

首例含 4,4'-联吡啶和乙酸锌的光致变色化合物

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摘要: 采用一种新方法得到一维配位聚合物 $[\text{Zn}(\text{CH}_3\text{COO})_2(4,4'\text{-bipy})]_n$ (**1**)。配合物 **1** 的晶体结构和荧光性质已经有详细报道, 但光致变色性质还没有相关的研究工作发表。通过研究化合物 **1** 在光照前后的紫外吸收光谱和顺磁共振谱, 表明化合物 **1** 具有电子转移光致变色性能。实验结果验证了我们提出的利用非光致变色单元设计电子转移光致变色材料的新方法是有效可行的。

关键词: 羧酸锌; 4,4'-联吡啶; 配位聚合物; 光致变色; 电子转移

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The First Photochromic Compound Containing 4,4'-Bipyridine and Zinc Acetate

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Abstract: The 1D coordination polymer $[\text{Zn}(\text{CH}_3\text{COO})_2(4,4'\text{-bipy})]_n$ (4,4'-bipy=4,4'-bipyridine) has been synthesized under a new way. Previous studies have revealed its crystal structure and luminescent properties. In this article, we demonstrate its electron-transfer photochromic behavior, which is conformed to our previously proposed design strategy for electron-transfer photochromic materials.

Key words: zinc carboxylate; 4,4'-bipyridine; coordination polymer; photochromism; electronic transfer

Photochromic materials have drawn wide attentions for their reversible color change that irradiated by light in the one or two directions^[1-2]. Especially, electron-transfer (ET) photochromic materials such as viologens^[3], naphthalene diimides^[4], dibenzobarrelenes^[5], salicylidene anilines^[6] and tetrathiafulvalenes^[7-8], provide various potential applications, for instance smart windows, optical data storage, solar cell, etc^[9]. Most of ET photochromic compounds were synthesized using the well-known ET photoactive units, such as viologen cation or inner salts and polyoxometallates^[10-12]. We have previously proposed a new design strategy for ET photochromic metal-organic complexes by the coordination between nonphotochromic units with lone

pairs of electrons and those with large π -conjugate structures, and developed a new class of ET photochromic compounds^[9]. 4,4'-bipyridine (4,4'-bipy) shows no ET photochromic behavior itself, and has been proved to be a good candidate to synthesize photochromic compounds by using the new strategy^[13-15].

The crystal structure and some physical properties of the 1D coordination polymer $[\text{Zn}(\text{CH}_3\text{COO})_2(4,4'\text{-bipy})]_n$ (**1**) have been clearly studied previously, revealing intraligand fluorescence emission and good thermal property^[16-17]. In this article, we elucidate the electron-transfer photochromic behavior of **1** for the first time, which demonstrates again the effectiveness of our previously proposed design strategy for

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electron-transfer photochromic materials.

1 Experimental

1.1 Material and instrument

Chemicals were commercially obtained and used without further purification. Water was deionized and distilled before use.

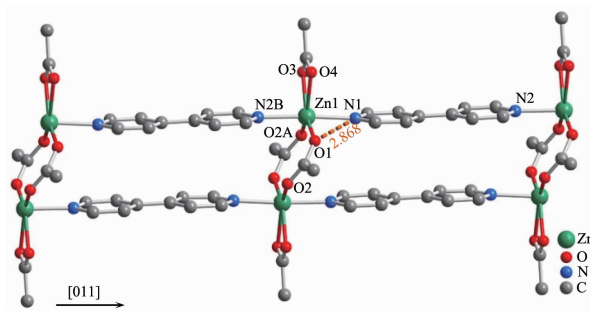
A PLS-SXE300C 300 W xenon lamp system equipped with an IR filter was used to prepare colored samples for FTIR, UV-Vis absorption spectra (UV-Vis), Powder X-ray diffraction (PXRD), and electron spin resonance (ESR) studies. The distances between the samples and the xenon lamp were around 25 cm. The FTIR spectra were recorded on a Bruker VERTEX 70 FT-IR spectrometer using KBr pellets in the range of 4 000~450 cm^{-1} . The UV-Vis spectra were recorded at room temperature on a PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer equipped with an integrating sphere in the wavelength range of 200~1 200 nm. BaSO_4 plates were used as a reference (100% reflection), on which the finely ground powder of the sample was coated. The PXRD patterns were collected with a Rigaku MiniFlex II diffractometer powered at 30 kV and 15 mA for Cu $K\alpha$ ($\lambda=0.154\ 18$ nm). The simulated pattern was produced using the Mercury Version 3.5.1 software (<http://www.ccdc.cam.ac.uk/products/mercury/>) and the reported single crystal reflection diffraction data. The ESR spectra were recorded on a Bruker ELEXSYS E500 spectrometer with a 9.847 GHz magnetic field in X band at room temperature. The elemental analyses of C, H, and N were measured on an Elementar Vario EL III microanalyzer.

1.2 Preparation of **1**

Colorless compound **1** has been previously synthesized by $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 4,4'-bipy by a solvent evaporation or hydrothermal method^[16-17]. In this work, a mixture of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (220 mg, 1.0 mmol), $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ (136 mg, 1.0 mmol), 4,4'-bipy (156 mg, 1.0 mmol) and trimethylamine (0.1 mL, 0.7 mmol) was solved in an aqueous solution (5 mL) and sealed into a 20 mL Teflon-lined stainless steel vessel under autogenous pressure and then heated at 120 $^\circ\text{C}$

for 84 h. Yellow block crystals of **1** were collected and dried in air with 33% yield (based on Zn). Anal. Calcd. (%) for $\text{ZnC}_{14}\text{H}_{14}\text{N}_2\text{O}_4$: C: 49.51; H: 4.15; N: 8.25%. Found: C: 49.46, H: 4.18, N: 8.48%. IR (KBr pellet, cm^{-1}): 3 042(w) 1 602(s br), 1 586(sh), 1 487(w), 1 422(s br), 1 332(w sh), 1 218(m), 1 067(m), 1 044(m), 1 005(m), 931(w), 818(s), 731(w), 673(m), 624(s), 469(w).

As reported, compound **1** features a 1D ladder-like chain structure, where $[\text{Zn}(\text{OAc})_2]_2$ dimers are double-bridged by 4,4'-bipy ligands along the [011] direction (Fig.1). The distance between N1 and O1 is about 0.286 8 nm, which is short enough to allow electron transfer happens^[18]. The phase purity of the crystalline samples used in this work was proved by the PXRD determination (Fig.2), elemental analysis and IR.



Symmetry codes: A: $-1-x, -y, -1-z$; B: $x, -1+y, -1+z$; Orange dash line presents the distance between N1...O1

Fig.1 1D ladder structure of **1**

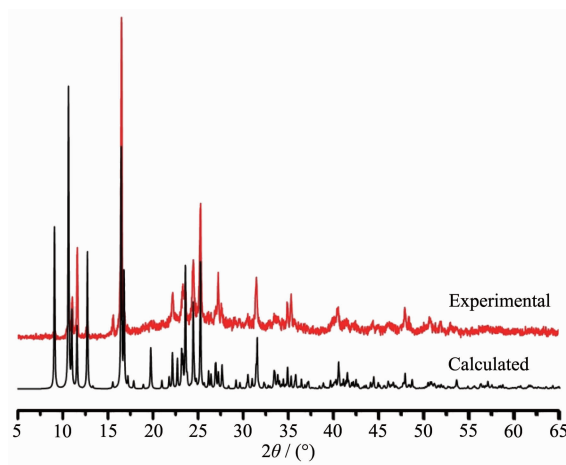


Fig.2 PXRD patterns of **1**

2 Results and discussion

Unlike traditional ways building ET photochromic

metal-organic complexes by choosing N-substitutedbipyridinium^[12], *N,N'*-disubstitutedbipyridinium^[10] or other photochromic units as electron acceptor, the new design strategy chooses nonphotochromic units such as 4,4'-bipy^[14-15] and tris(4-pyridyl)triazine^[13]. To the best of our knowledge, the photochromic behavior of **1** has never been reported. We found that the yellow sample of **1** turned to purple after irradiation by a 300 W Xenon lamp under ambient condition. The UV-Vis spectra after irradiation, demonstrated in Fig.3, show that the absorption has obviously change between 320 and 630 nm. The new generated peaks at 380 and 554 nm are the typical absorption bands of one-electron reduced species of 4,4'-bipy^[19-20]. After 120 minutes irradiation, the absorption turns to be saturated and comes to a stable state. The colored sample could be easily bleached after annealing at 100 °C for 30 min.

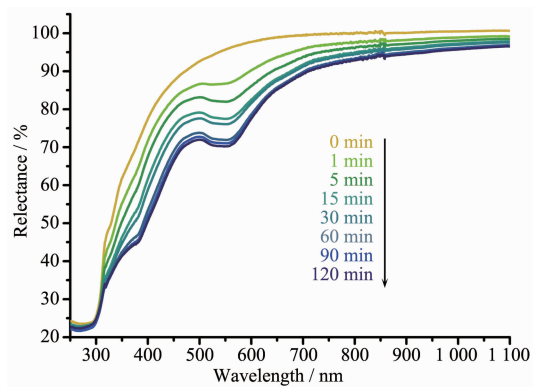


Fig.3 Time-dependent UV-Vis spectra of **1** upon irradiation by the Xe lamp under ambient condition, New absorption bands at 380 and 554 nm are the characteristic of 4,4'-bipy radical

An ESR study confirms the existence of radicals after light irradiation, suggesting that the photochromism of **1** is caused by an electron-transfer process. Before irradiation, the crystalline sample shows small ESR signal, which is caused by the ambient light during the determination since the samples are highly sensitive to the light. After irradiation, the one single-line signal at $g=2.003$ becomes multiple larger, which is characteristic of the free radical. After annealing at 100 °C for 30 min, the radical signal decreases apparently, illustrating that radical is generated during

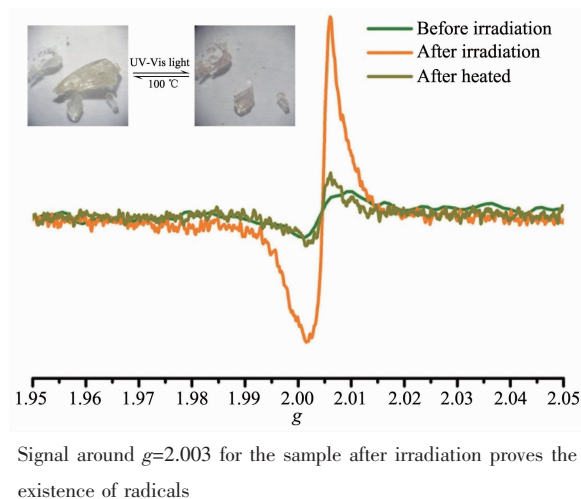


Fig.4 ESR spectra of **1**

the irradiation and disappeared after thermal bleaching. The appearance of radical signals after annealing is also caused by the ambient light during the determination.

3 Conclusions

In conclusion, we report here the electron-transfer photochromic behavior of **1**. This work proves that our previously proposed method for synthesis and design of electronic-transfer photochromic materials is relatively effective.

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