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Tuning up of chromism, luminescence in cadmium-viologen complexes through polymorphism strategy: Inkless erasable printing application

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ABSTRACT

In our work, polymorphism strategy has been successfully applied to tune up chromism and luminescence properties of viologen-based materials. Two polymorphs of viologen-based complexes of α-$CdBr_2(PHSQ)_2(H_2O)_2$ (**1**) and β-$CdBr_2(PHSQ)_2(H_2O)_2$ (**2**) (PHSQ = *N*-(4-sulfophenyl)-4,4′-bipyridinium) were synthesized by changing the solvent. They can both respond to UV light and electricity in the manner of chromism visible to the naked eye and the coloration states have good reversibility, through which an inkless erasable printing model has been established. But the coloration contrast of **1** is higher compared to **2**. Meanwhile, they both exhibit photoluminescence properties and the intensity of **1** is twice that of **2**, which is accompanied by photoquenching upon continuous UV light irradiation. The only divergence of disordered/ordered O atoms in the two crystalline compounds leads to significantly different chromic and luminescent properties. Further explorations simultaneously demonstrate that the different chromic performance between **1** and **2** should attribute to the alteration of stimulus-induced (light/ electricity) electron transfer channels caused by the ordered/disordered O atoms in the complexes, which is achieved through C–H···O and O–H···O interactions to change crystal arrangement and structural rigidity, thus affect luminescent properties.

The 21st century has witnessed the advancement of technology and given birth to the age of intelligence. The demand for smart materials is rapidly increasing [1,2]. For decades, viologens have attracted much attention due to their unique characteristics including reversible redox states and good electron-accepting properties [3]. They have been applied to extensive fields [4-6]. By multiple synthetic methods [3,7], various viologens and their derivatives with unique structures and outstanding functions have appeared. Furthermore, the viologen family can be enriched from the raw material of 4,4′-bipyridines through isomers and bipyridinium precursor skeletons [8].

In recent years, incorporating viologen derivatives as building blocks into metal complexes for constructing smart materials has been research focus from the perspective of coordination chemistry [9-12]. For one thing, viologen-based complexes can retain or even enhance the properties of the respective components [13,14], for instance, chromism of viologen [15,16] and luminescence of metal ions [17]. For another, the synergistic effect between the functionalized metal ions and bipyridine molecules can generate new properties, through which viologen-based complexes can be utilized to develop excellent multistimulus-responsive materials together with optical switches [18,19]. This greatly expands the scope of smart materials [20,21]. Electron transfer has always been a recognized mechanism of viologen-based chromic materials [22,23], which can be regulated from many aspects. However, it remains a considerable challenge to precisely control electron transfer pathways between the electron-deficient viologens and electron-donating moieties [24]. In addition, the research on viologen-based complexes with definite structures that bring about multifunctional properties such as chromism and luminescence is still lacking [25].

Fortunately, the importance of crystalline polymorph has been recognized due to the fact that it not only can act as an effective way to tune various properties, but also its study can pro-

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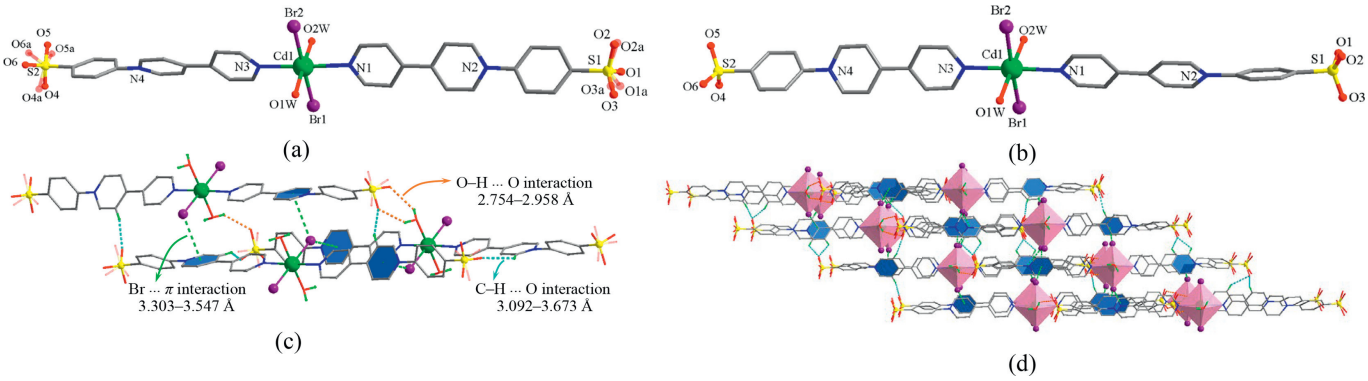

Fig. 1. Crystal structures of **1** and **2.** Asymmetric unit in **1** (a) and **2** (b), supramolecular interactions in **1** (c), as well as 3D supramolecular structure of **1** (d). Green, red, purple, blue, gray and yellow represent atoms of Cd, O, Br, N, C and S, respectively.

vide straightforward correlation between the molecular arrangement/packing manner and properties [26-29]. Polymorphs can be defined as isomers at the individual crystal level resulting from the possibility of at least two different arrangements of the molecules in the solid state, which has been received by most chemists today [26]. Furthermore, the crystal arrangement/packing is significantly influenced by noncovalent intermolecular interactions (*e.g.*, hydrogen bond, van der Waals, $\pi\cdots\pi$, and C–H$\cdots\pi$ interactions) [30]. Despite the advantages of polymorphs, there remain problems that the polymorphism phenomenon is poorly understood, synthesis and selective separation of two or more polymorphs is challenging, as well as regulatory capability of polymorphism in chromic behaviors of viologen-based materials is unclear [31], which requires further explorations.

In this work, by employing different solvents, two polymorphs of viologen-based complexes of α-$CdBr_2(PHSQ)_2(H_2O)_2$ (**1**) and β-$CdBr_2(PHSQ)_2(H_2O)_2$ (**2**) (PHSQ = *N*-(4-sulfophenyl)–4,4′-bipyridinium) have been synthesized using PHSQ ligand and $CdBr_2$ through solvothermal method, which exhibit significantly different properties solely due to tiny differences in crystal structure. There exist disordered sulfonic acid O atoms in **1**, while it is not the case for **2**. Under the irradiation of ultraviolet (UV) light, they both exhibit color changes, of which **1** has higher coloration contrast. At the same time, they can both response to electricity and experience coloration processes. In addition, the two compounds are found to have photoluminescence properties. But the fluorescence intensity of **1** is twice higher than that of **2**. Upon continuous exposure to UV light, their fluorescence intensity decreases.

X-ray single crystal diffraction analysis demonstrates that compounds **1** and **2** belong to the monoclinic system and crystallize in the $P2_1/n$ space group (Table S1 in Supporting information). As shown in Figs. 1a and b, their asymmetric units both consist of one Cd ion, two PHSQ molecules, two Br ions, and two water molecules. The Cd ion adopts an octahedral coordination mode through coordinating with two Br ions, two water molecules, and two N atoms, of which N atoms come from PHSQ ligands. The adjacent PHSQ ligands adopt a "head-to-head" mode, which are bridged by a Cd ion to form a minimal structural unit. These units extend into three-dimensional (3D) supramolecular networks through hydrogen bonds and Br$\cdots\pi$ interactions (Fig. 1 and Fig. S1 in Supporting information). One type of hydrogen bond is formed between the O atoms of sulfonic acid groups in PHSQ ligands and the O–H moieties of the coordinated H_2O (O–H$\cdots$O), the other exists between the sulfonic acid O atoms and the C–H moieties of pyridine rings in PHSQ ligands (C–H$\cdots$O). And the Br$\cdots\pi$ interactions are found between coordinated Br ions and pyridine rings of PHSQ ligands. The specific description of structure can be seen in section S5 (Supporting information), from which we can see

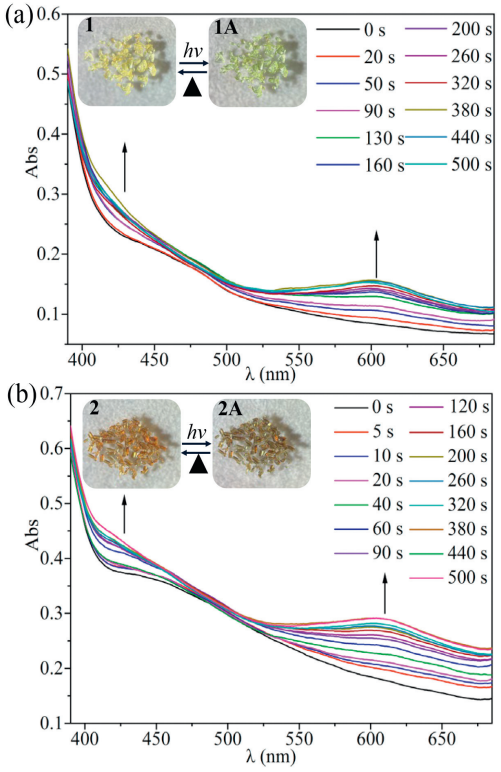

Fig. 2. Time-dependent UV–vis adsorption spectra of **1** (a) and **2** (b) under continuous UV light irradiation. Inset: Photochromic process induced by UV light and bleaching phenomenon through heating at 120 °C.

the influence of disordered/ordered O atoms on crystal structure through hydrogen bonding interactions.

Due to the fact that viologen-based materials generally can respond to UV light and display color changes [10], we explored the photochromic properties of the two compounds. As shown in Fig. 2a, the color of **1** changed from yellow (**1**) to green (**1A**) under UV light irradiation. The yellowish-green crystal (**1A**) faded after being left in the air for 18 h or in an environment of 120 °C for 0.5 h. It manifests that the coloration of **1** exhibits fast response speed and excellent reversibility. To preliminarily figure out the reason for the chromic process, corresponding UV–vis absorption spectrum was obtained, which showed the appearance of two new absorption bands near 430 nm and 605 nm for **1** upon sustained exposure to UV light of 365 nm. Meanwhile, absorption intensity increased along with the illumination time increasing and the coloration reached saturation after 440 s. A similar coloration phe-

nomenon can also be found in compound **2** (Fig. 2b), which experienced color change from orange-yellow (**2**) to orange-green (**2A**). Two absorption peaks appearing after illumination are located at 430 nm and 610 nm. Linear function fitting of absorbance data at 605 nm for **1** and 610 nm for **2** was further carried out (Figs. S2a and b in Supporting information). We can conclude that their photochromic behaviors follow first-order reaction kinetics.

Afterwards, we preliminarily explored the photochromic mechanisms of **1** and **2** through experimental characterizations of X-ray diffraction (PXRD), Fourier transform infrared (FT-IR) spectra, electron paramagnetic resonance (EPR) measurements and X-ray photoelectron spectroscopy (XPS) together with theoretical calculations. PXRD patterns before and after irradiation are basically consistent with that of theoretical simulations (Fig. S3 in Supporting information), and the IR spectra of the two compounds show almost no change before and after illumination (Fig. S4 in Supporting information), which indicate that the two compounds have a high-purity crystalline phase and there are no significant crystal structure changes during chromic processes. EPR measurements of **1** and **2** after coloration both show a strong single-line signal with $g = 1.998$ (Fig. S5 in Supporting information), indicating the occurrence of electron transfer. Moreover, this statement is confirmed by the disappearance of free radical signals after bleaching processes through heating the two compounds. As is well known, viologen-based ligands have redox activity [3], it is speculated that the photochromic phenomenon is caused by the generation of PHSQ radical.

Despite the above results, the determination of electron transfer pathways for viologen-based materials is considerably crucial to further elucidate the chromic mechanism, to get its controlling factors and to provide guidance for designing excellent chromic materials. First, we investigated the donor and acceptor of electron transfer through XPS (Fig. S6 in Supporting information). For compound **1**, the electron may be transferred from the S or O atoms to the pyridine rings of PHSQ ligands. Being different from **1**, the electron transfer of compound **2** is from Br^- ions to N^+ cations of pyridine ring in PHSQ ligand. The details can be found in section S7 (Supporting information).

Theoretical calculations were further carried out to provide insights that can unravel the mystery of chromic mechanisms of the two compounds. We firstly obtained energy band structure and partial density of states (PDOS) by Vienna *Ab initio* Simulation Package (VASP) based on density functional theory (DFT). As shown in Figs. S7a, S7b, S8a and S8b (Supporting information), the indirect bandgaps of compounds **1** and **2** agree well with that of the experimental values estimated by the solid UV–vis absorption spectra, indicating reliability of the calculations. When shifting attention to the PDOS in Figs. S7c and S8c (Supporting information), we found that the valence bands near Fermi level (set to 0 eV) of these two compounds are mainly contributed by Br and O atoms, and the conduction bands are mainly contributed by C and N atoms. To identify the electron transfer pathways of the two compounds, we got electronic cloud distribution in valence band maximum (VBM) and conduction band minimum (CBM). Calculation results indicated that the HOMO and LUMO of **1** belong to n orbital being located at O atoms of the sulfonic acid group and π^* orbiral of pyridine rings (Figs. S9a and c in Supporting information), respectively. While for compound **2**, the HOMO and LUMO are respectively attributed to n orbital centered on Br ions and π^* orbiral of pyridine rings (Figs. S9b and d in Supporting information). So, our calculations can conclude that the two compounds have different electron transfer pathways.

The additional photocurrent and impedance results are concluded in section S7, which indicate that the compound **1** generates more free radicals compared to **2** through electron transfer in chromic processes.

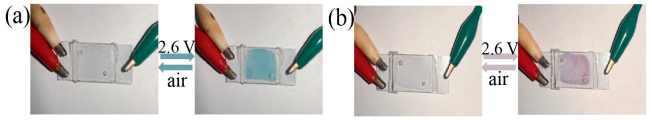

Fig. 3. Electrochromism of compounds **1** (a) and **2** (b).

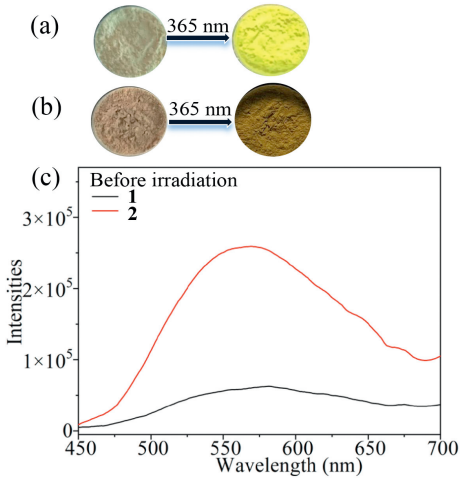

Fig. 4. Photoluminescence of compounds **1** (a) and **2** (b), as well as their emission spectra (c).

It is well known that viologen-based materials are electrically sensitive and have reversible electrochromic properties [3]. To investigate electrochromic behaviors of the two compounds, we prepared electrochromic devices (EDCs) based on solutions and conductive glass with tin indium oxide coating (ITO) acted as the active component of the electrode. When a voltage of 2.6 V was applied to ECD with DMF solution of **1**, a color change from light yellow to blue-green was observed (Fig. 3a). Being similar with **1**, EDC of **2** in mixed solution of DMSO and DMF also underwent color changes under the stimulation of external voltage of 2.6 V, which was from yellow to purple (Fig. 3b). And the colored EDCs can fade after being exposed to air for 1 h. As shown in Figs. S13a and b (Supporting information), the UV–vis absorption spectra of initial EDCs for **1** and **2** are similar to counterparts in their solid state. Meanwhile, characteristic absorption bands of **1** and **2** emerged after applying voltage are similar to that in the photochromic processes, and the intensity of the new absorption bands increase with the extension of voltage application time. It suggests that electrochromism of the two compounds also originates from the generation of free radicals through electron transfer.

The photoluminescence characteristics play an important role in expanding the application scope of multistimulus-responsive chromic materials [27]. We thus measured and analyzed the photoluminescence properties of the two compounds. Emission spectra before and after persistent irradiation together with excitation emission spectra of the compounds were both obtained (Fig. 4, Figs. S14 and S15 in Supporting information). The results show that **1** and **2** exhibit significantly different luminescence properties. For one thing, upon excitation by 365 nm of light, **1** has maximum fluorescence emission centered at 568 nm, while that of **2** has a slight redshift compared to **1**, which is located at 580 nm. For another, the fluorescence intensity of **1** is twice higher than that of **2**. We also monitored the fluorescence intensity changes of the two compounds during photochromic processes. With increasing illumination time, the fluorescence intensity of the two compounds both decreases. In addition, the fluorescence lifetime decreases with the deepening of color change (Figs. S16 and S17 in Supporting information), indicating that the occurrence of photoquenching during

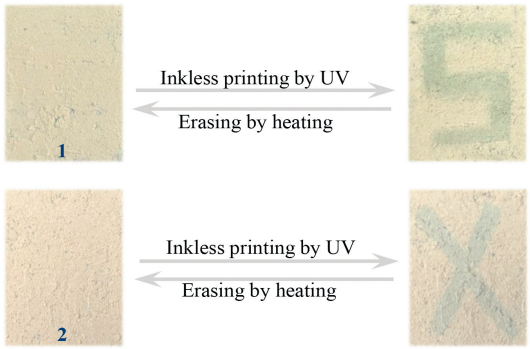

Fig. 5. Inkless erasable printing model of compounds **1** and **2**.

photochromism and fluorescence quenching is a dynamic process. Non radiative transition caused by molecular vibrations is an important factor that affects luminescence intensity, which can be used to explain the significant differences of luminescent properties in **1** and **2**. Due to the disordered sulfonic acid O atoms in compound **1**, it has more possibilities for building hydrogen bonds, which is functional to increase the structural rigidity and thus reduce non radiative transitions.

Based on the chromic properties of these two compounds, we have established an inkless erasable printing model. As shown in Fig. 5, the letters 'S' and 'X' were successfully printed out after respectively covering the corresponding molds on the surfaces of glass plates coated with two powder samples and irradiating with UV light. Upon subsequent heating, the original form can be restored, enabling repeated printing. The stability and reversibility of coloration states for **1** and **2** not only enable inkless printing needs but also achieve recycling, in line with the development concept of green chemistry.

Despite the multiple properties of chromism, photoluminescence, and photoquenching existing in these two compounds, thermal stability is an important parameter for the practical application of multistimulus-responsive materials, which is confirmed through thermogravimetric analysis (TGA). As shown in Fig. S18 (Supporting information), the weight loss process for the two compounds can be divided into two steps. The first step occurs approximately between 30 °C and 125 °C, attributing to the loss of coordinated water molecules. The second step is assigned to the collapse of the structure starting from 400 °C until 800 °C. The results indicate that these two compounds have good and comparable stability.

To sum up, two polymorphs of multistimulus-responsive viologen-based complexes exhibit photochromism and electrochromism with fast response speed, excellent reversibility, as well as photoluminescence accompanied by photoquenching upon sustained UV irradiation. The slight difference of crystal structure in the two compounds makes them exhibit significantly different chromic and luminescent properties, due to the disordered sulfonic acid O atoms of **1** provide more possibilities for the formation of O–H···O and C–H···O interactions. Experimental characterizations and theoretical calculations indicate that the two compounds have different electron transfer pathways. On the one hand, the type of electron transfer pathway is greatly influenced by the internal interactions and microstructure of the crystal. On the other hand, luminescent performance can be improved through increasing the number of hydrogen bonds that are helpful for the construction of rigid structures. So, our work provides a perspective on regulating chromism, luminescence through polymorphism strategy. Finally, we have established an inkless erasable printing model that conforms to the concept of green development.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yanting Yang: Writing – review & editing, Writing – original draft, Data curation, Conceptualization. **Guorong Wang:** Software. **Kangjing Li:** Methodology. **Wen Yang:** Investigation. **Jing Zhang:** Formal analysis. **Jian Zhang:** Software. **Shili Li:** Funding acquisition. **Xianming Zhang:** Resources, Funding acquisition.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.110123.

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