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Chiral Induction in the Ionothermal Synthesis of a 3-D Coordination Polymer

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Coordination polymers (sometimes known as metal organic frameworks, MOFs) constitute one of the most exciting developments in recent nanoporous science, with potential applications in many areas.[1,2] Ionothermal synthesis,[3−5] the use of an ionic liquid[6] as solvent and structure directing agent in the preparation of crystalline solids, offers many advantages over traditional hydrothermal and solvothermal materials synthesis methods. The change from molecular to ionic reaction media leads to new types of material being accessible, with structural properties that can be traced directly to the chemistry of the ionic liquid.[3] Here we report the use of ionic liquids (ILs) as reaction media in the preparation of a new coordination polymer material. Significantly, the use of an enantiopure anion as one component of the IL induces chirality in the resulting solid, despite the fact that the anion is not occluded by the material and that the solid itself is built from only nonchiral building blocks.

Control of chirality in solids is an important goal as there are many potential applications.[7] Two recent approaches have been particularly successful in the synthesis of chiral coordination polymers. Both of them rely on using chiral units to form the framework of the material. The first method uses a chiral organic bridging ligand to link the metal centers in the framework. Kim et al.[8] used D-tartaric acid as the organic linker in a zinc metal organic framework, and Lin and co-workers have used similar methodologies with great success.[9,10] The alternative method, used by Rosseinsky and co-workers, uses a chiral co-ligand that does not bridge the metal centers but forces chirality by coordinating to the metal center.[11,12]

There is also the possibility of forming chiral solids from achiral building blocks, which would remove the need for a chiral center in the building units and so vastly increase the potential number of chiral solids. However, unless there are other factors at work, the bulk material will generally contain a 50:50 (racemic) mixture of the two enantiomorphs, even if individual crystals are themselves homochiral. Crystals may spontaneously form as one enantiomorph in excess over the other, but there is no current way to control this process, except by seeding with crystals of the required chirality.[13] The challenge is how to induce the spontaneous crystallization of only one enantiomorph.

The large Coulombic interactions in ILs mean that the liquid is highly structured and show relatively long-range correlations and a three-dimensional distribution that reflects the asymmetry of the ions.[14] In the case of a chiral ionic liquid, one might expect this long-range asymmetric distribution to reflect the chirality of the ions present. This could have major implications for structure direction in ionothermal synthesis, as one can imagine more efficient transfer of chiral information from the ionic liquid to the solid than is the case in situations, for example, where the chirality of the environment is diluted by the presence of nonchiral molecular solvents. Figure 1 shows this situation schematically.

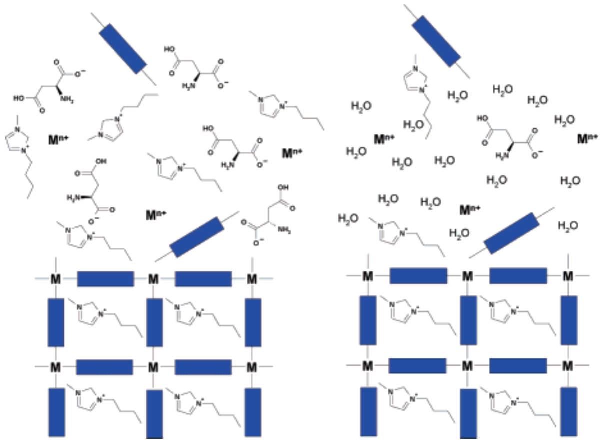

Figure 1. Schematic diagram of the synthesis of a templated coordination polymer in an IL with a chiral anion under ionothermal conditions (left) where the IL is the solvent and under hydrothermal conditions (right) where the chirality of the system is diluted by the presence of nonchiral solvent molecules (water). Our theory is that, because of the highly structured asymmetric distribution of ILs, transfer of chiral information from the IL to the growing framework is more likely in the ionothermal case.

Chirality can be introduced into ionic liquids by altering the structure of the cation or the anion or both. The simplest preparation of a chiral ionic liquid involves ion exchange of the anion with chiral species such as L-aspartate. The preparation of chiral cations is known[15] but is synthetically more challenging. Use of the chiral ionic liquid 1-butyl 3-methylimidazolium L-aspartate produces SIMOF-1 ($(BMIm)_2[Ni(TMA-H)_2(H_2O)_2]$, Figure 2), a homochiral material that crystallizes in space group $P4_12_12$.[16] Proving that the bulk solid is homochiral is actually a nontrivial problem. In principle, the only way to do this directly is to ascertain the absolute structure of each crystal in the sample. Clearly, this is impractical, but 10 high-quality single-crystal X-ray determinations on different samples all revealed the absolute structure to be the same (see Supporting Information). If the bulk material was a racemic mixture, the probability of 10 crystals all being of the same chirality is small (1 in 2^{10}), indicating that, at the very least, the bulk samples consist predominantly of the same enantiomorph, and that they are probably chirally pure. The bulk samples of SIMOF-1 consist entirely of nicely shaped crystals that all look equivalent to the naked eye, which means that any bias in the choice of crystal associated with one enantiomorph having, for example, larger crystals than the other is also unlikely.

There are certain pieces of evidence that point toward chiral induction being the likely reason for the effect we have seen. Without the chiral component of the ionic liquid, the achiral SIMOF-2 ($(BMIm)_2[Ni_3(TMA-H)_4(H_2O)_2]$, Figure 3) is formed using 1-butyl 3-methylimidazolium bromide under the same synthesis conditions. This is good evidence in itself. In addition, replacing L-aspartate with D-aspartate in the ionic liquid induces a material (SIMOF-1a) which crystallizes with the opposite chirality.

The structure of SIMOF-1 consists of octahedrally coordinated nickel. Each nickel atom is bound to four trimesate (TMA) and

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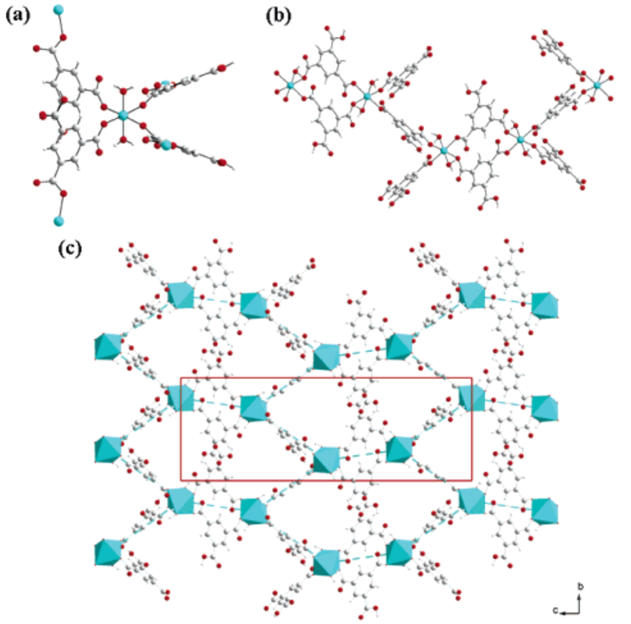

Figure 2. The structure of chiral SIMOF-1: (a) arrangement of four TMA units around each Ni; (b) helical chiral unit that runs parallel to the 4_1 axis of symmetry in the structure; (c) overall structure viewed parallel to the crystallographic *a*-axis. Ni-centered polyhedra = cyan, C = gray, O = red. Nickel atoms are also shown in cyan. For clarity, the ionic liquid cation is not shown in (c).

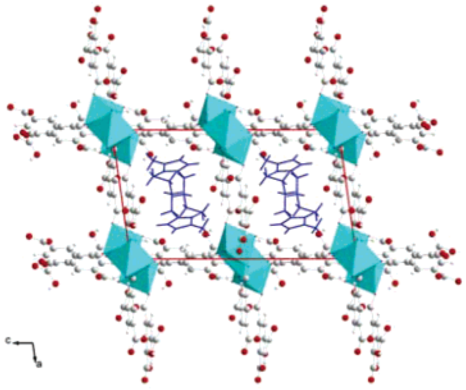

Figure 3. The framework structure of achiral SIMOF-2 viewed parallel to the crystallographic *b*-axis. Key as for Figure 2. The occluded ionic liquid cations are shown as blue wire molecules.

two water molecules (Figure 2a). Each trimesate dianion acts as a 120° bent linker between two nickel atoms, the final carboxylate group being protonated and not coordinated to a nickel. The spatial arrangement of the four linking trimesate anions around each nickel leads to a pseudotetrahedral building unit, which in turn connects to four other metal centers to form a diamondoid network (Schläfli symbol 6^6). The chirality in the structure is the result of the 4_1 axis in the symmetry, which leads to a helical arrangement of the pseudotetrahedral units, all of which have the same handedness (Figure 2b), and these are connected to form the overall three-dimensional framework (Figure 2c). The ionic liquid cation is strongly held inside the pores in the structure, and as yet, we have been unable to remove it without causing the structure to collapse.

In conclusion, we report a chiral induction effect in the ionothermal synthesis of a coordination polymer. Such an effect may open up new opportunities in the preparation of chiral materials. Current studies in our laboratory are aimed at determining the generality of this approach to the synthesis of chiral solids or whether it is confined to specific cases such as the one reported here.

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Supporting Information Available: Crystallographic information (CIF) for SIMOF-1 and SIMOF-1a, and full details of the synthesis of the coordination polymers. This material is available free charge via Internet at http://pubs.acs.org.

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(16) **Crystal data for SIMOF-1**: tetragonal $P4_12_12$, $a = 11.1813(4)$ Å, $c = 31.552(1)$ Å, $V = 3944.7(3)$ Å^3, R_1 (3599 reflections) = 0.025, wR_2 (3738 reflections) = 0.062. Flack absolute structure parameter = 0.019(10) [1419 Friedel pairs measured, with a total Friedel coverage of 61%]. A total of 10 crystal structure determinations were carried out on crystals picked at random from samples of SIMOF-1. Care was taken to pick crystals that looked as different as possible, with different crystal sizes and slightly different morphologies all sampled. The quality of the refinements was good, and all of the Flack absolute structure parameters measured had values near zero with small standard uncertainties indicating that all the crystals have the same chirality. An incorrect model with the opposite chirality would lead to a Flack parameter of around 1. See Table S1 in the Supporting Information for details of all of the refinement *R* factors and Flack absolute structure parameter values. **Crystal data for SIMOF-1a**: tetragonal $P4_32_12$, $a = 11.192(2)$ Å, $c = 31.561(6)$ Å, $V = 3953(1)$ Å^3, R_1 (4598 reflections) = 0.050, wR_2 (5424 reflections) = 0.127. Flack absolute structure parameter = -0.090(17). [Total Friedel coverage of 65%]. **Crystal data for SIMOF-2**: monoclinic $P2_1/c$, $a = 10.693(1)$ Å, $b = 13.722(1)$ Å, $c = 18.562(2)$ Å, $\beta = 98.160(7)°$, $V = 2696.1(4)$ Å^3, R_1 (1832 reflections) = 0.062, wR_2 (2285 reflections) = 0.159.

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