Achievement of Bulky Homochirality in Zeolitic Imidazolate-Related Frameworks

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S Supporting Information

ABSTRACT: Before this work, adding chiral C centers into zeolitic imidazolate frameworks (ZIFs) has never been realized. Presented here are the first examples on achieving bulky homochirality in ZIF systems, and three homochiral zeolitic imidazolate-related frameworks with sodalite and dia topologies are successfully synthesized by employing enantiopure imidazolate derivatives. The results open a new blueprint on the synthetic design of homochiral ZIFs for future applications.

norganic zeolites and zeolitic metal–organic frameworks (MOFs) have received much attention in recent years owing to their fascinating tetrahedral structures, high stability, and wide potential applications in various areas, such as gas adsorption and separation, luminescence, catalysis, and so on.¹⁻⁶ Among them, zeolitic imidazolate frameworks (ZIFs) built from tetrahedrally coordinated divalent cations $(M^{2+} = Zn^{2+} \text{ or } Co^{2+})$ and uninegative imidazolate ligands are of special merit in the employment of various imidazolate derivatives.^{2,3} It is commonly known to add a chiral C center in the organic ligand, so that the homochiral MOFs with such enantiopure ligands may be generated for special enantioselective applications, which are not available with pure inorganic zeolites. Despite the fact that it is not difficult to make enantiopure imidazolate ligands, so far homochiral ZIFs based on enantiopure imidazolate ligands have never been reported.

In this work, two presynthesized enantiopure imidazolate derivatives, (S)-2-(1-hydroxyethyl)benzimidazole [(S)-OHbim] and (R)-2-(1-hydroxyethyl)benzimidazole [(R)-OHbim], have been used to realize a pair of homochiral zeolitic imidazolate-related frameworks (HZIrFs) with sodalite (SOD) topology for the first time. The successful achievement of bulky homochirality and zeotype structures in these HZIrFs is dependent on not only the addition of a chiral C center to a benzimidazole ligand but also the help of another Smethyltetrazole (5-Hmtz) ligand (Scheme 1).^{4e} Moreover, the combining assembly of enantiopure OH-bim, achiral 5-Hmtz,





and tetrahedral Zn²⁺ ion under different conditions leads to structural diversity. Both SOD- and dia-type frameworks have been obtained. Thus, we report here the details of these HZIrFs, namely, $Zn_2(5-mtz)_3[(R)-OH-bim]\cdot DMF$ (HZIrF-1R; DMF = *N*,*N*-dimethylformamide), $Zn_2(5-mtz)_3[(S)-OH-bim]\cdot DMF$ (HZIrF-1S), and dia-type $Zn_2(5-mtz)_3[(R)-OH-bim]\cdot DMF$ (HZIrF-2R).

Colorless crystals of HZIrF-1 were solvothermally synthesized by the self-assembly of $Zn(CH_2COO)_2 \cdot 2H_2O$, 5-Hmtz, and (S)-OH-bim [or(R)-OH-bim] in a mixed DMF and ethanol solvent. Both HZIrF-1S and HZIrF-1R crystallize in the space group of R3 with opposite absolute configuration. In the structure of HZIrF-1R, each Zn²⁺ center has tetrahedral geometry and is coordinated by three N atoms from three 5-mtz ligands and one N atom from the (*R*)-OH-bim ligand (Figure 1a). Either the 5mtz or (R)-OH-bim ligand is a μ_2 -linker similar to 2methylimidazole in ZIF-8. A similar coordination environment is presented in HZIrF-1R (Figure 1b). It is notable that the -OH group in the (R)-OH-bim ligand has weak interactions with the Zn^{2+} center. A cage (4⁶·6⁴) substructure consisting of 24 Zn atoms, 9 (R)-OH-bim ligands, and 27 5-mtz ligands is observed (Figure 1c), which is a typical SOD cage with 4- and 6-membered rings (Figure 1d).8 The 4-ring windows are blocked by the substitutes of OH-bim and 5-mtz, just leaving 6-ring windows with an effective size of about 3.3 Å (Figure S1). Each (R)-OHbim bridges two Zn centers, with the Zn…Zn distance being 5.854 Å, and the Zn…Zn distances separated by 5-mtz are from 6.084 to 6.170 Å. The bond angle of Zn–OH-bim–Zn is ca. 138°, and the bond angles of Zn-mtz-Zn are ca. 153° and 157°. As a result, both enantiopure and achiral ligands link the tetrahedral Zn centers into a three-dimensional (3D) framework with SOD topology (Figure 1e,f). The solvent-accessible volume of ca. 44.1% of the crystal volume was found by the PLATON program.⁹ These voids were filled by the structurally ordered DMF molecules.

With additional HBF₄ in the synthesis system of HZIrF-1, another dia-type HZIrF-2R was obtained. This result reveals that the pH plays an important role in tuning the structures of HZIrFs. HZIrF-2R crystallizes in monoclinic C2 and shows a 3D open framework with dia topology. The coordination environment in HZIrF-2R is very similar to that in HZIrF-1R, where the tetrahedral Zn centers are connected by the μ_2 -5-mtz and μ_2 -(*R*)-OH-bim ligands (Figure 2a). A typical cage substructure including 10 Zn atoms, 3 (*R*)-OH-bim ligands, and 9 5-mtz

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Figure 1. Coordination environment in **HZIrF-1R** (a) and **HZIrF-1S** (b). SOD cage of **HZIrF-1R** (c and d). 3D framework of **HZIrF-1R** (e) and SOD topology (f) along the *c* axis.



Figure 2. (a) Coordination environment in HZIrF-2R. (b) Cage in HZIrF-2R. (c) 3D framework of HZIrF-2R along the c axis. (d) dia topology of HZIrF-2R.

ligands is presented (Figure 2b). The different spatial arrangements of these ligands around Zn centers make a totally different framework of HZIrF-2R (Figure 2c,d). The one-dimensional channels along the *c* axis are filled by the structurally defined DMF molecules. The effective window size is about 4.5×5.0 Å.

The total potential solvent-accessible volume is ca. 910 Å³ per unit cell volume, and the pore volume ratio is 32.9%, as calculated with the *PLATON* program.

To characterize the porosity of HZIrF-1R and HZIrF-2R, methanol-exchanged samples were degassed by supercritical CO_2 , and N_2 gas sorption experiments at 77 K on the activated samples were measured. For HZIrF-1R, it has only ca. 31 cm³/g N_2 uptake at 77 K (Figure S8), although it has 44.1% of solvent-accessible volume, which may be mainly attributed to the narrow window size. Further, CO_2 gas sorption experiments at 195 K were also measured, and it exhibits typical type I reversible sorption isotherms and takes up CO_2 to 220 cm³/g, corresponding to Langmuir and Brunauer–Emmett–Teller (BET) surface areas of 1082 and 1026 m²/g, respectively (Figure 3). A single data point at a relative pressure of 0.95 gives a



Figure 3. Sorption isotherms for HZIrF-1R and HZIrF-2R at different temperatures. CO_2 uptake for HZIrF-1R at (a) 195, (b) 273, and (c) 293 K. N_2 uptake for HZIrF-2R at 77 K (d). Solid symbols represent adsorption, and open symbols represent desorption.

maximun pore volume of $0.26 \text{ cm}^3/\text{g}$ by the Horvath–Kawazoe equation. For HZIrF-2R, N₂ gas sorption experiments at 77 K were measured, and it exhibits type I reversible sorption isotherms with a little hysteresis, corresponding to Langmuir and BET surface areas of 415 and 285 m²/g, respectively. A single data point at a relative pressure of 0.98 gives a maximun pore volume of 0.16 cm³/g by the Horvath–Kawazoe equation. The hysteresis loop of HZIrF-2R existed mainly because the samples were partly amorphous after being degassed (Figure S7).

The adsorption isotherms of CO₂ for HZIrF-1R were also measured up to 1 bar at 273 and 293 K (Figure 3). The CO₂ uptake values were 73 cm³/g (3.84 mmol/g) at 273 K and 40 cm³/g (2.75 mmol/g) at 293 K. In comparison, the CO₂ uptake value of the SOD-type MAF-4 was only 29.3 cm³/g at the same conditions.^{2c} The isosteric heats of adsorption (Q_{st}) for HZIrF-IR was calculated using the adsorption data collected at 273 and 293 K. At zero coverage, the enthalpy of CO₂ adsorption for HZIrF-1R is 23 kJ/mol (Figures S9 and S10), also higher than that of MAF-4 (14.9 kJ/mol). The results show that the uncoordinated N-heteroatom sites of tetrazole ligands may remarkably increase the uptake and enthalpy of CO₂. Furthermore, the CO₂ uptake capacity of HZIrF-1R is also higher than that of the currently best-performing ZIF-69 (70 cm³/g) under the same conditions (273 K and 1 atm).^{2c}

The enantiopure environments within **HZIrF-1R** motivated us to explore its potential for chiral recognition. Considering the small window size of HZIrF-1R (ca. 3.3 Å) and the rich H-bond environment of the surface, it can be used to recognize the chiral molecules, e.g., carvone including carbonyl O atom as the H-bond acceptor, although carvone molecules can hardly enter the pores. So, we just used the as-synthesized crystal samples (average size of 0.1 mm) without guest exchange to do such experiments. A solution of D-carvone and L-carvone in an ethanol solvent with the same concentration (10^{-3} mol/L) and amount (1.5 mL) was placed in the cell. Then the same amounts of the as-synthesized samples of HZIrF-1R were added, and the circular dichroism (CD) signal was recorded. As shown in Figure 4, the intensity of



Figure 4. Enantioselective recognition of carvone in ethanol solutions.

L-carvone decreased more drastically than that of D-carvone by using the same amount of the HZIrF-1R samples, although the CD intensity of both solutions decreased with increasing HZIrF-1R samples. This may mean that the interactions between the HZIrF-1R samples and L-carvone are stronger than those of Dcarvone. This result suggests that HZIrF-1R shows a different recognition ability to D-carvone and L-carvone.

In summary, we first achieved the homochiral construction of ZIFs and present here three HZIrFs with SOD and dia topologies. The results open a new blueprint on the synthetic design of homochiral ZIFs for future applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02337.

Experimental details, TGA diagrams, powder X-ray diffractions, sorption isotherms, and CD, UV–vis, and FT-IR spectra (PDF) CIF file (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Gier, T. E.; Bu, X.; Feng, P.; Stucky, G. D. Nature 1998, 395, 154-157. (b) Li, H. L.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. Science 1999, 283, 1145–1147. (c) Cooper, E. R.; Andrews, C. D.; Wheatley, P. S.; Webb, P. B.; Wormald, P.; Morris, R. E. Nature 2004, 430, 1012-1016. (d) Feng, P. Y.; Bu, X. H.; Zheng, N. F. Acc. Chem. Res. 2005, 38, 293-303. (e) Yu, J. H.; Xu, R. R. Acc. Chem. Res. 2010, 43, 1195-1204. (f) Morris, R. E.; Cejka, J. Nat. Chem. 2015, 7, 381-388. (g) Lin, H. Y.; Chin, C. Y.; Huang, H. L.; Huang, W. Y.; Sie, M. J.; Huang, L. H.; Lee, Y. H.; Lin, C. H.; Lii, K. H.; Bu, X.; Wang, S. L. Science 2013, 339, 811-813. (2) (a) Tian, Y. Q.; Cai, C. X.; Ren, X. M.; Duan, C. Y.; Xu, Y.; Gao, S.; You, X. Z. Chem. - Eur. J. 2003, 9, 5673-5685. (b) Huang, X.-C.; Lin, Y.-Y.; Zhang, J. P.; Chen, X.-M. Angew. Chem., Int. Ed. 2006, 45, 1557-1559. (c) Zhang, J.-P.; Zhu, A.-X.; Lin, R.-B.; Qi, X.-L.; Chen, X.-M. Adv. Mater. 2011, 23, 1268-1271. (d) Zhang, J.-P.; Zhang, Y.-B.; Lin, J.-B.; Chen, X.-M. Chem. Rev. 2012, 112, 1001-1033. (e) He, C. T.; Jiang, L.; Ye, Z. M.; Krishna, R.; Zhong, Z. S.; Liao, P. Q.; Xu, J.; Ouyang, G.; Zhang, J. P.; Chen, X. M. J. Am. Chem. Soc. 2015, 137, 7217-7220.

(3) (a) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Science* **2008**, *319*, 939–943. (b) Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2010**, *43*, 58–67.

(4) (a) Zhang, J.; Wu, T.; Zhou, C.; Chen, S.; Feng, P.; Bu, X. Angew. Chem., Int. Ed. 2009, 48, 2542–2545. (b) Wu, T.; Zhang, J.; Zhou, C.; Wang, L.; Bu, X.; Feng, P. J. Am. Chem. Soc. 2009, 131, 6111–6113. (c) Zhang, H. X.; Wang, F.; Yang, H.; Tan, Y. X.; Zhang, J.; Bu, X. J. Am. Chem. Soc. 2011, 133, 11884–11887. (d) Wang, F.; Liu, Z. S.; Yang, H.; Tan, Y. X.; Zhang, J. Angew. Chem., Int. Ed. 2011, 50, 450–453. (e) Wang, F.; Fu, H.-R.; Kang, Y.; Zhang, J. Chem. Commun. 2014, 50, 12065– 12068.

(5) (a) Liu, Y. L.; Kravtsov, V. C.; Larsen, R.; Eddaoudi, M. Chem. Commun. 2006, 1488–1490. (b) Nouar, F.; Eckert, J.; Eubank, J. F.; Forster, P.; Eddaoudi, M. J. Am. Chem. Soc. 2009, 131, 2864–2870.
(c) Zheng, S.; Zuo, F.; Wu, T.; Irfanoglu, B.; Chou, C.; Nieto, R. A.; Feng, P.; Bu, X. Angew. Chem., Int. Ed. 2011, 50, 1849–1852.

(6) (a) Li, P.; He, Y.; Zhao, Y.; Weng, L.; Wang, H.; Krishna, R.; Wu, H.; Zhou, W.; O'Keeffe, M.; Han, Y.; Chen, B. Angew. Chem., Int. Ed. 2014, 54, 574-577. (b) Zhang, Y.-B.; Furukawa, H.; Ko, N.; Nie, W.; Park, H. J.; Okajima, S.; Cordova, K. E.; Deng, H.; Kim, J.; Yaghi, O. M. J. Am. Chem. Soc. 2015, 137, 2641-2650. (c) Xiong, W. W.; Miao, J.; Ye, K.; Wang, Y.; Liu, B.; Zhang, Q. Angew. Chem., Int. Ed. 2014, 54, 546-550. (d) Zhai, Q.-G.; Lin, Q.; Wu, T.; Wang, L.; Zheng, S.; Bu, X.; Feng, P. Chem. Mater. 2012, 24, 2624-2626. (e) Zhang, X.; Liu, W.; Wei, G. Z.; Banerjee, D.; Hu, Z.; Li, J. J. Am. Chem. Soc. 2014, 136, 14230-14236. (f) Liu, T.-F.; Feng, D.; Chen, Y.-P.; Zou, L.; Bosch, M.; Yuan, S.; Wei, Z.; Fordham, S.; Wang, K.; Zhou, H.-C. J. Am. Chem. Soc. 2015, 137, 413-419. (g) Feng, D.; Wang, K.; Su, J.; Liu, T.-F.; Park, J.; Wei, Z.; Bosch, M.; Yakovenko, A.; Zou, X.; Zhou, H.-C. Angew. Chem., Int. Ed. 2015, 54, 149-154. (h) Lu, H. S.; Bai, L.; Xiong, W. W.; Li, P.; Ding, J.; Zhang, G.; Wu, T.; Zhao, Y.; Lee, J. M.; Yang, Y.; Geng, B.; Zhang, Q. Inorg. Chem. 2014, 53, 8529-8537. (i) Gao, J.; Ye, K.; Yang, L.; Xiong, W.-W.; Ye, L.; Wang, Y.; Zhang, Q. Inorg. Chem. 2014, 53, 691-693.

(7) (a) Kim, K.; Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. Nature 2000, 404, 982–986. (b) Morris, R. E.; Bu, X. Nat. Chem. 2010, 2, 353–361. (c) Ma, L.; Falkowski, J. M.; Abney, C.; Lin, W. Nat. Chem. 2010, 2, 838–846. (d) Wanderley, M. M.; Wang, C.; Wu, C.-D.; Lin, W. J. Am. Chem. Soc. 2012, 134, 9050–9053. (e) Zhao, M.; Ou, S.; Wu, C.-D. Acc. Chem. Res. 2014, 47, 1199–1207. (f) Yoon, M.; Srirambalaji, R.; Kim, K. Chem. Rev. 2012, 112, 1196–1231. (g) Mo, K.; Yang, Y.; Cui, Y. J. Am. Chem. Soc. 2014, 136, 1746–1749.

(8) Blatov, V. A. Struct. Chem. 2012, 23, 955-963.

(9) Van der Sluis, P.; Spek, A. L. Acta Crystallogr., Sect. A: Found. Crystallogr. **1990**, 46, 194–201.