

A 3D Chiral Hydrogen Bond Framework Based on Phenanthroline Hydrogen 4,5-Dichlorophthalate: Crystal Structure and Luminescent Properties

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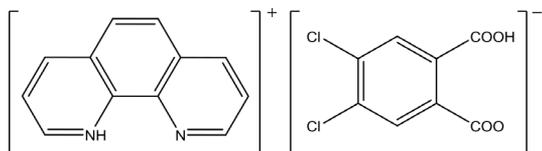
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A salt with the composition $[C_{12}H_9N_2][C_8H_3Cl_2O_4]$ (**1**) with 4,5-dichlorophthalic acid and 1,10-phenanthroline (phen) has been synthesized and characterized by IR, UV spectroscopy, elemental analysis, and X-ray crystallography. Compound **1** represents a 3D chiral supramolecular framework containing monohelical chains (2_1 axis) through multiform C–H \cdots O, O–H \cdots O, N–H \cdots N intramolecular hydrogen bonds and C–H \cdots O, N–H \cdots O intermolecular hydrogen bonds. Otherwise, two types of face-to-face $\pi\cdots\pi$ interactions between the aromatic rings are found in the solid state. The luminescent properties of compound **1** were investigated in the solid state at room temperature.

Key words: Hydrogen Bond, Crystalline Salt, Helix, Luminescence Properties

Introduction

Supramolecular crystalline salts have attracted significant interest due to their potential applications in fields as diverse as chemistry, biology and materials science [1–4]. Hydrogen bonds and $\pi\cdots\pi$ interactions in synthons represent two important classes of intermolecular forces, with which many excellent structures have been reported to demonstrate how the rational design and assembly of supramolecular solids can be achieved [5–7]. These materials are attractive to chemists not only for the variety of topologies and intriguing frameworks, but also for their interesting catalytic, electric and optical properties [8–10].



Scheme 1. Chemical formula drawing of compound **1**.

Organic carboxylic acids and nitrogen-containing organic molecules as hydrogen-bonded synthons find broad use to form complicated structures in the field of crystal engineering [11–13]. The design and construction of a chiral framework sustained by hydrogen bonds represents a considerable synthetic challenge since this has to be achieved *via* spatial organi-

zation of simple achiral synthons without any chiral auxiliaries [6, 14]. As a part of our continuing investigations on functional supramolecular systems and their photoluminescent properties [4, 13, 15], in the present paper a chiral crystalline salt $[C_{12}H_9N_2][C_8H_3Cl_2O_4]$ (**1**) was synthesized and characterized by single-crystal X-ray diffraction (Scheme 1). Compound **1** exhibits strong fluorescent emission in the solid state at r. t.

Experimental Section

General

Materials: All chemicals were reagent grade quality obtained from commercial sources and used without further purification.

Instrumentation: Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded from KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{-1} region. The UV/Vis spectra were measured in methanol solution with a Hitachi U-4100 spectrophotometer, and the luminescence spectra were obtained on a Hitachi F-7000 fluorescence spectrophotometer.

Synthesis

Compound **1** was synthesized by a hydrothermal method. A mixture of 4,5-dichlorophthalic acid (0.037 g, 0.15 mmol), 1,10-phenanthroline (0.027 g, 0.15 mmol) and NaOH (0.008 g, 0.2 mmol) in 3 mL of MeOH and 5 mL of water

Table 1. Summary of crystal data and refinement results for the title compound.

Formula	C ₂₀ H ₁₂ Cl ₂ N ₂ O ₄
<i>M_r</i>	415.22
Crystal size, mm ³	0.18 × 0.16 × 0.15
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
<i>a</i> , Å	6.4232(13)
<i>b</i> , Å	7.5415(16)
<i>c</i> , Å	18.347(4)
β, deg	94.698(3)
<i>V</i> , Å ³	885.8(3)
<i>Z</i>	2
<i>D</i> _{calcd} , g cm ⁻³	1.56
μ(MoK _α), cm ⁻¹	4.0
θ range for data collection, deg	2.70–28.27
<i>F</i> (000), e	424
<i>hkl</i> range	−7 ≤ <i>h</i> ≤ 2, −9 ≤ <i>k</i> ≤ 9, −21 ≤ <i>l</i> ≤ 20
Refl. measured / unique / <i>R</i> _{int}	3592 / 2910 / 0.011
Param. refined	253
<i>R</i> 1(<i>F</i>) / <i>wR</i> 2(<i>F</i> ²) [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0308 / 0.0789
<i>R</i> 1(<i>F</i>) / <i>wR</i> 2(<i>F</i> ²) (all refl.)	0.0337 / 0.0811
<i>x</i> (Flack)	0.06(6)
Gof (<i>F</i> ²)	1.033
Δρ _{fin} (max / min), e Å ⁻³	0.15 / −0.20

Table 2. Selected bond lengths (Å) and angles (deg) of the title compound.

O(1)–C(13)	1.215(3)	O(2)–C(13)	1.283(3)
O(3)–C(14)	1.273(3)	O(4)–C(14)	1.227(3)
C(13)–C(15)	1.524(3)	C(14)–C(16)	1.526(3)
C(15)–C(20)	1.393(3)	C(15)–C(16)	1.413(3)
C(16)–C(17)	1.381(3)		
O(1)–C(13)–O(2)	121.6(2)	O(4)–C(14)–O(3)	123.2(2)
O(2)–C(13)–C(15)	119.63(18)	O(3)–C(14)–C(16)	119.43(18)
O(4)–C(14)–C(16)	117.3(2)	C(20)–C(15)–C(13)	112.76(18)
C(20)–C(15)–C(16)	117.96(19)	C(17)–C(16)–C(15)	118.34(19)
C(16)–C(15)–C(13)	129.26(18)	C(15)–C(16)–C(14)	128.18(18)
C(17)–C(16)–C(14)	113.46(18)		

was stirred for 0.5 h, sealed in a 30 mL Teflon-lined stainless-steel bomb and heated at 160 °C for 96 h. Then the autoclave was cooled to r. t., and colorless block shaped crystals were isolated and washed with distilled water. Yield: 21 %. – Elemental analysis for C₂₀H₁₂Cl₂N₂O₄: calcd. C 57.85, H 2.91, N 6.75; found C 57.78, H 2.95, N 6.85.

X-Ray crystallographic study

A suitable single crystal of size 0.18 × 0.16 × 0.15 mm³ as obtained above was selected for the crystallographic study and mounted on a Bruker SMART APEX CCD diffractometer with ω and φ scan mode. All diffraction measurements were performed at room temperature using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The structure was solved by Direct Methods and refined by full-matrix least-squares on *F*² using the SHELXS/L 97 program

suite [16]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques, and all hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. Space group, lattice parameters and other relevant information are listed in Table 1. Relevant interatomic bond lengths and angles for **1** are given in Table 2.

CCDC 843320 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

IR and UV spectra

In the IR spectrum of compound **1**, two strong broad bands at 3440 and 3077 cm⁻¹ are assigned to the ν(OH) and ν(NH) stretching vibrations, which agrees well with those of the relevant components [17, 18]. Compound **1** shows several bands at 1695, 1599 and 1575 cm⁻¹ which can be attributed to the ν(OCO) stretching vibrations of the carboxyl units. Their identity was finally confirmed by X-ray crystallography. The UV spectrum of compound **1** in methanol solution displays a strong absorption peak at 268 nm, which can be assigned to the *n*-π* transition.

Crystal and molecular structure

The structure analysis by single-crystal X-ray diffraction revealed that compound **1** forms a 3D chiral supramolecular framework which contains helical chains on a 2₁ axis. The asymmetric unit consists of a 4,5-dichlorophthalic acid monoanion and a phenanthroline mono cation. As shown in Fig. 1, one hydrogen atom of an O(4) atom in a carboxyl

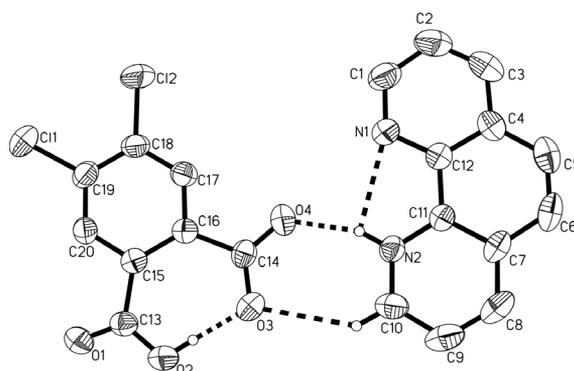


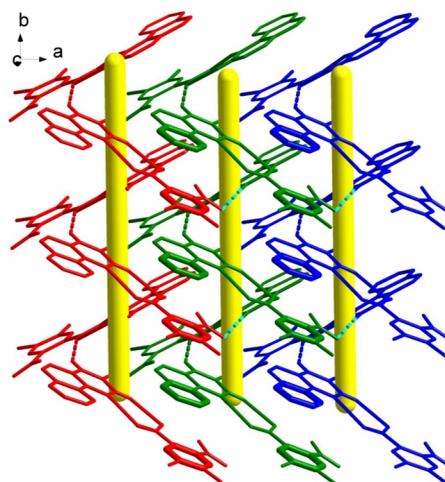
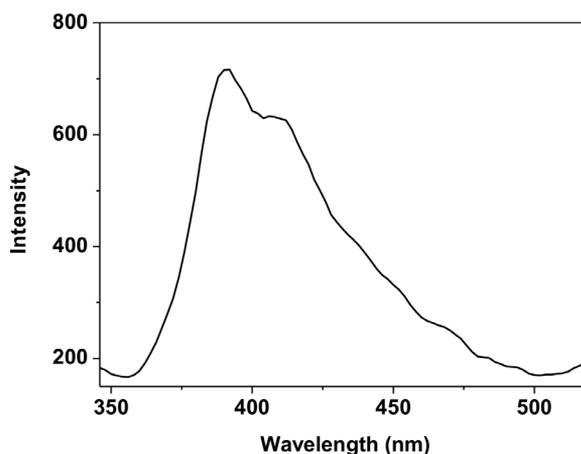
Fig. 1. ORTEP drawing of compound **1** with atom numbering scheme adopted. Hydrogen bonds are shown as dashed lines; displacement ellipsoids at the 50 % probability level.

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(D–H···A)	Symmetry transformation for A
N(1)–H(2A)···O(4)	0.86	1.88	2.697(2)	159	
N(2)–H(2A)···N(1)	0.86	2.40	2.737(3)	104	
O(2)–H(2C)···O(3)	0.82	1.58	2.395(3)	178	
C(8)–H(8A)···O(3)	0.93	2.52	3.298(3)	141	$1 - x, -1/2 + y, 1 - z$
C(9)–H(9A)···O(1)	0.93	2.47	3.392(3)	169	$-x, 1/2 + y, 1 - z$
C(10)–H(10A)···O(3)	0.93	2.53	3.300(3)	141	

Table 3. Hydrogen bonding interactions (Å, deg) in **1**.

group of 4,5-dichlorophthalic acid is transferred to an N(2) atom of phenanthroline (phen). The typical character of the structure of compound **1** is the existence of multiple strong intramolecular hydrogen bonds in each component and intermolecular hydrogen bonds between 4,5-dichlorophthalate anion and protonated phen (Table 3). An intramolecular hydrogen bond O(2)–H(2C)···O(3) is found in the acid component (Fig. 1). As for O(2)–H(2C)···O(3), the distance of O(2)···O(3) is 2.395(3) Å, suggesting a strong hydrogen bond with the angle O(2)–H(2C)···O(3) of 178°. An N(2)–H(2A)···N(1) intramolecular hydrogen bond is found in the protonated cation with an N(2)···N(1) distance of 2.737(3) Å and an N(2)–2(2A)···N(1) angle of 104°. Moreover, there is a pair of intermolecular hydrogen bonds, C(10)–10(10A)···O(3) and N(2)–2(2A)···O(4), between the protonated nitrogen atom N(2) and one carbon atom C(10) in the cation and two carboxylate oxygen atoms O(3), O(4) of the 4,5-dichlorophthalic acetate to closely link cation and anion.

The chiral assembly from achiral components on the basis of helical motifs is of current interest as one of the most attractive and evocative strategies due to the intrinsic chiral character of helicates [19–21]. Herein, single-crystal structure analysis shows that (achiral) **1** crystallizes in the chiral monoclinic space group $P2_1$ as conglomerate. The single crystals are enantiomerically pure, the one chosen exhibits *M* helicity by a spontaneous resolution process. Fig. 2 shows the chiral infinite monohelical chains around the 2_1 axis at $(-1/2, y, 1/2)$ constructed by intrachain C(8)–8(8A)···O(3) ($1 - x, -1/2 + y, 1 - z$) hydrogen bonds between adjacent units in the dimeric structures. The helical pitch is 7.5415(16) Å along the crystallographic *b* axis, which results in one full rotation around the 2_1 helical axis. Furthermore, adjacent 2_1 helical chains are linked by interchain hydrogen bonds C(9)–9(9A)···O(1) ($-x, 1/2 + y, 1 - z$) to construct a multi-helical array. Additionally, two kinds of face-to-face π ··· π interactions involving two parallel rings from adjacent he-

Fig. 2 (color online). Supramolecular structure of compound **1** showing 2_1 helical chains around the yellow axes and hydrogen bonds (dashed line); π ··· π interactions are between rings drawn with increased thickness.Fig. 3. The emission spectrum ($\lambda_{\text{ex}} = 280$ nm) of compound **1** in the solid state at r. t.

lical chains are found in the solid state, and probably play an important role in stabilizing the framework. The π ··· π interaction between the aromatic rings [C(15)–15(20)] and [N(1)C(1)–1(4)C(12)] is

characterized by centroid-centroid separations of 3.80 and 3.76 Å, and the shortest interplanar atom...atom distances are 3.44 and 3.51 Å, respectively. Studies on crystal engineering reveal that these kinds of intermolecular force are important in molecular structure and molecular packing [22]. Herein, the above shown multiform intermolecular interactions are substantially strong, and the chiralities of helical units are extended into 3D supramolecular frameworks to construct a chiral species.

Luminescence properties

The solid-state luminescent properties of compound **1** were investigated at r.t. As shown in Fig. 3, upon excitation at 280 nm, compound **1** shows the

main luminescent emission peak at 387 nm and a shoulder emission at 420 nm. Compared to that of 4,5-dichlorophthalic acid and phen by literature [23, 24], the photophysical properties of compound **1** may be attributed to the π - π^* and n - π^* transitions on the basis of the emission of acid and phen. The observed variation in the luminescent is perhaps due to the presence of multiform strong hydrogen bond interactions in the supramolecular crystal structure of **1**.

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