

Supramolecular Isomerism in Honeycomb Metal–Organic Frameworks Driven by CH $\cdots\pi$ Interactions: Homochiral Crystallization from an Achiral Ligand through Chiral Inducement

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Received March 30, 2010

The solvothermal reaction of Zn(NO₃)₂·6H₂O and 4,4',4''-(2,4,6-trimethylbenzene-1,3,5-triyl)tribenzoic acid (H₃TMTA) in *N,N*-diethylformamide or *N,N*-dimethylacetamide gave rise to two layered honeycomb frameworks. The different stacking arrangements of the 2D layers generate achiral (α -1) and chiral (β -1) architectures, which are supramolecular isomers. The homochiral crystallization of β -1 can be achieved through chiral inducement, which is confirmed by circular dichroism spectra.

The recent rapid development of supramolecular isomerism has provided a good opportunity for seeking novel functional materials and a better understanding of the factors that influence the crystal growth.^{1–4} In the past decades, the

temperature-,⁵ solvent-,⁶ template-,⁷ guest-,⁸ and catenation-induced⁹ formation of supramolecular isomerism has been reported and has introduced more invaluable factors and strategies in the design and synthesis of novel coordination complexes with desired topologies and special functionalities. For instance, catenation isomerism in [Cu₃(TATB)₂(H₂O)₃]_n (TATB = 4,4',4''-*s*-triazine-2,4,6-triyltribenzoate) has resulted in two functional porous metal–organic frameworks (MOFs) with quite different adsorption properties.⁹ Recently, we reported two nanotubular isomers, based on squares and a helix, that were influenced by the reaction concentration.¹⁰ However, there are no reports on supramolecular isomerism that was induced by different stacking arrangements driven by supramolecular interactions such as CH $\cdots\pi$ interactions in layered frameworks.

For a layered framework, there are two different arrangements of the layers: one is interpenetrating, and the other is stacking. For the stacking arrangement of the layers, which may generate chirality from stacking around one fixed axis, there are infinite arrangements, such as AAAA, ABAB, ABCDEF, etc. (Scheme 1), which are supramolecular isomers mutually. In our previous work, we applied a planar tricarboxylate ligand, 4,4',4''-*s*-triazine-2,4,6-triyltribenzoate (H₃TATB), in the construction of porous MOFs.^{9,11} In

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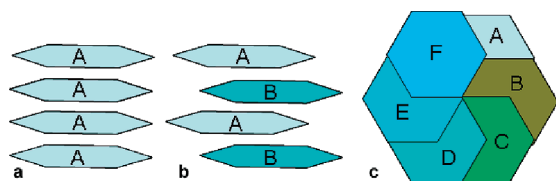
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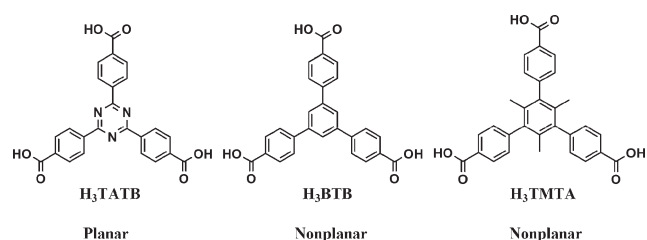
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Scheme 1. Different Stacking Arrangements for Layered Complexes: (a and b) Side View Showing AAAA and ABAB Stacking, Respectively; (c) Top View Showing Chiral ABCDEF Stacking around One Axis



Scheme 2. The Planar and Nonplanar Tricarboxylate Ligands



continuing our work, recently, we designed a new nonplanar ligand, 4,4',4''-(2,4,6-trimethylbenzene-1,3,5-triyl)tribenzoic acid (H_3TMTA). Compared to H_3TATB and H_3BTB , H_3TMTA is much more nonplanar, with its three carboxylate groups almost being vertical with the central benzene ring (Scheme 2). When rigid secondary building units (SBUs), such as $M_2(COO)_4$ ($M = Cu, Zn$) or $M_2(COO)_3$ ($M = Zn, Co$), are connected, a two-dimensional (2D) layered framework will be generated. In this Communication, we report two isomeric honeycomb frameworks, $Zn_2(TMTA)(H_2O)_2 \cdot NO_3 \cdot 6H_2O \cdot DEF$ ($\alpha-1$), $Zn_2(TMTA)(H_2O)_2 \cdot NO_3 \cdot 2H_2O \cdot 0.5DMA$ ($\beta-1$), which possess an achiral framework of $\alpha-1$ and a chiral framework of $\beta-1$, caused by different stacking arrangements of the layers.

Solvothermal reactions of $Zn(NO_3)_2 \cdot 6H_2O$ and H_3TMTA in N,N' -diethylformamide (DEF) or N,N -dimethylacetamide (DMA) resulted in the formation of a large amount of colorless prismatic crystals of $\alpha-1$ and $\beta-1$, respectively, which were structurally characterized by single-crystal X-ray diffraction,¹² elemental analysis, and thermogravimetric analysis (TGA). $\alpha-1$ and $\beta-1$ are isomeric structures in different crystal systems and space groups. $\alpha-1$ crystallizes in the orthorhombic space group $Cmcm$, while $\beta-1$ crystallizes in the hexagonal chiral space group P_{6122} .

Both $\alpha-1$ and $\beta-1$ adopt the dinuclear $Zn_2(COO)_3$ clusters as SBUs and possess 2D honeycomb frameworks (Figure 1). It should be pointed out that, compared to $M_2(COO)_4$ SBUs, the three-connected $M_2(COO)_3$ SBUs are quite rare in the construction of functional MOFs.¹³ All of the zinc ions in $\alpha-1$ and $\beta-1$ are four-coordinated by three oxygen atoms from

(12) Crystal data for $\alpha-1$: $C_{35}H_{48}N_2O_{18}Zn_2$, $M = 915.49$, orthorhombic, space group $Cmcm$, $a = 16.841(6)$ Å, $b = 27.981(10)$ Å, $c = 10.298(4)$ Å, $U = 4853(3)$ Å³, $Z = 4$, $D_c = 1.253$ Mg m⁻³, $\mu(Mo K\alpha) = 1.053$ mm⁻¹, $T = 293$ K, 16874 reflections collected. Refinement of 1181 reflections (118 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0945$, $wR2 = 0.2576$, and $GOF = 1.077$. Crystal data for $\beta-1$: $C_{32.50}H_{34.5}N_{1.5}O_{13.5}Zn_2$, $M = 792.86$, hexagonal, space group P_{6122} , $a = b = 16.5812(11)$ Å, $c = 28.105(4)$ Å, $U = 6691.9(11)$ Å³, $Z = 6$, $D_c = 1.180$ Mg m⁻³, $\mu(Mo K\alpha) = 1.128$ mm⁻¹, $T = 293$ K, 22788 reflections collected. Refinement of 2375 reflections (187 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0787$, $wR2 = 0.2129$, and $GOF = 1.126$.

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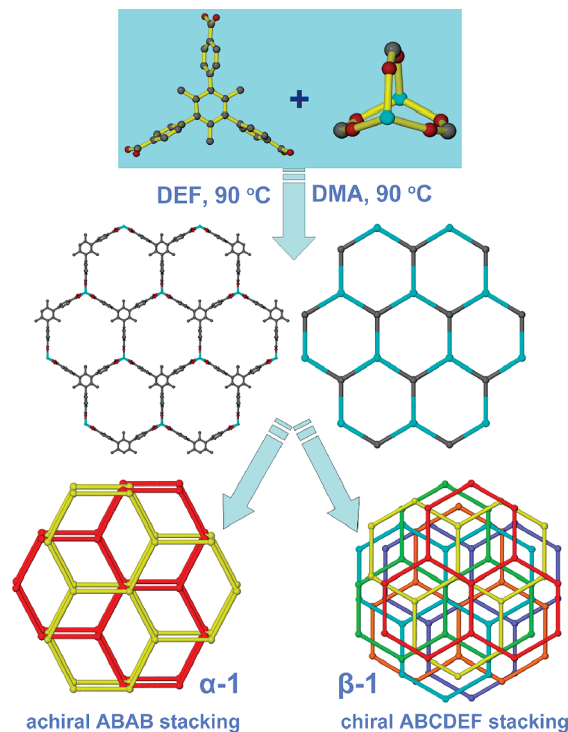


Figure 1. Formation of two isomeric supramolecular architectures. Each isomer consists of 2D honeycomb layers based on TMTA and $Zn_2(COO)_3$ SBUs. The different stacking arrangements (ABAB and ABCDEF in different colors, respectively) of the layers resulted in the formation of isomers with achiral and chiral architectures.

different TMTA ligands and one-coordinated by a water molecule in a tetrahedral geometry (Supporting Information), as found in the previous results.¹⁴ As expected, the TMTA ligand is nonplanar, with the average dihedral angles between the central benzene ring and the three side benzene rings of 90.0 and 99.6° and the resulting dihedral angles between the carboxylate groups and the central benzene ring of 90.0 and 100.8° for $\alpha-1$ and $\beta-1$, respectively. Thus, each $Zn_2(COO)_3$ SBU attaches to three TMTA ligands, and every TMTA connects three $Zn_2(COO)_3$ SBUs to generate a cationic honeycomb framework. The charge is balanced by a free nitrate ion, which is confirmed by elemental analysis and TGA. Although $\alpha-1$ and $\beta-1$ possess similar 2D layered frameworks, the stacking arrangements of the layers are quite different, generating supramolecular isomerism.

In $\alpha-1$, the 2D cationic layers adopt ABAB stacking to give rise to a three-dimensional (3D) achiral supramolecular architecture with a distance between layers of 10.3 Å. There are no significant supramolecular interactions among the layers. Different from $\alpha-1$, the 2D cationic layers in $\beta-1$ adopt ABCDEF stacking, resulting in the formation of a 3D chiral supramolecular architecture with a layer-to-layer distance of 4.63 Å, which is significantly shorter than that in $\alpha-1$. There are $CH \cdots \pi$ interactions (3.529 and 3.597 Å) between the side benzene rings in one layer and the central benzene rings in its adjacent layer. These supramolecular interactions connect the TMTA ligands in different layers to give rise to a one-dimensional (1D) 6_1 helical chain, as shown in Figure 2a,b. All of the TMTA ligands are arranged around the 6_1 helical axes. Because of the rigidity of the 2D layer and the

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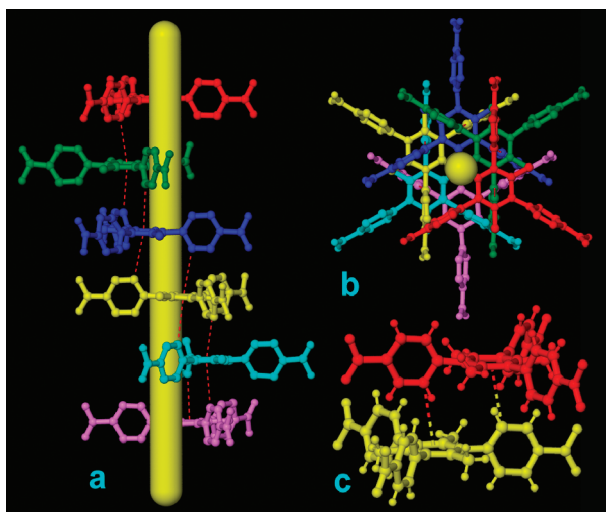


Figure 2. (a and b) Side and top views of the 1D 6_1 helical chain generated through $\text{CH}\cdots\pi$ interactions between the side benzene ring in one layer and the central benzene ring in its adjacent layer in β -1. (c) Highlighted view of $\text{CH}\cdots\pi$ interactions between two TMTA ligands.

directionality of $\text{CH}\cdots\pi$ interactions, the same chirality of the helical chains is preserved. Thus, the whole structure is chiral. In the past decades, many MOFs possessing 2D honeycomb or other topological layers have been widely synthesized and documented.^{15–17} However, most of them are interpenetrating or stacking one another through supramolecular interactions among the layers to give rise to achiral frameworks; there are no reports on 3D chiral supramolecular architectures generated from 2D honeycomb layers through $\text{CH}\cdots\pi$ interactions based on achiral ligands prior to this report. Because of the different stacking modes (ABAB vs ABCDEF), α -1 possesses more void volume than β -1 does. The solvent-accessible volumes calculated from PLATON¹⁸ are 49.2 and 43.2% for α -1 and β -1, respectively.

TGA for α -1 and β -1 showed that both complexes can be stable up to 400 °C. For α -1, the first weight loss of 5.2% from 50 to 141 °C corresponds to the loss of three uncoordinated water molecules (calcd: 5.9%); the second weight loss of 26.0% from 142 to 437 °C corresponds to the loss of three uncoordinated water molecules, one NO_3^- , one uncoordinated DEF molecule, and two coordinated water molecules (calcd: 27.6%), and after 437 °C, α -1 starts to decompose. For β -1, the first weight loss of 14.7% from 50 to 232 °C corresponds to the loss of 0.5 uncoordinated DMA molecule, two uncoordinated water molecules, and two coordinated water molecules (calcd: 14.4%); the second weight loss of 7.2% from 233 to 414 °C corresponds to the loss of one NO_3^- anion (calcd: 7.9%), and after 430 °C, β -1 starts to decompose.

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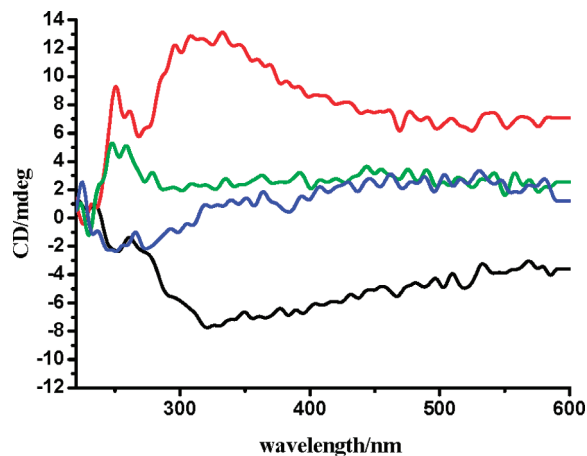


Figure 3. Solid-state CD spectra of β -1 through chiral induction [blue line, (S)-tna; green line, (R)-tna; black line, (S)- β -1; red line, (R)- β -1].

It has been reported that bulk homochiral crystallization from achiral precursors can be achieved through chiral induction.¹⁹ In our work, the chiral molecule (*S* or *R*)-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)acetamide (tna; Figure S3 in the Supporting Information) was selected as a chiral-induced reagent. Powder X-ray diffraction reveals that the samples, after the addition of a chiral molecule, possess the same structure with β -1 (Supporting Information). The chiral bulk sample of tna- β -1 exhibits circular dichroism (CD) with an exciton-coupled split Cotton effect, positive or negative for the absolute helicity with chiral induction by (*R*)- or (*S*)-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)acetamide, respectively. The CD signal is quite different with the chiral molecule (Figure 3), indicating that P_{6122} or P_{6522} is the preferred configuration in the bulk sample of β -1 through chiral induction.

In conclusion, two new isomeric MOFs (α -1 and β -1) possessing 2D honeycomb layers have been synthesized and characterized based on a newly developed nonplanar tricarboxylate ligand. The layers in α -1 adopt a ABAB stacking mode to give rise to an achiral 3D supramolecular architecture. Because of $\text{CH}\cdots\pi$ interactions in β -1, the layers adopt an ABCDEF stacking mode to generate a chiral 3D supramolecular architecture. To our best knowledge, α -1 and β -1 represent the first isomeric MOFs that were generated from the different stacking arrangements of 2D honeycomb layers to provide achiral or chiral architectures driven by $\text{CH}\cdots\pi$ interactions. Further studies will focus on the synthesis of other supramolecular isomers with different stacking arrangements of the layers, as well as decoration of the layers to construct novel MOFs based on TMTA ligands.

Acknowledgment. We are grateful for financial support from the NSF of China (Grants 90922014 and 20701025), the NSF of Shandong Province (Grants Y2008B01 and BS2009CL007), and Shandong University.

Supporting Information Available: Experimental procedures, structural figures, and TGA as well as crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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