NLO Photoswitching

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Electron-Transfer Photochromism To Switch Bulk Second-Order Nonlinear Optical Properties with High Contrast**

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Abstract: *The first bulk electron-transfer photochromic compound with intrinsic second-order nonlinear optical (NLO) photoswitching properties has been synthesized. This system employs an electron-transfer photoactive asymmetric viologen ligand coordinated to a zinc(II) center.*

Photochromic compounds have attracted much attention for their useful physicochemical properties that can be switched between two states. As such, the use of light as an external trigger to switch the second-order nonlinear optical (NLO) activity has been increasingly addressed for nondestructive data storage or opto-optical switching in the emerging field of photonic devices.[1–3] The reversible photoswitching of second-order NLO properties can be seen in a large number of photochromic compounds.[4,5] For most of these compounds, the photoswitching was realized in the liquid or film form in the presence of external optical/electric fields or special supported media. The polarities of bulk second-order NLO materials are intrinsic, and their photoswitching does not require the above severe conditions. However, it is still a significant challenge to obtain new photoswitchable NLO materials in the bulk.

So far, the photoswitching of NLO properties in established bulk photochromic materials all experience a large molecular isomerization reaction accompanied by hydrogen atom transfer.[6] The large isomerization and atom migration in a bulk material require enough steric space for a sharp inversion of configuration, generally resulting in limited contrast for the photoswitching of NLO properties. An electron transfer (ET) photochromic process could overcome these adverse factors.[1e,7] To our knowledge, bulk ET photochromic compounds with intrinsic photoswitchable second-order NLO properties are unknown.

Herein, we report the first bulk ET photochromic compound $[ZnBr_2(\mu\text{-CEbpy})]\cdot 3H_2O$ (**1**, CEbpy = *N*-carboxyethyl-4,4′-bipyridinium) with intrinsic photoswitchable second-order NLO properties, caused by the synergetic interaction between an ET photoactive asymmetric ligand and a metal center with acentric coordination geometry.

Compound **1** crystallizes in the acentric space group *Cc* (No. 9). The single-crystal X-ray structure of **1** shows that the compound coordinates to form a one-dimensional (1D) infinite zigzag chain extending along the [1 1 2] direction, where each zinc(II) center is tetrahedrally coordinated by two μ-bridging CEbpy ligands and two terminal bromide atoms (see Figure S3 in the Supporting Information). Each 1D infinite chain cross-stacks alternately along the *c*-axis, with each asymmetric unit in a monoclinic configuration, to form a channel structure that accommodates hydrogen-bonded chains of water molecules (Figure 1 and Figure S4 in the Supporting Information). It has been well-established that the viologen cation has an excellent electron-withdrawing nature. It is expected that substitution at one end of the molecule with an electron-donating group should enhance the polarity of the viologen moiety and promote the formation of an acentric push–pull system. In **1**, two donor groups, CH_2COO^- and Br^-, and one acceptor group, 4,4′-bipyridinium, produce the intrinsic polarity in a -[(4,4′-bipyridinium)$ZnBr_2(OOCCH_2)$]- unit (Figure S5a). The continuous head-to-tail linking of such units generates a 1D polar chain structure (Figure S5b). As shown in Figure 1, the cross-stacking of the polar chains according to the acentric space group (*Cc*) gives rise to the macroscopic polarization of **1** in the bulk.

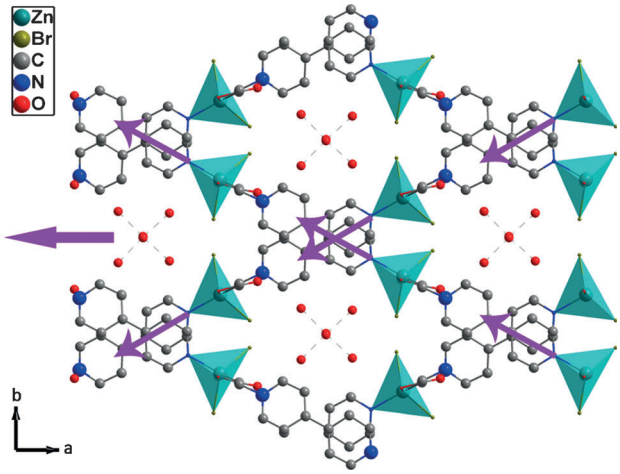

Figure 1. Molecular packing in a crystal of **1** viewed along the *c*-axis. The violet arrows indicates the whole remnant polarity. $[ZnBr_2O_2]$ tetrahedra are shaded in cyan. Dashed lines denote hydrogen bonds.

Upon continuous irradiation with a 300 W xenon lamp at room temperature in air, the crystalline sample of **1** (denoted

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1A) showed a color change from colorless to deep blue within 35 minutes (Figure 2). The deep blue photoproduct (**1B**) undergoes the reverse transformation in the dark under an oxygen atmosphere after more than 3 days (Figure 2). After this reverse transformation, the decolored sample can

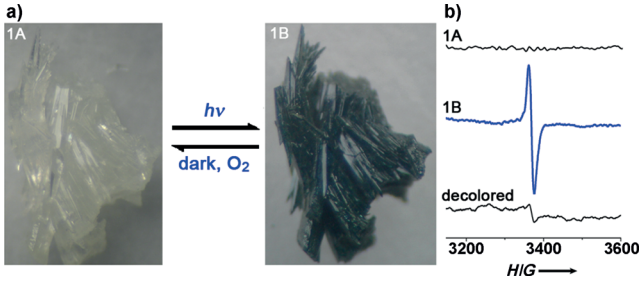

Figure 2. a) Color change of **1A** to form **1B** after irradiation with a 300 W Xe lamp at room temperature in air, and the reverse transformation in darkness under an oxygen atmosphere. b) The corresponding ESR spectra before irradiation (**1A**), after irradiation (**1B**), and after the reverse transformation (decolored).

undergo the photochromic color change again after irradiation (Figure S6). In the UV/Vis diffuse reflectance absorption spectrum of **1B**, a characteristic broad band was detected at approximately $\lambda = 615$ nm, which almost disappears after decoloration (Figure S7). ESR spectroscopy studies showed that no ESR signal could be detected before irradiation, but a symmetric single-line radical signal with a g value of 2.0020 emerged after coloration (Figure 2). Such a radical signal almost disappeared after decoloration, reflecting the reversible nature of this photochromism. Both single-crystal and powder X-ray diffraction data verified that no obvious structural change occurred during the photochromism (Figure S2 and Table S2 in the Supporting Information). These spectral features resemble those of viologen cation radicals detected in other viologen compounds,[8] suggesting that the color change arises from the photoinduced ET and the generation of radicals in the crystalline compound.

In similar photochromic compounds, the coordinated bromine atom and the oxygen atom from the carboxy group have been confirmed using XPS (X-ray photoelectron spectroscopy) experiments to be good electron donors under photoirradiation.[9] The precursor CEbpy·3 H_2O, used to prepare **1**, is photochromic (Figure S1) and the distance between the oxygen atom of the carboxy group and the nearest nitrogen atom on the pyridinium ring is approximately 2.7 Å. This distance is favorable for interaction between the carboxylate donor and the viologen acceptor. These conditions indicate that the photoexcited electron could be transferred between the 4,4′-bipyridinium group and the Br atom or carboxylate moiety.[10,11]

Second-harmonic generation (SHG) measurements with sieved powdered samples (150–200 μm) indicated that the crystalline sample **1A** displays a macroscopic SHG response approximately 0.8 times that of KH_2PO_4 (KDP) and is phase-matchable (Figure S8). The most striking feature of **1A** is that its SHG response becomes very small after photoinduced coloration, suggesting the photoswitching of NLO properties. A fundamental laser ($\lambda = 1907$ nm) was used for the SHG measurement and no absorption of **1A** and **1B** was considered in the range of $\lambda = 800$–1100 nm (Figure S7), so the SHG variation is not attributed to the absorption change. Upon irradiation with a Xe lamp, the SHG intensity of compound **1** dropped gradually and reached approximately 30% of the original value after 35 minutes (Figure 3), displaying a higher

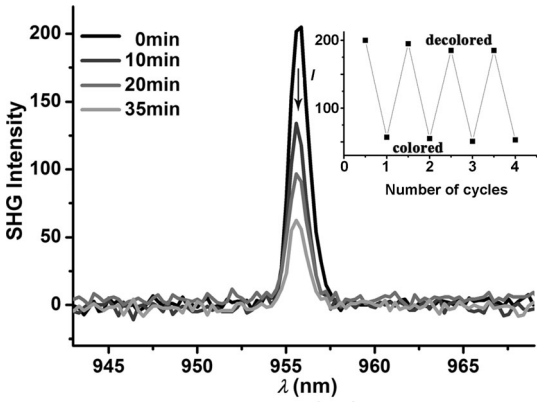

Figure 3. Variation of the SHG intensity upon irradiation of compound **1A** by a 300 W Xe lamp over different time periods. Inset: The photoswitching of the SHG signal intensity, indicating conversion of **1A** to **1B** and the reverse process, for four cycles.

contrast than the reported values of 40–90% for other bulk photoswitchable NLO materials.[6] The SHG intensity detected for **1** after decoloration was close to that measured for the compound before irradiation. The switching of SHG intensity between **1A** and **1B** can be cycled at least four times (Figure 3, inset).

To understand the electron structure and photophysical processes measured for compound **1**, calculations of partial electron density of states (PED) were performed using the DFT method. The calculations showed that the majority of the electron distribution of the highest valance band (HVB) near the Fermi level (set at 0 eV) is located on the oxygen atom of the carboxy group and the bromine atom, whereas that of the lowest conduction band (LCB) is concentrated on the 4,4′-bipyridinium group (Figure 4). The complete localization of the electron distribution on the HVB and LCB means the electron could transfer from the carboxy group or the bromine atom to the 4,4′-bipyridinium group.[12] On the basis of structural and Bader charge analysis, the NLO behavior of **1** should originate from the superposition of the polar unit, as shown in the Figure S5. We calculated approximately the dipole moment of the unit cell in two stable states with different spin multiplicities (before irradiation, $S = 0$; after irradiation, $S = 1$) by using an ab initio code Gaussian package at the B3LYP/(6-31+G*) level. The dipole moment of 20.25 Debye before irradiation is almost three times greater than that calculated after irradiation (6.61 Debye), which is almost consistent with the experimental result.

Considering the photophysical process described, we suggest that the drop of SHG intensity in compound **1** occurs because of the lower polarity of **1B** compared to that of **1A**, which arises from a photoinduced change in the electronic structure of the 1D chain. The polarity of **1A** is a result of the asymmetric disposition of the different electron

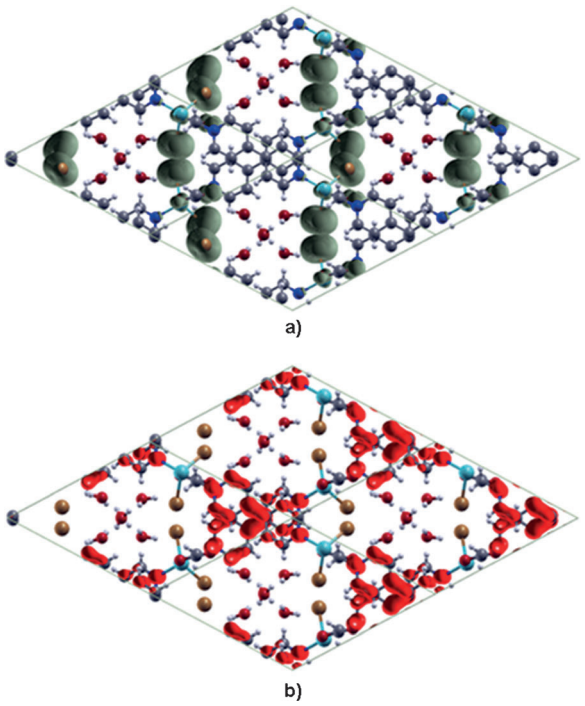

Figure 4. A 2×2 cell view of the PED for compound **1**, calculated using the DFT method, showing a) the valence band (green/gray) and b) the conduction band (red). Atom color: Br = brown; O = red; H = white; C = gray; N = green; Zn = cyan.

densities between the donor groups (CH_2COO^- or Br^-) and the acceptor group (viologen). For **1B**, the photoinduced ET weakens the different electron densities between the donor and acceptor groups and thus obviously lowers the domain polarity. The relaxation of the electron cloud in the polar chain weakens the whole remnant polarity of the compound; the more electron transfer initiated by the photoirradiation, the smaller the value of the SHG response. This is a likely explanation why there only a weak SHG signal detected for **1B**. The change of the electronic structure determines NLO photoswitching.

In conclusion, the first ET photochromic bulk compound with photoswitchable NLO properties has been successfully designed and synthesized. This work demonstrates the effectiveness of ET photochromism for the reversible photoswitching of bulk NLO properties, and reveals a new approach to realize photoswitching of bulk second-order NLO materials. In future, we will continue to explore new photochromic bulk coordination compounds based on electron transfer, considering their flexible coordination modes and structural design.

Experimental Section

The coordination compound $[ZnBr_2(\mu\text{-CEbpy})]\cdot 3H_2O$ (**1**) was obtained as cone-shaped crystals following the reaction of $ZnBr_2$ (0.2 mmol) and CEbpy·$3H_2O$ (0.2 mmol) in aqueous solution at room temperature. A single phase was obtained in 53% yield (based on Zn). The phase purity was confirmed by powder X-ray diffraction (Figure S2). Elem. Anal. calcd for $C_{12}H_{16}N_2O_5ZnBr_2$: C, 29.2; H, 3.27; N, 5.68%. Found: C, 29.7; H, 2.94; N, 5.72%.

CCDC 1009402, 1009403 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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