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## Chiral template induced homochiral MOFs built from achiral components: SHG enhancement and enantioselective sensing of chiral alkalines by ion-exchange

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**A pair of chiral template induced anionic homochiral frameworks constructed upon achiral components has been synthesized. Ion-exchange of counter cations with polar or chiral organic cations enhances the SHG efficiency of the frameworks. Enantioselective sensing of chiral alkalines can be achieved by the SHG response.**

Exploring new second-order non-linear optical (NLO) materials continues to attract world-wide interest because of their potential applications in the domain of opto-electronics and photonics.<sup>1</sup> Early research efforts have been focused mainly on inorganic oxide or conjugated organic compounds.<sup>2</sup> Currently, metal-organic frameworks (MOFs), a class of newly developed inorganic-organic hybrid materials have emerged as promising candidates for second-order NLO materials because they can combine the high nonlinear optical coefficients of the organic molecules with excellent physical properties of the inorganics.<sup>3</sup> In addition, the almost unlimited combination of inorganic building blocks and organic linkers would, in principle, lead to a huge number of MOFs, enabling the large-scale screening and design of new NLO-active MOF materials. However, up to now, it is still a big challenge to obtain MOF materials with high SHG properties, because there are several limitations, for example it is difficult to control the MOF structure and a more reliable method to synthesize acentric MOFs is required. Very recently, inclusion of the ordered organic dipolar chromophores in a microporous MOF has been reported, which opens up new possibilities in the area of NLO MOF materials.<sup>4</sup>

Meanwhile, homochiral metal-organic frameworks (HMOFs) have attracted much attention owing to their promising applications in the fields such as enantioselective separation and sensing, asymmetry catalysis, and SHG materials.<sup>5</sup> As far as is known, most HMOFs prepared so far consist of enantiopure

organic ligands that ensure the homochirality of the resulting crystals.<sup>6</sup> However, because of the limited availability and the high cost of enantiopure ligands, it is extremely desirable to fabricate HMOFs from achiral constructing blocks. For this purpose, the greatest trouble is not the generation of chirality, but rather how to prepare an enantiomeric bias to favour one handedness. It is commonly known that achiral components crystallized in chiral symmetry tend to be an agglomeration, defined as an equal mixture of crystals with opposite handedness or racemic twins.<sup>7</sup> Hence, a more predictable approach for homochiral crystallization with achiral components would be to employ an additional chiral source to induce a given handedness.<sup>8</sup> Despite the fact that chiral MOFs can also be obtained from achiral precursors *via* spontaneous resolution,<sup>7</sup> up to now, only several examples of homochiral frameworks formed by achiral ligands have been documented.<sup>9</sup> Moreover, chiral template-induced ionic HMOFs, where the frameworks are built from achiral components and the chiral templates act only as counter ions in the pores have not been seen before. It can be expected that these ionic HMOFs may afford a feasible proposal to adjust the SHG intensity through ion-exchange of the chiral templates with various optically active organic molecules<sup>4</sup> and can sense the enantiomorphous molecules by chiral recognition and SHG response.

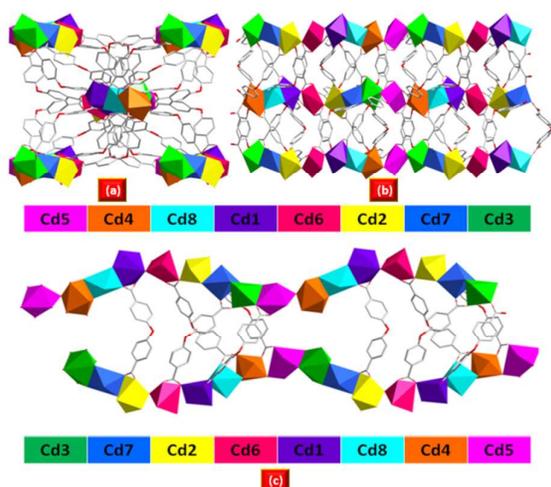
In this work, we select d<sup>10</sup> transition metal Cd(II) as a metal node, which can avoid unwanted d–d transitions in the visible region, semi-rigid 4,4'-oxybisbenzoic acid (H<sub>2</sub>OBA) as a linker to connect the metal nodes and easily protonated L- or D-2-amino-1-propanol (L- or D-APA) as chiral inducing agents to synthesize a pair of anionic HMOFs, {[L-HAPA]<sub>4</sub>[Cd<sub>8</sub>(OBA)<sub>10</sub>]} (**1L**) and {[D-HAPA]<sub>4</sub>[Cd<sub>8</sub>(OBA)<sub>10</sub>]} (**1D**). The SHG intensity of **1L** can be significantly increased by partly replacing HAPA<sup>+</sup> cations in **1L** with polar organic molecules such as 4-nitroaniline and some chiral alkalines. Moreover, these homochiral frameworks are capable to sense, for the first time, chiral alkaline molecules by enantioselective ion-exchange and the variation of SHG efficiency.

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**Fig. 1** (a) View of one inorganic Cd chain is bridged by OBA<sup>2-</sup> with four Cd chains of reversed order. (b) A 2D ladder-like sheet of **1L** viewed from the *b*-axis. (c) Schematic showing of the connection of two adjacent inorganic Cd chains of **1L**.

**1L** and **1D** are obtained as colourless crystals by the solvothermal reactions of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O with H<sub>2</sub>OBA in the presence of L- or D -APA in ethanol at 150°C for 3 days in high yields. Here, the APA acts a template to induce homochirality of the products. Interestingly, the APA is protonated at its primary amino group and the resulting cation serves not only as the homochiral inducing agent, but also as the charge balancer. Single crystal X-ray diffraction analysis shows that **1L** and **1D** crystallize into the chiral space groups of P2<sub>1</sub>. Due to the fact that the structure of **1D** is essentially the same as that of **1L**, only the structure of **1L** is discussed in detail. The asymmetry unit of **1L** consists of eight crystallographically independent Cd(II) ions, ten unique OBA<sup>2-</sup> ligands and four L-HAPA<sup>+</sup> counter cations (Fig. S1). The Cd1, Cd2, Cd3, Cd4 and Cd5 ions are seven-coordinated by carboxylate oxygen atoms in a twisted pentagonal geometry, while Cd6, Cd7 and Cd8 ions are six-coordinated by carboxylate oxygen atoms in a distorted octahedral coordination geometry. In **1L**, the carboxylate groups adopt either bidentate chelating-bridging or bidentate bridging modes to coordinate to the Cd(II) ions (Fig. S2). The Cd–O bond lengths vary from 2.193(8) to 2.606(10) Å, which are in the normal range.

The structure of **1L** can be regarded as a 3D framework assembled from parallel inorganic chains with OBA<sup>2-</sup> as the bridging ligands. The inorganic chain is composed of eight Cd(II) ions and can be described as a {Cd5–Cd4–Cd8–Cd1–Cd6–Cd2–Cd7–Cd3}<sub>n</sub> chain. When viewed from the *c*-axis, every such Cd chain is connected by OBA<sup>2-</sup> ligands to other four Cd chains with reversed sequence, to construct a 3D chiral microporous metal-organic framework (Fig. 1).

To further determine the absolute configurations of the enantiomers, the solid-state CD spectra for **1L** and **1D** were measured. The bulk samples of **1L** and **1D** display approximate mirror-image curves in the region of 200–500 nm, showing that they are enantiomers of each other (Fig. S3). This result is in good agreement with the structures determined by single

crystal X-ray diffraction. The XRD of **1L** and **1D** were recorded to check the phase purity. The experimental data matches well with the simulated XRD pattern, indicating the phase purity of the as-synthesized samples (Fig. S4). The thermal stabilities of **1L** and **1D** were examined by thermogravimetric analysis. The TGA curve of **1L** indicates that there is no obvious mass change from room temperature to 150°C. The L-HAPA<sup>+</sup> cations are lost from 150 to 300°C, followed by decomposition of the framework (Fig. S5).

Enlightened by the fact that the cationic Me<sub>2</sub>NH<sub>2</sub><sup>+</sup> molecules can be readily exchanged by metal cations and some cationic organic molecules,<sup>4, 10</sup> and there are chiral zigzag channels along *b* axis of about 5.15 × 10.74 Å<sup>2</sup> in this compound, we try to examine the potential of **1L** to encapsulate the cations of NLO chromophore 4-nitroaniline and some chiral alkamine molecules (Scheme S1) to improve the SHG activity of **1L**. Firstly, compound **1L** was soaking in an ethanol solution containing Li<sup>+</sup> ions for 24 h, and this process was repeated three times with fresh Li<sup>+</sup>-ethanol solution to afford Li<sup>+</sup>@**1L**. The content of Li<sup>+</sup> was approximate 76.1% as measured by ICP-AES. Immersion of Li<sup>+</sup>@**1L** in ethanol solutions containing organic cations generated by protonation of 4-nitroaniline and chiral alkamines with acetic acid for 5 days gives HA<sup>+</sup>@**1L**, L-HPA<sup>+</sup>@**1L** and L-HPG<sup>+</sup>@**1L** (A = 4-nitroaniline; L-PA = L-phenylalaninol and L-PG = L-phenylglycinol). Compared to Me<sub>2</sub>NH<sub>2</sub><sup>+</sup>, Li<sup>+</sup> ions are more likely to be exchanged with these organic cations. Therefore, the contents of the organic cations in the channels of **1** can be estimated to be approximately 5.9, 12.1 and 12.7% for HA<sup>+</sup>, L-HPA<sup>+</sup> and L-HPG<sup>+</sup>, respectively, based on the reduced amount of Li<sup>+</sup> in **1L** after ion-exchange. All these inclusion compounds are highly crystalline materials which retain the original crystal structure of **1L**, as confirmed by XRD patterns (Fig. S4). The CD spectra of HA<sup>+</sup>@**1L**, L-PAH<sup>+</sup>@**1L** and L-HPG<sup>+</sup>@**1L** are nearly the same as that of **1L**, suggesting that the inclusion compounds have the same configuration as that of **1L** (Fig. S3).

Second-harmonic generation (SHG) measurements with the sieved powder samples of **1L** (100–150 μm) indicate that it displays a macroscopic SHG response approximately 0.5 times as that of the powder KH<sub>2</sub>PO<sub>4</sub> (KDP) and is phase-matchable (Fig. S7). Interestingly, the SHG response of HA<sup>+</sup>@**1L**, L-HPA<sup>+</sup>@**1L** and L-HPG<sup>+</sup>@**1L** is 1.2, 3.2 and 5.1 times that of KDP, suggesting that the NLO property of **1L** is distinctly enhanced by encapsulation of organic cations (Fig. 2a). We speculate that the high polarity and the π-conjugated push-pull character of 4-nitroaniline molecules are responsible for the enhancement of SHG effect. As for L-HPA<sup>+</sup>@**1L** and L-HPG<sup>+</sup>@**1L**, the increase of SHG should be attributed to the chirality of guest alkaminium cations which increase the overall polarity of the frameworks. The reason why the SHG intensity of HA<sup>+</sup>@**1L** is smaller than that of L-HPA<sup>+</sup>@**1L** and L-HPG<sup>+</sup>@**1L** could be due to the less content of 4-nitrobenzenaminium cations in **1L** compared to that of the alkaminium cations. In order to verify this point, we control the ion-exchange process so that the amount of guest L-HPA<sup>+</sup> and L-HPG<sup>+</sup> cations in **1L** is close to that of HA<sup>+</sup> (5.9%). The resultant three compounds indeed show approximately the same SHG efficiency (Fig. S8). For L-

HPA<sup>+</sup>@1L, the SHG effect increases with particle size and plateaus at a maximum value when the particle size is large enough, revealing the phase-matching behaviour (Fig. 2b).

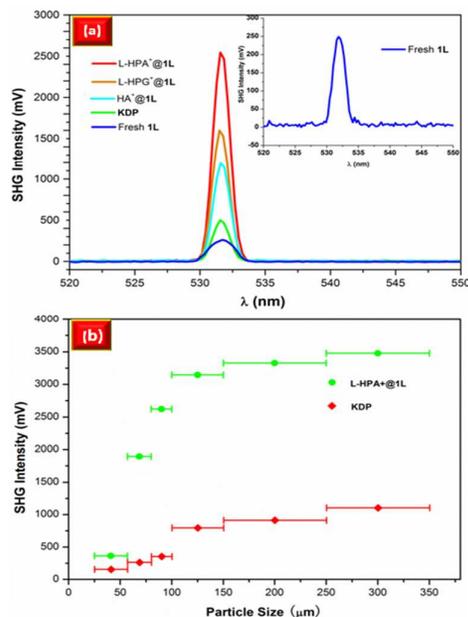


Fig. 2 (a) The SHG response of fresh 1L, HA<sup>+</sup>@1L, L-HPA<sup>+</sup>@1L, L-HPG<sup>+</sup>@1L and KDP. (b) Particle size dependence of the SHG intensity for L-HPA<sup>+</sup>@1L and KDP.

The ability of **1** to include organic cations by ion-exchange prompts us to explore the potential of **1** as enantioselective sensor for chiral alkalines. In principle, the chiral channels of **1L** should favour L-alkalines over D-alkalines. Thus, samples of Li<sup>+</sup>@1L were immersed in ethanol solutions containing cations of D-phenylalaninol and D-phenylglycinol respectively for five days to generate D-HPA<sup>+</sup>@1L and D-HPG<sup>+</sup>@1L. The ICP-AES results indicate that the contents of the D-alkaluminium cations in D-HPA<sup>+</sup>@1L and D-HPG<sup>+</sup>@1L are 0.23 and 0.27%, respectively, both of which are much less than those of the corresponding L-alkaluminium cations. In comparison with L-HPA<sup>+</sup>@1L and L-HPG<sup>+</sup>@1L, the SHG intensity of D-HPA<sup>+</sup>@1L and D-HPG<sup>+</sup>@1L is much smaller (Fig. 3). Thus, we can identify the absolute configuration of alkalines by combining chiral recognition of the anionic homochiral frameworks with NLO properties. It is worthy noting that SHG measurement is first utilized for enantioselective sensing of chiral molecules.

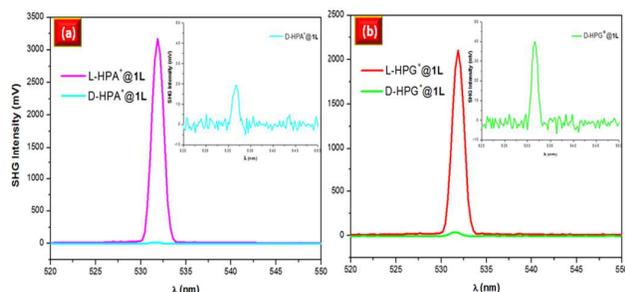


Fig. 3 (a) The SHG response of L-HPA<sup>+</sup>@1L and D-HPA<sup>+</sup>@1L. (b) The SHG response of L-HPG<sup>+</sup>@1L and D-HPG<sup>+</sup>@1L.

In summary, the homochiral crystallizations of two anionic enantiomeric metal-organic frameworks built from achiral components were achieved by using enantiopure L- or D-APA as chiral inducing agents. The protonated L- or D-APA species act as counter cations in the microporous channels which can be exchanged with  $\pi$ -conjugated organic cations, resulting in a significant improvement of the SHG efficiency. Furthermore, enantioselective sensing of chiral alkalines was first realized by combining the chiral recognition and SHG response of the anionic homochiral framework.

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## Notes and references

- (a) C. Chen, G. Liu, *Annu. Rev. Mater. Sci.*, 1986, **16**, 203; (b) H. S. Nalwa, *Appl. Organomet. Chem.*, 1991, **5**, 349; (c) S. R. Marder, J. W. Perry, C. P. Yakymyshyn, *Chem. Mater.*, 1994, **6**, 1137; (d) D. Burland, *Chem. Rev.*, 1994, **94**, 1; (e) M. Fiebig, V. V. Pavlov, R. V. Pisarev, *J. Opt. Soc. Am. B*, 2005, **22**, 96; (f) C. P. Shunemann, *Proc. SPIE-Int. Soc. Opt. Eng.* 2007, **6455**, 64550R-1; (g) S. Banerjee, C. D. Malliakas, J. I. Jang, J. B. Ketterson, M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2008, **130**, 12270; (h) T. K. Bera, J. I. Jang, J. B. Ketterson, M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2009, **131**, 75; (i) Q. Zhang, I. Chung, J. I. Jang, J. B. Ketterson, M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2009, **131**, 9896; (j) M. A. van der Veen, T. Verbiest, D. E. De Vos, *Microporous Mesoporous Mater.*, 2013, **166**, 102.
- (a) C. T. Chen, Y. B. Wang, B. C. Wu, K. C. Wu, W. L. Zeng and L. H. Yu, *Nature*, 1995, **373**, 322; (b) P. Becker, *Adv. Mater.*, 1998, **10**, 979; (c) J. H. Liao, G. M. Marking, K. F. Hsu, Y. Matsushita, M. D. Ewbank, R. Borwick, P. Cunningham, M. J. Rosker and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2003, **125**, 9484; (d) Q. Zhang, I. Chung, J. I. Jang, J. B. Ketterson and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2009, **131**, 9896.
- (a) O. R. Evans, W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; (b) O. R. Evans and W. B. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; (c) S. P. Anthony, K. Basavaiah and T. P. Radhakrishnan, *Cryst. Growth Des.*, 2005, **5**, 1663; (d) Q. Ye, Y. M. Song, G. X. Wang, K. Chen, D. W. Fu, P. W. H. Chan, J. S. Zhu, S. D. Huang and R. G. Xiong, *J. Am. Chem. Soc.*, 2006, **128**, 6554; (e) C. Wang, T. Zhang, W. Lin, *Chem. Rev.*, 2012, **112**, 1084; (f) S. Dang, J. H. Zhang, Z. M. Sun and H. J. Zhang, *Chem. Commun.*, 2012, 48, 11139; (g) H. B. Zhang, P. Lin, X. C. Shan, F. L. Du, Q. P. Li and S. W. Du, *Chem. Commun.*, 2013, **49**, 2231; (h) Y. H. Han, C. B. Tian, Q. H. Li and S. W. Du, *J. Mater. Chem. C*, 2014, **2**, 8065.
- J. C. Yu, Y. J. Cui, C. D. Wu, Y. Yang, Z. Y. Wang, M. O. Keeffe, B. L. Chen and G. D. Qian, *Angew. Chem. Int. Ed.*, 2012, **51**, 10542.
- (a) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (b) L. Ma, C. Abney and W. B. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248; (c) S. M. Xie, Z. J. Zhang, Z. Y. Wang and L. M. Yuan, *J. Am. Chem. Soc.*, 2011, **133**, 11892; (d) W. Zhang and R. G. Xiong, *Chem. Rev.*, 2012, **112**,

- 1163; (e) Y. Liu, W. M. Xuan and Y. Cui, *Adv. Mater.*, 2010, **22**, 4112; (f) M. Zhao, S. Ou and C. D. Wu, *Acc. Chem. Res.*, 2014, **47**, 1199; (g) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196; (h) J. Zhang, S. M. Chen, A. Zingiryan and X. H. Bu, *J. Am. Chem. Soc.*, 2008, **130**, 17246; (i) X. Jing, C. He, D. P. Dong, L. L. Yan and C. Y. Duan, *Angew. Chem., Int. Ed.*, 2012, **51**, 10127; (j) Z. G. Gu, S. Grosjean, S. Bräse, C. Wöll and L. Heinke, *Chem. Commun.*, 2015, **51**, 8998.
- 6 (a) B. Kesanli and W. Lin, *Coord. Chem. Rev.*, 2003, **246**, 305; (b) C.-D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940; (c) R.-G. Xiong, X.-Z. You, B. F. Abrahams, Z. Xue and C.-M. Che, *Angew. Chem., Int. Ed.*, 2001, **40**, 4422; (d) E. V. Anokhina, Y. B. Go, Y. Lee, T. Vogt and A. J. Jacobson, *J. Am. Chem. Soc.*, 2006, **128**, 9957; (f) D. N. Dybtsev, A. L. Nuzhdin, H. Chun, K. P. Bryliakov, E. P. Talsi, V. P. Fedin and K. Kim, *Angew. Chem., Int. Ed.*, 2006, **45**, 916.
- 7 (a) L. Pe'rez-García and D. B. Amabilino, *Chem. Soc. Rev.*, 2002, **31**, 342; (b) Y. H. Han, C. B. Tian and S. W. Du, *Dalton Trans.*, 2014, **43**, 11461; (c) H. B. Zhang, S. T. Wu, C. B. Tian, Z. J. Lin, Z. H. Li, P. Lin and S. W. Du, *CrystEngComm*, 2012, **14**, 4165; (d) Y. H. Han, C. B. Tian and S. W. Du, *Dalton Trans.*, 2014, **43**, 11461; (e) K. K. Bisht and E. Suresh, *J. Am. Chem. Soc.*, 2013, **135**, 15690; (f) K. K. Bisht and E. Suresh, *Inorg. Chem.*, 2012, **51**, 9577 (g) J. Su, L. D. Yao, M. Zhao, H. Wang, Q. Zhang, L. J. Cheng, J. Zhang, S. Y. Zhang, J. Y. Wu and Y. P. Tan, *Inorg. Chem.*, 2015, **54**, 6169 (h) S. M. Chen, J. Zhang and X. H. Bu, *Inorg. Chem.*, 2009, **48**, 6356 (i) S. A. Yuan, Y. K. Deng, W. M. Xuan, X. P. Wang, S. N. Wang, J. M. Dou and D. Sun, *CrystEngComm*, 2014, **16**, 3829.
- 8 R. E. Morris, and X. H. Bu, *Nat. Chem.*, 2010, **2**, 353.
- 9 (a) Z. Lin, A. M. Z. Slawin and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 4880; (b) J. Zhang, S. M. Chen, T. Wu, P. Y. Feng and X. H. Bu, *J. Am. Chem. Soc.*, 2008, **130**, 12882; (c) Y. Kang, S. M. Chen, F. Wang, J. Zhang and X. H. Bu, *Chem. Commun.*, 2011, **47**, 4950; (d) N. Chen, M. X. Li, P. Yang, X. He, M. Shao and S. R. Zhu, *Cryst. Growth Des.*, 2013, **13**, 2650.
- 10 (a) T. G. Douglas, G. W. F. Antek, J. M. Adam and S. S. Melanie, *J. Am. Chem. Soc.*, 2013, **135**, 10586; (b) J. C. Yu, Y. J. Cui, H. Xu, Y. Yang, Z. Y. Wang, B. L. Chen and G. D. Qian, *Nat. Chem.*, 2013, **4**, 2019; (c) S. Masaaki, K. Hidetaka, K. Kenichi, T. Masaki and Y. Miho, *J. Am. Chem. Soc.*, 2014, **136**, 1702.