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Induction in urothermal synthesis of chiral porous materials from achiral precursors†

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Special asymmetric crystallization of porous framework materials from achiral precursors under urothermal conditions is successfully achieved by using an enantiopure liquid as a co-solvent and chirality induction agent, which provides a new strategy for the synthesis of homochiral porous materials containing only achiral building blocks.

Homochirality plays an important role in chemical, biological and pharmaceutical sciences. Catalytic asymmetric synthesis of enantioenriched organic compounds represents an essential feature of these sciences.[1] Currently, there is wide interest in creating homochiral porous materials as heterogeneous catalysts for enantioselective catalysis, separation *etc*.[2,3] Most homochiral porous solids prepared so far consist of enantiopure organic ligands that impart homochirality to the resulting crystals.[3–5]

Because of the limited availability and very often the high cost of enantiopure ligands, it is highly desirable to create homochiral porous materials from achiral starting precursors. For this purpose, the greatest challenge is not the generation of chirality, but rather how to create an enantiomeric bias to favor one handedness, a question that also exists in organic asymmetric synthesis. It is commonly known that achiral components crystallizing in chiral symmetry tend to be a conglomerate, defined as an equal mixture of crystals with opposite handedness or racemic twins.[6]

Symmetry breaking during crystallization from achiral precursors without an enantiopure source is also known.[7] This is conceptually similar to asymmetric autocatalysis in organic synthesis—a process of automultiplication of a chiral compound in which the chiral product acts as a chiral catalyst for its own production. However, such symmetry breaking is unpredictable and chirality control from run to run is generally not possible.

In ordinary catalytic asymmetric synthesis, an enantiopure catalyst different from the product is often used to promote the asymmetric induction. A similar idea was introduced to develop a more predictable method for asymmetric crystallization: the use of an additional chiral source to induce a given handedness.[8–10] A recent discovery by Morris *et al.* demonstrated that the chiral ionic liquid solvent containing L-aspartate can induce the homochiral crystallization of an interesting compound from achiral precursors.[9a] We also found that the use of alkaloids such as (−)-cinchonidine or (+)-cinchonine can lead to asymmetric induction during crystallization from achiral precursors.[10a] Another notable example is the nucleotide-catalyzed conversion of racemic zeolite-type zincophosphate into enantioenriched crystals.[10b]

Comparable to catalytic asymmetric synthesis for organic molecules, a new concept of catalytic asymmetric crystallization for porous crystalline materials emerged here and created more opportunities for the development of novel homochiral porous materials with potential applications in enantioselective processes. As only a few examples of catalytic asymmetric crystallization are known to date, a systematic exploration of the asymmetric induction effect in various chemical environments becomes increasingly important for the understanding on the catalytic mechanism and its wide applications.[9b]

Recently, it has been demonstrated that the use of urea derivatives as solvents opened a new urothermal method for the synthesis of a wide range of crystalline materials.[11] Such a method is well suited for the creation of porous framework materials with active open metal sites, which also well fits the requirements of catalysts for enantioselective processes. However, the urothermal syntheses of homochiral porous materials remain unknown to date.

In this work, we first explore catalytic asymmetric crystallization of microporous framework materials from achiral precursors by using mixed achiral and enantiopure solvents. The homochiral induction reaction reported here is performed under a mixed solvent system containing a room-temperature achiral solid—ethyleneurea (e-urea) hemihydrate with a melting point of only 55 °C and an enantiopure liquid (−)-carvone (or (+)-carvone). The combination of such two solvents leads to the homochiral crystallization of a 3D

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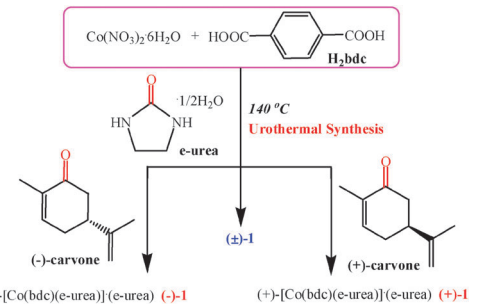

Scheme 1 Synthetic conditions of the compounds.

microporous material [Co(bdc)(e-urea)]·(e-urea) (**1**; H_2bdc = 1,4-benzenedicarboxylic acid) (Scheme 1).

The reaction of $Co(NO_3)_2{\cdot}6H_2O$ and 1,4-benzenedicarboxylic acid in ethyleneurea hemihydrate at 140 °C produces red crystals of [Co(bdc)(e-urea)]·(e-urea) (**1**), which crystallizes in a chiral space group $P4_122$ and has permanent microporosity.‡ The solid-state circular dichroism (CD) measurements verified that the bulk sample has no optical activity, but it encouraged us to investigate the asymmetric induction effect for such a special system.

An enantiopure liquid (−)-carvone as a co-solvent was employed to induce the asymmetric crystallization of **1**. The selection of (−)-carvone is not random, but based on the careful consideration of the structural features of **1**. In the structure of **1**, the solvent molecule e-urea has a dual role as both bridging ligand and template. Relying on the coordinate interaction between carbonyl oxygen and metal ions (*i.e.*, –C═O–M), the e-urea molecule bridges the Co centers into a 4_1 helix along the *c* axis (Fig. 1a and b). The resulting 4_1 helices with the same handedness are further linked up by the bdc ligands to form a 3D chiral framework with large rectangular channels along the *c* axis (Fig. 1c and d). Thus, how to ensure the 4_1 helices in each crystal have the same handedness is the key point to synthesize the homochiral bulk product. As the carbonyl group of e-urea ligand affect the formation of the

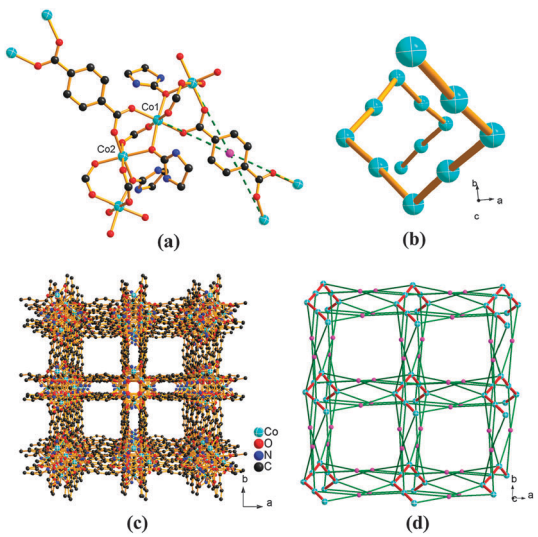

Fig. 1 (a) The coordination environments in **1**, where one bdc ligand is reduced into a 4-connected planar node (purple dot); (b) the 4_1 helix presented in **1**; (c) the 3D porous framework of **1**; (d) the structural topology of **1**.

4_1 helix, the replacement of e-urea ligand to an enantiopure ligand with carbonyl group should control the absolute handedness of the 4_1 helix. The correlation between the enantiopure components and the absolute helicity is well-known in the DNA structures and was also demonstrated in our recent reports on metal–organic frameworks.[12] Three commercial available enantiopure chemicals with the carbonyl group, (−)-carvone, (+)-carvone and (+)-camphor, were selected to investigate the induction effect. Unfortunately, the use of (+)-camphor did not achieve the asymmetric crystallization (no CD signal), which may be due to the low solubility of (+)-camphor in e-urea solvent.

Successfully, the mixed solvent of achiral e-urea and enantiopure (−)-carvone in the 4.3 : 1 molar ratio induced the asymmetric crystallization of (−)-**1**. (−)-**1** crystallized in the $P4_122$ space group. Crystal structures of five randomly selected crystals were refined using single-crystal X-ray diffraction data and all of them belong to the $P4_122$ space group with the Flack parameters that suggest the $P4_122$ (rather than $P4_322$) is the preferred configuration (Table S1, ESI†) in the bulk sample. Further evidence comes from the solid-state CD spectroscopy. The CD spectrum for samples obtained from four separate synthetic batches catalyzed with (−)-carvone show that the bulk sample of (−)-**1** consistently exhibits negative CD signals. In contrast, replacing (−)-carvone with (+)-carvone induces the bulk sample of (+)-**1** which crystallizes with the opposite chirality ($P4_322$ space group, Table S2, ESI†) and exhibits positive CD signals (Fig. 2).

A possible homochirality transfer might come from the existence of the enantiopure carvone in the channels of the framework. But it is not true for the case reported here. The evidence is that all samples prepared with or without carvone have very similar IR spectra (Fig. S3, ESI†). No additional signals of carvone in the IR spectra of (−)-**1** and (+)-**1** can be found. Furthermore, the as-synthesized crystals of (−)-**1** were dissolved by 0.1 mol L^{-1} HNO_3 solution, the EI-MS measurements of the obtained solvent indicate no typical peaks of carvone (Fig. S5-6, ESI†). So it is impossible for the enantiopure carvone to be trapped into the channels, and homochirality transfer must be associated with other induction effect.

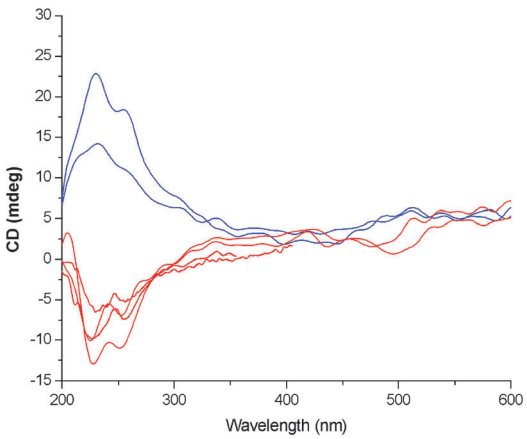

Fig. 2 The solid-state CD spectra of samples of **1** prepared with (−)-carvone (red lines) or (+)-carvone (blue lines) as the co-solvent.

The asymmetric crystallization of (−)-**1** is believed to result from cooperative interactions between (−)-carvone and e-urea during the nucleation of [Co(bdc)(e-urea)] frameworks. (−)-Carvone is capable of directly participating in the nucleation and crystallization process, which allows the control of the absolute helicity of [Co(bdc)(e-urea)] frameworks. On the other hand, because e-urea has a stronger binding ability due to the presence of hydrogen bonding interactions with the main framework, e-urea eventually replaces (−)-carvone in the final crystals.

As established in the former studies, asymmetric induction in the synthesis of homochiral solids from achiral precursors can be classified into two categories, one is to use the enantiopure solvents and another is to use enantiopure additives to achieve the required effect.[9,10] The enantiopure solvents could provide an asymmetric environment for crystallization and enantioselection, but most of them are expensive and limited to use widely. Small amounts of enantiopure additives also affect asymmetric nucleation or crystal growth, but they need relatively strong interactions with the main framework to drive the induction effects. The successful chiral induction presented in this work by using mixed achiral and enantiopure solvents reveals a new effect which just fills the gap between the above two effects and bears both merits. Such an enantiopure co-solvent effect not only generates relatively rich chiral environment, but also controls the enantiomeric excess.

In the as-synthesized form of **1**, large channels are filled with disordered e-urea molecules. The pore volume ratio is 33.4% as calculated with the PLATON program.[13] The permanent porosity of **1** was confirmed by gas adsorption measurements (Fig. S7, ESI†). The Langmuir surface area of **1** is 146.7 $m^2 g^{-1}$. Thermogravimetric analysis indicated that the framework of **1** has no weight loss before 250 °C (Fig. S8, ESI†).

Topological analysis indicates the structure of **1** has a previously unknown (4,6)-connected 3-nodal network with total Schläfli symbol of $(3^2.6^2.7^2)(3^4.4^2.6^4.7^5)$ by considering the bdc ligands and the Co centers as the 4-connected and 6-connected nodes, respectively (Fig. 1d).[14] The ideal space group for such an unusual net is $P4_122$ (No. 91), indicating the intrinsic chirality of the framework. The special feature for this net is the presence of the parallel helices with the same handedness, which is similar to other intrinsic chiral nets, such as quartz and zeolite β.[15]

Specifically, this work has brought major synthetic and conceptual advances for homochiral framework materials. The first is the successful application of urothermal synthesis; the asymmetric crystallization *via* induction is known in hydrothermal,[10b] solvothermal[10a] and ionothermal[9a] conditions, but it is for the first time known in urothermal conditions. The second advance is the generation of chirality from achiral precursors into intrinsic chiral nets at the single crystal level, which is mostly dependent on the special urothermal environment. The rich coordinate and hydrogen bonding behavior of the e-urea ligands might control the connectivity between the Co centers and the bdc ligands, and they become the driving force for the chirality and finally link the Co centers into helices. The third advance is the employment of an enantiopure co-solvent to induce bulk homochirality. The absolute chirality of the intrinsically chiral helix present in the network can be related to the stereochemistry of the starting enantiopure carvone.

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‡ Crystal data for **1**: tetragonal, space group $P4(1)22$, $a = b = 11.3358(2)$ Å, $c = 24.9541(9)$ Å, $V = 3206.61(14)$ $Å^3$, $Z = 4$, Flack parameter = 0.11(7), 2851 independent reflections ($R_{int} = 0.1356$). The final R_1 ($wR(F^2)$) = 0.0989 (0.2621) ($I > 2\sigma(I)$). The structures were solved by direct methods and refined on F^2 full-matrix least-squares using the SHELXTL-97 program package.

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