Chiroptical Activity from an Achiral Biological Metal−Organic Framework

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Ⓢ *Supporting Information*

ABSTRACT: Chiroptical activity is observed from an achiral adenine-containing metal−organic framework (MOF) named ZnFDCA. Such a seemingly counterintuitive phenomenon can, in fact, be predicted by the intrinsic crystal symmetry of $\bar{4}2m$ point group. Although theoretically allowed, examples of optically active achiral crystals are extremely rare. ZnFDCA is the first reported achiral MOF showing optical activity, as demonstrated by a pair of circular dichroism signals with opposite signs and enhanced intensity. Moreover, simply through adding an amino substituent to adenine, the chiroptical activity, as well as nonlinear optical activity, of the analogous MOF, namely ZnFDCA-NH$_2$, disappears due to diverse packing pattern giving rise to centrosymmetric crystal symmetry.

Since Louis Pasteurs' famous experiments in 1848, where a pair of mirror-image forms of tartrate crystals were observed and meticulously separated by hand and their solutions could rotate polarized light in opposite directions, optical activity has been naturally correlated to molecular chirality,[1] and chiroptical measurements have become indispensable tools for studies on chirality.[2,3] The implication of this discovery has also triggered unceasing interest in the relation between molecular chirality and life phenomena given the fact that crucial biomolecules, e.g., DNA and proteins, are enantiopure optically active.[4]

Although it may be a widely held notion that chiroptical activity can only be identified for chiral species, this statement is not strictly correct.[5−7] A chiral entity cannot superimpose with its mirror image; they are said to be an enantiomorphous pair.[1] Albeit counterintuitive, nonenantiomorphous (achiral) species can be optically active; in fact, it has been long established theoretically that optical activity can also arise from achiral crystals of certain crystallographic symmetry.[6,7] As shown in Scheme 1 (left), of the total 32 crystal point groups, besides 11 chiral point groups, chiroptical activity can also be predicted for crystals of four achiral point groups (*m*, *mm*2, $\bar{4}$, and $\bar{4}2m$).

Scheme 1. Relationship between Chirality, Crystal Symmetry, and Optical Activity (Left); Occurrence of Optical Activity from an Achiral Entity with $\bar{4}2m$ Point Group (Right)
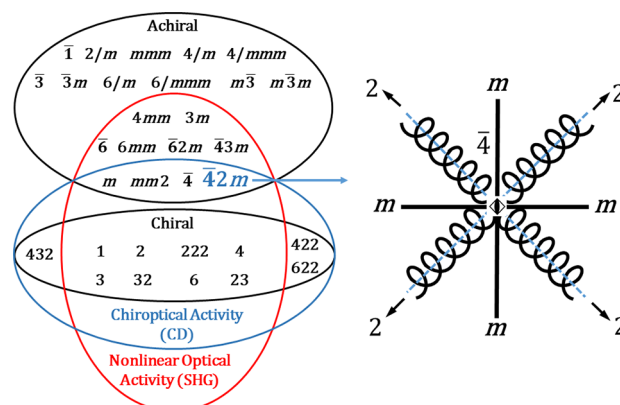
The occurrence of optical activity from achiral crystals of these four point groups is solely determined by their symmetry irrespective of how the atoms are arranged therein.[6] A phenomenological representation may help to understand (Scheme 1, right). For the $\bar{4}2m$ point group, one may imagine two forms of rotatory power of which one-half are right-handed and one-half left-handed, both perpendicular to 4-fold inversion axis. In principle, such an achiral crystal is able to generate chiroptical signals with both positive and negative signs when subject to different directions of the incident light, although the signals of opposite signs may completely counterbalance one another along 4-fold inversion axis.

Nevertheless, experimental observations on optical activity from achiral crystals were extremely rare.[5−7] Previously studied examples were mostly inorganic and organic crystals.[7] Most recently, there was a report on racemic crystals of discrete coordination complexes,[8,9] which crystallize in the achiral *mm*2 point group, exhibiting solid-state circular dichroism (CD)

signals. Notably, therein the CD signal intensity was very weak, and a pair of CD spectra with opposite signs was absent.[8] To the best of our knowledge, there was no report on achiral coordination networks, or metal−organic frameworks (MOFs), showing optical activity prior to the present work.

Herein, we report an emerging achiral biological MOF,[10−15] namely, $[Zn(FDC)(Ade)]\cdot 0.5DMF$ (denoted as ZnFDCA; H_2FDC = 2,5-furandicarboxylic acid, Ade = adenine, DMF = N,N-dimethylformamide), which crystallizes in the $I\bar{4}m2$ space group (belonging to $\bar{4}2m$ point group), and shows chiroptical activity (see the Supporting Information for experimental section and crystal data). ZnFDCA features a networked structure in contrast to those achiral crystals of discrete compounds reported to show optical activity.[5−9] In this layer structure (Figure 1, middle), each Zn^{II} ion adopts a 4-
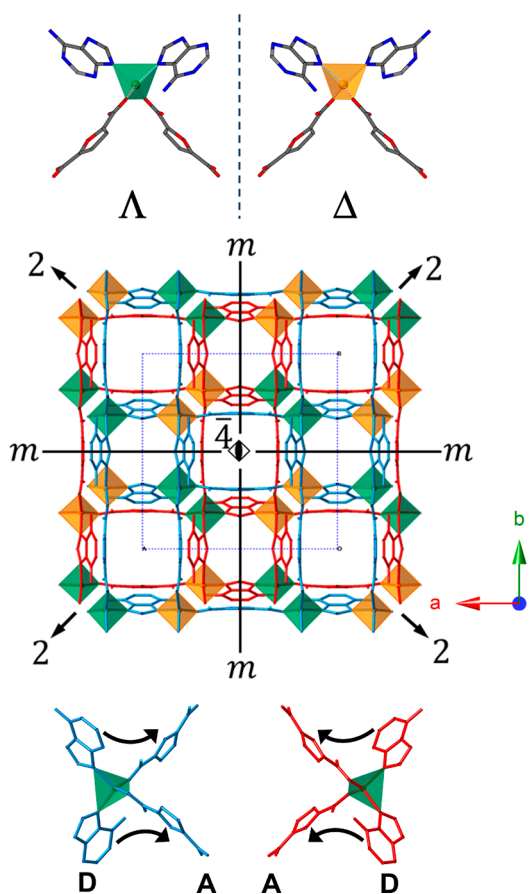

Figure 1. Overall layer stacking arrangement of ZnFDCA marked with point symmetry operations of $\bar{4}2m$ (middle). Adjacent layers are colored in blue and red, and the Zn^{II} ions with Λ and Δ absolute configurations are shown in green and yellow tetrahedra, respectively. A pair of Zn^{II} ions of opposite configurations with respect to the mirror plane are shown at the top, and the representative donor−acceptor structure responsible for nonlinear optical activity is depicted at the bottom (only one-half of disordered adenine is shown).

coordinated, tetrahedral configuration fulfilled with two FDC^{2-} and two Ade ligands. The overall architecture is a two-dimensional (4,4) layer (**sql** net, Figure S4a), parallel to the ab plane, which is composed of alternately arranged large and small grids (with dimensions of 9.8×9.8 and 5.9×5.9 Å², respectively, based on Zn···Zn distances), corresponding to the lengths of FDC^{2-} and Ade linkers (Figure S1d). In addition, the layers are reinforced by extensive intra- and interlayer

hydrogen-bonding between adenine-N/amino and carboxyl-O sites (Figure S1e and Table S4), giving rise to a neat and ordered stacking arrangement of tetragonal crystal symmetry.

The abstract symmetry operations of the $\bar{4}2m$ point group, which is responsible for the chiroptical activity, has fully manifested in the real crystal of ZnFDCA (cf. Scheme 1, right and Figure 1, middle). The crystal structure has a 4-fold inversion main axis, which passes through the centers of adjacent rectangles, each formed from two FDC^{2-} and two Ade linkers, across the layers. Through careful examination, one can identify a pair of enantiomorphous building blocks, i.e., tetrahedral Zn^{II} centers of Λ and Δ absolute configurations[3] (Figure 1, top), which are equally arranged on opposite sides of the two existing mirror planes, leading to an ensemble of achiral crystal. Notably, different from the situation of racemic molecules in liquid or solution, the optical activity of each pair of Zn^{II} tetrahedra would not counterbalance with one another in all directions, which is attributed to their special alignment in crystal.[6] Indeed, there can be observed that tetrahedral Zn^{II} centers of the same configuration (either Λ or Δ) running along one of the two 2-fold axes normal to each other (Figure 1, middle).

As expected, CD signals were observed for the measured ZnFDCA samples (Figure 2a). In a typical measurement, a piece of single crystal with a suitable size (approximately $1.0 \times 0.7 \times 0.4$ mm³) was randomly picked out, first arranged to
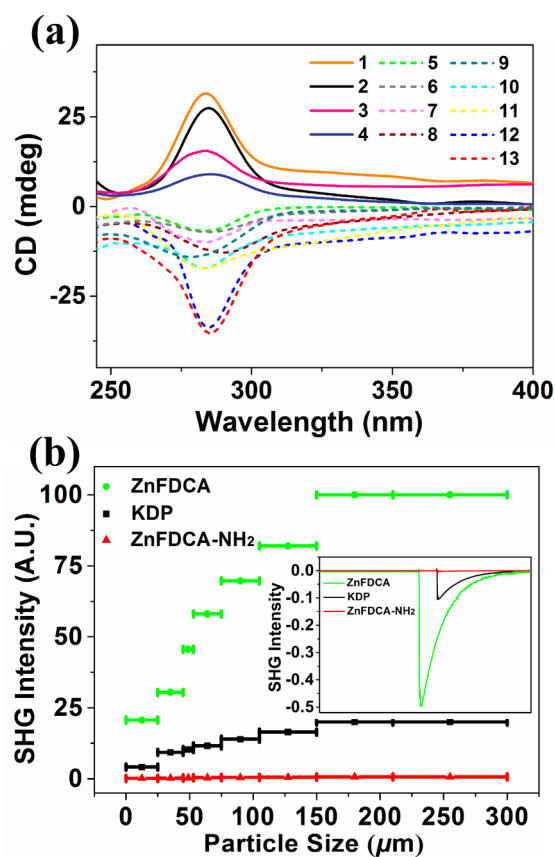
Figure 2. (a) Solid-state CD spectra of ZnFDCA measured by using a randomly selected piece of single crystal, tableted, and diluted by KCl (13 trials). (b) Comparison of measured SHG signal intensity versus particle size of ZnFDCA, ZnFDCA-NH₂, and KDP reference (laser radiation λ = 1064 nm). Inset: oscilloscope traces of the SHG signals (particle size 150−210 μm).

single-crystal X-ray diffraction analysis and then for CD spectral measurement. For a total of 20 trials, four samples showed positive sign and nine showed negative sign, whereas the signals for the remaining seven samples were negligible. Such a result is reasonable because each single crystal was crushed and tableted for the solid-state CD measurement. In this case, the anisotropically optical activity from achiral crystals might be diminished to some extent. Even so, the CD signal intensity recorded here is much stronger compared with the recent report of Gautier et al.[8] The CD signals here were reproducible, giving a broad band with the peaks at ∼280−285 nm. Moreover, both positive and negative signals were successfully recorded, unambiguously demonstrating chiroptical activity from an achiral MOF crystallized in the $\bar{4}2m$ point group. It would be valuable to perform more accurate measurements by employing an intact single-crystal sample, although such experiments are challenging.[9]

The solid-state UV−vis absorption spectrum of ZnFDCA was measured (Figure S11), which showed a broad band covering the 230−290 nm wavelength. It is assigned to the interaction between the two ligands given that the absorption bands of free ligands, H_2FDC (225−305 nm) and Ade (235−295 nm), are close to each other. The correspondence between UV−vis and CD spectra indicate the optical activity of ZnFDCA, attributed to tetrahedral Zn^{II} centers of Λ and Δ absolute configurations, has transferred to the organic components of the MOF.

We have solved the single-crystal structures of all 13 trials showing optical activity prior to the CD spectra measurements (Table S5). For a noncentrosymmetric crystal structure, a Flack parameter can also be obtained, which shows the correctness of the refinement. For making the Flack parameter close to zero, two configurations are adopted, between which the a- and b-axes are swapped (Figure S5). Because this is merely an artifact in structure determination, we intend not to establish any correlation with the optical activity observed.

Under the crystal symmetry investigated (i.e., noncentrosymmetric $\bar{4}2m$ point group, see Scheme 1, left), ZnFDCA is also expected to show nonlinear optical activity.[16] We have performed measurements on powder samples of ZnFDCA to evaluate its second harmonic generation (SHG) efficiency (Figure 2b). The results reveal that ZnFDCA is phase-matchable and exhibits impressive SHG responses ∼5-times that of the KH_2PO_4 (KDP) reference. Through inspection of crystal structure (Figure 1, bottom), one can identify the local donor−acceptor (D-A) structure (i.e., from electron-donating adenine-NH_2 to electron-withdrawing carboxyl substituents), which is usually responsible for strong second-order nonlinear optical activity (see Figures S13 and S14 and Table S6 for further discussions).[16]

For comparison, we introduced 2,6-diaminopurine in place of adenine in ZnFDCA to prepare an analogous MOF, namely, $[Zn(FDC)(Ade-NH_2)]\cdot0.5H_2O$ (denoted as ZnFDCA-NH_2; Ade-NH_2 = 2,6-diaminopurine, see the Supporting Information for experimental section and crystal data). Interestingly, simply through adding an amino substituent to the biological component of the targeted MOF, the overall packing and crystal symmetry, as well as optical activity, have altered drastically. Under a polarizing microscope, the obvious dark/bright reflection for anisotropic crystals of ZnFDCA can no longer be observed for ZnFDCA-NH_2 (Figure 3, top).

ZnFDCA-NH_2 crystallizes in an orthorhombic space group $Pccn$ with a unit cell very close to a tetragonal one (a =
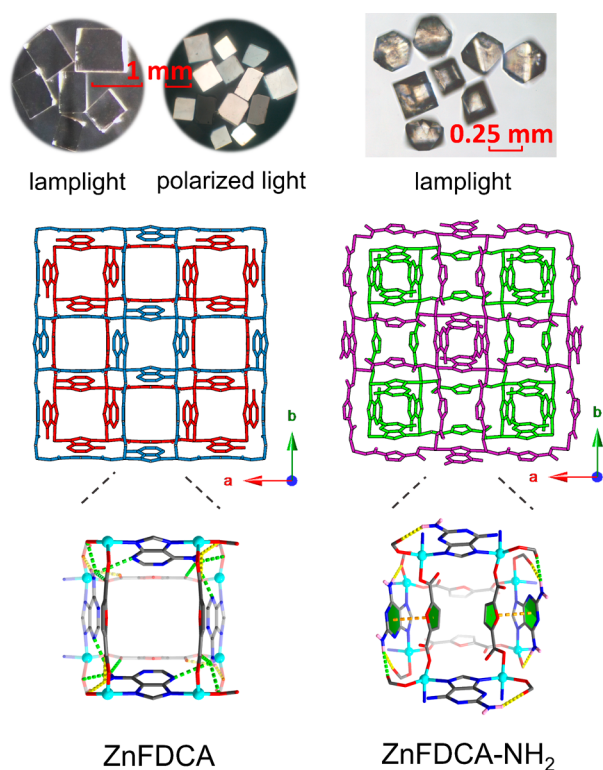
Figure 3. Comparison on images of single crystals, overall packing patterns, and local structural details of ZnFDCA (left) and ZnFDCA-NH_2 (right). In packing diagrams (middle), adjacent layers are colored in blue and red for ZnFDCA and in green and purple for ZnFDCA-NH_2. In zoom-in local views (bottom), intralayer hydrogen bonds are shown in yellow dashed lines, and interlayer ones are shown in green. The rings with π−π stacking are highlighted in green. Note that the orientations of Ade and Ade-NH_2 are different.

15.0337(1) Å, b = 15.0402(1) Å). Although the (4,4)-grid layer retains (with dimensions of 9.2 × 9.3 and 5.9 × 5.8 Å^2, based on Zn⋯Zn distances, Figure S2d), the orientations of the ligands differ from those of ZnFDCA (Figure 3, middle), resulting in the same **sql** net but with slight distortion (Figure S4b). There are abundant intra- and interlayer hydrogen bonding among the ligands for both ZnFDCA and ZnFDCA-NH_2, but for ZnFDCA-NH_2 interlayer π−π stacking force also exists (Figure 3, bottom, see also Figure S2e and Table S4). It can be seen that its neighboring layers stack together in such a way that the FDC ligands protrude into the interior cavity enclosed by the Ade-NH_2 ligands, giving rise to π−π interactions (∼3.431 Å) between furan and pyrimidine rings of adjacent layers, which is absent in ZnFDCA (cf. Figures S1 and S2 for side views).

Consequently, CD spectra recorded for ZnFDCA-NH_2 samples gave negligible signals (Figure S12), and the accompanying second-order nonlinear optical activity also vanished (see Figure 2b). Comparing the two MOF analogues, it is concluded that local effects (i.e., supramolecular interactions, configurational distortion, ligand orientation, and donor−acceptor structure) are subject to global effect (i.e., crystal symmetry), which plays a decisive role in the occurrence of CD and SHG activity for ZnFDCA.

Indeed, chiral species are optically active but not vice versa. The present contribution provides strong new evidence for the theoretical prediction that achiral crystals of certain point symmetry are capable of exhibiting optical activity and

represents the first report of such a counterintuitive phenomenon in the field of MOFs. This finding is validated by a pair of CD spectra with opposite signs and enhanced intensity and strengthened by comparison with a centrosymmetric analogous MOF without CD or SHG activity. We anticipate further studies, perhaps with more accurate physical measurements, to fully unveil the mysteries beneath.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b06725.

> Experimental section, crystal data and physical measurements (PDF)
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Notes
The authors declare no competing financial interest.

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