

Communication

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Kamal Kumar Bisht, and Eringathodi Suresh

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

Kamal Kumar Bisht<sup>†,‡</sup> and Eringathodi Suresh<sup>\*,†,‡</sup>

<sup>†</sup>Analytical Department and Centralized Instrument Facility, Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR–CSMCRI) G. B. Marg, Bhavnagar –364 002, Gujarat, India.

<sup>‡</sup>Academy of Scientific and Innovative Research (AcSIR–CSMCRI) G. B. Marg, Bhavnagar –364 002, Gujarat, India.

## Supporting Information

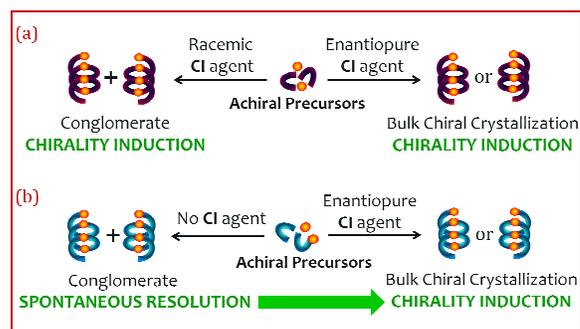
**ABSTRACT:** It is observed that conglomerate crystallization of achiral precursors yielding racemate MOFs/CPs can be driven to absolute homochiral crystallization of desired enantiomorph by utilizing suitable chiral induction agent. In a series of crystallization experiments isostructural Zn and Co homochiral CPs (**1P**, **1M** and **2P**, **2M**) are prepared using the achiral precursors. In presence of enantiopure camphoric acid, 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, non-linear optics and chiral recognition.<sup>1–4</sup> The straight forward way to synthesize homochiral CPs/MOFs is the use of enantiopure building blocks which translate their inherent chirality to the resultant framework by “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 linker for the construction of homochiral MOFs.<sup>3,4</sup> The prime indirect ways 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 most celebrated chiral inducing agents.<sup>7</sup> The use of cinchona alkaloids as chiral induction agent was first demonstrated by Zhang, et al. for the construction of homochiral microporous MOFs.<sup>7a</sup> Recently Duan et.al, have further explored the cinchona alkaloids as

chiral induction agent 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 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 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 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.

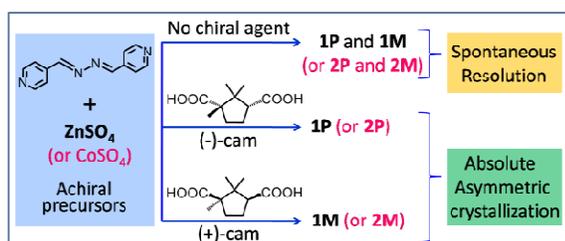
**Scheme 1. Cartoon depiction of the chiral induction (CI) agent driven conglomeration and bulk asymmetric crystallization processes (for example, reference 10) (a); spontaneous resolution driven conglomeration and the asymmetric coercing of same process via CI agent leading to absolute asymmetric crystallization (present study) (b).**



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 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 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 of achiral building blocks, we accentuate on the cooperative operation of spontaneous resolution and chiral induction. To be precise, we have employed a chiral induction agent to maneuver the fate of 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 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.

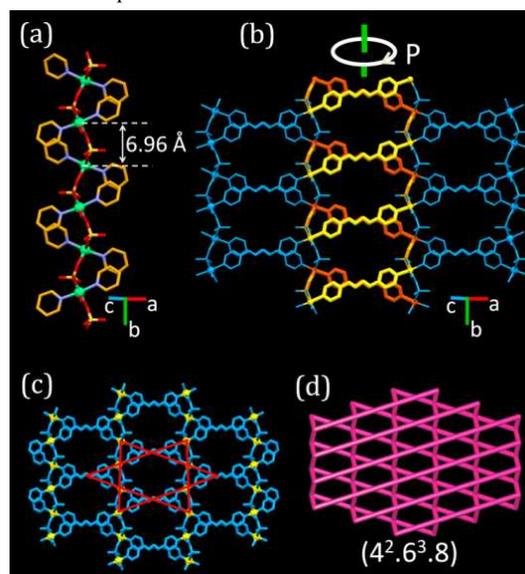
**Scheme 2. Depiction of studied crystallization processes: Contribution of enantiopure camphoric acid induces the absolute asymmetric crystallization of 2D homochiral CPs and absence of CI agent leads to conglomerate products.**



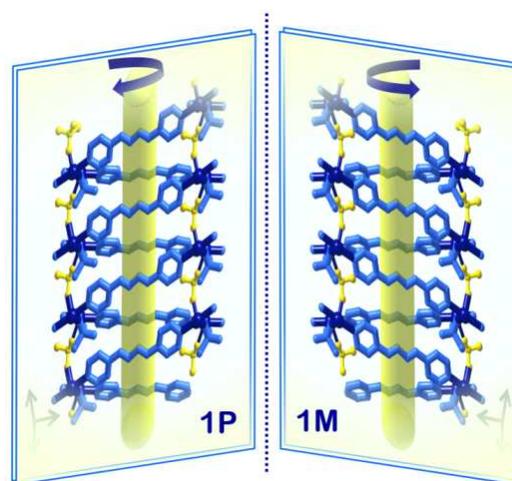
Herein we report two enantiomeric pairs (**1P**, **1M** and **2P**, **2M**) of isostructural 2-dimensional metal organic frameworks  $[\text{Zn}(\text{SO}_4)(\text{L})(\text{H}_2\text{O})_2]_n$  (**1**) and  $[\text{Co}(\text{SO}_4)(\text{L})(\text{H}_2\text{O})_2]_n$  (**2**) (where **L** = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene) comprising of 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 occurred upon diffusing the alcoholic solution of ligand (**L**) into the aqueous metal sulphate solution. We further show that the enantiopure camphoric acid (cam) can act as chirality inducing agent to achieve bulk absolute chiral CPs with 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 (–)-cam whereas (+)-cam directs the exclusive formation of absolute negative homohelical CPs **1M** and **2M** (supporting information S1).

All the four compounds crystallize in chiral space group  $C_2$  and possess a two dimensional network with intrinsic chirality. The Zn and Co CPs are isotypic; hence the structural description is restricted to the Zn CPs **1P** and **1M**. **1P** and **1M** contain two crystallographically independent  $[\text{Zn}(\text{SO}_4)(\text{L})(\text{H}_2\text{O})_2]_n$  entities with 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  $\mu_2-\kappa^2$  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 zigzag chain for both the molecules present in the asymmetric unit is 6.96 Å ( $\text{Zn1}\cdots\text{Zn1}$ ) and 6.03 Å ( $\text{Zn2}\cdots\text{Zn2}$ ) respectively.  $\text{Zn}\cdots\text{O}$  distance involving the water ranges from 2.087(2) to 2.170(2) Å, 2.109(2) to 2.123(2) Å and the sulfato bridged oxygens is 2.071(2) to 2.098(2) Å, 2.150(2) Å, 2.165(2) Å *apropos* Zn1 and Zn2 respectively. The  $[\text{Zn}(\text{H}_2\text{O})_2(\mu-\text{SO}_4)]$  chains running parallel to the *b*-axis are further coupled by **L** with alternate metal centre in cross chain mode fabricating a right (P) and left (M) handed heli-

cal 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 into  $[\text{Zn}(\mu-\text{SO}_4)(\text{L})(\text{H}_2\text{O})_2]_n$  two dimensional network (Figure 1c) in which the same  $\text{M}\cdots\text{M}$  cross-chain distance ( $\text{Zn1}\cdots\text{Zn1} / \text{Zn2}\cdots\text{Zn2} = 15.59\text{Å}$ ) is retained for both the molecules present in **1P**. Accordingly, the *trans* axial position occupied by the terminal nitrogen atoms from two different **L** molecules completes the octahedral coordination around  $\text{M}^{+2}$  in which  $\text{Zn}\cdots\text{N}$  distance range from 2.140(3) to 2.120(3) and 2.125(3) to 2.151(3) for Zn1 and Zn2 respectively. Average dihedral angle between the two peripheral pyridine rings of the rigid ligand **L** being 8.69° and 8.78°, indicating only marginal twist in these ligands to make effective coordination with the metal in both the zinc complexes.



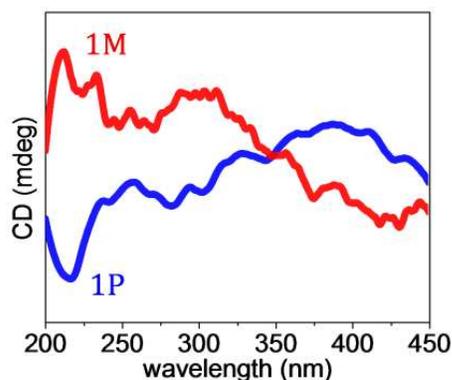
**Figure 1.** (a)  $[\text{Zn}(\text{H}_2\text{O})_2(\mu-\text{SO}_4)]$  chain running parallel to the *b*-axis; (b) coupling of  $[\text{Zn}(\text{H}_2\text{O})_2(\mu-\text{SO}_4)]$  chains by **L** at alternate metal centres fabricate a right (P) handed helical coil in **1P**; (c) P-homohelices fuse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

Concomitant effect of  $\mu_2$ - $\kappa^2$  bridging mode of the screw related metal centers by the sulfate 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 enantiomorphous networks ( $4^2.6^3.8$ ) in **1P** and **1M** (Figure 1d). Packing diagram of **1P** revealed that both 2D nets present in the asymmetric unit (involving Zn1 and Zn2) are arranged in ABAB pattern. Independent 2D nets are associated by O-H...O hydrogen bonding interactions between the coordinated water molecules and sulphate 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 length and bond angles; details of hydrogen bonding interactions for all the 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 trend operating in various experiments, six crystals were randomly picked from each crystallization batch and analyzed by single crystal X-ray diffraction techniques. Flack parameter value of the collected crystal data sets revealed that Zn CP crystallized in the presence of (–)-cam exclusively possess 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 remaining were **1M**. Similar batch experiments carried out for Co CPs also showed identical end results. Crystallographic details, Flack parameter values and observed helicity for Zn and Co CPs obtained from different batch crystallization experiments are presented in the Tables S4–S9.



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

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 six random crystals from the both Zn and Co CPs crystallized in the presence of enantiopure camphoric acids and ten crystals from the 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 virtually mirror symmetric relation as depicted in Figure 3. Hence, the absolute chirality of 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 conglomerate (Figure S6). As anticipated, 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 supports 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 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 results in the predominant formation of desired enantiomorph.

Both Zn and Co CPs showed thermal stability upto ca 280 °C after liberating the lattice guests in the temperature range 60–150 and 50–160 °C respectively (Figure S7). Luminescent properties of both CPs were also explored and observed that upon excitation at 295 nm; both CPs emit at 365 nm which could be assigned to the intra-ligand 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 of 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 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** is originated by the self assembly of homo-helical 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. Present study highlights the feasibility of 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 of 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>.

## AUTHOR INFORMATION

### Corresponding Author

[suresh@csmcri.org](mailto:suresh@csmcri.org); [suresh123@rediffmail.com](mailto:suresh123@rediffmail.com)

### Notes

The authors declare no competing financial interests.

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