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ABSTRACT: A homochiral microporous hydrogen-bonded organic framework (HOF-2) based on a BINOL derivative has been synthesized and structurally characterized to be a uninodal 6-connected \{3^56^7\} network. This new HOF exhibits not only a permanent porosity with the BET of 237.6 m² g⁻¹ but also, more importantly, a highly enantioselective separation of chiral secondary alcohols with ee value up to 92% for 1-phenylethanol.

Porous hydrogen-bonded organic frameworks (HOFs)¹² have lagged significantly behind metal–organic frameworks (MOFs)³⁴ in terms of their development on their framework design, topological rationalization, and functional exploration, although the concepts of constructing such porous materials by making use of hydrogen bonding and coordination bonding, respectively, were proposed during the same time period as those of MOFs.⁵,⁶ Such a situation is mainly due to the weaker hydrogen-bonding interactions within HOFs, which are typically not strong enough to stabilize the frameworks and establish their permanent porosities.⁷ It is, therefore, not surprising that only recently a few HOFs have been shown to possess permanent porosities⁸–¹¹ although a large number of HOFs have been structurally characterized and reported in the literature. Nevertheless, it is expected that the establishment of these few porous HOFs will initiate the rebounding interest in the exploration of functional porous HOF materials for their potential applications in gas storage and separation, sensing, and heterogeneous catalysis. Thus, further research endeavors to figure out the basic and strong hydrogen-bonding motifs to stabilize the frameworks, rationalizing that the basic principles for constructing the frameworks of the desired topologies and controlling the pore sizes, dimensions, and functionalities of the porous HOF materials for their diverse applications are warranted. Specifically, new hydrogen-bonding motifs need to be explored for the construction of porous HOFs and examined comprehensively on their universal applicability and feasibility to build a series of expanded HOFs whose pore sizes and functionalities can be systematically tuned and explored for their applications.

The hydrogen-bonding motif of 2,4-diaminotriazinyl (DAT), pioneered by Wuest, is of particular interest for constructing functional porous HOFs.⁶ This motif has recently been utilized not only to assemble a series of structurally porous HOFs¹² but also to achieve the first porous HOF-1 for the highly selective separation of C₂H₂/C₂H₄ at room temperature.⁷ Given the fact that 1,1′-bi-2-naphthol (BINOL) is a very powerful organic backbone for asymmetric induction,¹³,¹⁴ we incorporated the (R)-BINOL scaffold into 2,4-diaminotriazinyl hydrogen-bonding motif to synthesize a new chiral organic building block for the self-assembly of HOFs (Scheme 1).

Scheme 1. Organic Building Block To Build HOF-2

Herein we report the crystal structure of this new homochiral HOF-2 of the uninodal 6-connected \{3^56^7\} network topology. More importantly, this homochiral HOF-2 exhibits highly enantioselective separation of chiral secondary alcohols, with the enantiometric excess (ee) up to 92% for 1-phenylethanol because of the specific recognition of HOF-2 for the 1-phenylethanol molecule.

The chiral organic building block, shown in Scheme 1, can be readily synthesized in 52% yield by reacting known chiral nitrile with dicyandiamide (see Scheme S1 in the Supporting Information [SI]).

Single crystals of HOF-2 suitable for X-ray diffraction study can be easily obtained by slow evaporation of a solution of the organic building block in 2-methoxyethanol at room temperature. The purity of HOF-2 was confirmed by ¹H NMR spectroscopy, thermogravimetric analysis (TGA), and powder X-ray diffraction (PXRD) (Figures S1–S3 in the SI).

The single-crystal X-ray structure of HOF-2 reveals that it crystallizes in a chiral space group P6₅.¹⁶ HOF-2 is a three-dimensional porous material in which each organic building block is connected with six neighboring ones by multiple strong hydrogen bonds (Table S1 in the SI) among the 2,4-
diaminotriazine groups (Figure 1a. Topologically, it can be viewed as a uninodal 6-connected \( \{3^5\{6^7\}\} \) network (Figure 1b). There exist one-dimensional hexagonal pores with a diameter of about 4.8 Å along the \( \epsilon \) axis and (b) the uninodal 6-connected \( \{3^5\{6^7\}\} \) network topology. X-ray crystal structure of HOF-2 featuring (a) multiple hydrogen bonding (light-blue dashed lines) among adjacent units to form three-dimensional hydrogen-bonded organic framework exhibiting 1D hexagonal pores with the diameter of about 4.8 Å along the \( \epsilon \) axis, and (d) the chiral cavities of the framework for the specific recognition of R-1-PEA which is further enforced by the hydrogen-bonding interactions among the –OH groups of R-1-PEA (green molecule) and oxygen atoms of the diethoxy groups from the HOF-2 framework. Comparison of X-ray crystal structures of (e) HOF-2\( \supset \)S-1-PEA and (f) HOF-2\( \supset \)R-1-PEA, indicating the different recognition of the HOF-2 for these two enantiomers (C, gray; H, white; N, pink; O, red).

Figure 1. X-ray crystal structure of HOF-2 featuring (a) multiple hydrogen bonding (light-blue dashed lines) among adjacent units to form three-dimensional hydrogen-bonded organic framework exhibiting 1D hexagonal pores with the diameter of about 4.8 Å along the \( \epsilon \) axis, and (b) the uninodal 6-connected \( \{3^5\{6^7\}\} \) network topology. X-ray single-crystal structure of the 1-PEA included HOF-2, which is prepared by soaking single crystals of the as-synthesized HOF-2 in racemic 1-PEA. The crystal structure clearly indicates that HOF-2 exclusively encapsulates S-1-PEA molecules and oxygen atoms of the diethoxy groups of the HOF-2 framework (d(O3–OH) groups of R-1-PEA). Furthermore, the specific recognition of HOF-2 for the chiral aromatic 1-PEA (ee of 92\%) is remarkable. In fact, HOF-2 is superior to our best demonstrated MOF (ee of 82\%) for such an industrially important separation, given the fact that the chiral secondary alcohols are valuable intermediates in the synthesis of a variety of pharmaceutical, agricultural, and fine chemicals.

Table 1. Resolution of Racemic Secondary Alcohols with HOF-2a at Room Temperaturea

<table>
<thead>
<tr>
<th>entry</th>
<th>secondary alcohols</th>
<th>ee (%)b,c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-phenylethanol</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>1-(4-chlorophenyl)ethanol</td>
<td>79</td>
</tr>
<tr>
<td>3</td>
<td>2-butanol</td>
<td>77</td>
</tr>
<tr>
<td>4</td>
<td>1-(3-chlorophenyl)ethanol</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>2-pentanol</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>2-hexanol</td>
<td>&lt;10</td>
</tr>
<tr>
<td>7</td>
<td>2-heptanol</td>
<td>&lt;4</td>
</tr>
</tbody>
</table>

aSee SI for experimental details. bDetermined by HPLC. cR isomers are preferred.
more importantly, we have also demonstrated the motif for the construction of porous robust HOFs, but even in the near future.

ASSOCIATED CONTENT

Supporting Information
Crystallographic data, TGA, PXRDs, HPLC plots, isotherm fit parameters, gas sorption isotherms, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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REFERENCES