

Host–Guest Chirality Interplay: A Mutually Induced Formation of a Chiral ZMOF and Its Double-Helix Polymer Guests

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Supporting Information

ABSTRACT: A novel homochiral zeolite-like metal–organic framework (ZMOF), [(Cu₄I₄) (dabco)₂]·[Cu₂(bbimb)]·3DMF (**JLU-Liu23**, dabco = 1,4-diazabicyclo[2.2.2]-octane, H₂bbimb = 1,3-bis(2-benzimidazol)-benzene, DMF = *N,N*-dimethylformamide), has been successfully constructed to host unprecedented DNA-like [Cu₂(bbimb)]_n polymers with double-helicity. The host–guest chirality interplay permitted the induced formation of an unusual gyroid MOF with homochirality and helical channels in the framework for the first time, **JLU-Liu23**. Importantly, the enantiomeric pairs (**23P**, **23M**) can be promoted and isolated in the presence of appropriate chiral inducing agents, affording enantioselective separation of chiral molecules as well as small gas molecules.

Over the past two decades, metal–organic frameworks (MOFs) have received great attention from academia and industry alike, because of their intriguing variety of architectures and topologies¹ and their great prospective to address challenges in applications pertaining to gas adsorption and separation, luminescent, sensing, and catalysis.² Homochiral MOFs with appropriate enantioselective separation are highly desirable host materials for the chemical and pharmaceutical industries.³ Various strategies have been pursued and developed to construct homochiral MOFs from enantiopure or achiral ligands.^{4–9} Commonly, the MOF homochirality is transmitted from the molecular building units to the whole framework. Whereas MOF homochirality resulting from enclosed DNA-like polymer, with absolute double-helicity, in the MOF structure is yet to be realized and observed.

To address this challenge, hosting a DNA-like polymer in a MOF structure, the MOF host material should be envisioned and elected to enclose a pore system (one-dimensional (1D) channels) with a suitable surface contour and functionality which can direct the host–guest interactions and promote the

assembly of helical polymers. Interestingly, numerous inorganic zeolites enclose the desired 1D channel types, but their restricted pore sizes associated with functionalization difficulties prohibit their use to host polymers with double-helicity.¹⁰ Accordingly, we target zeolite-like MOFs (ZMOFs), a subclass of MOFs that resemble zeolites in their topologies, due to their hybrid character and relatively large pore system that can be potentially regulated to accommodate polymers with double-helicity. It is anticipated that hosting a DNA-like polymer in the ZMOF pore system may generate homochirality from a prospective guest–host transformation. Noticeably, the DNA and zeolites entail two distinct chemistries, nevertheless making and hosting DNA-like polymers in zeolite-like structures offer potential to connect the two classes of materials and plausibly gain insights into the mechanism of chiral transformation.

Herein, we report a novel homochiral zeolitic MOF [(Cu₄I₄) (dabco)₂]·[Cu₂(bbimb)]·3DMF (**JLU-Liu23**, dabco = 1,4-diazabicyclo[2.2.2]-octane, H₂bbimb = 1,3-bis(2-benzimidazol)-benzene, DMF = *N,N*-dimethylformamide). The [(Cu₄I₄) (dabco)₂]_n framework, having a zeolite-like topology, hosts DNA-like [Cu₂(bbimb)]_n polymers with double-helicity. Markedly, the enclosed DNA-like polymers induced helical channels in the resultant framework, **JLU-Liu23**, a scarce gyroid MOF with homochirality. The **JLU-Liu23** high stability and chiral channels offer enantioselective separation of chiral molecules as well as small gas molecules.

It is notable that **JLU-Liu23** was prepared from achiral precursors, and thus both enantiomeric pairs (**23P**, **23M**) were observed. D deservedly, by employing a chiral induction strategy reported by Bu et al.,^{7c} the associated structures based solely on **23P** or **23M** can be absolutely promoted in the presence of different chiral inducing agents.

Yellow block crystals of **JLU-Liu23** were synthesized by the solvothermal reaction from a mixture of CuI, dabco, H₂bbimb, and HNO₃ in DMF at 105 °C for 12 h. Interestingly, **JLU-**

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Liu23 spontaneously crystallizes in the chiral space group $P6_3$. The resultant structure encloses two interpenetrated chiral structures: (i) a chiral three-periodic zeolitic framework composed of four-connected $[\text{Cu}_4\text{I}_4]$ clusters bridged by dabco ligands and formulated as $[\text{Cu}_4\text{I}_4(\text{dabco})_2]_n$, and (ii) a chiral DNA-like double-helical chain based on $\text{Cu}(\text{I})$ ions linked by bbimb ligands and formulated as $[\text{Cu}_2(\text{bbimb})]_n$.

In the chiral host framework $[\text{Cu}_4\text{I}_4(\text{dabco})_2]_n$ of **JLU-Liu23**, each $[\text{Cu}_4\text{I}_4]$ cluster is coordinated to four dabco ligands, while each dabco ligand, regarded as a two-coordinated linker, bridges two $[\text{Cu}_4\text{I}_4]$ clusters (Figures 1a and S1). From a topological

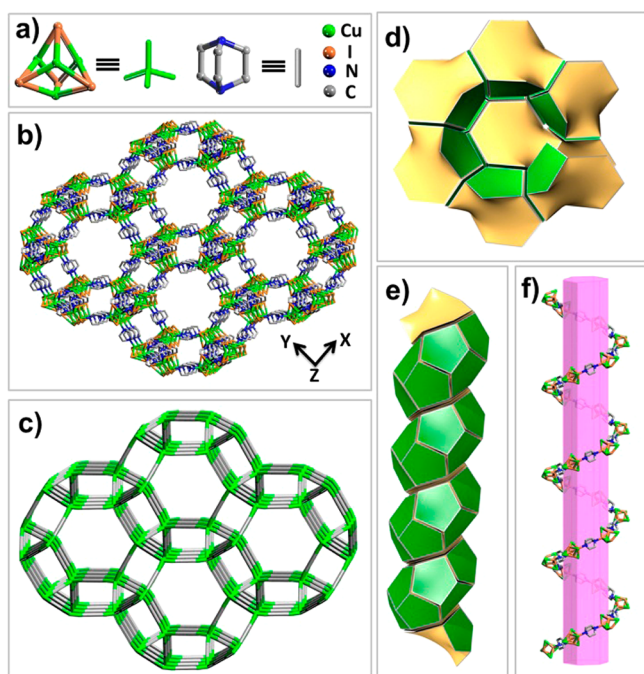


Figure 1. A structure description of **JLU-Liu23**: (a) $[\text{Cu}_4\text{I}_4]$ cluster viewed as a four-connected tetrahedral node, dabco viewed as a two-coordinated linker; (b) three-periodic framework viewed along the $[001]$ direction; (c) topological representation of the **unj** net; (d and e) tiling representation of the helical channel; (f) big right-handed helix.

analysis perspective, the $[\text{Cu}_4\text{I}_4]$ can be reduced to a four-connected node and the dabco ligands to a two-connected linear bridge. This reduction resulted in the derivation of five-membered ring units that are further linked together to form a three-periodic neutral framework with helical channels running along the $[001]$ direction (Figure 1b). The host framework $[\text{Cu}_4\text{I}_4(\text{dabco})_2]_n$ underlying topology is the four-connected zeolite-like **unj** topology (Figure 1c). From the tiling aspect, the helical channel is enclosed by a helical ribbon formed by five-membered rings sharing edges (Figure 1d,e) and two types of right-handed helix composed by $[\text{Cu}_4\text{I}_4]$ clusters and dabco ligands linked together to yield the helical channel (Figures 1f and S2). It is to note that all the helical channels are of right handedness (Figure 1f), and subsequently the three-periodic framework possesses intrinsic homochirality.

To the best of our knowledge, **JLU-Liu23** exhibits a rare example of chiral MOFs with a zeolite-like topology compared to the reported ZIFs and ZMOFs.¹¹ It is notable to mention that in the past decade, great efforts have been devoted to construct zeolite-like frameworks based on $[\text{Cu}_4\text{I}_4]$ clusters and dabco ligands.¹² Nevertheless no chiral zeolite-like MOF has

been reported so far in such a system, and COZ-1 remains the only related known porous zeolitic MOF.^{12c}

Another prominent structural feature of **JLU-Liu23** is the DNA-like double-helix guest located in the helical channels of the three-periodic zeolitic framework, **unj**-ZMOF (Figure 2a–

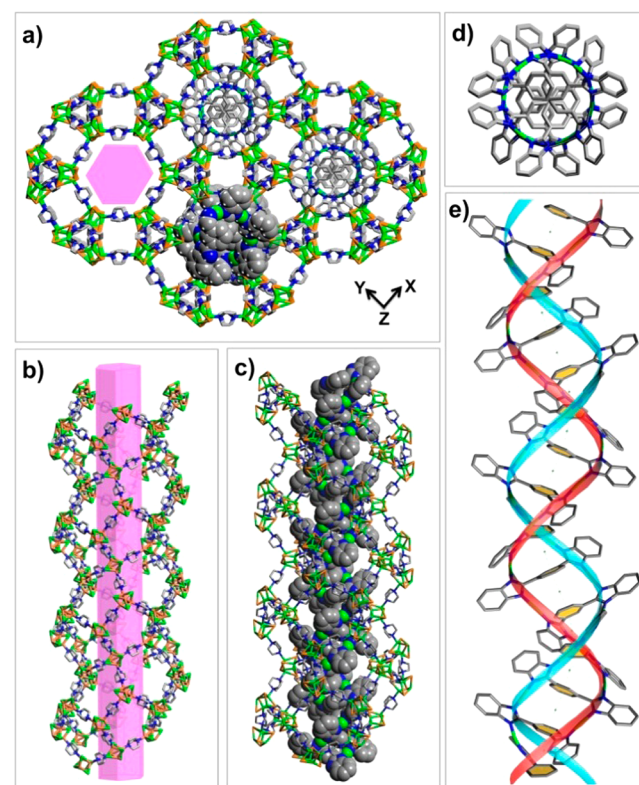


Figure 2. (a) The structure of **JLU-Liu23** showing the interpenetrated 3D framework and double-helical chain. (b) Helical channel formed by helical five-ring ribbons. (c) Double-helical chain filled in the helical channel. (d and e) DNA-like double-helical chain viewed along the $[001]$ and $[110]$ directions, respectively.

(c). In its structure, each Cu^+ ion is coordinated to two nitrogen atoms from two distinct chelating μ_4 -bbimb ligands, in a linear fashion, generating a right-handed helical chain. Two helical chains, running around the 6_1 screw axis, are interconnected with each other via bbimb ligands to form a right-handed double-helix (Figure 2d,e). Additionally, the neighboring benzene rings in the double helix are at close proximity of 4.1 Å and thus supporting the occurrence of weak π - π stacking interactions between the two strands. Interestingly, the hosted double-helical chain resembles the double helix occurring in the DNA structure, except that the hydrogen-bonding pair (interactions) between the two strands is substituted by the central benzene rings of the neighboring two bbimb ligands (as shown in yellow color in Figure 2e). The diameter of the double-helical chain is 17.2 Å, and the screw-pitch is 22.8 Å, which are relatively smaller than 20 and 34 Å observed in DNA helix, respectively (Figure S5). It is worth noting that the mimicking of the DNA double-helical chains has been reported for other materials,¹³ nevertheless MOF structures containing DNA-like double-helix feature are scarce.¹⁴

To the best of our knowledge, the previously reported chiral MOFs are mainly comprised of a sole type of a chiral structure. Whereas, the **JLU-Liu23** encompasses concurrently two distinct chiral structures that are interpenetrated. Such an

unprecedented occurrence represents the first example in MOF chemistry. To gain a better insight in the formation of **JLU-Liu23**, we further analyzed the structure and found that the bbimb ligands are highly distorted with a dihedral angle between the central benzene ring and benzimidazole rings of 55° , a feature that plausibly favors the coordination of Cu(I) ions with the two N-donor centers in a linear fashion and subsequently promotes the formation of double-helical chains (Figure S6). Interestingly, the single-helical chains composing the host framework, $[\text{Cu}_4\text{I}_4(\text{dabco})_2]_n$, are aligned in the same direction with the guest double-helical chains. The two structures, host and guest, are intertwined via multiple C–H $\cdots\pi$ interactions as evidenced by the observed distances between the H atoms of the dabco rings and the centroids of the imidazole and phenyl rings of 2.85, 3.20, and 3.51 Å, respectively (Figures 3 and S7). Eventually, the C–H $\cdots\pi$

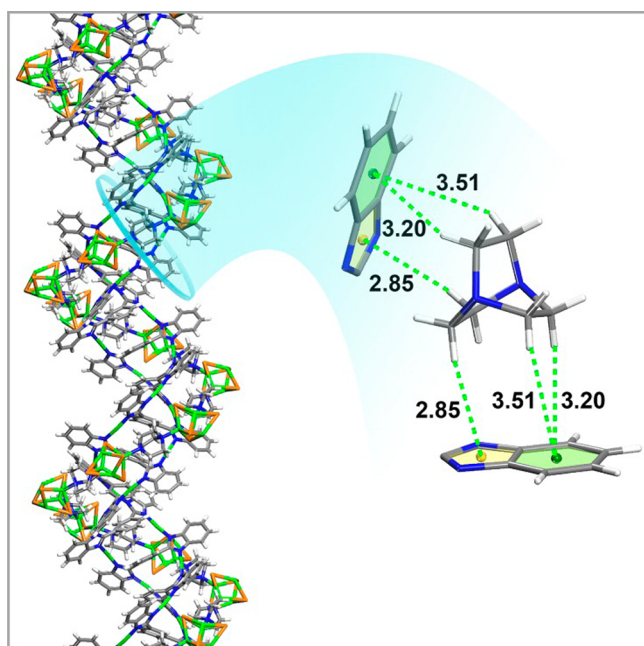


Figure 3. Structure of **JLU-Liu23** showing the DNA-like double-helical chain interwoven with helical chain of the host framework (left) and the multiple C–H $\cdots\pi$ interactions between the dabco molecules and the benzimidazole rings (right).

interactions play a key role in the plausible transmission of the chirality from the double helix to the framework and subsequently promote the formation of the homochiral framework.¹⁵ Plausibly, the occurring spontaneous resolution of the chiral **JLU-Liu23** can be attributed to the directing cooperative effects of the twisted configuration of bbimb ligands and the supramolecular interactions, i.e., π – π stacking and C–H $\cdots\pi$ interactions. Conceivably, the DNA-like double helices can be regarded as a chiral template directing and inducing the formation of the resultant homochiral **unj-ZMOF**, **JLU-Liu23**. The unprecedented occurrence of the DNA-like double helix and its reasonable templating effect, as in the formation of **JLU-Liu23**, offers great potential for the construction of novel chiral MOFs.

Furthermore, the CD spectra reaffirms that the bulk sample of **JLU-Liu23** is homochiral, indicating that the resultant crystals are optically active even without the presence of chiral precursors in the original synthesis. In order to isolate the

opposite handedness enantiomer and to further investigate the spontaneous resolution and the chiral induction phenomenon, we performed similar reactions in the presence of various chiral inducing agents. Indeed, the **JLU-Liu23M** has been prepared using *S*-Binol or (–)-cinchonidine as a chiral inducer, which crystallizes in the $P6_322$ space group. Similarly, the introduction of *R*-Binol or (+)-cinchonine resulted in the formation of **JLU-Liu23P** that crystallizes in the $P6_122$ space group with the opposite handedness. The absolute configurations of bulk materials were confirmed by single crystal X-ray diffraction studies (Table S1). The CD and UV spectra for the three as-synthesized compounds, **JLU-Liu23**, **JLU-Liu23M** and **JLU-Liu23P**, were recorded and are shown in Figure S12. The UV spectra are almost identical and revealed four absorption bands at 360, 298, 230, and 213 nm. On the other hand, the CD spectra showed three positive CD signals for **JLU-Liu23P** at 282, 224, and 210 nm and opposite (negative) CD signals for **JLU-Liu23M**. It is notable that since dabco is not UV active, the CD signals should be mainly associated with the twisted bbimb ligands (see SI).

In order to explore the adsorption properties of **JLU-Liu23**, we performed various gas adsorption studies. Remarkably, even though the chiral channels of the framework are filled by the helical chains, the theoretical solvent-accessible free volume of **JLU-Liu23** was estimated by PLATON to be 48.4% of the total crystal volume. Thermogravimetric analysis (TGA) of **JLU-Liu23** revealed that the DMF guest molecules in the helical channels can be fully exchanged by ethanol molecules and that the resulting **JLU-Liu23** is stable in air and most organic solvents. The permanent porosity of **JLU-Liu23** was supported by the reversible Type-I N_2 adsorption isotherm (Figure S15), characteristic of a microporous material. The Langmuir and BET surface areas for **JLU-Liu23** were estimated to be 811 and 584 m^2/g , respectively. It is noteworthy that **JLU-Liu23** exhibits the highest surface area among the reported MOFs based on $[\text{Cu}_4\text{I}_4]$ clusters and dabco ligands, higher than that the reported surface area for COZ-1 (514 $\text{m}^2 \text{g}^{-1}$).^{10c} **JLU-Liu23** displays adsorption property for other gases, such as H_2 , CO_2 , CH_4 , C_2H_6 , and C_3H_8 , and exhibits relatively high selectivity for the evaluated gas pairs, CO_2/CH_4 , $\text{C}_2\text{H}_6/\text{CH}_4$, and $\text{C}_3\text{H}_8/\text{CH}_4$ (Figures S16–23).

The permanent porosity of **JLU-Liu23** and the chirality of its pore system prompted us to explore its potential for the enantioselective separation of racemic compounds. The enantioselective sorption properties of **JLU-Liu23** for methyl lactate were evaluated by single crystal studies, and the associated **JLU-Liu23M** single crystal, immersed in the racemic mixture, was resolved. After establishing the optimized separation conditions, the results showed that **JLU-Liu23M** exhibits an enantioselectivity up to 27% enantiomeric excess (ee) value for methyl lactate (Figure S24). This result is comparable to the reported homochiral porous MOFs, such as $[\text{Cd}_9((R)\text{-PIA})_6(\text{TIB})_4(\text{H}_2\text{O})_{12}] \cdot 3\text{H}_2\text{O}$ and $[\text{Cd}_9((S)\text{-PIA})_6(\text{TIB})_4(\text{H}_2\text{O})_{12}] \cdot 3\text{H}_2\text{O}$.^{5c}

In summary, the induced transmission of DNA-like polymer, with absolute double-helicity, chirality to a MOF structure by the directional weak C–H $\cdots\pi$ interactions has permitted the formation of a novel homochiral zeolite-like MOF, **unj-ZMOF**, **JLU-Liu23**. The DNA-like polymers induced the helical channels in the host **JLU-Liu23** framework, an unusual gyrooid **unj-ZMOF** with homochirality. Remarkably, absolute chiral crystallization of **23P** and **23M** with opposite handedness was achieved in the presence of the proper chiral induction agents.

Notably, the chiral **JLU-Liu23** exhibits good enantioselectivity. This study reveals a novel strategy based on the chirality interplay between the host and guest and its potential for the construction of new homochiral zeolite-like MOFs (ZMOFs).

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12516.

Experimental details, additional structure figures and descriptions, physical measurements (PXRD, TGA, CD), gas chromatograph, gases adsorption and selectivity for **JLU-Liu23** (PDF)

X-ray crystallographic data (CIF)

X-ray crystallographic data (CIF)

X-ray crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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