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Synthesis of an Enantipure Tetrazole-Based Homochiral $Cu^{I,II}$-MOF for Enantioselective Separation

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Supporting Information

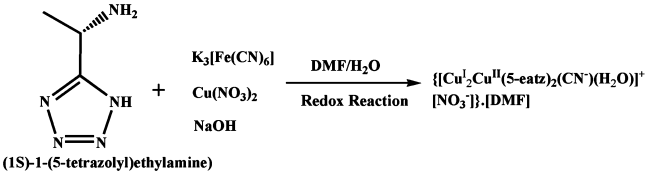
ABSTRACT: An enantipure (1*S*)-1-(5-tetrazolyl)-ethylamine (5-eatz) ligand was first employed to construct a homochiral porous metal−organic framework, $\{[Cu^{I}_2Cu^{II}(5\text{-eatz})_2(CN^-)(H_2O)]^+[NO_3^-]\}\cdot[DMF]$ (**1**), with unusual ligand-unsupported Cu···Cu interactions. Such a compound shows high stability in water and common organic solvents. Remarkably, it has high enantioselectivity toward (*R*,*S*)-1-phenylethanol and (*R*,*S*)-1-phenylpropanol with enantiomeric excess values of up to 42% and 48%, respectively.

In recent years, homochiral metal−organic frameworks (MOFs) have emerged as ideal platforms for enantiomer separation and asymmetric catalysis because of their high porosity, size, and shape selectivity.[1−4] Basically, the combination of porosity and chirality is not on its own enough to enable strong enantioselectivity. To design homochiral MOFs as enantioselective adsorbents, the driving force to efficiently discriminate two opposite enantiomers should be considered.[5,6] A homochiral MOF should have chiral recognition sites that can work synergistically to induce enantioselective separation.[7,8] Thus, the synthesis of a desired homochiral MOF for efffciently enantioselective separation should consider the interactions between the chiral framework and chiral guests.

In this work, we choose an enantipure tetrazole[9] to assemble with a Cu ion, targeting a homochiral MOF, $\{[Cu^{I}_2Cu^{II}(5\text{-eatz})_2(CN^-)(H_2O)]^+[NO_3^-]\}\cdot[DMF]$ [**1**; 5-eatz = (1*S*)-1-(5-tetrazolyl)ethylamine], for enantioselective separation of racemic alcohols. Compound **1** has 1D channels, and it can effectively separate racemic 1-phenylethanol or 1-phenylpropanol. Moreover, it can be readily recycled and reused without any apparent loss of performance.

The purple crystals of **1** were solvothermally synthesized at 100 °C for 2 days with a mixture of 5-eatz, NaOH, $K_3[Fe(CN)_6]$, and $Cu(NO_3)_2$ in the mixed solvent of DMF, H_2O, and EtOH (Scheme 1). Here, $K_3[Fe(CN)_6]$ can dissociate CN^-, which is a bridging ligand in compound **1**. The structure and composition of **1** were characterized by single-crystal X-ray diffraction and elemental analyses. Its phase purity and thermal stability were studied by powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA), respectively. Compound **1** presents good stability in aqueous solution and other organic solvents (Figure S1).

Scheme 1. Synthesis Route of Compound 1



Compound **1** crystallizes in the tetragonal space group $P2_12_12_1$. There are three Cu ions, two 5-eatz ligands, one CN^-, one H_2O molecule, and a NO_3^- in the asymmetric unit. Both Cu^I and Cu^{II} exist in the structure, which can be proven by the X-ray photoelectron microscopy pattern (Figure S2). Cu^I1 and Cu^I3 show three-coordinate modes, while $Cu^{II}2$ has an octahedral geometry (Figure 1a). Cu^I1 (or Cu^I3) is coordinated by two 5-eatz ligands and a CN^- ligand. The octahedral $Cu^{II}2$ is chelated by two 5-eatz ligands and coordinated by one NO_3^- and one H_2O molecule (Figure 1a). The $Cu^{II}(5\text{-eatz})_2$ subunits are connected to a Z-type chain by two Cu^I ions. The resulting chains are further linked into a layer by CN^- ligands (Figure 1b). Finally, the wavelike layers are connected into a 3D framework by

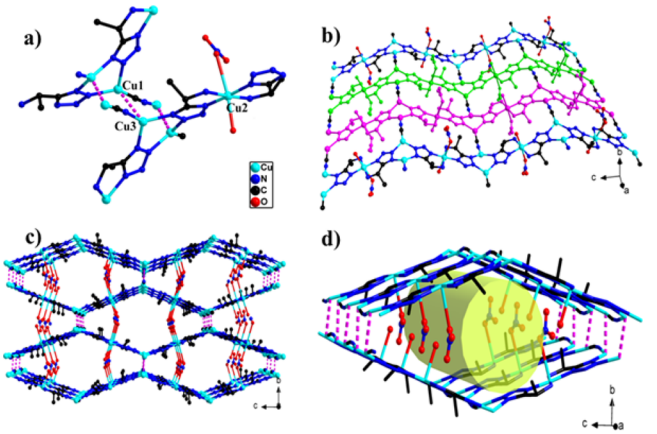


Figure 1. (a) Coordination environment of **1**. (b) Wave layer in **1**. The green and violet colors highlight the Z-type chains. (c) 3D framework of **1** with 1D channels along the *a* axis. (d) Clear presentation of NO_3^- and H_2O molecules in the channel.

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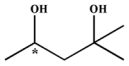
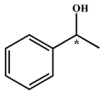
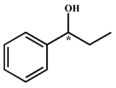
ligand-unsupported Cu···Cu interactions. Strong Cu···Cu interactions, with a distance of 2.695 Å, are observed between the layers. The 3D framework of **1** shows 1D channels along the *a* axis. The size of each channel is ca. 8.0 Å × 7.0 Å (Figure 1c). To emphasize, there are NO_3^- and H_2O molecules hanging along the wall of the 1D pore, which can form hydrogen bonding with the guest (Figure 1d). The void volume of the pores was calculated using *PLATON* to be 27% of the unit cell volume. The CO_2 gas adsorption was measured to evaluate the porosity of **1**. The adsorption isotherm curves show that **1** can take up 30, 40, and 92 $cm^3\ g^{-1}$ CO_2 gas at 292, 273, and 195 K, respectively (Figure S3). The low adsorption capacities indicate that **1** has a low superficial area.

Because **1** is a homochiral MOF, the enantioselective separation of 2-butanol, 2-methyl-2,4-pentadiol, (*R*,*S*)-1-phenylethanol, and (*R*,*S*)-1-phenylpropanol was explored (Tables S1–S4). Interestingly, the gas chromatography (GC) results reveal that the enantioselectivity of **1** toward is different from that of aliphatic alcohols. As shown in Table 1, the ee values of aromatic

Table 1. Enantioselective Separation for Racemates at Room Temperature[a]

Entry	Substrate	ee[b], %
1		—
2		—
3		42 (R)
4		48 (R)

[a]For details, see the Experimental Section in the Supporting Information. [b]Determined by GC (letters in brackets specify the preferable isomer), and the deviations for the ee values are less than 5%.

alcohols, (*R*,*S*)-1-phenylethanol and (*R*,*S*)-1-phenylpropanol, released by **1** can reach 42% and 48%, respectively. However, **1** shows low ee percentage values toward 2-butanol and 2-methyl-2,4-pentadiol. The recycle experiments reveal that the enantioselective efficiency maintains the same level with no reduction after four cycles. Meanwhile, the structure of **1** is intact after recycled experiments (Figure 2b).

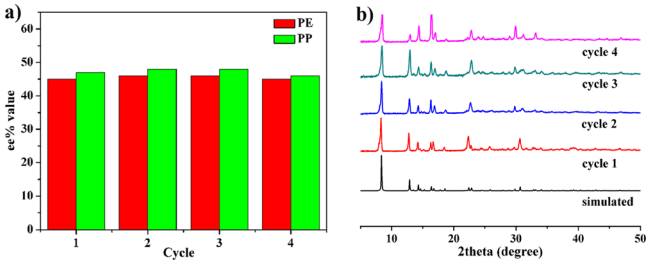


Figure 2. (a) ee values of chiral samples in chiral separation recycled experiments. (b) PXRD patterns of **1** after recycled experiments.

Because the window of the 1D channel is too narrow, access of large molecules is likely impossible. Thus, enantioselective separation may occur on the chiral surface of compound **1**. Thus, the reason why **1** can enantioselectively separate aromatic alcohols but not aliphatic alcohols is comprehensible. For aromatic alcohols, enantioselective separation can be explained by the three-point rule.[7] Interactions between the surface of **1** and aromatic alcohols may include $\pi\cdots\pi$ interaction, hydrogen-bonding interaction, and stereochemical interaction of a chiral carbon. The 5-eatz ligands on the surface of **1** tend to adsorb *R*-configuration aromatic alcohols (Figure 3). For aliphatic

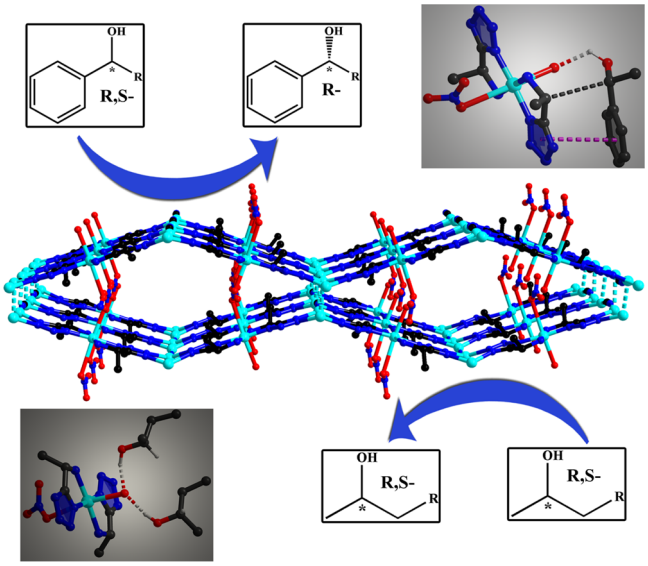


Figure 3. Possible interactions between the chiral framework and chiral aromatic alcohols.

alcohols, the interactions between **1** and the aliphatic alcohols include merely hydrogen bonding, which could not agree with the three-point rule. Thus, the *R* and *S* configurations can both interact with **1** through hydrogen bonding. Finally, no enantioselectivity for aliphatic alcohols can be achieved.

In conclusion, a homochiral MOF with an enantipure 5-eatz ligand and unusual ligand-unsupported Cu···Cu interactions has been successfully synthesized. It has high enantioselectivity toward (*R*,*S*)-1-phenylethanol and (*R*,*S*)-1-phenylpropanol. Also, enantioselectivity is attributed to interactions between the surface of **1** and the aliphatic alcohols.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02514.

Experimental details, TGA diagram, and PXRD (PDF)
CIF file (CCDC 1510073) (CIF)

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Notes

The authors declare no competing financial interest.

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