Homochiral Cu(I) coordination polymer based on achiral precursors and its photocatalytic property

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A homochiral three-dimensional framework material, [Cu_7(4-bpt)$_6$(CN)(H_2O)] **(1)** (4-bpt = 3,5-bis(4-pyridyl)-1,2,4-triazole) has been successfully synthesized by solvothermal reaction, which generated through an unusual spontaneous asymmetrical crystallization from achiral precursors, and its photocatalytic properties on degradation of organic dyes are also investigated.

Introduction

Chirality is crucial in biological processes, which influence many fields such as biology, medicine, biotechnology and agriculture. Recently, great efforts have been made to design and construct the chirally coordination polymers, not only because of their intriguing variety of architecture, but also their potential application in enantioselective catalysis, chiral separation, optical materials.[1-6] Three distinct synthesis strategies can be used to synthesize homochiral materials. The most common one is using a chiral component as a starting point to construct homochiral frameworks. This method has been demonstrated successfully on many occasions.[7-10] The second and third methods are all based on the asymmetric crystallization of achiral building blocks. Recently, Morris and Bu developed controllable symmetry breaking by chiral induction,[11] which using inductive reagent, such as chiral solvent, additive or template to achieve homochirality from achiral precursors. This is a new direction and a fertile field for the development of homochiral materials.[12-16] The third method is only by preparing from achiral components via spontaneous self-resolution during crystal growth. Because of spontaneous resolution process often resulted in a mixture of racemic mixture, so random symmetry breaking crystallization without any chiral source is particular rare. So, finding out the driving force for symmetric breaking crystallization is very important to understand the generation of chiral. Previous research indicated that some supparmolecular interaction, such as hydrogen bond or π-π interaction, the conformation of an organic ligand, or the twisted topology may result in the origin of the chirality.[17-19] Other factors might also affect the chirality of compound. For example, helix axis plays an important role to build chiral framework.[20, 21] While adopting an intrinsically chiral topology is other recommendable approach toward the construction of chiral three-dimensional (3D)

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x frameworks from achiral precursors.[22] So, exploring intrinsically chiral topologies from so many metal–organic frameworks is very necessary. On the other hand, photocatalysis is a new technology for the treatment of all kinds of contaminants, which has received great research attention in the catalysis field. Some metal−organic frameworks (MOFs) have been demonstrated to be efficient photocatalysts on the green degradation of organic pollutants.[23, 24] However, such kinds of applications of MOFs on ultraviolet-light-driven photocatalysis are just beginning to emerge. How to achieve inexpensive, stable, and efficient MOFs photocatalysts is still a big challenge.

In this work, we reported a homochiral 3D framework material. [Cu_7(4-bpt)$_6$(CN)(H_2O)] **(1)** (4-bpt **=** 3,5-bis(4-pyridyl)-1,2,4-triazole), constructed from achiral precursors, also it has a new (3,4)-connected topology with intrinsic chirality. At the same time, the photocatalytic activity of complex **1** was also investigated by degradation of Rhodamine B under UV−vis light.

Results and discussion

Red block crystals of compound **1** was solverthermally synthesized by mixing Cu(NO_3)$_2$2.5H_2O and 4-abpt in DMA and water. A single crystal X-ray diffraction study showed that it crystallizes in the chiral monoclinic space group *C*2 with a Flack parameter of 0.03(2) demonstrates the homochirality of the single crystal. As shown in Fig. 1, the structure of **1** possesses four unique metal sites, adopting three kinds of coordination modes, namely two-, three- and four-coordination. Cu3 is in a liner geometry, coordinated by two μ_3-bridging 4-bpt ligands (Scheme S1). Cu1 and Cu4 are all in distorted trigonal geometries. However, the details of coordination environment of these copper atoms are different. Cu1 is coordinated by three triazole ring nitrogen donors from three different 4-bpt ligands, while Cu4 is coordinated by two triazole ring nitrogen atoms from two 4-bpt ligands and one oxygen atom form water molecule. Cu4 is located at a site with twofold symmetry. Cu2 is coordinated by three pyridyl ring nitrogen atoms of three different 4-bpt ligands and one cyanide group. The special stretch vibration of CN^- at 2121 cm^{-1} was observed in the infrared spectrum of **1** (Fig. S1), which further demonstrates the presence of the cyanide anion in this structure. The generation mechanism of the cyanide anion should be similar to other reported examples under solvothermal conditions.[25] At the same time, it has also been found that 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole in situ generated 3,5-bis(3-pyridyl)-1,2,4-triazole (4-bpt) ligand during the syntheses of compound **1.** The L ligand is deprotonated to balance the charges of the whole structure according to chemical and structural information (Scheme 1). 4-bpt ligands exhibit μ_3-bridging mode as tridentate ligand, which is not common to see. This asymmetric coordination mode of ligand may benefit to the chirality of compound. Both μ_3-L ligands and μ_2-CN ligands bridge the Cu(I) centers into a 3-D framework (Fig. 2) showing one kind of helice along the b-axis. The right-handed one is bridged by the L ligands between the Cu2 ions with a pitch of 15.5740 A. (Fig. S2)

An extraordinary structural feature of **1** is the observation of a new intrinsically chiral topology. Topological analysis was performed by the Topos[26-29] and Systre[30-32] programs. The framework of **1** can be reduced as a trinodal network with two planar three-connected (Cu1 atom and μ_3-L ligands) nodes and one tetrahedral four-connected (Cu2 atom) node (Fig. 3). The net exhibits 2_1 helices with the same handedness along the b-axis. This net can be specified by the vertex symbol of [$8_2.10_2.8_2.10_2.8_2.10_2$] and short Schlafli symbol of $\{6;8^2\}_3\{6^3\}\{8^3;10^3\}$. Further analysis by the Systre program reveals the ideal space group of this net is R32, retaining the chirality. The result shows the intrinsic chirality of this new (3,4)-connected net. It also demonstrates that the chirality of compound **1** is based on intrinsically chiral topology. For the heterocoordinate (3,4)-connected nets, there are four kinds of chiral topologies are listed in the RCSR database,[33] such as dmf, hst, pth-a and sto, and one named fir type reported by Lu.[22] Here, a intrinsically new (3,4)-connected topology with intrinsic chirality was observed in this 3-D Cu(I) compound from achiral precursors.

This compound is interesting in that: 1) 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole in situ generated 3,5-bis(3-pyridyl)-1,2,4-triazole (4-bpt). 2) The cyanide anion was generated under solvothermal conditions 3) new (3,4)-connected topology with intrinsic chirality.

The Dichroism Spectra (CD) Analysis

Circular dichroism(CD) spectra is the most common way of gaining as much evidence as is possible for the homochirality or enantioenrichment of bulk material. The bulk samples of **1** from parallel solverthermal syntheses were measured in the solid-state using MOS-405 spectropolarimeter. The CD spectra exhibit negative CD signal at about 240 nm (Fig. 4). These result confirmed the single-crystal analyses, providing an additional evidence for the asymmetric crystallization. In order to better validate the homochirality of **1**. 10 crystals were randomly picked out from the same crystallization and analyzed using single crystal X-ray diffraction. The Flack parameters of nine crystals are close to zero whereas the other one are close to one (Table S1). The results demonstrate that the product is enantioenriched.

PXRD Patterns and Thermal Analysis

Red block crystals of compound **1** were simply obtained by reacting achiral organic ligand 4-abpt with copper salt under solvethermal conditions. All major peaks of experimental powder X-ray pattern (PXRD) of compound **1** match quite well with that of the simulated PXRD, indicating reasonable crystalline phase purity (Fig. S3).

To characterize the compound more fully in terms of thermal stability, its thermal behaviours were studied by TGA. Upon heating, there is no obvious weight loss from 35~460 °C. A rapid weight loss is observed up to 460 °C, where the complex starts to decompose into the final product of Cu. This result may suggest that compound **1** is a high thermal stable material (Fig. S4).

Photoluminescence and photocatalytic property

The photoluminescent properties of **1** have been explored at room temperature in the solid state (Fig.S5). Compound **1** displays a green emission band with a peak maximum at 616 nm (excitation at 370 nm), which was assigned to metal-to-ligand charge transfer triple excited states [MLCT]. The diffuse reflectivity spectra of the powdered crystal samples were recorded by UNICO ultraviolet spectrophotometer (Fig. S6). The lowest energy peak at 450 nm can be assigned to a metal-to-ligand charge transfer. The values of the band gap for **1** obtained from corresponding MLCT transitions is 2.168 eV, which indicate that compound **1** may be potential photocatalysts.

In order to evaluate its photocatalytic activity, the degradation ability of organic dyes Rhodamine B (RhB) in water under UV light was studied (Fig. 5). For comparison, the photocatalytic performance of RhB in the absence of catalyst and commercial TiO_2 were also assessed under the identical experimental conditions. The decomposition of RhB was monitored by the characteristic absorption band at 555 nm. As illustrated in Fig. 6, the absorbance of RhB versus reaction time under UV light irradiation was plotted. After irradiation for 10 min, the degradation rate of RhB for complex **1** attains 69.4% (RhB 22.4%, TiO_2 53.2%) while the degradation rate increase dramatically to 92.9 % after further 20 min photoexcitation (TiO_2 83.5%). It should be noted that complex **1** are powdered from large crystals as sample and hence have less accessible active centers than the same amount of the nanosized TiO_2. Complex **1** is insoluble in aqueous media of photocatalytic test which excluded the possibility of the catalytic activities result from soluble species instead of the complex **1**. Thus it is complex itself possesses remarkable photocatalytic properties of RhB. After repeating the photocatalytic degradation of RhB three times, photocatalytic efficiency for sample 1 decrease slightly. The PXRD patterns at the end of each repeated bleaching experiment are almost the same as that of the as-prepared sample (Fig. S3).

The simplified model of photocatalytic reaction mechanism of complex **1** was proposed as follows. Because the HOMO is mainly contributed by oxygen and (or) nitrogen 2p bonding orbitals (valence band, VB) and the LUMO by empty transition metal orbitals (conduction band, CB). Under UV light irradiation, electrons (e^-) in the HOMO (VB) of MOF were excited to its LUMO (CB), with same amount of holes (h^+) left in VB. The HOMO strongly demands one electron to return to its stable state. Therefore, one electron was captured from water molecules, which was oxygenated into •OH active species. Meanwhile, the electrons (e^-) in LUMO could be combined with the oxygen adsorbed on the surfaces of MOF to form $•O2^-$, then they might transform to the hydroxyl radicals (•OH). Then the formed •OH radicals could cleave the C-N bond and stepwise N-deethylation of RhB until total degradation.[34]

Experimental

Materials and Instrumentation，The ligand 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole was prepared according to the literature method.[35] Other chemicals were of reagent grade and used as purchased without further purification. C, H, and N analyses were performed on a Vario EL III elemental analyzer. Infrared spectra were recorded with a Nicolet A370 FT-IR spectrometer using KBr pellets in 400–4000 cm^{-1} range. Thermogravimetric analyses (TG-DSC) were completed on a Netzsch STA 449C thermal analyzer at a heating rate of 10 $°C·min^{-1}$

under N_2 atmosphere. The solid-state circular dichroism (CD) spectra were recorded on a MOS-450 spectropolarimeter using KCl pellets. The phase purity and crystallinity of each product were checked by powder X-ray diffraction (PXRD) using a Rigaku Miniflex2 diffractometer with Cu-Kα radiation (λ=1.54056 Å).The luminescent data were investigated in the solid state at room temperature. The photoluminescent (PL) spectra were recorded on a HORIBA Jobin-Yvon FluoroMax-4 fluorescence spectrophotometer. The photochemical reactor employed in this study was comprised of a jacketed quartz tube with a high-pressure mercury lamp of 125 W (Philips) placed inside. For the degradation studies, samples were collected before filtered through millipore membrane filters, and centrifuged to remove the catalyst particles prior to analysis on UNICO ultraviolet spectrophotometer (UV-2102PC).

Synthesis of [Cu_7(4-bpt)$_6$(CN)(H_2O)] (1): 4-abpt (0.10 mmol, 23.8 mg) and $Cu(NO_3)_2$•$2.5H_2O$ (0.15 mmol, 34.9 mg) were dissolved in 3 mL of DMA, 10 mL of H_2O. The mixture was sealed in a Teflon-lined stainless steel vessel (25 mL), which was heated at 160 °C for 3 days and then cooled to room temperature at a rate of 10 °C/h. Red polyhedron crystals of **1** were collected in 32% yield (0.009 g, based on 4-abpt).Anal. Calcd for $C_{73}H_{50}N_{31}OCu_7$: C, 48.12; H, 2.76; N, 23.83%. Found: C, 48.53; H, 3.03; N, 23.62%. IR (KBr pellet, cm^{-1}): 3422 m, 3033 w, 2121s, 1602 s, 1559 s, 1434 s, 998 m, 853m, 748s, 727 s, 687 m.

X-ray Crystallography. The single-crystal X-ray diffractional data of **1** was collected on a Bruker Smart Apex-II CCD diffractometer with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) at room temperature. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. The structure was solved by the direct methods and refined on F^2 by full-matrix least- square techniques using the SHELXTL program.[36] For complex **1**, the bridging cyanide group between two Cu atoms was disordered with respect to the C and N termini; this disorder was treated by performing test refinements with C and N atoms with partial occupancies. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed geometrically and refined using the riding model. Crystallographic data and structural refinement parameters are summarized in Table S1. Selected bond distances and bond angles are listed in Table S2.

Conclusions

In summary, a homochiral three-dimensional framework material has been constructed from achiral precursors by solvothermal reaction, It has been found that this compound has a new (3,4)-connected topology with intrinsic chirality. It reveals a new possibility for the construction of lowly-connected chiral framework materials. At the same time, this complex itself possesses remarkable photocatalytic properties of RhB, which show that it is a good candidate for potential application in catalysis.

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Notes and references

‡ Additional crystallographic data for compound **1** in CIF format, TGA, PXRD and IR in PDF format. CCDC 932369.

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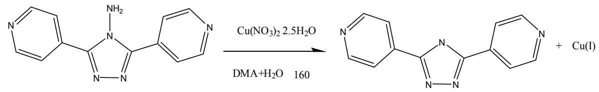
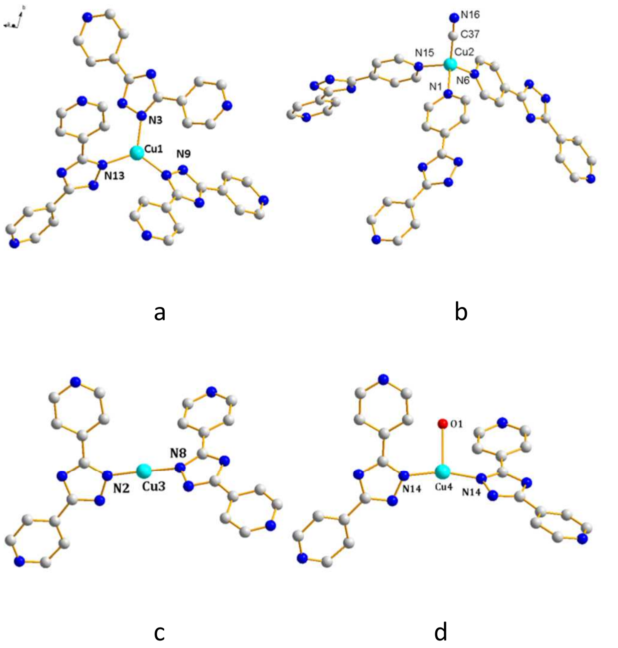


Scheme 1 One-Pot Solvothermal Generation of a 3,5-Bis(2-pyridyl)-1,2,4-triazolate (bpt) Anion



a b

c d

Fig. 1 The different coordination geometries of Cu^I center in compound **1**.

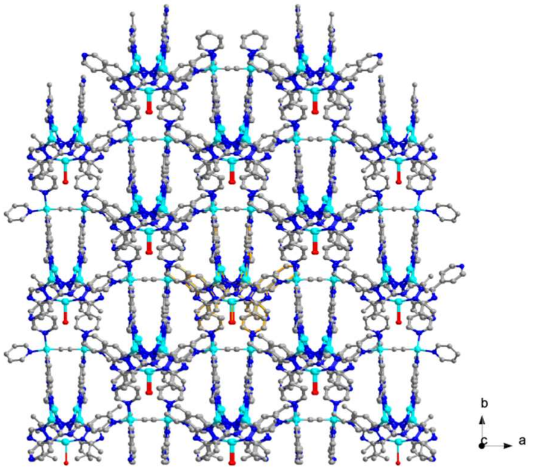


Fig.2 3D structure in compound **1**.

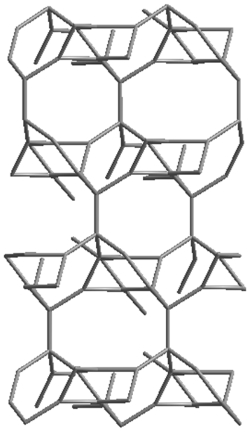


Fig.3 New chirality (3,4)-connected topology in compound **1**.

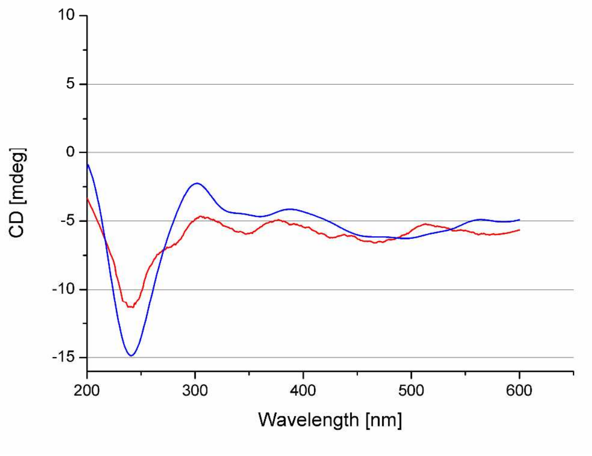


Fig.4 The solid-state circular dichroism spectrum of **1** from two batches.

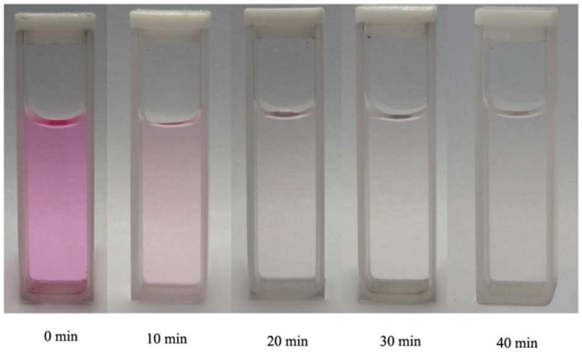


Fig. 5 Color change photograph image of RhB solutions with time in the presence of compound **1** monitored by UV−vis spectra.

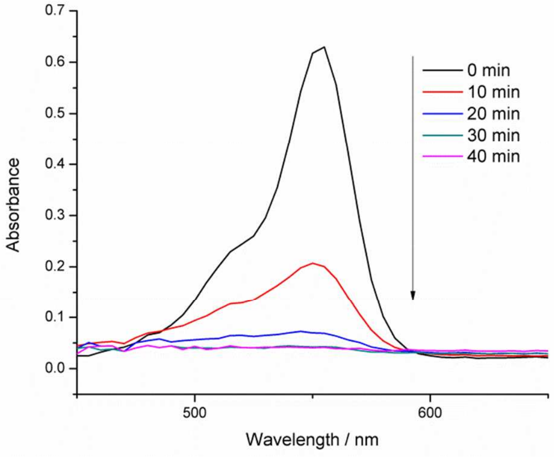


Fig. 6 Photocatalytic decomposition of RhB solution under UV light in the presence of **1**.

Homochiral Cu(I) coordination polymer based on achiral precursors and its photocatalytic property

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A homochiral three-dimensional framework material, [Cu_7(4-bpt)$_6$(CN)(H_2O)] (**1**) (4-bpt = 3,5-bis(4-pyridyl)-1,2,4-triazole) has been successfully synthesized by solvothermal reaction, which generated through an unusual spontaneous asymmetrical crystallization from achiral precursors without any enantiopure additive, and its photocatalytic properties on degradation of organic dyes are also investigated.