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Particular Handedness Excess through Symmetry-Breaking Crystallization of a 3D Cobalt Phosphonate

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S *Supporting Information*

ABSTRACT: A 3D chiral cobalt phosphonate has been obtained from achiral precursors in the absence of chiral inducers. Remarkably, the bulk sample is largely enantio-enriched with particular handedness through symmetry-breaking crystallization in spite of multiple repeated experiments. Moreover, protonation of this chiral material introduces Brønsted acid sites, the structure of which is unique to the heterogeneous phase for the ring opening of epoxies.

The current increasing interest in chiral inorganic–organic hybrid materials mainly stems from their enormous potentials in asymmetric catalysis, nonlinear optics, and chiral recognition.[1] Despite its great importance, the generation of chirality remains a great challenge. Great efforts have been made to achieve chirality in solid materials. The straightforward way is to employ enantiopure bridge[2,3] or auxiliary ligands,[4] during the process of which the inherent chirality of the enantiopure ligand can be imparted to the resultant sample. The other effective strategy is to fall back on the help of an additional chiral source as a chiral catalyst, a template, or a solvent,[5,6] wherein the existence of the chiral auxiliary ligand can affect the growth of nucleation in the reaction system. However, both of the methodologies suffer from limited availability and the very high cost of the enantiopure ligands. Therefore, there is a highly desirable requirement to obtain chiral materials from achiral precursors. Chirality can be generated from achiral precursors,[5a,7] deriving from the spatial organization (e.g., helix) of achiral building blocks. It is necessary to stress that the generation of chirality is not the purpose. The greatest challenge is the creation of an enantiomeric bias to favor one-handedness because the resultant sample obtained through spontaneous resolution tends to be a conglomerate, defined as an equal mixture of crystals with opposite handedness or racemic twins.[8] As mentioned above, realizing asymmetric chiral amplification from achiral precursors through symmetry breaking still reamins one of the most challenging tasks, although there have been several such examples.[9]

On the other hand, the chemistry of metal phosphonates has been expanding rapidly in recent years because of their versatile structural features and potential applications.[10] Although a variety of metal phosphonates have been reported, those with chirality are very few, and most of them are built from enantiopure phosphonate ligands,[11] while examples characterized as enantio-enriched through symmetry-breaking crystallization are relative rare. As far as we know, Zheng et al. did elegant work on the study of metal phosphonates[12] and reported the only two notable cases with enantiomeric excess accomplished by using asymmetry achiral ligands,[12d,e] the structures of which feature chiral layering.

In this Communication, we identify an unusual phenomenon that the bulk sample is largely enantio-enriched with particular handedness through symmetry-breaking crystallization in spite of multiple repeated experiments. The resulting compound $Co(H_2L)(4,4'\text{-bipy})\cdot H_2O$ [**1**; H_4L = thiophene-2-phosphonic acid (Scheme S1) and 4,4′-bipy = 4,4′-bipyridine] presents a 3D chiral metal phosphonate framework built from achiral precursors in the absence of chiral sources. In addition, compound **1** displays excellent catalytic activity due to protonation of the phosphonate ligands.

A mixture of $Co(NO_3)_2\cdot H_2O$, H_4L, and 4,4′-bipy in a 2:1:2 molar ratio in aqueous solution at 100 °C gives pink blocky crystals of compound **1M** (or **1P**). The purity of as-synthesized **1** was confirmed by similarities between the simulated and experimental powder X-ray diffraction (PXRD) patterns (Figure S1). A single-crystal X-ray diffraction study showed that **1M** crystallizes in the chiral space group $P2_1$ with a Flack parameter of 0.021(1), indicating enantiomeric purity of the single crystals despite the use of achiral reagents. Each asymmetric unit includes one crystallographically independent cobalt(II) cation, one protonated $\{H_2L\}^{2-}$ anion, one 4,4′-bipy ligand, and one water molecule (Figure S2). Each cobalt(II) center is five-coordinated in a distorted trigonal-bipyramidal geometry environment with two nitrogen atoms from two 4,4′-bipy ligands and three oxygen atoms from three different phosphonic ligands in a monodentate fashion. One phosphonate group of each $\{H_2L\}^{2-}$ linker bonds two cobalt atoms in a dimonodentate fashion, and the other phosphonate group coordinates to one cobalt center in a monodentate fashion. Such a connection results in an infinite 3D (3,5)-connected hms net (Figures 1 and S3).[13] It is worth noting that each cobalt(II) ion, ligated by two nonplanar bidentate 4,4′-bipy and three conformationally changed $\{H_2L\}^{2-}$ ligands, becomes an asymmetric center, and the interconnection of

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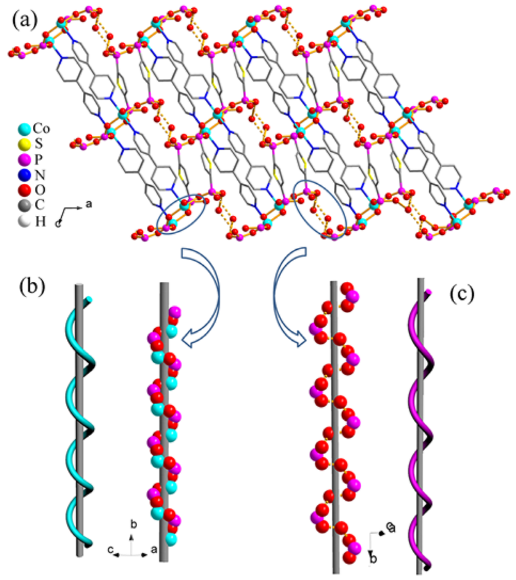

Figure 1. (a) One set of the 3D framework in **1M** along the *b* axis. A space-filling view of the left-handed helical −Co−O−P−O−Co− chains (b) and the −O−P−O···H−O−H···O−P−O− chains (c) as well as their corresponding highlighted pitch. Hydrogen atoms bonded to carbon atoms are omitted for clarity in part a.

neighboring cobalt(II) ions results in a left-handed 2_1 helical inorganic chain viewed along the (1,0,1) axis (Figure 1b). Lattice water molecules are located among adjacent phosphonate groups from different $\{H_2L\}^{2-}$ linkers through strong hydrogen-bonding interactions (Figure 1a). It is worth noting that the hydrogen bonds exist not only between phosphonate oxygen atoms and water molecules but also between neighboring protonated and nonprotonated phosphonate groups, with O−H···O lengths ranging from 2.582 to 3.024 Å (Figure S4). It is especially interesting that the arrangement of lattice water molecules produces a left-handed −O−P−O···H−O−H···O−P−O− helical chain (Figure 1c).

In order to investigate the absolute configurations of compound **1**, 26 crystals were randomly picked, and the corresponding crystal structures were refined by single-crystal X-ray diffraction data with the same set of atomic coordinates. The results reveal that all of them crystallize in space group $P2_1$, and the Flack absolute structure parameter from each refinement of 25 crystals is close to 0, whereas the other one is close to 1 (Table S2). It must be highlighted that 10 of the 26 crystals are from one batch, 5 of them from another one, 3 of them from a third one, and the other 8 crystals are from different reactors; it is possible that the bulk sample is largely enantio-enriched with particular handedness in spite of multiple repeated experiments. In order to get a better insight into the chirality of **1**, ultraviolet−visible diffuse-reflectance (UV−vis DRS) and solid-state circular dichroism (CD) spectra on 10 single crystals picked from different reactor as well as a bulk sample from another hydrothermal synthesis were measured. As shown in Figure 2, the maximum absorption frequency (λ_{max} = 260 nm) observed in the solid-state UV experiment is parallel to the dichroic signals (λ_{max} = 260−270 nm) in the CD spectra, indicating that the bulk sample of **1** is enantio-enriched. Remarkably, all of the results of the CD spectra show a significant signal with nine negative and one positive from 10 single crystals and one negative from the bulk sample. Both the Cotton effect displayed in the CD spectra and the structural refinements of 26 crystals demonstrate that the bulk sample of **1** is enantio-enriched with left-handed helical chains (**1M** ≫ **1P**).

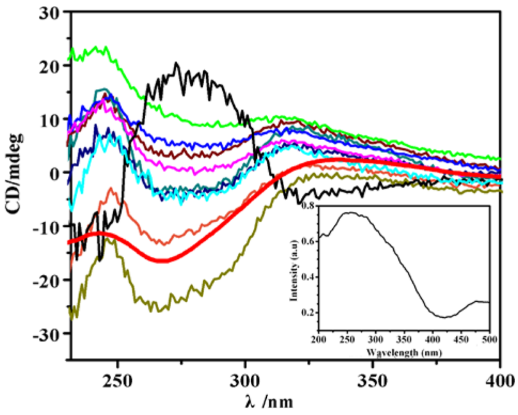

Figure 2. Solid-state CD spectra of 10 randomly selected crystals as well as the bulk sample (labeled in bold red). Inset: solid-state UV−vis spectra of compound **1** in $BaSO_4$ plates at room temperature.

As established in the former structure analyses, the origin of the chirality of the single crystal is particular interesting because there are no driving forces, such as enantiopure catalysts. In addition, the unique feature of this work is that the bulk sample is largely enantio-enriched with particular handedness in spite of multiple repeated experiments. Considering that the impact of hydrogen bonding has been discussed in previous reports,[14] CD measurement was performed on several desolvated crystals (Figure S6) to gain further insight into the role of intermolecular hydrogen-bonding interaction. The appearance of CD signals from the desolvated samples indicates that hydrogen bonding is not the key factor for the formation of chirality in this work. Meanwhile, it is worth noting that the phosphonate ligand H_4L itself is rigid and symmetrical, while it becomes asymmetric due to a tiny distortion angle upon bonding to a cobalt(II) ion (Figure S10). Then the mirror between the inherent right- and left-handed helices is broken once the conformation is twisted, with the chirality emerging. Thus, the twisted conformation of the $\{H_2L\}^{2-}$ linker is the conclusive factor for the symmetry-breaking phenomenon. The enantiomeric excess of particular handedness in this work is suspected of being associated with the cooperative effect from the dual ligands, the contribution of which to symmetry-breaking crystallization has been observed previously.[7b] The coordination bonds are strong, selective, and directional for chirally discriminative interactions.[8,9d,15] The $\{H_2L\}^{2-}$ linker might preferentially take the conformation adopted in **1M**, and then the seed effects the formation of left-handedness of bulk crystals over right-handedness, leading to an enantiomeric excess of particular handedness. Such an unusual phenomenon is similar to that of homochirally biological helices to a certain extent, such as a DNA molecule, amino acid, glucose, and so on, the origin of which is a result of the combined action of many factors and is still unknown to humans up to now. The following work will be focused on exploration of the external forces that trigger the conformational changes.

Considering the protonation of the two phosphonate groups per $\{H_2L\}^{2-}$ anion, there is a possibility of the introduction of Brønsted acid sites, and the catalytic performance of **1** was investigated in the ring-opening reaction of styrene oxide with methanol at 60 °C. The only reaction product, 2-methoxy-2-phenylethanol, was obtained with conversion and selectivity over 99% after 2.5 h, indicating that compound **1** possesses excellent catalytic activity. It is worth noting that no reaction occurred in the absence of the catalyst under similar conditions, and such values of the activity and selectivity are high among the metal–organic-framework-based heterogeneous catalysts reported.[16] In order to gain better insight into the nature of the catalytic action, the ring-opening reaction of styrene oxide with methanol was also carried out using the ligand H_4L and $Co(NO_3)_2{\cdot}7H_2O$ as the catalyst instead of **1**, respectively. The results clearly prove that compound **1** plays the role of a Brønsted acid rather than a Lewis acid catalyst. The recyclability of catalyst **1** was investigated for three consecutive batch runs. Both the conversion and selectivity remain high and equal to those in the first run. Furthermore, the PXRD pattern of the catalyst after the third run demonstrates that the structural integrity of compound **1** remains unaltered throughout the catalytic tests performed (Table S3).

In conclusion, herein we demonstrate an unusual phenomenon that the bulk sample is largely enantio-enriched with particular handedness through symmetry-breaking crystallization in spite of multiple repeated experiments. The chirality of **1** was verified by single-crystal X-ray diffraction in combination with solid-state CD spectroscopy. Moreover, protonation of this chiral material introduces Brønsted acid sites, the structure of which is unique to the heterogeneous phase for the ring opening of epoxies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02187.

> Experimental details, additional structural figures, crystallographic refinement details, photographs of crystals, PXRD, catalytic details, thermogravimetric analysis curve, and IR spectra (PDF)
> CCDC 1418906 (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Yoon, M.; Srirambalaji, R.; Kim, K. *Chem. Rev.* **2012**, *112*, 1196–1231. (b) Xuan, W. M.; Zhu, C. F.; Liu, Y.; Cui, Y. *Chem. Soc. Rev.* **2012**, *41*, 1677–1695. (c) Suh, K.; Yutkin, M. P.; Dybtsev, D. N.; Fedin, V. P.; Kim, K. *Chem. Commun.* **2012**, *48*, 513–515. (d) Ma, L. Q.; Falkowski, J. M.; Abney, C.; Lin, W. B. *Nat. Chem.* **2010**, *2*, 838–846. (e) Yang, Q.; Chen, Z.; Hu, J.; Hao, Y.; Li, Y.; Lu, Q.; Zheng, H. *Chem. Commun.* **2013**, *49*, 3585–3587. (f) Liu, D.-S.; Sui, Y.; Chen, W.-T.; Feng, P. *Cryst. Growth Des.* **2015**, *15*, 4020–4025.

(2) (a) Vaidhyanathan, R.; Bradshaw, D.; Rebilly, J.-N.; Barrio, J. P.; Gould, J. A.; Berry, N. G.; Rosseinsky, M. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6495–6499. (b) Wu, C.-D.; Lin, W. B. *Angew. Chem., Int. Ed.* **2005**, *44*, 1958–1961. (c) Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. B. *J. Am. Chem. Soc.* **2005**, *127*, 8940–8941. (d) Li, Z. J.; Yao, J.; Tao, Q.; Jiang, L.; Lu, T. B. *Inorg. Chem.* **2013**, *52*, 11694–11696.

(3) (a) Zhang, J.; Chen, S.; Zingiryan, A.; Bu, X. H. *J. Am. Chem. Soc.* **2008**, *130*, 17246–17247. (b) Zhang, J.; Chen, S.; Bu, X. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 5434–5437. (c) Zhang, J.; Bu, X. H. *Chem. Commun.* **2009**, 206–208.

(4) Kepert, C. J.; Prior, T. J.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 5158–5168.

(5) (a) Morris, R. E.; Bu, X. H. *Nat. Chem.* **2010**, *2*, 353. (b) Bisht, K. K.; Suresh, E. *J. Am. Chem. Soc.* **2013**, *135*, 15690–15693. (c) Zang, H.-Y.; Miras, H. N.; Long, D.-L.; Rausch, B.; Cronin, L. *Angew. Chem., Int. Ed.* **2013**, *52*, 6903–6906. (d) Morris, R. E. *Chem. Commun.* **2009**, 2990–2998. (e) Wang, S.; Zang, H.; Sun, C.; Xu, G.; Wang, X.; Shao, K.; Lan, Y.; Su, Z. *CrystEngComm* **2010**, *12*, 3458–3462.

(6) (a) Kang, Y.; Chen, S.; Wang, F.; Zhang, J.; Bu, X. H. *Chem. Commun.* **2011**, *47*, 4950–4952. (b) Zhang, J.; Chen, S.; Nieto, R. A.; Wu, T.; Feng, P.; Bu, X. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 1267–1270. (c) Lin, Z.; Slawin, A. M. Z.; Morris, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 4880–4881. (d) Marino, N.; Armentano, D.; Pardo, E.; Vallejo, J.; Neve, F.; Di Donna, L.; De Munno, G. *Chem. Sci.* **2015**, *6*, 4300–4305.

(7) (a) Chen, S.-C.; Zhang, J.; Yu, R.-M.; Wu, X.-Y.; Xie, Y.-M.; Wang, F.; Lu, C.-Z. *Chem. Commun.* **2010**, *46*, 1449–1451. (b) Zhou, T. H.; Zhang, J.; Zhang, H. X.; Feng, R.; Mao, J.-G. *Chem. Commun.* **2011**, *47*, 8862–8864. (c) Yi, F.-Y.; Zhang, J.; Zhang, H.-X.; Sun, Z.-M. *Chem. Commun.* **2012**, *48*, 10419–10421.

(8) Pérez-García, L.; Amabilino, D. B. *Chem. Soc. Rev.* **2002**, *31*, 342–356.

(9) (a) Kondepudi, D. K.; Kaufman, R. J.; Singh, N. *Science* **1990**, *250*, 975–976. (b) Sun, Q.; Bai, Y.; He, G.; Duan, C.; Lin, Z.; Meng, Q. *Chem. Commun.* **2006**, 2777–2779. (c) Wu, S. – T.; Wu, Y. – R.; Kang, Q.-Q.; Zhang, H.; Long, L.-S.; Zheng, Z.; Huang, R.-B.; Zheng, L.-S. *Angew. Chem., Int. Ed.* **2007**, *46*, 8475–8479. (d) Ezuhara, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3279–3283.

(10) (a) Shimizu, G. K. H.; Vaidhyanathan, R.; Taylor, J. M. *Chem. Soc. Rev.* **2009**, *38*, 1430–1449. (b) Mao, J.-G. *Coord. Chem. Rev.* **2007**, *251*, 1493–1520. (c) Zheng, Y.-Z.; Evangelisti, M.; Tuna, F.; Winpenny, R. E. P. *J. Am. Chem. Soc.* **2012**, *134*, 1057–1065. (d) Taylor, J. M.; Mah, R. K.; Moudrakovski, I. L.; Ratcliffe, C. I.; Vaidhyanathan, R.; Shimizu, G. K. H. *J. Am. Chem. Soc.* **2010**, *132*, 14055–14057.

(11) (a) Fredoueil, F.; Evain, M.; Massiot, D.; Bujoli-Doeuff, M.; Bujoli, B. *J. Mater. Chem.* **2001**, *11*, 1106–1113. (b) Yue, Q.; Yang, J.; Li, G.-H.; Li, G.-D.; Chen, J.-S. *Inorg. Chem.* **2006**, *45*, 4431–4439. (c) Shi, X.; Zhu, G. S.; Qiu, S. L.; Huang, K.; Yu, J.; Xu, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6482–6485. (d) Evans, O. R.; Ngo, H. L.; Lin, W. B. *J. Am. Chem. Soc.* **2001**, *123*, 10395–10396. (e) Ngo, H. L.; Lin, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 14298–14299. (f) Liu, X.-G.; Bao, S.-S.; Li, Y.-Z.; Zheng, L. M. *Inorg. Chem.* **2008**, *47*, 5525–5527.

(12) (a) Zeng, D.; Ren, M.; Bao, S.-S.; Feng, J.-S.; Li, L.; Zheng, L.-M. *Chem. Commun.* **2015**, *51*, 2649–2652. (b) Liu, X.-G.; Bao, S.-S.; Huang, J.; Otsubo, K.; Feng, J.-S.; Ren, M.; Hu, F.-C.; Sun, Z.; Zheng, L.-M.; Wei, S.; Kitagawa, H. *Chem. Commun.* **2015**, *51*, 15141–15144. (c) Nie, W.-X.; Bao, S.-S.; Zeng, D.; Guo, L.-R.; Zheng, L.-M. *Chem. Commun.* **2014**, *50*, 10622–10625. (d) Yang, X.-J.; Bao, S.-S.; Zheng, T.; Zheng, L.-M. *Chem. Commun.* **2012**, *48*, 6565–6567. (e) Hou, S.-Z.; Cao, D.-K.; Li, Y.-Z.; Zheng, L. M. *Inorg. Chem.* **2008**, *47*, 10211–10213.

(13) Blatov, V. A. *Struct. Chem.* **2012**, *23*, 955–963.

(14) Gao, E.-Q.; Yue, Y.-F.; Bai, S.-Q.; He, Z.; Yan, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 1419–1429.

(15) (a) Katsuki, I.; Motoda, Y.; Sunatsuki, Y.; Matsumoto, N.; Nakashima, T.; Kojima, M. *J. Am. Chem. Soc.* **2002**, *124*, 629–640. (b) Tabellion, F. M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1529–1532.

(16) (a) Vilela, S. M. F.; Ananias, D.; Gomes, A. C.; Valente, A. A.; Carlos, L. D.; Cavaleiro, J. A. S.; Rocha, J.; Tomé, J. P. C.; Paz, A. A. *J. Mater. Chem.* **2012**, *22*, 18354–18371. (b) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *Chem. - Eur. J.* **2010**, *16*, 8530–8536. (c) Jiang, D.; Mallat, T.; Krumeich, F.; Baiker, A. *J. Catal.* **2008**, *257*, 390–395.