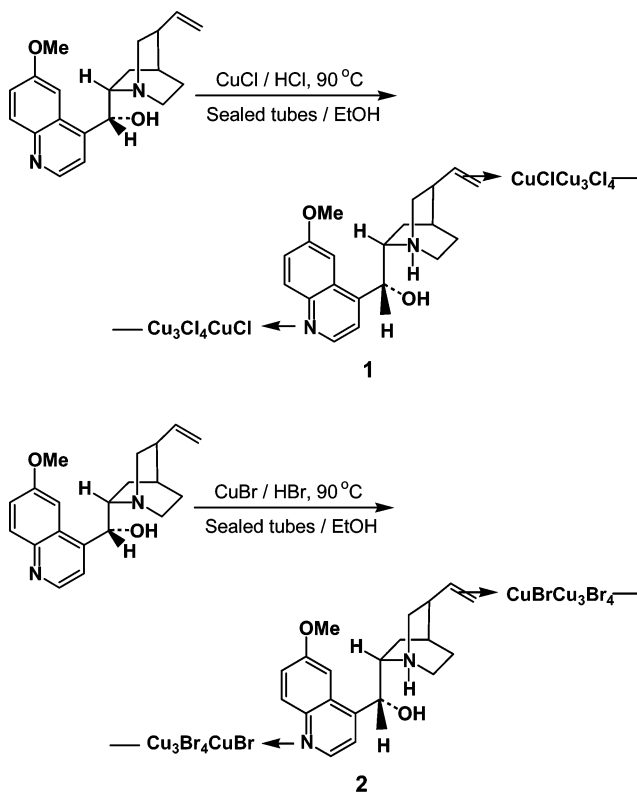
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**Summary:** Solvothermal reactions of quinine with  $\text{Cu}^{\text{I}}\text{Cl}$  or  $\text{Cu}^{\text{I}}\text{Br}$  yield the two highly stable homochiral copper(I)–olefin coordination polymers  $\text{Cu}_8\text{Cl}_{10}(\text{H-quinine})_2$  (**1**) and  $\text{Cu}_8\text{Br}_{10}(\text{H-quinine})_2$  (**2**), respectively, in which both **1** and **2** are 2D layered networks and are isostructural. The electric hysteresis loop of **1** clearly shows it displays a typical ferroelectric behavior with a remanent polarization ( $P_r$ ) of ca.  $0.12 \mu\text{C cm}^{-2}$ .

Through the use of bridging ligands of appropriate size, shape, and stereochemistry it is possible to assemble coordination networks that possess novel and potentially useful physical properties such as optoelectronic behavior. In recent times there has been an intensive focus on the design and synthesis of homochiral coordination polymers<sup>1–8</sup> and their contributions

Scheme 1



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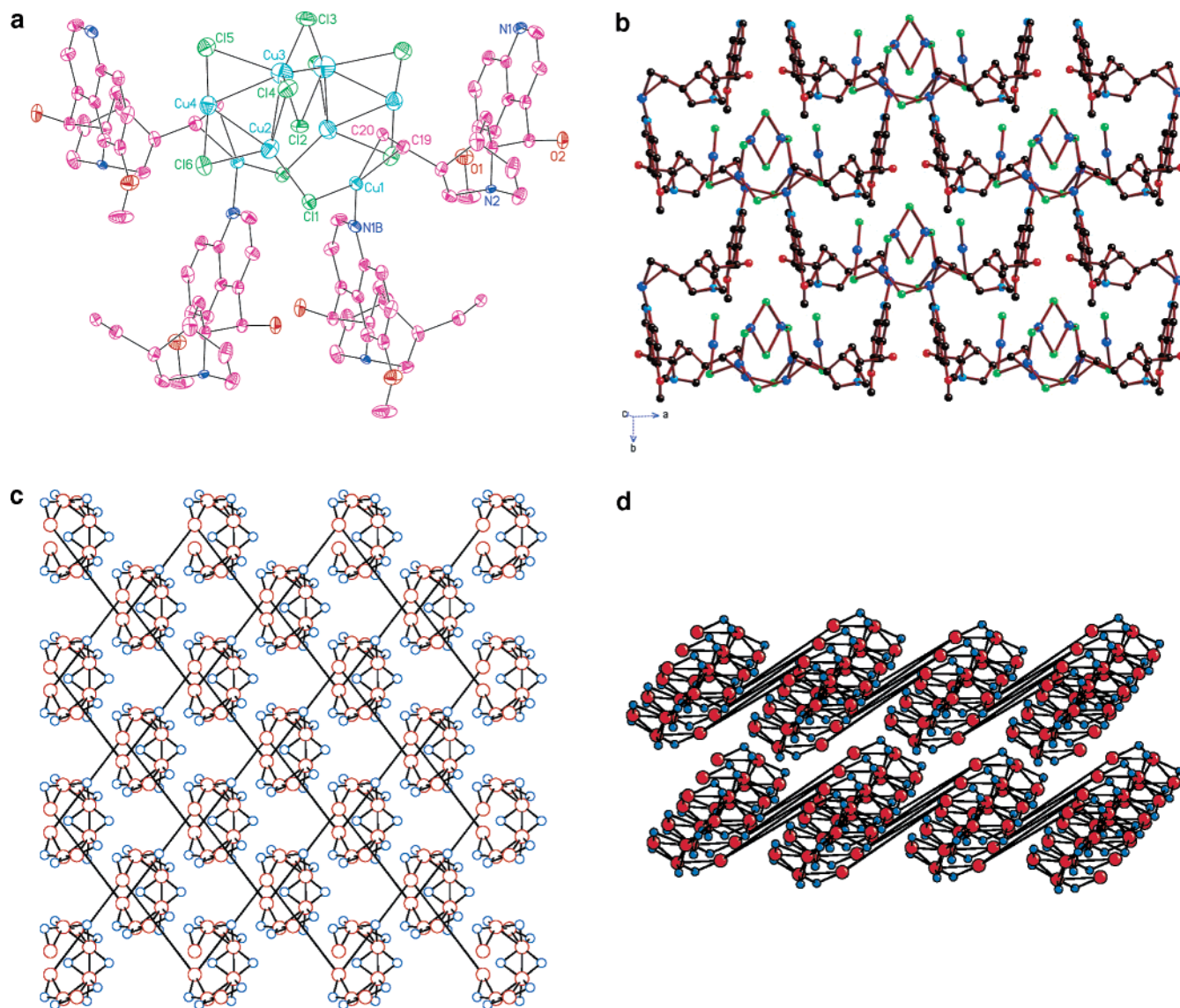
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to our understanding of the homochirality exhibited by a variety of essential biomolecules.<sup>8d</sup>

In the synthesis of coordination polymers a large number of chiral materials have been generated from achiral molecular building blocks. Such materials are of interest because the adoption of an acentric space group in their structures may lead to potential applications in areas such as second-harmonic generation, piezoelectricity, pyroelectricity, and ferroelectricity.<sup>9</sup> Although individual crystals of many compounds may be chiral, the bulk material is, however, often a racemic mixture of crystals, thus limiting their potential uses. *Enantiopure* coordination polymers where all crystals possess the same handedness have the added advantage of offering applications in heterogeneous asymmetric catalysis, enantioselective separation, and ferroelectric materials such as liquid crystals. We reported recently



**Figure 1.** (a) ORTEP view of an asymmetric unit of compound **1** showing 30% probability displacement ellipsoids in which the Cu<sub>8</sub>Cl<sub>10</sub><sup>2-</sup> aggregate is bound to four monoprotonated quinine units. A vertical 2-fold axis passes through Cl3. The H atoms are omitted for clarity. (b) 2-D network of **1** that extends in the *a*-*b* plane. Twofold axes run parallel to the *b* direction. Color code: Cu, blue; Cl, green; O, red; N, pale blue; C, black. H atoms have been omitted for clarity. (c) Simplified square network representation of **1** and **2** in which longer straight line stand for quinine ligand. (d) Arrangement of the simplified adjacent layers of 2D networks of **1** and **2**. A vertical 2-fold axis passes through Br3. The H atoms are omitted for clarity.

the first enantiopure coordination polymer used for the separation of a racemic mixture.<sup>7a</sup> This coordination polymer was constructed by linking Cd(II) centers with bridging chiral anions (quitenine—a modified quinine) to form a polymer that has the same connectivity as

diamond. This *enantiopure* coordination polymer led to successful separation of a racemic mixture of (*R*)- and (*S*)-2-butanol or (*R*)- and (*S*)-2-methyl-1-butanol by selective absorption of only one enantiomer into the asymmetric adamantane-type cavities.

We have been investigating coordination networks involving copper–olefin interactions.<sup>10</sup> Our success in this area and in the generation of homochiral materials prompted us to study the preparation of copper–olefin, homochiral networks with enantioselective or ferroelectric properties. Although such *network* materials are,

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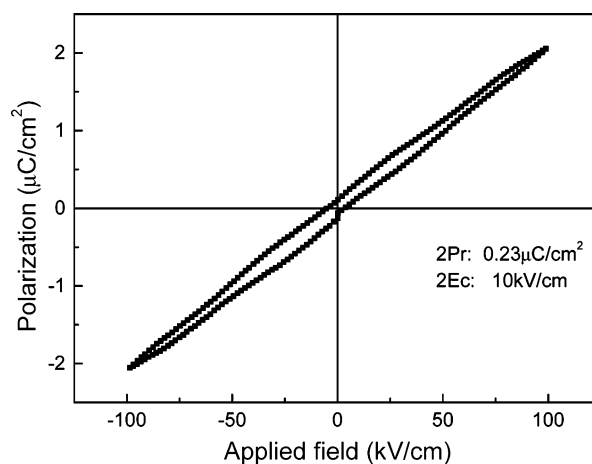
to our knowledge, not known, two *discrete* enantiopure olefin–copper complexes were recently reported.<sup>11</sup>

Inspired by some elegant work by Beck and co-workers on the coordination chemistry of quinine,<sup>12</sup> we studied the synthesis of enantiopure coordination polymers involving olefin–Cu(I) bonds. Herein we report the synthesis, solid-state structures, and thermal stabilities of  $\text{Cu}_8\text{Cl}_{10}(\text{H-quinine})_2$  (**1**) and  $\text{Cu}_8\text{Br}_{10}(\text{H-quinine})_2$  (**2**), which represent, to our knowledge, the first example of homochiral coordination polymers with copper–olefin bonds. A preliminary investigation of their enantioselective and ferroelectric behaviors is also reported.

**1** and **2** were obtained by the reactions of CuCl (or CuBr), quinine, and HCl (or HBr) in ethanol under solvothermal conditions at 90 °C (Scheme 1) (see Supporting Information). Thermogravimetric analysis (TGA) of these polycrystalline complexes showed no weight loss below ca. 260 and 265 °C for **1** and **2**, respectively. EPR spectra of **1** and **2** were silent, confirming that the oxidation state of Cu ions in these two solid complexes is +1.

The crystal structure of **1** reveals that the quinine is only monoprotonated and acts as a bridging ligand, as shown in Figure 1a (see Supporting Information). In this structure a 2-fold axis passes through an irregular discrete  $[\text{Cu}_8\text{Cl}_{10}]^{2-}$  aggregate. The terminal copper centers (Cu1) are coordinated by a quinoline nitrogen of one H-quinine, a C=C moiety of another H-quinine, and a bridging chloride ion. The remaining copper centers, Cu2, Cu3, and Cu4, are in approximately trigonal, pyramidal, and linear coordination environments of chloride ions, respectively. An unusual feature of this anion is the sharp kink at Cl6 with a Cu2–Cl6–Cu4 angle of 74.20(8)°. This brings Cu2 and Cu4 into close contact (2.700(2) Å) and allows Cl5 to form a weak interaction with Cu3 (2.727(3) Å). Each  $[\text{Cu}_8\text{Cl}_{10}]^{2-}$  aggregate is linked to four other equivalent aggregates through the bridging H-quinines, resulting in a 2D layered network (Figure 1b,c). The arrangement of adjacent layers of the 2D network is AA type packing, as shown in Figure 1d. Similarly, **2**, the bromide analogue, is isostructural with **1**, but in this case the angle at Br6 is 67.17(8)°, allowing Br5 to make a contact of 2.652(3) Å with Cu3 (Figure 1e) (see Supporting Information<sup>13</sup>). In addition, Cu2 and Cu4 are only separated by 2.611(3) Å. As a result, **1** and **2**, to the best of our knowledge, represent the first example of a homochiral metal-organic coordination polymer containing olefin–copper(I).

A preliminary attempt of enantioselective separation of racemic *sec*-butylamine under solvothermal conditions was unsuccessful. Interestingly, **1** and **2** crystallize



**Figure 2.** Electric hysteresis loop of **1** in the form of a pellet, obtained in Virtual Ground Mode at room temperature.

in polar point groups (space group  $C_2$ , which belongs to the  $C_2$  point group), in which their ferroelectric properties are expected. This prompts us to investigate their ferroelectric properties. The experimental results (Figure 2) clearly indicated that the electric hysteresis loop of **1** was a typical of a ferroelectric compound with a remanent polarization (Pr) of ca.  $0.12 \mu\text{C cm}^{-2}$  and coercive field (Ec) of  $5.0 \text{ kV cm}^{-1}$ , while the spontaneous polarization values (Ps) of ferroelectric  $\text{KH}_2\text{PO}_4$  (KDP) and triglycine sulfate (TGS) are  $5.0$  and  $3.0 \mu\text{C cm}^{-2}$ , respectively.<sup>14</sup> (Due to a leaking circuit, we failed to measure the hysteresis loop of **2**). The ferroelectric property ( $P_s \approx 2.0 \mu\text{C cm}^{-2}$ ) of **1** is comparable to those found in KDP and TGS.<sup>15</sup> To our knowledge, **1** represents the first example of polar coordination polymers with ferroelectric properties.

In conclusion, the solvothermal synthesis technique provides a powerful synthetic method to give organometallic compounds which are not readily accessible with unique properties.

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**Supporting Information Available:** Tables of atomic coordinates, thermal parameters, bond distances and angles for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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