



单一手性一价铜配位聚合物:晶体结构,荧光,SHG 响应及介电性质

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A Homochiral Cu(I) Coordination Polymer: Crystal Structure, Luminescent, SHG Response and Dielectric Property

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Abstract: Under hydrothermal conditions, homochiral ligand (4a*R*,8a*R*)-2,3-di(thiophen-2-yl)-decahydroquinoxaline (DTDCQ) reacted with CuBr to give 1D helical chain complexes [(DTHHQ)CuBr]_n (**1**). Single crystal X-ray determination shows that compound **1** crystallize in chiral space groups *P*₂₁*2*₁*2*₁ and the experimental result indicated that **1** has SHG (second harmonic generation) active with approximate responses 0.4 times that of urea. Fluorescent analysis showed it exhibits one intense emission band at 377 nm when the exciting radiation was set at 340 nm. Dielectric constant of compound **1** were measured at different frequencies at room temperature. CCDC: 745354.

Key words: chiral; Cu(I); coordination polymer; fluorescence; permittivity; SHG

Many solid-state physical properties, such as pyroelectricity, piezoelectricity, ferroelectricity, nonlinear optical, second harmonic generation (SHG), and triboluminescence are only found in chiral or noncentrosymmetric bulk materials^[1-5]. Of particular importance are non-linear optical (NLO) function (especially SHG) and ferroelectric properties because of their practical importance in areas such as telecommunications, optical storage and information processing^[6-9]. In recent years, much of the attention in this field has been

focused on developing inorganic compounds^[10-14]. In contrast, studies toward developing non-linear optical materials based on metal-organic compound (MOC) have remained sparse^[15-17]. While metal coordination compounds have received widespread attention in recent years because of the ability of the organic inorganic hybrid material to possess the useful properties of both organic (chromophore, chirality, and tailorable) and inorganic (physical properties and coordination mode) compounds within a single molecular-scale composite. In addition,

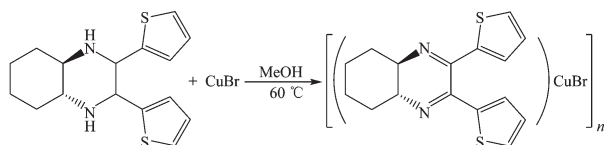
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metal organic complexes offer not only increased synthetic flexibility for optimization of hyperpolarizability but also well-defined metal centers and oxidation states, which, in turn, would provide the ability to fine-tune the electronic properties of the surrounding ligands^[18]. We have realized that the homochiral compounds should be good candidates, which easily crystallize in non-centrosymmetric point groups leading to SHG response. In this article, we wish to describe our successful development of crystal-engineering strategies toward using homochiral DTDCQ with Cu(I) ion to construct organic-inorganic compound that can crystallize in chiral space groups as shown in Scheme 1 and report the synthesis, structure, luminescent, SHG response and dielectric properties of a 1D homochiral Cu(I) complexes, [(DTHHQ)CuBr]_n.



Scheme 1

1 Experimental section

1.1 Material and instrument

Chemicals and solvents in this work were commercially obtained and used without any further purification. Infrared spectra were recorded on SHIMADZU IRprestige-21 FTIR-8400S spectrometer in the spectral range 4 000~400 cm⁻¹, with the samples in the form of potassium bromide pellets. ¹H NMR spectra were recorded a Bruke DRX500 NMR spectrometer. The solid-state fluorescent spectra by SHIMADZU RF-5301PC. Dielectric constant was conducted using an automatic impedance TongHui2828 Analyzer with frequency of 20 to 1 MHz, and pellet sample was made through high-pressure of 8 MPa. the second-order nonlinear optical intensity was estimated by measuring a powder sample 80~150 μm in diameter in the form of a pellet relative to urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1 064 nm was used to generate a SHG signal from powder samples. The backscattered SHG light was collected by a spherical concave mirror and passed through a filter

that transmits only 532 nm radiation^[19].

1.2 preparation of ligand DTDCQ

(4a*R*,8a*R*)-2,3-di (thiophen-2-yl)-4a,5,6,7,8a-hexahydroquinoxaline (2.0 g, 6.9 mmol) (DTHHQ) was dissolved in methanol (30 mL) and NaBH₄ (0.3 g) was added to the solution portionally. The mixture was stirred at room temperature for 3 h. The resulting solution was poured into ice water (200 mL), then extracted with methylene chloride (30 mL×2). The organic phase was washed with saturated sodium chloride aqueous solution (20 mL), then dried with anhydrous sodium sulfate. After removed the solvent, the residue was recrystallized from properly amount of ethanol to afford DTDCQ as a yellowish crystalline powder in 98.2% yield. IR (KBr, cm⁻¹): 3 292(w), 3 069(m), 2 918(s), 2 850(s), 2 823(m), 2 807(m), 1 542(w), 1 444(m), 1 375(w), 1 363(w), 1 308(w), 1 284(m), 1250(w), 1 234(w), 1 209(w), 1 183(w), 1 169(w), 1 131(s), 1 110(w), 1 071(w), 1 040(w), 966(w), 897(m), 853(m), 835(m), 818(s), 756(s), 726(s), 704(vs), 646(w), 616(w), 569(w), 531(w), 510(w), 494(m), 455(w). ¹H NMR, δ(ppm):7.15(d, *J*=4.9 Hz, 2H, Ar-H), 6.80(dd, *J*=3.4 Hz, 2H, Ar-H), 6.61(s, 2H,), 4.13(s, 2H), 2.63(s, 2H), 1.97(2H), 1.79(2H), 1.72(2H), 1.41(s, 4H).

1.3 Preparation of complexes

[(DTHHQ)CuBr]_n (1)

CuBr (2.5 mmol, 0.36 g) and DTDCQ (1 mmol, 0.3 g) were placed in a thick Pyrex tube (ca. 20 cm in length). After addition of methanol (1mL) and water (1mL), the tube was frozen with liquid N₂, evacuated under vacuum, and seal with a torch. The tube was heated at 70 °C for five days to give red block crystals. The yield of [(DTHHQ)CuBr]_n (1) was 45% based on DTDCQ. IR (KBr, cm⁻¹): 3 180(s), 3 104(w), 2 933(s), 2 855(m), 1 610(m), 1 583(w), 1 531(m), 1 508(w), 1 444(m), 1 422(s), 1 346(w), 1 296(m), 1 251(m), 1 238(m), 1 126, 1 049(m), 1 006(m), 962(w), 926(w), 897(w), 871(w), 852(m), 836(m), 761(w), 719(vs), 703(s), 611(w), 576(w), 538(w), 476(w), 445(w).

1.4 Crystal structure determination

A single crystal of the title complex with approximate dimensions 0.18 mm×0.16 mm×0.14 mm was selected for data collection at 293(2) K, using a Rigaku

SCXmini diffractionmeter by the ω scan technique at room temperature with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). Bruker Smart 1K CCD system diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). The structure parameters were obtained by CrystalClear^[20] with the θ range for data collection from 3.42 to 25.98°. Of the 15 569 reflections collected, there were 3 373 unique reflections ($R_{\text{int}}=0.115\ 7$). The absorption correction was carried out by multi-scan method. The structure was solved

by direct methods with SHELXS-97 and refined by full matrix least squares on F^2 with SHELXL-97^[21-22]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms were added theoretically and refined with riding model and fixed isotropic thermal parameters. Detailed data collection and refinement of the compound **1** are summarized in Table 1, and the selected bond distances and angles are listed in Table 2.

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

Empirical formula	C ₁₆ H ₁₆ N ₂ S ₂ CuBr	Crystal size / mm	0.1800×0.1600×0.1400
Formula weight	443.88	θ range for data collection / (°)	3.42–25.98
Temperature	293(2) K	Limiting indices	$-7 \leq h \leq 7, -11 \leq k \leq 11, -37 \leq l \leq 37$
Wavelength / nm	0.071073	Reflections collected	15 569
Crystal system	Orthorhombic	Independent reflections (R_{int})	3 373 (0.115 7)
Space group	$P2_12_12_1$	Completeness to $\theta=25.98$ / %	99.7
a / nm	0.59230(7)	Absorption correction	Semi-empirical from equivalents
b / nm	0.94858(13)	Refinement method	Full-matrix least-squares on F^2
c / nm	3.0568(4)	Data / restraints / parameters	3373 / 0 / 199
Volume / nm ³	1.7174(4)	Goodness-of-fit on F^2	1.092
Z	4	Final R indices [$I > 2\sigma(I)$]	$R_1=0.061\ 4, wR_2=0.104\ 1$
D_c (Mg·m ⁻³)	1.717	R indices (all data)	$R_1=0.095\ 9, wR_2=0.115\ 4$
μ / mm ⁻¹	3.838	Absolute structure parameter	0.016(19)
$F(000)$	888	Largest diff. peak and hole / (e·nm ⁻³)	834 and -786

Table 2 Selected bond-length (nm) and bond-angle (deg) of compound **1**

Br(1)-Cu(1)	0.233 41(13)	Br(1)-Cu(1) ⁱ	0.245 16(13)	Cu(1)-N(1)	0.199 8(6)
Cu(1)-Br(1) ⁱⁱ	0.245 16(13)	Cu(1)-S(2)	0.273 2(2)		
Cu(1)-Br(1)-Cu(1) ⁱ	105.98(4)	N(1)-Cu(1)-Br(1)	133.18(17)	N(1)-Cu(1)-Br(1) ⁱⁱ	106.02(18)
Br(1)-Cu(1)-Br(1) ⁱⁱ	119.32(4)	N(1)-Cu(1)-S(2)	77.99(18)	Br(1)-Cu(1)-S(2)	106.58(6)
Br(1)ii-Cu(1)-S(2)	96.08(6)	C(6)-N(1)-Cu(1)	121.4(5)	C(12)-N(1)-Cu(1)	120.9(5)
C(16)-S(2)-Cu(1)	133.7(3)	C(13)-S(2)-Cu(1)	83.3(3)		

Symmetry transformations used to generate equivalent atoms: ⁱ $x-1/2, -y+1/2, -z$; ⁱⁱ $x+1/2, -y+1/2, -z$.

2 Results and discussion

The ligand DTDCQ react with CuBr under hydrothermal conditions, we didn't get complex including DTDCQ ligand, however we do get another unexpected compound [(DTHHQ)CuBr]_n. This may be due to DTDCQ ligand unstable under hydrothermal conditions and DTDCQ dehydrogenation reaction occurred. The asymmetric unit of **1** consist of one crystallographically

independent Cu(I) atom, one DTHHQ ligand and one μ_2 -Br atom (Fig.1). The Coordination environment of **1** with the atomic labeling is shown in Fig.2. The Cu(I) ion is coordinated by two bridging μ_2 -Br, one S atom and one N atom of DTHHQ ligand. The angles around Cu, in the range of 77.99°~133.18°, which suggests that the geometry around this tetracoordinated Cu atom is distorted tetrahedral. The N atom and the S atom from DTHHQ ligand chelate Cu atom to form a stable five-

member ring along the N(1)-C(12)-C(13)-S(2)-Cu(1) bond sequence (Fig.1). Further, the Cu atoms are linked by μ_2 -Br atoms to form a 1D helical chain along the Cu \cdots Br \cdots Cu \cdots Br \cdots Cu bond sequence (Fig.3). While the

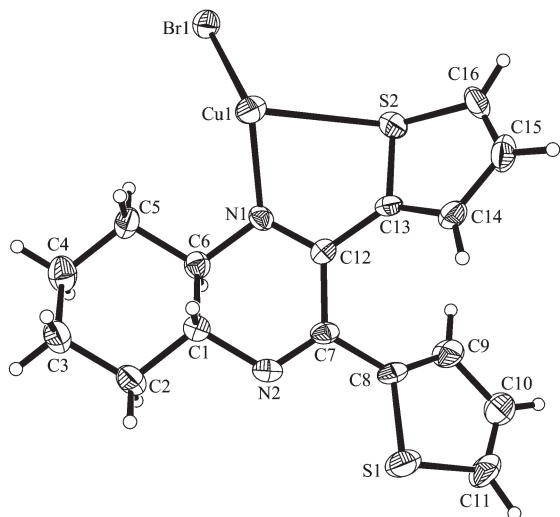


Fig.1 ORTEP view of asymmetric unit for compound **1**, displacement ellipsoids are drawn at the 30% probability level

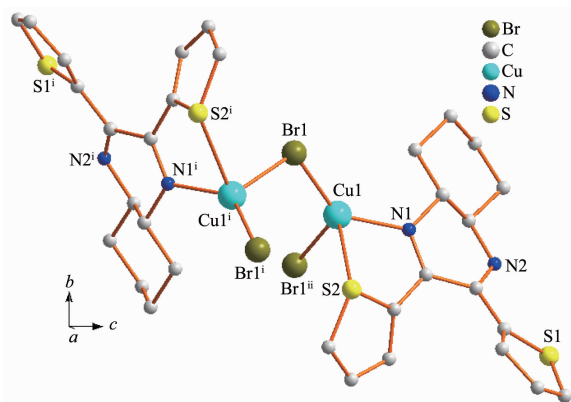


Fig.2 View of the coordination environment of Cu(I) in complex **1**, Hydrogen atoms have been omitted for clarity.

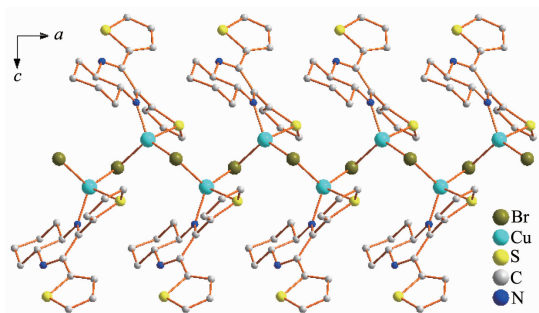


Fig.3 A perspective view of 1D chain representation of complex **1** along *b*-axis in which H atoms are omitted for clarity

bond lengths of Cu-N (0.199 4(6) nm) are slightly shorter than those found in the three coordination compounds mentioned above^[23-25] (0.205 5, 0.205 2, 0.204 8 nm), the two bridging Cu-Br bonds are 0.245 2 nm and 0.233 4 nm, respectively, which are shorter than those found in the coordination compounds mentioned above (0.248 5~0.257 9 nm)^[26-27]. In addition, the Cu-S bond lengths (0.273 2 nm) in complex **1** is obviously longer than that of analogous complexes (0.23~0.25 nm)^[27]. The angles of Cu(1)-Br(1)-Cu(1B) and Br(1A)-Cu(1)-Br(1) are 105.98° and 119.32°, respectively. The angle between the two thiophen ring (the plane C(13)-C(14)-C(15)-C(16)-S(2) and the plane C(8)-C(9)-C(10)-C(11)-S(1)) is 56.276°.

Of particular interest are the photoluminescent spectra of powdered (**1**). Fluorescence efficiency can be correlated with many structural features of chemicals including π - π^* and n - π^* transitions, structural rigidity, noncovalent interactions (e.g. hydrogen bonds, π - π interactions, and hydrophilic and hydrophobic interactions), interior intermolecular energy transfers, and photoinduced electron transfers^[28,29]. The solid-state fluorescent spectra for (**1**) at room temperature reveal maximal emission peaks at 377 nm (the exciting radiation set at 340 nm) as shown in Fig.4. The emission band may be attributable to the π - π^* transition of thiophen ring.

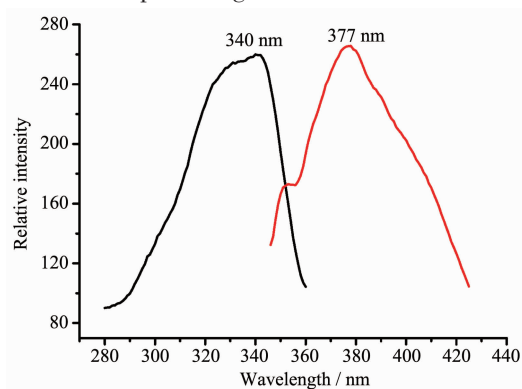


Fig.4 Fluorescent excitation (left) and emission (right) spectra of compound **1**

The permittivity ($\epsilon = \epsilon_1 - i\epsilon_2$, in which ϵ_1 and ϵ_2 are the corresponding real part and imaginary part of dielectric constant, dielectric dissipation factor $D = \tan \delta = \epsilon_2 / \epsilon_1$) of powdered samples of **1** in the form of pellets were measured. The frequency dependence of permittivity was taken at room-temperature as shown in Fig.5, it is interesting to note that the ϵ_1 at a lower

frequency reaches a maximum value 6 (200 Hz), which obviously drops to 2.7 at a relatively higher frequency of 1 MHz. This behavior is similar to that found for the perovskite-related oxide $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ^[30-32] and the previously reported homochiral zinc-quitenine coordination polymer^[33], both show a significant decline. Also the dielectric dissipation measurement reveals the similar trend (Fig.5).

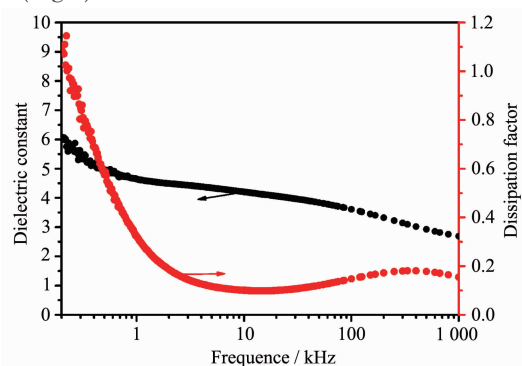


Fig.5 Dielectric constants and dielectric dissipation of compound **1** at frequency range from 200 Hz to 1 MHz at 293 K

It is known that a non-centrosymmetric structure may have second-order non-linear optic (NLO) effects, given that the complexes (**1**) crystallize in chiral space groups $P2_12_12_1$ which belongs to crystal class 222 and point group (D_2), because of the ligand coordination enhancing the rigidity of ligand, a good donor acceptor system is formed, which is essential for SHG effect, so we performed quasi-Kurtz^[19] SHG measurements on powder sample of **1** to confirm its acentricity as well as to evaluate its potential application as second-order NLO material. The compound **1** displays a second harmonic generation (SHG) activity with a response of approximately 0.4 times than that of urea.

In conclusion, a novel homochiral 1D helical complexes $[(\text{DTHHQ})\text{CuBr}]_n$ (**1**) was prepared through employing chiral ligand Under hydrothermal conditions .we studied fluorescence properties, SHG response and permittivity of the Coordination polymer. This class of materials provides a new impetus to construction of novel functional materials with potentially useful physical properties.

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