

## 发光的二维 Cu(I)分子箱 $[\text{CuCl}(\text{DBBD})_2]_n$

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### Luminescent Copper(I) 2D Molecular Box Containing Atropisomeric Biquinoline-based Ligands

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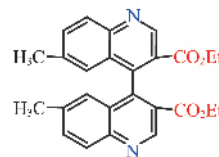
**Abstract:** Hydrothermal treatment of CuCl and atropisomeric ligand racemic-diethyl (*R,S*)-4,4'-biquinoline-6,6'-diethyl-3,3'-dicarboxylate (DBBD) (**1**) in the presence of H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH over 4 days at 104~109 °C yielded colorless block crystals  $[\text{CuCl}(\text{DBBD})_2]_n$  (**2**). The compound exhibits strong red fluorescent emission with a wavelength of 650 nm. The crystal of  $[\text{CuCl}(\text{DBBD})_2]_n$  belongs to monoclinic system with space group *C2/c*, and *a*=1.656 58(17) nm, *b*=2.025 0(2) nm, *c*=1.548 73(16) nm,  $\beta$ =107.879(2)°, *V*=4.944 4(9) nm<sup>3</sup>, *D<sub>c</sub>*=1.417 g·cm<sup>-3</sup>, *Z*=8. CCDC: 292932.

**Key words:** Cu(I); coordination polymer; synthesis; crystal structure; luminescent property

The luminescent property of copper(I) coordination compounds acquired extensive research, many organic ligands with nitrogen atom as a soft base, which coordinates to copper(I) salt as a soft acid, were induced in such luminescent material<sup>[1-6]</sup>, while is still a challenge for inorganic chemist to get copper(I) coordination polymer with strong luminescent property. However, in order to induce a multi-dentate organic ligand may result in the formation of the copper coordination polymer, the ligands like bipyridine derivatives have been winning scientists' intention, while there is no information about biquinoline which be used as a bidentates ligands in fluorescent copper(I) coordination polymer. Herein we report the

synthesis and characterization of 2D sheet copper(I) coordination polymer (**2**) involving such ligand with axial rotation that displays luminescent in solid state at room temperature.

The solvothermal treatment of CuCl and diethyl (*R,S*)-4,4'-biquinoline-6,6'-diethyl-3,3'-dicarboxylate (DBBD) (**1**) (Scheme 1) at 104~109 °C yielded colorless block crystal  $[\text{CuCl}(\text{DBBD})_2]_n$  (**2**) (Scheme 2). Fig.1 shows the structural unit and framework through



Scheme 1 Structure of compound **1**

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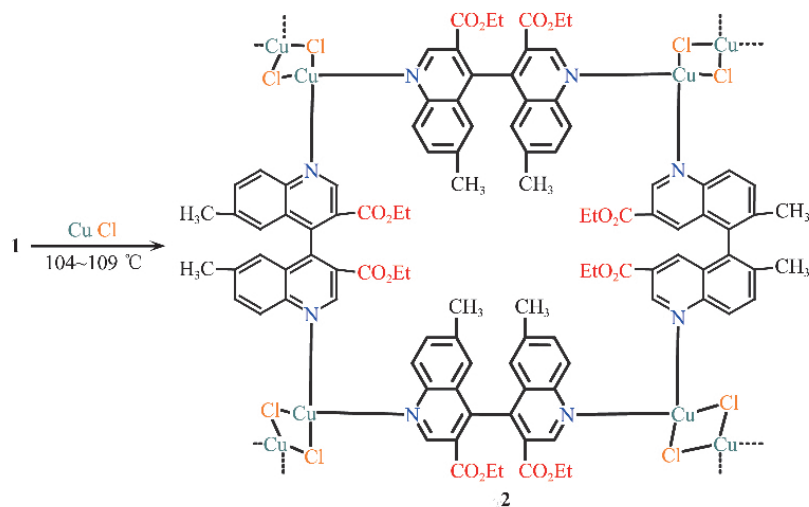
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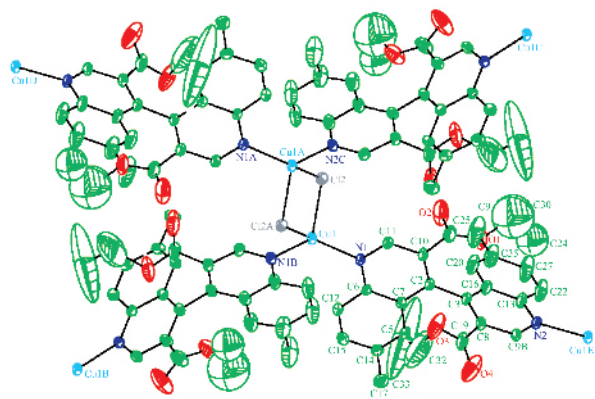
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the investigations of X-ray single crystal diffractions. The local coordination environment around each copper(I) center can be best described as a slightly distorted tetrahedron. Each copper coordinates to two chlorine atoms and two nitrogen atoms from two different ligands, in which chloride anion act as a  $\mu_2$ -

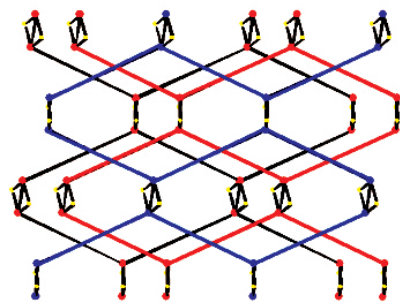
bridging mode to link to two different copper atoms, that is, there are two bridging chlorines between two copper centers. As seen from the packing structure of **2**, 2D layered structures stack together with ABAB... sequence to extend in third-dimension direction as shown in Fig.2.



Scheme 2



Hydrogen atoms are omitted for clarity  
Fig.1 Crystal structure of **2** drawn at 30% ellipsoids probability



2D layered structure stack together with ABAB sequence to extend in third-dimension direction  
Fig.2 Simplified packing structure of **2** the red sheet is top, the blue one is middle and the black one is bottom (long line stands for **1**)

The emission spectrum of **2** in the solid state at room temperature, shown in Fig.3, displays a maximum wavelength at ca. 650 nm.

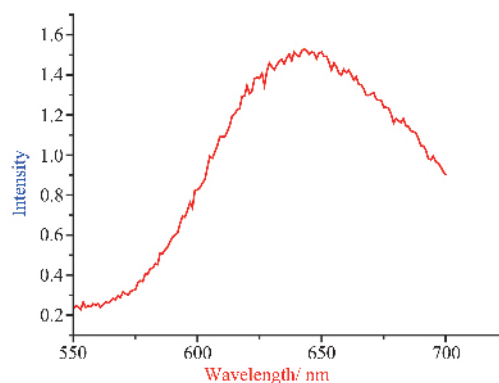


Fig.3 Solid-state emission spectrum of **2** at room temperature

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