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Spontaneous symmetry breaking of Co(II) metal-organic frameworks from achiral precursors *via* asymmetrical crystallization

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The racemic conglomerate (1P-NH₃ + 1M-NH₃) and enantioenriched bulk samples (1P-H₂O or 1M-NH₃) of Co(II) metal-organic frameworks were obtained from achiral precursors under different solvothermal conditions. The bulk homochirality was generated through asymmetrical crystallization in the absence of any chiral additives confirmed by single crystal X-ray diffraction and CD spectroscopy.

Homochirality is an essential feature of life and plays a vital role on various biological functions. Recently, homochiral crystalline solids, especially metal-organic frameworks (MOFs) with tunable cavities and high porosity have gained increasing attractiveness for their potential applications in asymmetrical catalysis, chiral separation, optical materials and magnetisms.¹ However, it is not easy to obtain bulk homochiral crystalline solids, though it is not rare for individual crystal being chirally pure itself through spontaneous resolution.² There are two common approaches to obtain bulk homochirality. One is to use chiral building blocks (chiral ligands,³ chiral auxiliary ligands⁴ or chiral templates,⁵ etc.) by a "chirality conservation" process from the precursors to the final as-made crystals. In this way, the chiral components are finally incorporated into the product. For example, Kim and coworkers applied chiral D-tartaric acid derivative as the primary linker/ligand to synthesize a chiral three-dimensional (3D) MOF successfully.^{3a} Another approach is to combine achiral precursors together with enantiopure solvents, chiral additives or even circularly polarized light which can induce the bulk sample to be desired handedness (a process often called asymmetric crystallization).⁶ Morris et al. obtained the homochiral compound from achiral precursors through the chiral ionic liquid solvent containing L-aspartate.^{6a} Bu and Zhang et al. demonstrated that chiral camphoric acid^{6b,c} or cinchonine^{6d} as additives had the ability to induce the bulk crystalline solids to be enantiopure or

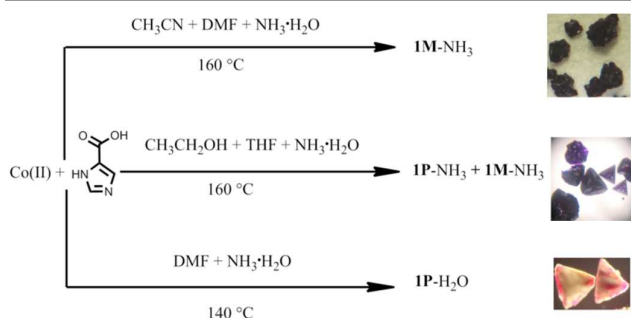
enantioenriched. Aoyama and coworker also have proved that chirality can be controlled by seeding.⁷ Because of the limited availability and the high cost of chiral agents, it is quite desirable and highly challenging to create bulk homochirality without any chiral sources.

In the absence of any enantiopure agents, the bulk homochirality can also be generated from achiral precursors through crystallization (a process called symmetry breaking if no chiral source is present) upon external stimuli such as stirring,⁸ chemical manipulation,⁹ or an abrasion/grinding technique.¹⁰ For instance, Kondepudi et al. have successfully obtained enantiopure or enantioenriched bulk crystals of NaClO₄ under stirring. Even though there is postulation that homochirality in crystalline state is thermodynamically-driven,¹¹ or Viedma's experiments demonstrate that cryptochiral environmental impurities may induce selective chiral symmetry breaking during crystallization,¹² to acquire homochiral bulk crystalline solids through symmetry breaking must be based on statistical fluctuation of initial nucleation events (e.g., single-colony growth induced by secondary nucleation). Though in a given experiment bulk homochirality could be yielded through symmetry breaking, the chirality sense is not controllable and predictable from run-to-run.

In this work, we observed that when varying the reaction solvents and temperature, racemic conglomerate **1P-NH₃** and **1M-NH₃** could be changed to the bulk homochiral (or enantioenriched) **1P-H₂O** and **1M-NH₃** with only achiral precursors (**1P-H₂O** = [(Co)₆(L)₆(H₂O)]·xH₂O, **1P-NH₃/1M-NH₃** = [(Co)₆(L)₆(NH₃)]·xH₂O, H₂L = 2H-imidazole-4-carboxylic acid, P and M denote the right- and left-handed helix in the corresponding framework, respectively). It should be noted that **1P-H₂O** and **1M-NH₃** are more accurately pseudo-enantiomorphs because their composition differs from coordinated solvent molecules. The enantiometric nature of **1P-H₂O** and **1M-NH₃** was confirmed by single-crystal X-ray diffraction (SCXRD) and solid-state circular dichroism (CD). Interestingly, we can readily distinguish between the enantiomers from their difference in both morphology and color with naked eyes, which, to our knowledge, is quite rare since Pasteur separated the crystals of enantiomeric tartaric acid by tweezers according to their different morphologies.¹³

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† Electronic Supplementary Information (ESI) available: Details of synthesis, characterizations and structure determinations, CD spectra, Uv-Vis, TGA, gas adsorption, PXRD, chiral GC. CCDC 1406644-1406646. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



Scheme 1. Schematic representation of the generation of conglomerate (**1P-NH₃** + **1M-NH₃**) or bulk homochiral **1P-H₂O** and **1M-NH₃** controlled by synthetic conditions.

The racemic conglomerate (**1P-NH₃** and **1M-NH₃**) was obtained when $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ solvothermally reacted with H_2L using ethanol, tetrahydrofuran (THF) and ammonia as solvents at 160 °C. There are two different kinds of crystals: one is blackish-purple and irregular; the other is also blackish-purple but triangular. Solid-state CD spectral analysis of these crystals with different morphologies shows that the handedness of each single crystal is random (either right-handed or left-handed). Unexpectedly, when the synthesis and crystallization were performed in mixed CH_3CN , DMF and ammonia solvents, we obtained blackish-purple and irregular crystals exclusively determined to be bulk homochiral crystals of **1M-NH₃** by SCXRD and CD analysis. Out of our expectation, we acquired reddish-purple and triangular crystals using DMF and ammonia as reaction solvents at 140 °C (scheme 1, see ESI† for experimental details). From the SCXRD analysis, we encountered a dilemma that we could not find any obvious differences between the reddish-purple crystals and the blackish-purple ones except that the helices in the structures of the reddish-purple single crystals are all right-handed opposite to **1M-NH₃**. We presume that the terminal coordinated solvent molecules in the reddish-purple crystals are H_2O molecules based on the following reasons: (1) the value of atomic scattering factor for N and O is close, so it is difficult to distinguish NH_3 and H_2O by crystallographic structural determination; (2) the magnetic properties **1M-NH₃** and the reddish-purple ones are very similar, excluding the probabilities that their different colors are caused by spin-crossover or different valence state of the Co atoms (*vide infra*);¹⁴ (3) from elemental analysis the content of N element of the reddish-purple crystalline solids decreases by *ca.* 1.2 wt%. (4) according to Hans Bethe's crystal field theory (CFT),¹⁵ H_2O is weaker field ligand than NH_3 , resulting in $\Delta_{(\text{NH}_3)} > \Delta_{(\text{H}_2\text{O})}$ (Δ denotes the crystal field splitting energy). In other words, the absorption band in visible light region of complexes with NH_3 as ligands (e.g., $\text{Co}(\text{NH}_3)_6^{2+}$) will be blue-shifted compared to those with H_2O as ligands (e.g., $\text{Co}(\text{H}_2\text{O})_6^{2+}$) and exhibit more darker color. In summary, the difference of the crystal color between blackish-purple and reddish-purple arises from the different coordinated solvent molecules. Therefore, the reddish-purple and triangular crystals are denoted as **1P-H₂O** which is chirally pure substantiated by SCXRD and CD analysis.

Both **1P-H₂O** and **1M-NH₃** crystallize in the chiral cubic space group $P2_13$ with all of Flack parameters close to zero, indicating enantiomeric purity of both single crystals. The asymmetric unit of **1P-H₂O** contains four crystallographically independent Co(II) centers.

Co1 center is coordinated by three O atoms and two N atoms from four different **L** ligands with geometry of distorted trigonal bipyramid. Co2 center is four-coordinated by three N atoms from three ligands and one terminal water molecule showing a tetrahedral geometry. Co3 site shows a slightly distorted octahedral geometry and is coordinated by six O atoms from six **L** ligands. Co4 center chelated by three **L** ligands displays CoO_3N_3 distorted octahedral coordination geometry (Fig. 1a). The Co-O (N) bond lengths are in the range of *ca.* 1.98–2.27 Å. The distance of adjacent Co(II) centers bridged by O atoms spans the range of *ca.* 3.09–3.53 Å. The structure of **1M-NH₃** is almost identical to **1P-H₂O** and the related bond angles of **1P-H₂O** and **1M-NH₃** are only slightly different except that the terminal coordinated H_2O molecule in Co2 center is replaced by NH_3 molecule ($\text{Co2-O1w} = 1.98$ Å, $\text{Co2-N5} = 1.94$ Å, Fig. S2–S3, Table S1, ESI†). From a topological viewpoint, the net of **1** can be rationalized to be a 3D 4-connected **lcv** net (Fig. S4, ESI†). The void cavities exist in **1** (Fig. 1b). The chirality arises from the helical arrangement of deprotonated ligands (**L**) and Co(II) cations (involving Co1 and Co2), wherein **1P-H₂O** and **1M-NH₃** contain right- and left-handed 2_1 screw axis with a pitch height of *ca.* 17.53 Å and 17.49 Å, respectively. Note that the right- and left-handed 2_1 helical chains are not genuine mirror-related due to the different terminal coordinated solvent molecules along the 2_1 helical chains (Fig. 1c).

The optical activity and enantiomeric nature of bulk samples of **1P-H₂O** and **1M-NH₃** were established by solid-state CD spectra. As shown in Fig. 2, the bulk sample of **1P-H₂O** exhibits a positive dichroic signal at *ca.* 300 nm while the **1M-NH₃** shows the opposite signal, which is in agreement with their UV-vis diffused reflectance spectra and manifests the enantioenriched (or a likely enantiopure) nature of bulk **1P-H₂O** and **1M-NH₃** (Fig. S5, ESI†). Bulk sample of **1** (containing both **1P-NH₃** and **1M-NH₃**) shows no dichroic signals suggesting the formation of racemic conglomerate through spontaneous resolution and different morphology does not correspond to the different chirality (see Fig. S6–S8 for more details, ESI†). The CD patterns of **1P-H₂O** and **1M-NH₃** are nearly mirror images of each other indicating the formation of a pair of

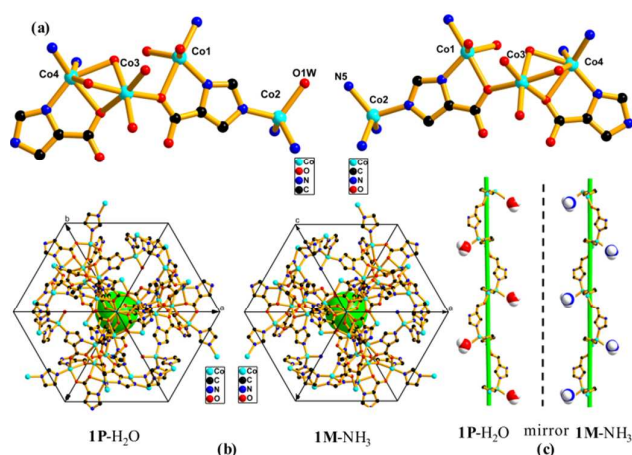


Fig. 1 (a) The coordination environments of Co(II) ions in **1P-H₂O** (left) and **1M-NH₃** (right). (b) a unit cell of **1P-H₂O** and **1M-NH₃** with green spheres showing the cavities viewed down [111] direction. (c) P and M 2_1 helical chains running along the *a*-axis showing the enantiomeric nature of **1P-H₂O** and **1M-NH₃** (H_2O and NH_3 molecules are shown in space-filling mode).

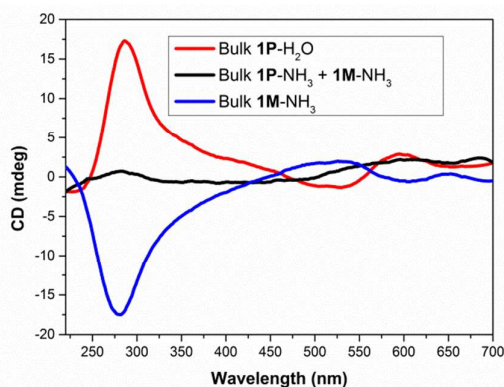


Fig. 2 Solid-state CD spectra of bulk samples of **1P-H₂O**, **1M-NH₃** and conglomerate **1**, respectively.

enantiomers. To get further information of optical activity of **1P-H₂O** and **1M-NH₃**, their bulk samples from 18 individual batches under parallel solvothermal syntheses were recorded with CD spectroscopy, respectively. It was a surprise that all of 18 samples of **1P-H₂O** exhibit positive signals at ca. 300 nm while those of **1M-NH₃** show the opposite signals (Fig. S9-S10, ESI[†]). However, the intensity of the CD signals moderately fluctuate (ca. ± 15 mdeg) indicate that some samples are enantioenriched instead of homochiral. So far, we failed to obtain the crystal structure of **1M-H₂O** somehow. Detailed CD measurements on 12 individual single crystals of **1P-H₂O** or **1M-NH₃** randomly picked from one crystallization experiment suggest that the enantiomeric excess (ee) is 100% (Fig. S11-S12, ESI[†]). We also randomly picked 10 reddish-purple and triangular and 10 blackish-purple of **1P-H₂O** and irregular single crystals of **1M-NH₃** for SCXRD analysis, respectively (Table S2-S3). All 10 crystals of **1P-H₂O** have P-helicity while those of **1M-NH₃** present M-helicity exclusively which again indicates the enantiomeric excess of **1P-H₂O** and **1M-NH₃**.

All of these results undoubtedly indicate the spontaneous symmetry breaking from achiral precursors *via* asymmetrical crystallization. Moreover, we can readily discriminate between **1P-H₂O** and **1M-NH₃** from different morphologies and colours of the crystals. To the best of our knowledge, such phenomenon is quite rare to date. The usual explanation for chiral symmetry breaking in one given experiment is secondary nucleation by which a randomly generated single mother crystal clones a large number of secondary crystals (e.g., through stirring) that are enantiomerically identical to itself.¹³ Because the handedness of the primary (mother) nucleus is random owing to no energy difference between the two enantiomers despite the theory that the parity violating energy difference (PVED) exists between enantiomers,¹⁶ the handedness distribution of multiple experiments should be stochastic. Nevertheless, several well-known examples about spontaneous symmetry breaking with nonstochastic distribution of handedness from achiral precursors have been reported.¹⁷ In order to explore the possible mechanism for the spontaneous symmetry breaking phenomenon observed in this work, we have checked all the reagents and solvents and found none of them were optically active. We conjecture that nonstochastic distribution of handedness in this case may be due to the sporadic presence of cryptochiral environmental impurities that act as the catalyst for the formation of

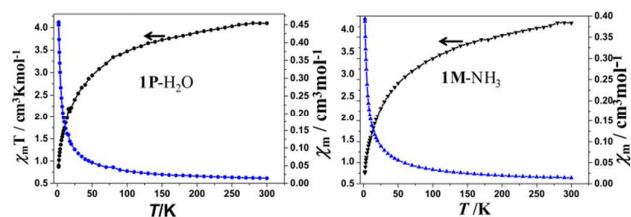


Fig. 3 Temperature dependence of χ_m (blue) and $\chi_m T$ (black) for **1P-H₂O** (left) and **1M-NH₃** (right) at 1 kOe.

one enantiomer and as the inhibitor for the formation of the opposite enantiomer.

The magnetic susceptibility data of **1P-H₂O** and **1M-NH₃** were measured at 1 kOe in the temperature range of 1.9–300 K. As shown in Fig. 3, the $\chi_m T$ values at 300 K are 4.09 and 4.14 $\text{cm}^3 \text{K mol}^{-1}$ for **1P-H₂O** and **1M-NH₃**, respectively, which are close to the spin-only value for two isolated Co(II) ions ($3.72 \text{ cm}^3 \text{K mol}^{-1}$, $S = 6/2$). During cooling process, the values of $\chi_m T$ gradually decreases from room temperature and reach a minimum at 1.9 K ($0.87 \text{ cm}^3 \text{K mol}^{-1}$ for **1P-H₂O**, $0.75 \text{ cm}^3 \text{K mol}^{-1}$ for **1M-NH₃**), suggesting antiferromagnetic behaviour. The magnetic susceptibility data in the temperature range of 20–300 K can be well fitted to the Curie-Weiss law expression where $C = 4.47 \text{ cm}^3 \text{K mol}^{-1}$, $\theta = -27.03 \text{ K}$ for **1P-H₂O**, and $C = 3.92 \text{ cm}^3 \text{K mol}^{-1}$, $\theta = -20.00 \text{ K}$ for **1M-NH₃**. The negative Weiss constants further confirm an antiferromagnetic interaction between the Co(II) ions (Fig. S13, ESI[†]).

The phase purity of **1** was confirmed by powder XRD (PXRD, Fig. S14, ESI[†]). The peaks of as-synthesized products are corresponding to those calculated from the data of single crystal diffraction except for the peaks of **1P-H₂O** with slightly widened and weakened, indicating that the increased framework distortion and decreased crystallinity of **1P-H₂O** after grinding for PXRD measurement. The pore volume void ratio of **1** is 49.8% calculated by the PLATON program. Thermogravimetric analysis (TGA) of **1P-H₂O** and **1M-NH₃** shows that the decomposition of the backbone occurs at about 300 °C (Fig. S15, ESI[†]). The permanent porosity of **1P-H₂O** was confirmed by CO₂ adsorption measurements, which shows a significant maximum adsorption of 102.46 cm^3/g at 195 K. A type I isotherm is observed, indicating that **1** is microporous (Fig. S16, ESI[†]). To investigate whether **1P-H₂O** and **1M-NH₃** allows enantioselective separation, its evacuated single-crystal were soaked in neat racemic 2-butanol. However, from chiral GC analysis, both **1P-H₂O** and **1M-NH₃** show very low enantioselectivity (Fig. S17 and Table S4, ESI[†]). This should be ascribed to weak interactions between the chiral 2-butanol molecules and the framework of **1P-H₂O** or **1M-NH₃**.¹⁸

In summary, we prepared enantioenriched three-dimensional Co(II) MOFs with achiral precursors through spontaneous symmetry breaking under different solvothermal reaction conditions. We can readily discriminate between the pseudo-enantiomers of **1P-H₂O** and **1M-NH₃** from the different color and morphology of the crystals with naked eyes. Notably, this compound is one kind of multifunctional materials integrating porosity, chirality and magnetism together.

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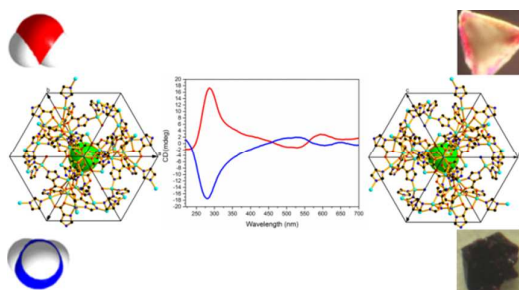
Notes and references

† Crystal data for **1P-NH₃**: C₂₄H₁₅Co₆N₁₃O₁₂, *M_r* = 1031.07, cubic, space group *P*2₁3, *a* = *b* = *c* = 17.4611(2) Å, *V* = 5323.71(11) Å³, *Z* = 4, *ρ*_{calcd} = 1.286 g cm⁻³, Flack parameter = -0.02(5), *R*₁ (*wR*₂) = 0.0557 (0.1716) and *S* = 1.096 for 2754 reflections with *I* > 2σ(*I*). Crystal data for **1M-NH₃**: C₂₄H₁₅Co₆N₁₃O₁₂, *M_r* = 1031.07, cubic, space group *P*2₁3, *a* = *b* = *c* = 17.4882(2) Å, *V* = 5348.54(11) Å³, *Z* = 4, *ρ*_{calcd} = 1.280 g cm⁻³, Flack parameter = 0.05(3), *R*₁ (*wR*₂) = 0.0378 (0.1075) and *S* = 1.090 for 3138 reflections with *I* > 2σ(*I*). Crystal data for **1P-H₂O**: C₂₄H₁₄Co₆N₁₂O₁₃, *M_r* = 1032.05, cubic, space group *P*2₁3, *a* = *b* = *c* = 17.5279(8) Å, *V* = 5385.0(4) Å³, *Z* = 4, *ρ*_{calcd} = 1.273 g cm⁻³, Flack parameter = 0.05(3), *R*₁ (*wR*₂) = 0.0372 (0.0991) and *S* = 1.056 for 3182 reflections with *I* > 2σ(*I*).

Measurement of solid CD spectra of bulk samples: A mixture of about 1 mg and 40 mg dried KCl powder was well-ground then press into a disk for the CD measurement

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Graphic Abstract



Enantioenriched 3D pseudo-enantiomorphs integrating porosity, chirality and magnetism together with different colour and morphology were obtained through spontaneous symmetry breaking.