DOI: 10.1002/ange.201108220

Photochromism

A Room-Temperature X-ray-Induced Photochromic Material for X-ray Detection**

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Radiation protection and detection has become an important subject because of the growing destruction of the atmospheric environment and the extensive use of high-energy radiation sources in industry, medical services, scientific instruments, and nuclear power plants. When irradiated by high-energy radiation, like X-ray radiation, species may not only release free electrons and characteristic X-rays but experience physical processes, such as photodecomposition, luminescence, ionization, and the formation of electron–hole pairs. Photographic plates, scintillation counters, ionization gauges, semiconductor detectors, and other devices have been developed and widely used in detecting X-rays based on these physical processes.[1] X-ray-sensitive materials used in these devices usually need electronic accessories or multi-step manipulations (typically for photographic plates) to deal with signals before useful information is obtained. New X-ray-sensitive materials that can directly provide the required information are needed.

If X-rays could be directly "visualized" by color, like for example the well-known pH test paper, X-ray detection would become very convenient and much cheaper because of the simplicity of the equipment and its manipulation. A material with this feature could be applied, to some extent, as a substitute for the commonly used photographic plate in medical imaging and industrial crack detection. In this way, the toxic liquid waste of developer and fixer could be avoided. Photochromic species generally show reversible color change upon external stimuli.[2] If X-rays behave as a stimulus, they are ideal candidates of such materials because they are recyclable.

There have been some excellent studies on X-ray-induced photochromic materials, like Prussian blue analogs,[3] Fe^{II} spin-crossover complexes,[4] manganite,[5] spinel,[6] cobalt dioxolene,[7] zinc phosphate with methylviologen cations,[8] BiOI/BiI-nylon11 composite films,[9] and oxometallates with impurities (such as $LiNbO_3$:Cu),[10] in strict accordance with the definition of photochromism.[2] However, to the best of our knowledge, examples of X-ray-induced photochromic materials are still rather rare in the literature. Even so, most of them only show X-ray-induced photochromism below room temperature,[3–7] which is not economic and convenient for use. Moreover, in the reported studies of X-ray-induced photochromic species, the adopted X-ray was either hard ($\lambda <$ 1 Å)[3,4] or soft ($\lambda >$ 1 Å),[5–10] but not both. Thus, it is desirable to develop new room-temperature X-ray-induced photochromic species which are susceptible to both hard and soft X-rays.

Herein, we present a room-temperature X-ray-induced photochromic metal–organic complex, [$ZnLBr_2$] (**1-Y**, Figure 1), which shows two advantages: 1) a susceptibility to hard and soft X-rays at room temperature with visual color change, which endows it a potential to detect X-rays; 2) a "green" recyclable material because it is reversible and has a high thermal stability and is easily recrystallized from water.

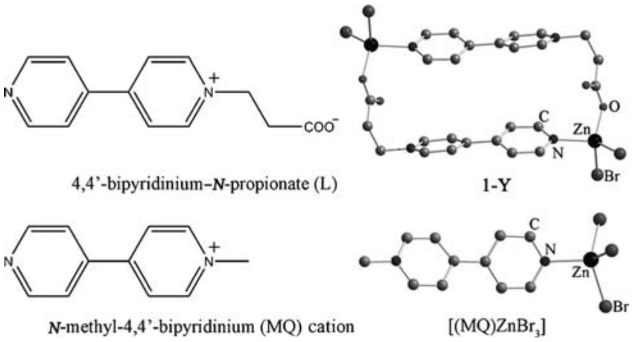

Figure 1. L and MQ ligands and molecular structures of **1-Y** and [$(MQ)ZnBr_3$]. H atoms are omitted for clarity.

The ligand 4,4′-bipyridinium-*N*-propionate (L) in **1-Y** is a neutral inner salt with an electron-donating carboxylate group and an electron-accepting 4,4′-bipyridinium group (Figure 1). It was obtained as a hydrated compound $L{\cdot}4H_2O$ (**2**) according to a similar reported synthetic procedure (see the Supporting Information).[11] Compound **2** is water-soluble and also hydroscopic in air. The reaction of **2** and $ZnBr_2$ in a molar ratio of 1:1 in aqueous solution and further evaporation in air yielded yellow crystals of **1-Y**. This compound readily recrystallizes from water and is relatively stable in air at room temperature. Thermogravimetric analysis, powder X-ray diffraction (PXRD) patterns, and IR spectra indicated that compound **1-Y** is thermally stable at

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[**] We gratefully acknowledge financial support from the NSF of China (grant numbers 90922013, 21101152, and 90922035) and the NSF for Distinguished Young Scholars of Fujian Province (grant number 2011J06006).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108220.

least at 250 °C (see Figure S1–S2 in the Supporting Information). As shown in Figure 1, compound **1-Y** is built upon discrete $(ZnLBr_2)_2$ molecules, where two $ZnBr_2$ salts are doubly bridged by two neutral L ligands. The 4,4′-bipyridinium groups in two adjacent L ligands are stacked at a distance of 4.956(5) Å, and thus no clear π–π stacking interaction is observed.

One important characteristic of **1-Y** is its X-ray-induced color change at room temperature. This color change was discovered unexpectedly during a single-crystal X-ray diffraction determination. As shown in Figure 2, compound **1-Y** turned blue after illumination by a hard X-ray source (Mo-K_α, $\lambda = 0.71073$ Å; powered at 4 kW). At the same time, two new absorption bands centered at 402 and 609 nm, respectively, emerged in the UV/Vis range (Figure 3). Compound **1-Y** is also sensitive to soft X-rays at room temperature. As shown in Figure 2, compound **1-Y** became blue after irradiation in a powder X-ray diffractometer (Cu-K_α, $\lambda = 1.54056$ Å; powered at 450 W). The diffuse reflectance spectra of the hard and soft X-ray-induced blue photoproducts (hereafter named as **1-HX-B** and **1-SX-B**, respectively) are very similar (Figure 3). Completed decoloration of **1-HX-B** and **1-SX-B** needs more than half a year in the dark at ambient temperature, but is easily achieved by heating the photoproducts up to 150 °C and keeping this temperature for 1 h (Figure 3). These coloration–decoloration processes are reversible (more than 10 times), which is indicative of X-ray-induced photochromism of **1-Y**. Both PXRD and IR analyses showed that the crystal structure and organic components of **1-Y** were left unchanged during its coloration–decoloration processes (see Figure S2 in the Supporting Information). Thus, compound **1-Y** is a highly robust X-ray-sensitive species which does not show irreversible irradiation damage.

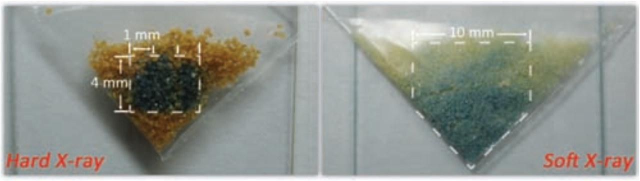

Figure 2. Hard X-ray- (Mo-K_α, $\lambda = 0.71073$ Å; irradiation time: 6 h per spot; three spots in total), and soft X-ray- (Cu-K_α, $\lambda = 1.54056$ Å; irradiation time: 7 h) induced photochromism of **1-Y**. The white dashed lines show X-ray irradiation areas in the single-crystal samples. The spot sizes of irradiation are labeled.

The exposure time, required for visual coloration, is an important parameter for an X-ray-sensitive material to detect X-rays. This value depends on energies of X-rays for **1-Y**. Visual coloration appeared in less than 30 s when **1-Y** was illuminated by Al-K_α radiation ($\lambda = 8.357$ Å) from an X-ray photoelectron spectrometer (powered at 150 W). More exposure time is needed for visual coloration when the X-rays become much harder. For example, about one hour is required when using the above-mentioned Mo-K_α ($\lambda = 0.71073$ Å) radiation source. Strictly speaking, compound **1-Y** seems more suitable to detect soft X-rays.

The quantitative evaluation is not accurate enough to detect X-rays through visual color change, just as it is the case for pH determination using test papers. Nevertheless, the coloration degree of **1-Y** can show its received radiation dosage to some extent. An in situ visualization system in the above-mentioned X-ray photoelectron spectrometer facilitates our evaluation of the degree of coloration of **1-Y**. Figure 4 shows the coloration process of **1-Y** when **1-Y** is irradiated by Al-K_α radiation. Clearly, the color became much deeper with increasing exposure time. If a film material of **1-Y** were prepared, it would play the same role as the photographic plate, but the detection by **1-Y** would be much easier than by the photographic plate.

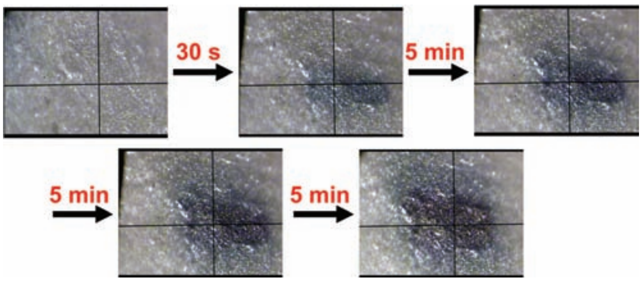

Figure 4. An X-ray-induced photochromic process of **1-Y**. The images were recorded in an X-ray photoelectron spectrometer ($\lambda = 8.357$ Å; powered at 150 W; spot size: 500 µm in diameter) using a tablet (0.8 mm in thickness) of powdered single crystals.

The high energy of X-rays can motivate an atom or a molecule to produce photoelectrons or secondary electrons. Electron transfer has been found to be one of the subsequent photophysical processes in some reported X-ray-induced photochromic species.[3,4,7–10] In this case, electron spin resonance (ESR) studies were carried out to make sure the presence of electron trans-

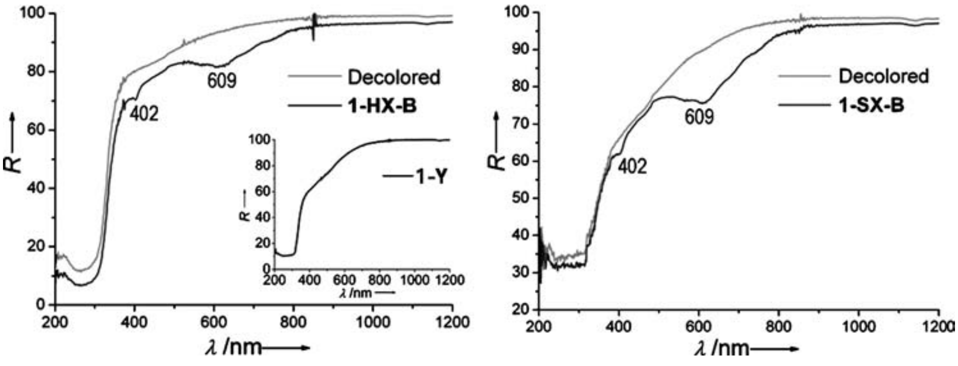

Figure 3. Diffuse reflectance (*R*) spectra of **1-Y** (inset), **1-HX-B**, and **1-SX-B**. All the curves were recored after decoloration using samples annealed at 150 °C for 1 h.

fer during X-ray irradiation. The experimental results showed that compound **1-Y** and its decolored samples are ESR silent but **1-HX-B** and **1-SX-B** display single line signals with g factors of 2.0029 and 1.9988, respectively (Figure 5). The zinc atom can be excluded to be a paramagnetic center because Zn^{I} and Zn^{III} atoms are unstable in this case. These g values are consistent with that of a free electron (2.0023), indicating that the paramagnetic centers of **1-HX-B** and **1-SX-B** should be radicals. So, the X-ray-induced photochromism of **1-Y** should also result from an electron-transfer process during X-ray irradiation.

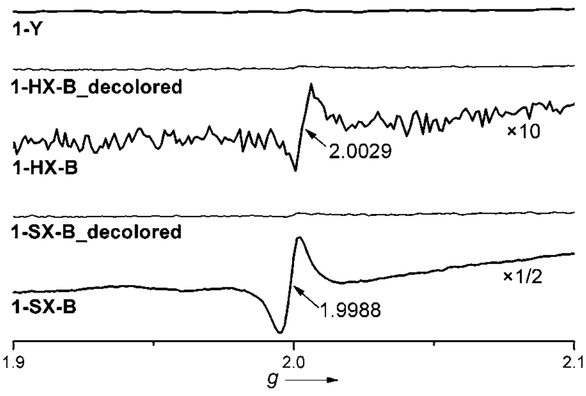

Figure 5. ESR curves of **1-Y**, **1-HX-B** after decoloration, **1-HX-B**, **1-SX-B** after decoloration, and **1-SX-B**.

In situ X-ray photoelectron spectroscopy (XPS) determination of the same sample can give us some insight into the X-ray-induced electron-transfer behavior of **1-Y**. As shown in Figure 6, the core-level spectrum of Br 3d varies remarkably after in situ X-ray irradiation. There are two normal Br $3d_{5/2}$ and $3d_{3/2}$ peaks of the negatively charged Br atom, lying at around 68.0 and 69.0 eV, respectively, before X-ray irradiation (see Figure S3a in the Supporting Information). A pair of weak components centered at around 70.1 and 71.1 eV, respectively, also appears in the Br 3d core-level spectrum, which should be attributed to the generation of partial neutral Br atoms during the XPS determination.[12] After in situ X-ray irradiation for one hour, the two major Br 3d peaks become weak, but the two components of the neutral Br atoms are prominently enhanced and shifted to a position with a higher binding energy (Figure 6 and Figure S3b in the Supporting Information). Therefore, the negatively charged Br atoms of **1-Y** lose electrons and become neutral upon X-ray irradiation. A minor shift toward a higher binding energy position for the Zn atom occurs after X-ray irradiation (Figure 6), which should be ascribed to the electron-withdrawing effect of more positive Br atoms and also indicates that the Zn atom is not an electron acceptor. Contrarily, the C 1s, N 1s, and O 1s core-level spectra are almost unchanged after in situ X-ray irradiation (Figure 6). Then, where is the electron acceptor in **1-Y**? Some literatures have reported the electron-accepting nature of the *N*-methyl-4,4′-bipyridinium (MQ) cation (Figure 1), which yields an $MQ^{\bullet}$ radical upon optical irradiation.[13] The new absorption bands around 609 nm of **1-HX-B** and **1-SX-B** are very similar to that of $MQ^{\bullet}$ (see Figure S4 in the Supporting Information).[13b] In addition, we found that $[(MQ)ZnBr_3]$ (Figure 1)[14] is slightly colored blue after X-ray irradiation (see Figure S5 in the Supporting Information), while $ZnBr_2$ is not sensitive to either soft or hard X-rays. So, the MQ group in L should be an electron-accepting unit. The undetectable variation of the N 1s core-level spectrum is a result of electron delocalization in the whole MQ group.

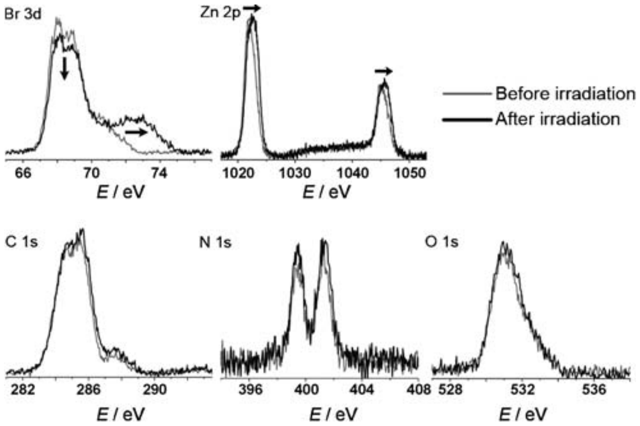

Figure 6. In situ measured XPS (Al-K_{α}) core-level spectra of **1-Y** before and after X-ray irradiation. The binding energies (E) are in units of electron volts. The arrows denote the shift.

Types of electron transfer in known X-ray-induced photochromic species are ligand-to-metal charge transfer,[7,9b] metal-to-metal charge transfer,[3] metal-centered transitions,[4] charge transfer between inorganic frameworks and organic templates,[8] and charge transfer between inorganic frameworks and doped metals.[10] In our case, the Br→L electron transfer is a key factor for the X-ray-induced photochromism of **1-Y**. This ligand-to-ligand charge transfer process is a new X-ray-induced electron-transfer mechanism. Secondary electrons originating from electron–phonon scattering in the crystal lattice of **1-Y** may be a main excitation source of this process.[15]

Compound **2** does not show visual coloration to Cu- and Mo-K_{α} X-rays even at exposure times longer than half a day. Compound **2** is also extremely hydroscopic in air and unstable at elevated temperatures (see Figure S6 in the Supporting Information). Compound $[(MQ)ZnBr_3]$ is sensitive to X-rays; however, its coloration is not only weaker than that of **1-Y** but its coloration also easily fades in air. A possible reason for this observation is that the bridging coordination to $ZnBr_2$ enhances the rigidity of the ligand L in **1-Y** which favors the stabilization of radicals. Compared to compound **2** and $[(MQ)ZnBr_3]$ compound **1-Y** has the advantage of being sensitive to X-rays.

In conclusion, we have synthesized a new and highly robust X-ray-sensitive material showing both soft and hard X-ray-induced photochromism at room temperature. A ligand-to-ligand electron-transfer mechanism has been proposed to elucidate its X-ray-induced photochromic phenomena. This material has a potential to detect X-rays, especially soft X-rays. To obtain an X-ray-induced photochromic species that shows fast response to both soft and hard X-rays is a challenge.

Received: November 22, 2011
Revised: January 25, 2012

Keywords: electron transfer · metal complexes · photochromism · radicals · X-ray detection

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