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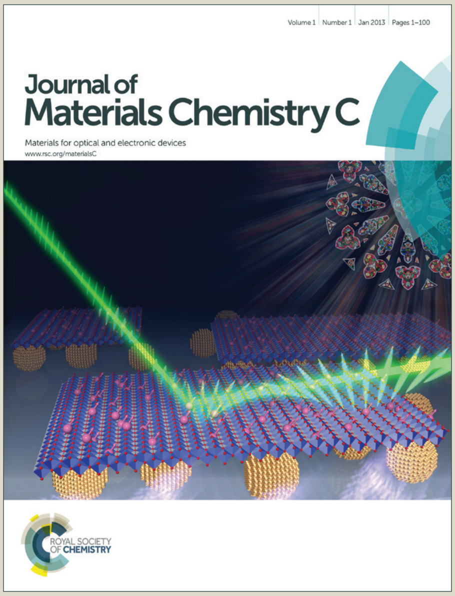

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Rare electron-transfer photochromic and thermochromic difunctional compounds

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Two new isostructural coordination compounds exhibit the rare difunctional properties of both electron-transfer (ET) photochromism and ET thermochromism, which are significantly affected by halogen atoms. The thermocrystallographic studies of the same single crystal have elucidated the electron-donating nature of the halogen atoms.

Exploration new di- or multifunction materials, such as multiferroic materials,[1] to meet application requirements in various fields has attracted more and more interesting. The color-changing materials, among the most common and useful species, can be variously modulated by external stimuli such as light, temperature, pH, and pressure.[2] Photochromic and thermochromic materials respectively can find potential application in various fields, including protection, decoration, display, memory, switches, photography, and so on.[3] If one material possesses both photochromism and thermochromism, the more extensive applications will be expected.[4] So far such materials are limited. Even so, they were mainly seen in photochromic compounds undergo large molecular structure isomerization, such as spirooxazines[5a] and Schiff bases[5b] and so on, while rarely in those experiencing ET processes.[6] Most ET photochromic compounds undergo only thermal bleaching processes with the increase of temperatures,[7a] and seldom exhibit spontaneous thermo coloration (thermochromism).[7b] It is still a significant challenge to obtain the both ET photochromic and ET thermochromic difunctional materials. To further guide the design and synthesis of such materials, it is crucial important to illustrate the key structural influence factors on the photochromic and thermochromic behaviours.

A variety of influencing factors for photochromic or thermochromic reactions based on ET processes have been researched.[8] For example, the molecular structure as well as the packing type, distance, and orientation between the electron donor and the electron acceptor affect the rate of the ET reactions. But it is still dazzled the change of the components will take what effect on both photo- and thermoinduced ET processes that give a color to a compound. To the best of our knowledge, the related researches have not been seen.

During our pursuing of new ET photochromic species,[9] we obtained two new both ET photochromic and ET thermochromic difunctional solid-state coordination compounds, that is, $[ZnX_2(CEbpy)]$ (CEbpy = 1-carboxyethyl-4,4'-bipyridine; X = Cl (**1**), Br (**2**)). It is interesting that they experience very different photochromic and thermochromic processes owing to the presence of different halogen atoms as the electron-donating groups.

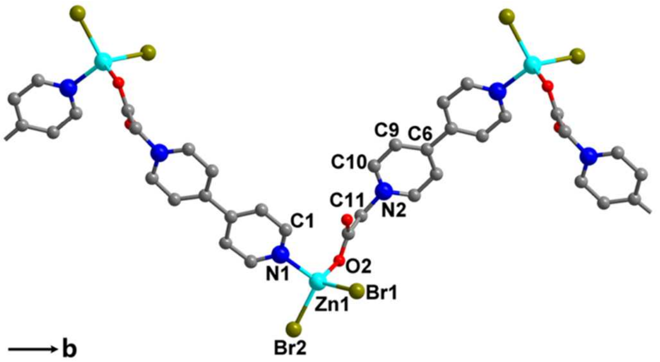

Fig. 1 A view of the 1D chain structure of **2** along the b-axis. Zn, Br, O, N, and C atoms are represented by cyan, yellowish brown, red, blue, and ray circles, respectively.

The reactions of zinc halide or zinc bromide with the photochromic precursor $CEbpy \cdot 3H_2O$ (Fig. S1, in the ESI) led to two new isostructural compounds **1** and **2**. Only the structure of **2** is discussed in detail as a representative. Compound **2** features a one-dimensional (1D) polymer $[ZnBr_2(\mu\text{-CEbpy})]_\infty$, where the zinc(II) centers are linked by the bidentate CEbpy ligands to form an infinite zigzag chain along the *b* axis (Fig. 1). The terminal Br atoms complete the tetrahedral coordination around each metal atom. The Zn-Br bond distances falling in the range of 2.377(1)−2.398(1) Å, Zn-O bond distance of 1.973(4) Å, and Zn-N bond distance of 2.082(4) Å (Table S2, in the ESI) are comparable to those reported for other zinc(II) compounds.[9b]

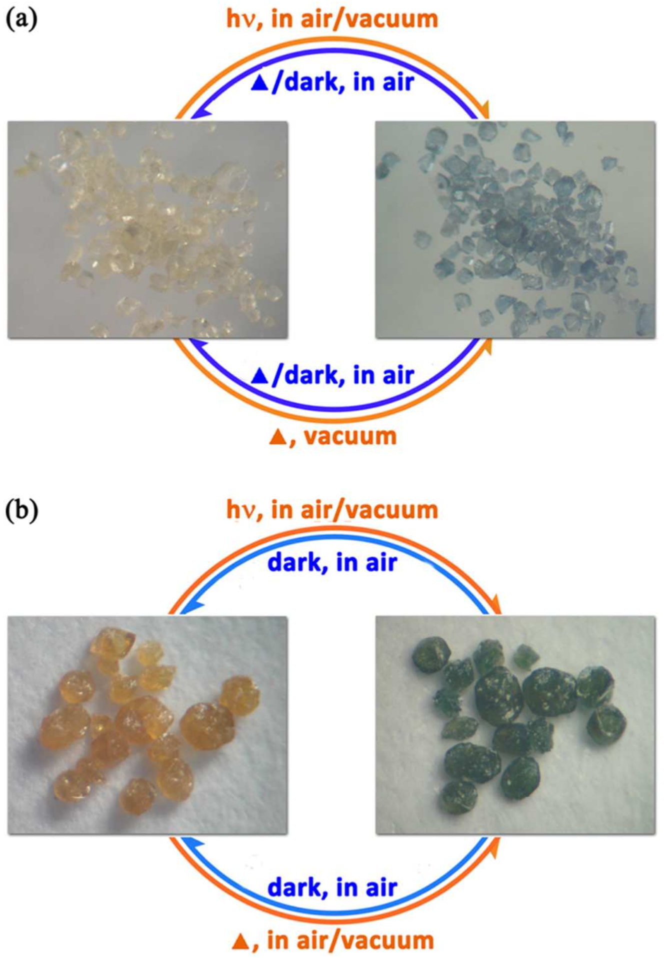

Fig. 2 Photochromic and thermochromic photographs of **1** (a) and **2** (b).

Compound **1** undergoes a photoinduced color change at ambient temperature *in air* or *under vacuum*. As shown in Fig. 2a, pale yellow crystals of **1** turned blue after irradiation by a 300 W Xe lamp. Two characteristic broad bands around 404 and 609 nm emerged in the UV-vis diffuse reflectance spectrum after coloration (Fig. 3a). An ESR study of the photoproduct (hereafter named as **1P**) has witnessed the single-line radical signal with a *g* value of 2.0051 (Fig. S3, ESI), closing to that of a free electron found at 2.0023. The decoloration of **1P** belongs to a thermo-bleaching progress. The new absorption bands of **1P** disappeared after annealing at 120 °C for 1 h *in air* or placed *in the dark in air* for more than 3 d (Fig. 3a).

Compound **2** also turned blue after photoirradiation at ambient temperature *in air* or *under vacuum* (Fig. 2b). Two new absorption bands around 406 and 609 nm appeared in the UV-vis diffuse reflectance spectrum of the photoproduct (hereafter named as **2P**). The ESR signal at *g* = 2.0011 demonstrates the generation of radicals (Fig. S3, ESI). The two new absorption bands disappeared completely when **2P** was placed *in the dark at ambient temperature in air* for more than 3 d (Fig. 3b).

The aforementioned UV-vis and ESR spectral features of photoproducts resemble those of viologen cation radicals,[7a, 9] which suggests that the color change of the crystalline compounds **1** and **2** arises from the photoinduced ET and the generation of CEbpy radicals. The photoinduced coloration–decoloration processes of **1** and **2** are reversible, which is indicative of their photochromic characteristics.

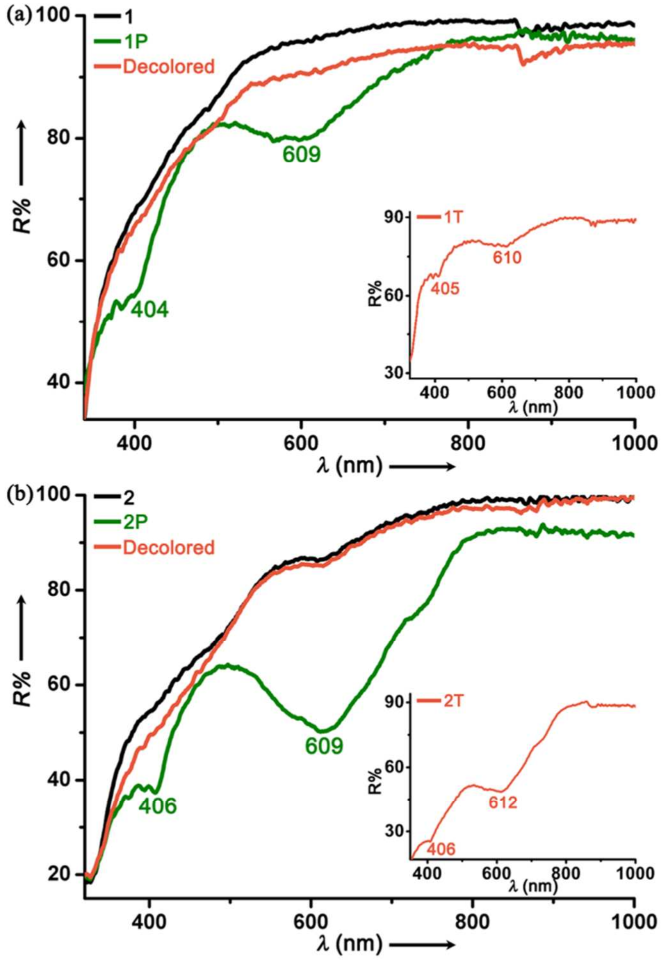

Fig. 3 UV-vis diffuse reflectance spectra of **1** (a) and **2** (b) by photo- or thermo-treatment.

Interestingly, after annealing at 100 °C for half an hour *in air* or *under vacuum*, compound **2** could undergo a thermo-coloration progress, while compound **1** just experienced the thermo-coloration progress *under vacuum*. As depicted in Fig. 3, new absorption bands around 405, 610 nm for **1** and 406, 612 nm for **2** emerged in the UV-vis spectra after thermo-coloration. ESR studies support that the heating process is also accompanied by the generation of single-line radical signals with *g* values of 2.0035 for **1** and 2.0028 for **2** (Fig. S3, ESI). The completed decoloration of the blue thermoproducts (**1T** and **2T**) needs more than 5 d *in the dark at ambient temperature in air*. The sample **1T** was also completely decolored through annealing at 120 °C for 1 h *in air*. These thermoinduced coloration–decoloration processes of **1** and **2** are reversible, which is indicative of their thermochromic characteristics. Powder XRD experiments indicated that no clear change of crystal structures happens in the photo- and thermoinduced coloration products (Fig. S2, ESI).

X-ray photoelectron spectroscopy (XPS) experiments, taking **2**, **2T** and **2P** as examples, were performed to probe the origin of the radicals. Upon heating, the C 1s and N 1s components of **2** were prominently shifted to positions with lower binding energies, while the opposite occurred for the Br 3d and O 1s components (Fig. S4, ESI). Hence, the thermochromism of **2** should originate from the electron transfer between the Br and O atoms and the 4,4'-bipyridinium moiety. Upon irradiation, the C 1s and N 1s components of **2** were also shifted to positions with lower binding energies, but the Br 3d and O 1s components almost remained unchanged (Fig. S5, ESI). This minor change may be caused by the hard penetration of light in the crystals.[10]

It is important to obtain the crystal structures of the same single crystal before and after a photo or thermo effect for a better understanding of the coloration mechanism of a compound. The photocrystallographic or thermocrystallographic researches of ET photochromic viologen compounds have been rarely developed.[11] In the both photochromic and thermochriomic crystalline compounds, the thermal process is much easier to realize the complete coloration of a single crystal than the optical one, which facilitates the crystallographic study of a colored sample.[12]

We take the crystal structures of **2** and **2T** as examples for thermocrystallographic analyses since **2T** is easily achieved *in air*. They show very similar crystal structures with only minor differences in molecular geometry. The biggest change was that the Zn-Br1 and Zn-Br2 bond distances were shorten by 0.006(1) and 0.003(1) Å, respectively, when **2** is converted to **2T** (Table S4, ESI). This suggests that the Br atom acts as an electron-donating group because the zinc(II) atom is too stable to be changed. As mentioned above, the CEbpy ligand forms a radical species after thermo-coloration. A smaller change in the bond lengths of CEbpy between **2** and **2T** is observed for N2-C11, N2-C10 and C6-C9 bonds with values of 0.014(7), 0.014(8) and 0.016(8) Å, respectively (Table S4, ESI). The other bond distances tend to shrink slightly. The structural variation between **1** and **1T** was very tiny, but the trend was similar to that occurred between **2** and **2T**(Table S3, ESI). These data demonstrate that the electron transfer from the halogen atom to the CEbpy ligand contributes to the thermo-coloration of **1** and **2**, which is consistent with the aforementioned XPS data. Therefore, the variation of different halogen atoms would influence the thermochromic behaviors, which has been well witnessed experimentally (Fig. 2 and 3).

It should be noted that the UV-vis spectrums of **1** and **2** show obvious new absorption bands after irradiation for 5 min (Fig. 3a and 3b), but the absorption intensity of **2P** is obviously larger than that of **1P**. Therefore, the light sensitivity of **1** and **2**, with Cl and Br atoms, respectively, is in the order of **1** < **2**. In addition, the thermoinduced coloration *in air* takes place only in compound **2**, and the absorption intensity of **2T** is larger than that of **1T** after annealing at 100 °C for an hour (Fig. 3 insert). Therefore, the heat sensitivity of **1** and **2**, with Cl and Br atoms, respectively, is also in the order of **1** < **2**. We think that the difference between 1 and 2 is caused by the different stability of halogen radicals in air, which should be related to the electronegativity of halogen.[13] Halogen atoms with lower electronegativity are more inclined to lose electrons, and thus the corresponding halogen radicals are less inclined to be reduced. The electronegativity of Br is smaller than that of Cl. Consequently, the Br• radical should be more stable than the Cl• radical in air. However, the detailed reason needs further elucidation in the future.

Conclusions

In summary, two new isostructural solid-state coordination compounds [ZnX_2CEbpy] (X = Cl, **1**; Br, **2**) with both photochromic and thermochromic properties have been obtained. Their different coordinated halogen atoms exert different influence on their photo- or thermoinduced colorations. The thermocrystallography was studied in the well-known viologen compound, which supported that the halogen atom as an electron donor plays an important role for ET. Our research results may provide new clues for design and synthesis of both ET photochromic and ET thermochromic difunctional materials.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Details of crystallographic studies, physical property measurements for **1** and **2** (in PDF and CIF format) are available]. See DOI: 10.1039/c000000x/.

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Rare Electron-Transfer Photochromic and Thermochromic Difunctional Compounds

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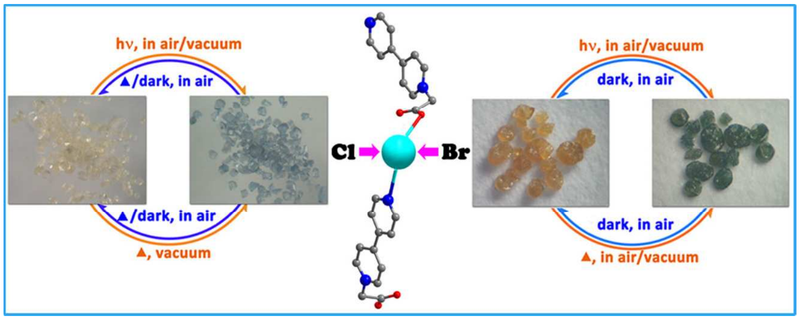
Graphical Abstract



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