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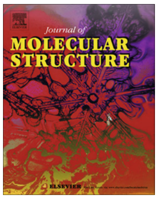


Spontaneous resolution in a new chiral purely organic crystal containing homochiral helical chains: Synthesis, crystal structure, and phosphorescence

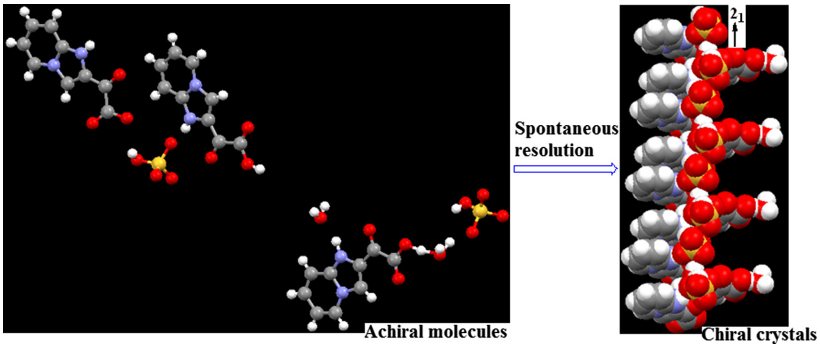
Chen Shen, Yiman Zhang, Guoping Yong *, Yumei Zhao

Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

HIGHLIGHTS

- A novel chiral purely organic crystal was prepared and structurally characterized.
- Spontaneous resolution occurred during the crystallization.
- Hydrogen bond and hydrophobic interactions induce the left-handed helical chain.
- Chirality of the originally formed helical chain is transferred uniformly.
- This chiral crystal exhibits interesting phosphorescent property.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel chiral purely organic crystal $[(\mathbf{A})(\mathrm{H}\mathbf{A}^{+}\mathrm{HSO}_4^{-})_2]\cdot 2\mathrm{H}_2\mathrm{O}$ (**1**) (**A** = 2-(imidazo [1,2-*a*]pyridin-2-yl)-2-oxoacetic acid) has been obtained through diffusion of acetone into sulfuric acid aqueous solution of **A**. This crystal was characterized by the elemental analysis, IR spectrum and the single crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic system, chiral space group $P2_1$, with $a = 10.092(2)$ Å, $b = 15.641(3)$ Å, $c = 10.551(2)$ Å, $\beta = 101.62(3)°$, and $Z = 2$. Compound **1** reveals left-handed 2_1 helical chain assembled by hydrogen bond and hydrophobic (short atomic contact) interactions, in which spontaneous resolution occurs. The left-handed chirality of the original helical chain is transferred uniformly to adjacent chain in a homochiral manner, through interchain hydrogen bond and hydrophobic interactions, resulting in the formation of chiral layer. Compound **1** also exhibits green phosphorescence.

Introduction

The supramolecular assembling process using noncovalent interactions such as hydrogen bond, π–π stacking, C–H–π and ion–π interaction, electrostatic, hydrophobic and charge-transfer interaction [1], has been recognized as a high-potential technique to construct functional molecular materials. Through noncovalent interactions, many novel organic solids with applications in the pharmaceutical [2], electronic [3], optical [4,5], luminescent [6], catalytic [7], ferroelectric [8], and magnetic [9,10] fields have been reported. Of these noncovalent interactions, the hydrogen bond is an important tool for creation of desired organic molecular arrangements and interesting properties. For example, hydrogen bond can induce the chiral helicity, creating the left- or right-handed helical assembly by the connection of each helical molecule through continuous intermolecular hydrogen bonds in the crystal packing [11]. Moreover, hydrogen-bonding functionalized tetrathiafulvalene

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* Corresponding author. Tel.: +86 551 6360 1584; fax: +86 551 6360 1592.
E-mail address: gpyong@ustc.edu.cn (G. Yong).

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derivatives have revealed high room-temperature conductivity (even metallic state conductivity), demonstrating that hydrogen bond plays a vital role in the design of purely organic conductors [12,13].

Chirality is of fundamental importance for life and plays a key role in biological system and pharmacy [14], as well as in advanced materials such as nonlinear optical devices [15,16], enantioselective synthesis and asymmetric catalysis [17,18]. Much interest has been focused on the construction of helical crystals using chiral or achiral molecules, because many important biopolymers such as DNA and peptides possess helical structures with a single right-handed chirality. In general, right- and left-handed helices are obtained in equal amounts as a meso compound when achiral or racemic building blocks are used [19]. A meso compound contains an equal amount of right- and left-handed helices in a single crystal, and each crystal is achiral and crystallizes in a central symmetrical space group. In some cases, however, spontaneous resolution occurs during the crystallization [20], yielding a conglomerate [21]. A conglomerate is a mechanical and enantiopure and crystallizes in a chiral space group. Even though the discovery of spontaneous resolution by Louis Pasteur [22] happened over 100 years ago, it is still a rare phenomenon and unpredictable, because the laws of physics determining the processes are not yet fully understood [20]. It has been found that noncovalent interactions such as hydrogen bond may play a key role in the process of spontaneous resolution [21,23,24]. Up to date, the spontaneous resolution mainly concerns with the metal complex crystals, however, the spontaneous resolution occurred in purely organic crystals is very scarce [7].

Recently, we found a new stacking-induced white light phosphorescent crystal based on 2-(imidazo[1,2-*a*]pyridin-2-yl)-2-oxoacetic acid [25]. Moreover, 2-(imidazo [1,2-*a*]pyridin-2-yl)-2-oxoacetic acid salts also exhibit different phosphorescent colors in solid state induced by crystal stacking structures or various noncovalent interactions (hydrogen bond, anion–π interaction, etc) [26]. As a part of our general research effort intending to extend the range of molecular materials, herein, we report the synthesis, crystal structure and phosphorescent property of a sulfate salt crystal based on 2-(imidazo[1,2-*a*]pyridin-2-yl)-2-oxoacetic acid (**A**), $[(\mathbf{A})(\mathrm{H}\mathbf{A}^{+}\mathrm{HSO}_4^{-})_2]\cdot 2\mathrm{H}_2\mathrm{O}$ (**1**). It is discovered that **1** is a chiral crystal with a chiral space group of $P2_1$. Such chirality appears only by spontaneous resolution during the crystallization of **1**, because **A** is an achiral starting material. A detailed structural investigation indicates that the hydrogen bond and hydrophobic (short atomic contact) interactions induce one-dimensional (1D) helical chain, and play a key role in the transfer of chirality between neighboring helical chains, leading to the 1D helical chains being packed in a homochiral manner.

Experimental

Materials and methods

2-(Imidazo[1,2-*a*]pyridin-2-yl)-2-oxoacetic acid (**A**) was synthesized as described previously [25]. All other reagents were commercially available and used as received. Microanalytical data (C, H and N) were collected on Vario ELIII elemental analyzer. FT-IR spectrum was recorded from KBr pellet in range 4000–400 cm^{-1} on a Bruker EQUINOX55 FT-IR spectrophotometer. The solid-state photoluminescence (PL) spectrum and the decay lifetime were determined at room temperature on a Fluorolog-3-TAU fluorescence spectrophotometer. The solid-state quantum yield was measured also on a Fluorolog-3-TAU fluorescence spectrophotometer equipped with a BaSO_4-coated integrating sphere, upon excitation at 365 nm.

Table 1
Crystal data and structure refinement for **1**.

Empirical formula	$C_{27}H_{26}N_6O_{19}S_2$
CCDC number	1030725
Formula weight	802.66
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1$
Unit cell dimensions	a = 10.092(2) Å, α = 90° b = 15.641(3) Å, β = 101.62(3)° c = 10.551(2) Å, γ = 90°
Volume	1631.3(6) $\mathrm{Å}^3$
Z	2
Calculated density	1.634 $\mathrm{mg/m}^3$
Absorption coefficient	0.261 mm^{-1}
$F(000)$	828
Sample size	0.40 × 0.36 × 0.30 mm^3
Theta range for data collection	3.27–26.37°
Reflections collected/unique	10074/6159 [R(int) = 0.0236]
Data/restraints/parameters	6159/1/529
Observed reflections	5302
Goodness-of-fit on F^2	1.019
Final R indices [I > 2sigma(I)]	R_1 = 0.0393, wR_2 = 0.0857
R indices (all data)	R_1 = 0.0494, wR_2 = 0.0924
Absolute structure parameter	−0.03(6)

Preparation of $[(\mathbf{A})(\mathrm{H}\mathbf{A}^{+}\mathrm{HSO}_4^{-})_2]\cdot 2\mathrm{H}_2\mathrm{O}$ (**1**) crystal

To a methanol solution (15 mL) of 2-(imidazo[1,2-*a*]pyridin-2-yl)-2-oxoacetic acid (0.19 g, 1.0 mmol) was dropwise added sulfuric acid aqueous solution (1:1, v/v). The solution was stirred for 20 min, and then the solution was filtered. Diffusion of acetone into above yellow solution for one week, yellow block crystals were isolated. The crystals were dried in air to give the title compound $[(\mathbf{A})(\mathrm{H}\mathbf{A}^{+}\mathrm{HSO}_4^{-})_2]\cdot 2\mathrm{H}_2\mathrm{O}$ (**1**), yield: 0.17 g (0.21 mmol), 21.00%. IR (KBr, cm^{-1}): 3515s(ν(OH)), 3077 m, 1724 m(ν(COOH)), 1698s(ν(COO^-)), 1651s(ν(C=O)), 1581 m (ν(C=N)), 1550m, 1461s, 1411s, 1366m, 1306s, 1252s, 1166s(HSO_4^-), 939m, 910m, 844m, 805m, 780m, 767m, 728m, 605m. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{27}H_{26}N_6O_{19}S_2$ (802.66) (%): C, 40.40; H, 3.26; N, 10.47. Found (%): C, 40.26; H, 3.15; N, 10.41.

X-ray crystallography

The X-ray diffraction measurement was performed on a Gemini S Ultra CCD diffractometer (Oxford diffraction Ltd.), and the data were collected at 293(2) by using graphite-monochromated Mo Kα (λ = 0.71073 Å). The structure was solved by direct method (SHELXL 97) and completed by difference Fourier method (SHELXL 97). Refinement was performed against F^2 by weighted full-matrix least-squares (SHELXL 97) [27], and empirical absorption correction (SCALE3 ABSPACK) was applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C—H hydrogen atoms were placed in geometrically calculated positions; the N—H and O—H hydrogen atoms were located in the difference Fourier map and kept fixed in that position. Weighted R factor (R_w) and all goodness of fit S are based on F^2, conventional R factor (R) is based on F.

Result and discussion

Crystal structure

The crystallographic data and details of structure refinement are listed in Table 1. As shown in Fig. 1, the crystal structure of **1** consists of one internal salt-type **A** in which the proton at