

# Spontaneous Resolution to Absolute Chiral Induction: Pseudo-Kagomé Type Homochiral Zn(II)/Co(II) Coordination Polymers with Achiral Precursors

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**S** Supporting Information

**ABSTRACT:** It is observed that conglomerate crystallization of achiral precursors yielding racemate metal organic frameworks/coordination polymers (MOFs/CPs) can be driven to absolute homochiral crystallization of the desired enantiomorph by utilizing a suitable chiral induction agent. In a series of crystallization experiments isostructural Zn and Co homochiral CPs (**1P**, **1M** and **2P**, **2M**) are prepared using the achiral precursors. In the presence of enantiopure camphoric acid, the crystallization process prefers absolute chiral induction over conglomerate formation which is established by single crystal X-ray diffraction and CD spectroscopy.

Chirality is an eminent feature of nature and plays an indispensable role in biological functions and material sciences. Designed synthesis of homochiral metal organic frameworks (MOFs) or coordination polymers (CPs) has been a frontier research field in recent years due to their prime importance in the field of asymmetric catalysis, magnetism, nonlinear optics, and chiral recognition.<sup>1–4</sup> The straightforward way to synthesize homochiral CPs/MOFs is the use of enantiopure building blocks which translate their inherent chirality to the resultant framework by a “chirality conservation” process. This methodology suffers from the high costs of enantiopure organic linkers. However, there are a few excellent reports on naturally occurring chiral organic molecules as linkers for the construction of homochiral MOFs.<sup>3,4</sup> The prime indirect approaches to synthesize chiral MOFs by achiral building blocks are ‘spontaneous resolution’ and ‘chirality induction’(CI).<sup>1</sup> The homochiral crystallization of CPs/MOFs from achiral building blocks still remains a scantily explored area. Self-assembly of chiral MOFs consisting of achiral building blocks by means of spontaneous resolution is an interesting phenomenon.<sup>5</sup> However, the handedness of individual nuclei during crystallization remains uncontrollable in the case of spontaneous resolution, and the products tend to be conglomerate except in a few cases where a rare course of symmetry breaking operates.<sup>6</sup> These unresolved conglomerates remain of less practical use. The other methodology, i.e., the use of chiral induction agents to achieve bulk homochiral MOFs is a powerful strategy, as it can accomplish absolute bulk chirality in the system. Camphoric acid and cinchona alkaloids

are the most celebrated chiral inducing agents.<sup>7</sup> The use of cinchona alkaloids as chiral induction agents was first demonstrated by Zhang et al. for the construction of homochiral microporous MOFs.<sup>7a</sup> Recently Duan et al. further explored the cinchona alkaloids as chiral induction agents to design catalytically active homochiral CPs from achiral precursors.<sup>7b</sup> Moreover, there are a couple of examples in which an enantiopure solvent has smartly been employed as a chirality induction agent.<sup>8,9</sup>

In a remarkable report, Bu et al. exploited the chirality induction competence of camphoric acid to direct the absolute chirality of an intrinsically chiral MOF composed of achiral building blocks.<sup>10</sup> They have shown that the racemic form of camphoric acid induces the formation of a conglomerate MOF; however, enantiopure camphoric acid could induce absolute bulk chirality in the same MOFs. Interestingly, a different achiral MOF was obtained in the absence of chiral induction agents.

Though there have been a few excellent reports demonstrating the phenomenon of chiral induction to synthesize bulk homochiral MOFs, the method remains elusive due to the unpredictability of a suitable chiral induction agent for a given set of precursors.<sup>11</sup> Aforesaid elegant reports indicate that the chirality induction agents work specifically on individual systems and often remain seminal for the construction of a desired network. Evidently, there is a realistic requirement to develop protocols to synthesize bulk homochiral MOFs.

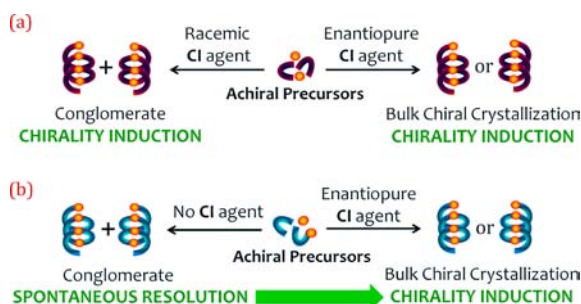
In our pursuit of novel chiral CPs/MOFs comprising achiral building blocks, we accentuate the cooperative operation of spontaneous resolution and chiral induction. To be precise, we have employed a chiral induction agent to maneuver the fate of the reaction from spontaneous resolution to the bulk homochiral crystallization of CPs as depicted in Scheme 1. As far as we know there have been no reports on utilizing the enantiopure agents in the crystallization process to yield bulk absolute chirality in CPs/MOFs from the achiral precursors which would otherwise yield spontaneous resolution in the absence of those enantiopure agents.

Herein we report two enantiomeric pairs (**1P**, **1M** and **2P**, **2M**) of isostructural two-dimensional metal organic frameworks  $[\text{Zn}(\text{SO}_4)(\text{L})(\text{H}_2\text{O})_2]_n$  (**1**) and  $[\text{Co}(\text{SO}_4)(\text{L})(\text{H}_2\text{O})_2]_n$

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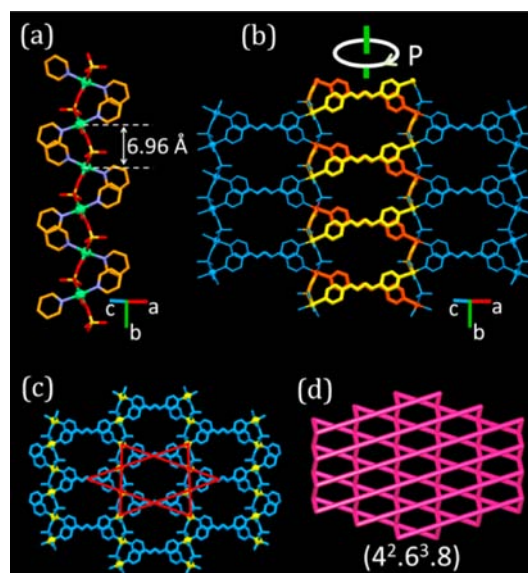
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**Scheme 1. Cartoon Depiction of the Chiral Induction (CI) Agent Driven Conglomeration and Bulk Asymmetric Crystallization Processes (for example, ref 10) (a); Spontaneous Resolution Driven Conglomeration and the Asymmetric Coercing of Same Process via CI Agent Leading to Absolute Asymmetric Crystallization (present study) (b)**

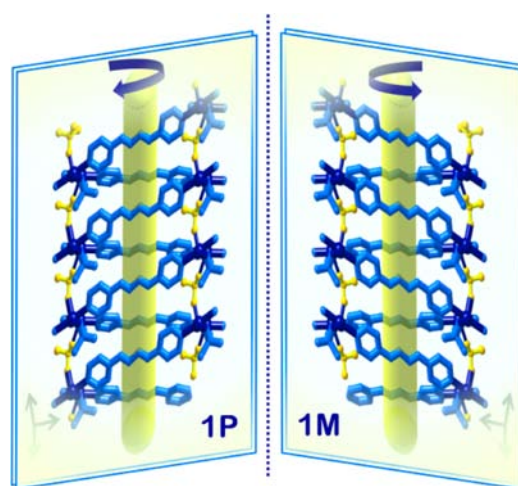


(2) (where  $L = 1,4\text{-bis}(4\text{-pyridyl})\text{-}2,3\text{-diaz}\text{-}1,3\text{-butadiene}$ ) comprising achiral building blocks by the spatial orientation of the ligand moiety coordinated to the metal. Either of the **1P/1M** and **2P/2M** pairs of chiral MOFs can be synthesized as a conglomerate by spontaneous resolution occurring upon diffusing the alcoholic solution of ligand ( $L$ ) into the aqueous metal sulfate solution. We further show that the enantiopure camphoric acid (*cam*) can act as a chirality inducing agent to achieve bulk absolute chiral CPs with the desired helicity (**1P**, **1M**, **2P**, and **2M**). In the chirality induction experiments enantiopure camphoric acid can coerce the enantio-enrichment of bulk samples. Thus, MOFs **1P** and **2P** with absolute positive homohelicity have been obtained in the presence of  $(-)\text{-cam}$  whereas  $(+)\text{-cam}$  directs the exclusive formation of absolute negative homohelical CPs **1M** and **2M** (Supporting Information S1).

All four compounds crystallize in chiral space group  $C_2$  and possess a two-dimensional network with intrinsic chirality. The Zn and Co CPs are isotopic; hence the structural description is restricted to the Zn CPs **1P** and **1M**. **1P** and **1M** contain two crystallographically independent  $[\text{Zn}(\text{SO}_4)(L)(\text{H}_2\text{O})_2]_n$  entities with an identical coordination environment (Figure S2). Coordination around the  $\text{Zn}^{2+}$  possesses a distorted octahedral  $\text{N}_2\text{O}_4$  geometry. The basal plane of each metal center is provided by two *cis* coordinated water molecules and oxygen atoms from two different sulfato groups oriented in *cis* disposition linking the adjacent screw related Zn(II) ions via  $\mu_2\text{-}\kappa^2$  binding mode to form a neutral zigzag  $[\text{Zn}(\text{H}_2\text{O})_2(\mu\text{-SO}_4)]_n$  chain motif running along the *b*-axis (Figure 1a). The adjoining  $\text{M}\cdots\text{M}$  distance within the zigzag chain for both molecules present in the asymmetric unit is  $6.96 \text{ \AA}$  ( $\text{Zn1}\cdots\text{Zn1}$ ) and  $6.03 \text{ \AA}$  ( $\text{Zn2}\cdots\text{Zn2}$ ) respectively. The  $\text{Zn}\cdots\text{O}$  distance involving the water ranges from  $2.087(2)$  to  $2.170(2) \text{ \AA}$ ,  $2.109(2)$  to  $2.123(2) \text{ \AA}$ , and that of the sulfato bridged oxygens is  $2.071(2)$  to  $2.098(2) \text{ \AA}$ ,  $2.150(2) \text{ \AA}$ ,  $2.165(2) \text{ \AA}$  *a*propos  $\text{Zn1}$  and  $\text{Zn2}$  respectively. The  $[\text{Zn}(\text{H}_2\text{O})_2(\mu\text{-SO}_4)]_n$  chains running parallel to the *b*-axis are further coupled by  $L$  with an alternate metal center in the cross chain mode fabricating a right (**P**) and left (**M**) handed helical coil in **1P** and **1M** respectively (Figures 1b, 2, and S3). Adjacent  $[\text{Zn}(\text{H}_2\text{O})_2(\mu\text{-SO}_4)]_n$  zigzag chains are connected by the binodal ligands  $L$  resulting in the  $[\text{Zn}(\mu\text{-SO}_4)(L)(\text{H}_2\text{O})_2]_n$  two-dimensional network (Figure 1c) in which the same  $\text{M}\cdots\text{M}$  cross-chain distance ( $\text{Zn1}\cdots\text{Zn1}/\text{Zn2}\cdots\text{Zn2} = 15.59 \text{ \AA}$ ) is retained for both molecules present in **1P**. Accordingly, the *trans* axial position occupied by the terminal



**Figure 1.** (a)  $[\text{Zn}(\text{H}_2\text{O})_2(\mu\text{-SO}_4)]$  chain running parallel to the *b*-axis; (b) coupling of  $[\text{Zn}(\text{H}_2\text{O})_2(\mu\text{-SO}_4)]$  chains by  $L$  at alternate metal centers fabricates a right (**P**) handed helical coil in **1P**; (c) **P**-homohelices fuse together to generate a 2D metal organic network; (d) the underlying intrinsically chiral pseudo-Kagomé type topology is depicted with a short vertex symbol  $(4^2.6^3.8)$ .



**Figure 2.** Mirror image relation of right and left handed helical motifs composed of achiral building blocks in enantiomorphs **1P** and **1M**.

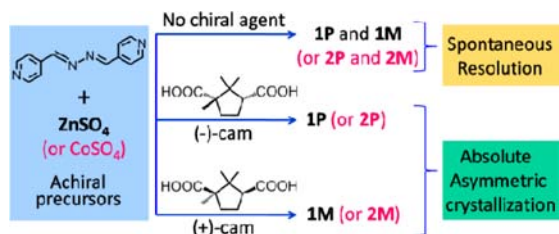
nitrogen atoms from two different  $L$  molecules completes the octahedral coordination around  $\text{M}^{+2}$  in which the  $\text{Zn}\cdots\text{N}$  distance ranges from  $2.140(3)$  to  $2.120(3)$  and  $2.125(3)$  to  $2.151(3)$  for  $\text{Zn1}$  and  $\text{Zn2}$  respectively. The average dihedral angles between the two peripheral pyridine rings of the rigid ligand  $L$  are  $8.69^\circ$  and  $8.78^\circ$ , indicating only a marginal twist in these ligands to effectively result in coordination with the metal in both zinc complexes.

The concomitant effect of the  $\mu_2\text{-}\kappa^2$  bridging mode of the screw related metal centers by the sulfato ligands and the cross chain bridging of the zigzag chains by  $L$  with alternate metal ions reinforce the construction of intrinsically chiral pseudo-Kagomé type two-dimensional enantiomeric networks  $(4^2.6^3.8)$  in **1P** and **1M** (Figure 1d). The packing diagram of **1P** revealed that both 2D nets present in the asymmetric unit (involving  $\text{Zn1}$  and  $\text{Zn2}$ ) are arranged in an ABAB pattern.

Independent 2D nets are associated by O–H...O hydrogen bonding interactions between the coordinated water molecules and sulfate oxygen between the A and B sheets. In addition to this O–H...O interaction, the lattice water molecules are also involved in O–H...O interactions between the coordinated water molecules and sulfate oxygens in bridging the 2D sheets with different metal centers and stabilizing the molecule in the crystal lattice. Albeit similar structural features including the helical nature and H-bonding interactions are observed in Co(II) complexes **2P** and **2M** also (Figure S4). Selected bond lengths and bond angles and details of hydrogen bonding interactions for all four complexes with hydrogen bonding parameters are given in Tables S2 and S3.

Three different crystallization experiments, particularly in the presence of (–)-cam, in presence of (+)-cam, and in the absence of camphoric acid were performed to distinguish and comprehend the spontaneous resolution and cooperative chirality induction phenomenon operative in the current system (Scheme 2). To establish the chiral crystallization

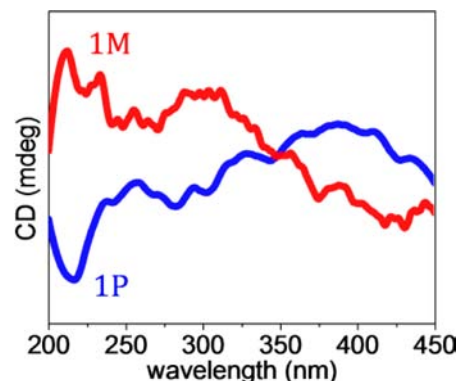
**Scheme 2. Depiction of Studied Crystallization Processes: Contribution of Enantiopure Camphoric Acid Induces the Absolute Asymmetric Crystallization of 2D Homochiral CPs and Absence of CI Agent Leads to Conglomerate Products**



trend operating in various experiments, six crystals were randomly picked from each crystallization batch and analyzed by single crystal X-ray diffraction techniques. The Flack parameter value of the collected crystal data sets revealed that the Zn CP crystallized in the presence of (–)-cam exclusively possesses right handed helicity; i.e., all six crystals were found to be **1P**. Similarly, six crystals selected from the batch crystallization carried out in the presence of (+)-cam were identical to **1M**, with left handed helicity. However, in the absence of (+)- or (–)-cam equal distribution of **1P** and **1M** was observed, as three crystals were **1P** and the remaining were **1M**. Similar batch experiments carried out for Co CPs also showed identical end results. Crystallographic details, Flack parameter values, and the observed helicity for Zn and Co CPs obtained from different batch crystallization experiments are presented in the Tables S4–S9.

In order to confirm the absolute configurations, individual crystals of **1P**, **1M** and **2P**, **2M** used for crystallographic studies were further characterized by solid-state circular dichroism (CD) spectroscopy, which furnished complementary results to the crystallographic findings. The Zn and Co CPs show electronic absorption spectra in the region ca. 295 nm (Figure S5). Hence, CD spectra for 6 random crystals from the both Zn and Co CPs crystallized in the presence of enantiopure camphoric acids and 10 crystals from each batch crystallized in the absence of camphoric acid were recorded using Nujol mull (Figure S6). Single crystals of both CPs grown in the presence of (–)-cam and (+)-cam showed a positive and negative dichroic signal at ca. 295 nm respectively. Representative CD

patterns for **1P** and **1M** possess a virtually mirror symmetric relation as depicted in Figure 3. Hence, the absolute chirality of



**Figure 3.** Representative CD spectra of enantiomorphs **1P** and **1M** depicting the mirror image relation for the dichroic signal at 295 nm.

the CPs prepared in the presence of enantiopure camphoric acid established by single crystal X-ray studies are also complemented by the CD data. Randomly picked individual crystals from the batch crystallized in the absence of enantiopure camphoric acid showed positive/negative dichroic signals varying from crystal to crystal, indicating the formation of a conglomerate (Figure S6). As anticipated, a mixture of a few crystals from the batch crystallized in the absence of CI agent (cam) did not show any dichroic signal (Figure S6). Thus, CD spectral data also support the conglomerate and predominant bulk homochiral crystallization of CPs in the absence or presence of enantiopure camphoric acid respectively. However, it is a challenging task to prove the absolute homochirality of the bulk sample because determination of the absolute configuration in each and every crystal by single crystal X-ray diffraction is not viable.<sup>9</sup> The results presented here, i.e., 36 (6 × 6) good quality single crystal data with refined Flack parameter values, indicate the crystallization experiments carried out in the presence of enantiopure camphoric acid result in the predominant formation of the desired enantiomorph.

Both Zn and Co CPs showed thermal stability up to ca. 280 °C after liberating the lattice guests in the temperature range 60–150 and 50–160 °C respectively (Figure S7). The luminescent properties of both CPs were also explored, and it was observed that, upon excitation at 295 nm, both CPs emit at 365 nm which could be assigned to the intraligand energy transfer. The overall quantum yields ( $\Phi_{\text{overall}}$ ) for Zn and Co CPs were 4.4 and 5.7 respectively which indicate the excellent fluorescent ability of these materials (Figure S8).

In summary, we demonstrated that the phenomenon of chirality induction can be applied to the CP/MOF systems comprising achiral building blocks which otherwise display spontaneous resolution. Absolute chiral crystallization for the isostructural Zn and Co coordination polymeric enantiomorphs  $[\text{Zn}(\text{SO}_4)(\text{L})(\text{H}_2\text{O})_2]_n$  and  $[\text{Co}(\text{SO}_4)(\text{L})(\text{H}_2\text{O})_2]_n$  has been achieved in the presence of a chirality induction agent (enantiopure camphoric acids). In the absence of camphoric acid conglomerate formation was observed. The bulk homochiral crystallization and conglomerate formation studies for the system are unambiguously established by crystallography and CD spectroscopy. Chirality in **1P/1M** and **2P/2M** originates from the self-assembly of homohelical motifs in the

intrinsically chiral pseudo-Kagomé type 2D network. Synthesized Zn and Co CPs show strong photoluminescence originating from the ligand-to-ligand energy transfer. The present study highlights the feasibility of the chirality induction process on the systems exhibiting spontaneous resolution and hence opens up new avenues for the selective crystallization of desired enantiomorphs in MOFs/CPs comprising achiral ligands. Acquiring insight from the present results, we are currently exploring the feasibility of chiral induction techniques in ternary MOF/CP conglomerates involving achiral dicarboxylate and flexible N-donor ligands.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental details, characterization data, CIF files, supporting figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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