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ARTICLE TYPE

Multi odd-even effects on cell parameters, melting points, and optical properties of chiral crystal solids based on *S*-naproxen

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A set of chiral crystal solids with odd and even number of carbon atoms based on *S*-naproxen have been prepared, ester *S*-naproxen-*R*$_1$ (*R*$_1$ = H, methyl, ethyl, *n*-propanyl, *n*-butanly, and *n*-amyl), alternatively crystallizing in the space group *P*2$_1$ and *P*2$_1$2$_1$2$_1$, respectively, which show multi odd-even effects on cell parameters, melting points, and optical properties.

Chiral crystal solids (CCSs) have received considerable attention in the field of material chemistry owing to a variety of technologically important properties such as second harmonic generation (SHG) nonlinear optical (NLO), and ferroelectricity.[1,2,3] Among of them, NLO-active and behaviors have widely been applied in NLO devices, signal processing, optical communication, and information storage.[4] So far, crystal engineering has extensively been provided insight into the preparation of the desired functional materials. Though there exist some progressive advances based on crystal engineering in the fabrication of CCSs,[2a,2e, 5,6] it remains the strenuous challenges in the design and syntheses of chiral and packing arrangement.

Odd-even effect has been observed in many homologues such as *n*-alkanes,[7] diols,[8] diamines,[8] diamides,[9] dicarboxylate esters,[10] dithiols,[11] diselenides,[12] and dicarboxylic acids,[13] which affects some physical properties such as melting temperature, density, solubility, wettability, tribological behavior, electrochemistry, and electron transfer.[14] Interestingly, most of them display symmetrical features of these structures. To date, the development and investigation of the compounds based on asymmetrical structure with single-side substitutes remains a great challenge, especially, chiral features with odd-even effects motifs. On the other hand, there exist one or two kinds of odd-even alternation for physical properties in the reported homologs. However, co-existence of multi-properties with odd-even alternation in homologs is still not documented so far. The multi odd-even alternation phenomena will help us understand the structure-property relationships and finely tune physical properties. Thus, the design and studies of these homologues with multi odd-even effect remain an unprecedented challenge.

During the investigation on CCSs with interesting NLO properties,[15] we have realized that chiral *S*-naproxen compounds easily construct CCSs with SHG responses.[16] *S*-naproxen and its derivatives possess some specific features: chiral, single ester, single-side substitutes and naphthene rings, which are propitious to dominate the intermolecular packing interactions. Herein, we report the syntheses, crystal structures, melting points, solid circular dichroism (CD), NLO, and photoluminescence properties of *S*-naproxene (**1**) and its ester derivatives **2-6** (*S*-naproxen-*R*$_1$, *R*$_1$ = methyl, ethyl, *n*-propanyl, *n*-butanly, and *n*-amyl for **2-6**, respectively), which were prepared by different alcohol solution reaction of naproxen under H_2SO_4 at refluxing temperature, respectively (Scheme 1, ESI).[†]

Interestingly, naproxen **1** and its derivatives **2-6** crystallize in two sets of different chiral space group, *P*2$_1$2$_1$2$_1$ and *P*2$_1$, repectively, though only the difference number of carbon chain exist in this set of naproxene derivatives (Table S1).[†] More notably, the type of chiral space group alternatively change upon the number of carbon atoms, which illustrates that there exists odd-even effects on space group for naproxen and its derivatives. It is predicted that the present study will provide us useful information for developing and designing some specific CCSs.

Single crystal X-ray crystallographic analysis of **1** reveals that compound **1** crystallizes in *P*2$_1$ space group, and an asymmetric unit of **1** contains one naproxen molecule (Fig. S1a). The hydrogen bondings are formed between two oxygen atoms from carboxylic group, which results in the formation of a 1D helix chain along the crystallographic *b* axis (Fig. 1a). Additionally, there exist the weak C-H$\cdots\pi$ packing interactions formed by CH_3O- group and naphthene rings. As a result, a supramolecular layer is generated through the interchain C-H$\cdots\pi$ packing interactions between carbon atoms of naphthene groups and naphthene rings, which further results in a 3D supramolecular framework by means of O-H$\cdots$O hydrogen bonds (Table S2, Fig. S1).

X-Ray crystal structural determination of **2** reveals that it crystallizes in *P*2$_1$2$_1$2$_1$ space group and consists of one methyl *S*-naproxen ester molecule in asymmetric unit (Fig. S2a). There are two types of weak C-H$\cdots\pi$ packing interactions, which are found between CH_3O- groups and naphthene rings, and between C atoms of naphthene rings, which result in the chiral 2D layer along the crystallographic *ab* plane (Fig. 1b). There exist weak C-H$\cdots$O interactions formed by C atoms of ester groups and O atoms of carboxylic ones. The 2D supramolecular layers are further constructed to a 3D supramolecular architecture through these weak interlayer interactions (Fig. S2, Table S3).

X-Ray structural analysis of **3** reveals that it shows *P*2$_1$ space group. An asymmetric unit contains one ethyl ***S***-naproxen ester

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molecule (Fig. S3a). There exist weak C-H···*π* interactions between carbon atoms of CH_3O- groups and naphthene rings, resulting into forming a 1D chain (Fig. 1c). The weak *π*···*π* packing interactions were observed. Through these packing interactions, a 2D layer supramolecular layer was generated along the crystallographic *ab* plane. Notably, there do not exist obvious interlayer packing interactions (Fig. S3).

The single-crystal structure analysis reveals that compound **4** crystallizes in $P2_12_12_1$ space group. An asymmetric unit is composed of one *n*-propanol *S*-naproxen ester molecule (Fig. S4a). It is observed that there exist weak C-H···*π* interactions between carbon aotms of CH_3O- group and naphthene rings of CH_3O-terminaed group, constructing a 1D chain (Fig. 1d). Notably, it is not found that the interchain interactions evidently occur. The nearest distance is 5.19 Å among CH_3O-terminaed naphthene rings (Fig. S4).

X-ray determine anaylsis indicates that compound **5** crystallizes in $P2_1$ space group. In an asymmetric unit, it is consisted of one *n*-butyl *S*-naproxen ester molecule (Fig. S5a). There exist weak C-H···*π* interactions between carbon atoms of CH_3O- group and CH_3O-terminaed naphthene rings, resulting into a 1D chain along the crystallographic *b* axis (Fig. 1e). It is observed that there exist weak C-H···*π* interactions between methyl carbon atoms of butyl group and carboxylic group-terminated naphthene rings, which consequently form a 2D supramolecular layer (Fig. S5). The weak C-H···O hydrogen bonds occur between chiral methyl carbon atoms and oxygen atoms from carboxylic group, resulting into a 3D architecture.

Single-crystal structure analysis reveal that compound **6** crystallizes in $P2_12_12_1$ space group. It is made of one *n*-amyl *S*-naproxen ester molecule in an asymmetric unit (Fig. S6a). It is observed that the weak C-H···*π* interactions formed by C atoms of CH_3O- groups and naphthene rings, forming a 1D chain (Fig. 1f). These 1D chains are further extended to a 2D supermolecular layer along the crystallogrpahic *ab* plane through the weak C-H···*π* packing interactions constructed by C atoms of naphthene rings and naphthene groups. Interestingly, the absence of strong packing interactions between the adjacent layers does occurs (Fig. S6).

As mentioned above, the existence of odd-even effects on cell parameters such as axis lengths, beta angles, cell volumes and space group obviously occurs with the length of carbon chain in ester groups (Fig. 2a-d). For so, we carefully compare the packing interactions among the crystal structures of these compounds. As illustrated in Fig. S7 and Table S4, the packing interactions exhibit the odd-even alternation, which may account for these phenomena and the following physical properties.

To further investigate physical properties of these compounds, their melting points, Uv-Vis, and solid CD spectra were examined. As illustrated in Fig. S8, it is observed that there exists the melting point alternation of naproxen and its derivatives, which may be attributed to the crystal-packing arrangements and intermolecular hydrogen interactions (Table S5). As shown in Fig. S9, the maximal adsorption peaks occur at 231.8, 232.1, 232.2, 232.0, 232.1, and 232.0 nm for **1**-**6**, respectively, which can be attributed to π-π* transition among organic molecules. Interestingly, the CD spectra display the Cotton effect (CE) (Fig. S10) from 239, 239, 238, 239, 239, 237, and 240 nm for **1**-**6**, respectively, which may be affiliated to π-π* transition band. Interestingly, compounds **1**, **3**, **5** and **2**, **4**, **6** display the positive and the negative CE, respectively, which illustrate the odd-effect alternation.

Given naphthene derivatives displaying interesting photoluminescence properties,[17] the solution photoluminescent spectra of compounds **1**–**6** at room temperature have been examined (Fig. S11). It is found that compound **1** exhibit an emission upon excitation at 230 nm with maxima at 351.8 nm, which might be assigned to the intraligand *π*-*π** transition.[18] Esters **2-6** exhibit blue photoluminescence with emission peaks at approximately 349.4 nm, 350.6 nm, 351.4 nm, 351.0 nm, 351.0 nm (λ_{ex} = 230 nm), respectively, which may be attributed to the emission of the intraligands.[18]

To further investigate the packing interactions effects on photoluminescent properties, the solid state luminescence spectra of compounds **1-6** at room temperature have been carried on. As illustrated in Fig. S12, the luminescent spectra of naproxen **1** display two emission peaks located at 353.8 nm and 357.0 nm (λ_{ex} = 230 nm), respectively, being assigned to the intraligand *π*-*π** transition.[18] Esters **2-6** also show blue luminescence with emission peaks at 357.8 nm, 356.6 nm, 359.2 nm, 356 nm, and 359.4 nm, respectively, upon the excitation at 230 nm, which can be attributed to the intraligand *π*-*π** transition.[18] Notably, it is found that the maximal peaks of these compounds display odd-even effects on photoluminescent properties (Fig. 3a). Compared to the photoluminescent spectra in solution, those of the solid state compounds **1-6** are similar. The presence of red-shifted phenomena occurs about 5.2 nm, 8.4 nm, 6.0 nm, 7.8 nm, 5.0 nm, and 8.4 nm, which can be ascribed to intermolecular *π*-*π* packing interactions at solid state. More importantly, it is observed that the red-shifted values also display the alternation trend in photoluminescent properties (Fig. 3b). The present results show that the alternation of photoluminescent spectra is in good agreement with that of packing interactions (Fig. 3 and Fig. S7). To our best knowledge, it is first example that it is observed odd-even effects on not only luminescence but also their accordant relationships. The present results provide us an excelent model to explain the nature of odd-even effect.

Given that compounds **1-6** crystallize in chiral space group associated with NLO property, we examine their NLO behaviors. Preliminary experimental results of compounds **1-6** indicate that they are SHG-active. The SHG efficiency of compounds **1-6** are weaker than that of urea,[19] which may be as a consequence of the absence of classical donor-acceptor system in the molecules.

In summary, we have successfully prepared a series of chiral crystal solids based on *S*-naproxen and its five derivatives, which display multi odd-even effects on cell parameters, space group, melting point, and optical properties, and exhibit moderate nonlinear optical activities. To our knowledge, it is first example that multi odd-even effects on cell parameters and optic properties occurs, which pave a way for exploring and tuning the organic materials with charming physical properties. Current studies on developing other chiral organic solids with interesting optoelectronic properties is under way in our laboratory.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis, elemental analysis, m.p., IR, crystal data, Tables, photoluminescent figures, crystallographic data in CIF and additional figures of **1-6**. See DOI: 10.1039/b000000x/

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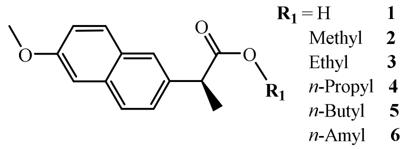
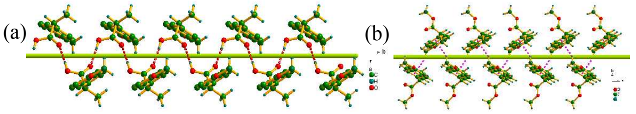


Scheme 1. A set of naproxen and its esters.



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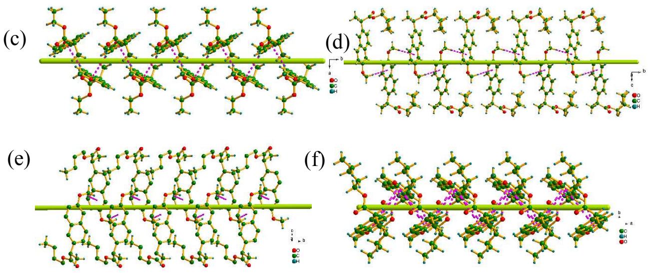

Fig. 1 (a)-(f) Perspective views of the chiral 1D chain in **1**-**6**, respectively.

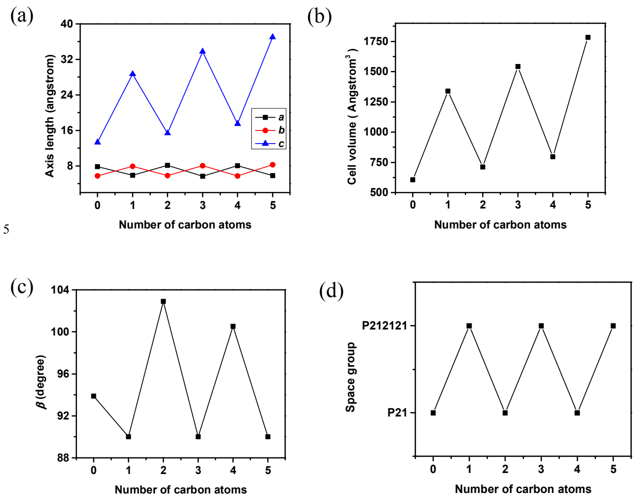

Fig. 2 The cell parameters alternation upon number of carbon atoms in ester groups. (a) axis lengths, (b) cell volumes, (c) β angles, and (d) space group. Note: Number of carbon atoms stands for substituent groups in naproxen and its derivatives.

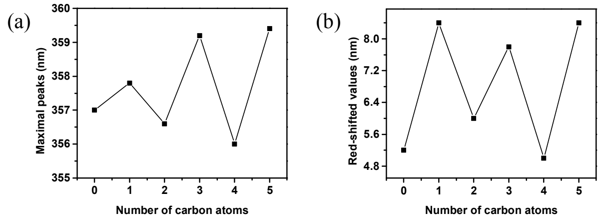

Fig. 3 (a) The maximal luminescent peaks of compounds **1**-**6** at solid state under room temperature as number of carbon atoms. (b) The red-shifted values of peaks between solid state and solution as number of carbon atoms.

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Synopsis

A set of chiral crystal solids with odd and even number of carbon atoms based on *S*-naproxen have been prepared, alternatively crystallizing in the space group $P2_1$ and $P2_12_12_1$, respectively, which show odd-even effects on cell parameters, melting points, and luminescent properties.

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