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Photochromic Metal Complexes of *N*-Methyl-4,4′-Bipyridinium: Mechanism and Influence of Halogen Atoms

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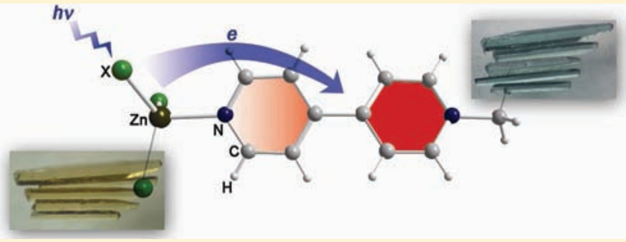
Supporting Information

ABSTRACT: Photochromism of *N*-methyl-4,4′-bipyridinium (MQ^+) salts and their metal complexes has never been reported. A series of MQ^+ coordinated halozinc complexes $[(MQ)ZnX_3]$ (X = Cl (**1**), Br (**2**), I (**3**)) and $[(MQ)ZnCl_{1.53}I_{1.47}]_2(MQ)ZnCl_{1.68}I_{1.32}$ (**4**), with better physicochemical stability than halide salts of the MQ^+ cation, have been found to exhibit different photochromic behaviors. Compounds **1**−**3** are isostructural, but only **1** and **2** show photochromism. Introduction of partial Cl atoms to nonphotochromic compound **3** yields compound **4**, which also displays photochromism. The photochromic response of **1**, **2**, and **4** indicates the presence of their long-lived charge separation states, which originate from X → MQ^+ electron transfer according to ESR and XPS measurements. Studies on the influence of different coordinated halogen atoms demonstrate that the Cl atom may be a more suitable electron donor than Br and I atoms to design redox photochromic metal complexes.



■ INTRODUCTION

Photochromic materials have real or potential applications in protection, display, high-density memory, switch, and many other high-tech areas.[1] A current focus of study in this area is to exploit new materials with better photochromic performances or various switching functions, such as luminescence,[2] electric conductivity,[3] magnetism,[4] and catalysis.[5] Coordination chemistry has been demonstrated to be an efficient approach to achieve this purpose.[6] Metal complexes show more structural diversity and rigidity than organic ligands themselves and display the ability to apply synergistic effects between inorganic and organic components. It has been thought that photochromic metal complexes should have better properties than traditional photochromic organic dyes if their efficient photochromic species were developed.[7] Incorporation of organic photochromic dyes, such as diarylethene derivatives and azo compounds, as ligands into metal complexes has gradually become hot in the past years.[8]

Redox photochromic materials play an increasing role for applications in such fields as catalysis[9] and optic, electric, or magnetic switch.[4d,10] The key to design and syntheses of such materials is to choose suitable electron donors and acceptors. Pyridinium derivatives, such as viologens (*N*,*N*′-disubstituted-bipyridinium), are typical electron acceptors and usually adopted to prepare redox photochromic materials.[11] Our group has also successfully obtained such photochromic materials based on viologens.[12] However, photochromic studies on metal complexes with coordinated pyridinium derivatives were rarely reported.[11f,13]

The *N*-methyl-4,4′-bipyridinium cation (MQ^+), as a typical pyridinium derivative, is a good electron acceptor.[14] A lot of work has been published on the electrochemical, nonlinear optical, and luminescent properties as well as Raman spectroscopy of MQ^+ complexes.[15] To the best of our knowledge, studies on photochromism of MQ^+ salts and their metal complexes have not been reported up to date. We and the Chen group have reported a series of MQ^+ coordinated halozinc complexes, $[(MQ)ZnX_3]$ (X = Cl (**1**), I (**3**)) and $[(MQ)ZnCl_{1.53}I_{1.47}]_2[(MQ)ZnCl_{1.68}I_{1.32}]$ (**4**).[15d,e] A new compound $[(MQ)ZnBr_3]$ (**2**), isostructural to **1** and **3**, was synthesized in this work. Herein, we first report the photochromism of these metal complexes and probe their photochromic mechanisms by electron spin resonance (ESR) spectra and X-ray photoelectron spectroscopy (XPS) measurements. We also investigate the influence of different coordinated halogen atoms on photochromic behaviors.

■ EXPERIMENTAL DETAILS

Materials. $ZnCl_2$, $ZnBr_2$, ZnI_2, 4,4′-bipyridine, 3-$ClCH_2CH_2COOH$, and 3-ICH_2CH_2COOH in AR grade were purchased commercially and used without further purification. Water was deionized and distilled before use. $MQX{\cdot}H_2O$ (X = Cl, I) were synthesized according to the same procedures reported in the literature.[15e]

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Determination. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using KBr pellets in the range of 4000−450 cm^{-1}. TGA spectra were measured on a Netzsch STA449C-QMS 403C thermal analysis-quadrupole mass spectrometer under a N_2 atmosphere with a ramp rate of 10 $K\cdot min^{-1}$. UV−visible (UV−vis) spectra were recorded at room temperature on a PerkinElmer Lambda 900 UV/vis/NIR spectrophotometer equipped with an integrating sphere in the wavelength range of 200−1200 nm. $BaSO_4$ plates were used as a reference (100% reflection), on which the finely ground power of the sample was coated. Powder X-ray diffraction (PXRD) patterns were collected with a Rigaku MiniFlex II diffractometer powered at 30 kV and 15 mA for Cu Kα (λ = 1.54056 Å). Simulated patterns were produced using the Mercury Version 1.4 software (http://www.ccdc.cam.ac.uk/products/mercury/) and single-crystal reflection diffraction data. ESR spectra were recorded on a Bruker ER-420 spectrometer with a 100 kHz magnetic field in X band at room temperature. The XPS study was performed in a ThermoFisher ESCALAB250 X-ray photoelectron spectrometer (powered at 150 W) using Al Kα radiation (λ = 8.357 Å). To compensate for surface charging effects, all XPS spectra were referenced to the C 1s neutral carbon peak at 284.6 eV.

X-ray Crystallographic Study. X-ray diffraction measurement of $[(MQ)ZnBr_3]$ was performed on a Rigaku SATURN70 CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity data sets were collected using an ω scan technique, and corrected for *Lp* effects. The primitive structure of $[(MQ)ZnBr_3]$ was solved by the direct method using the Siemens SHELXTL Version 5 package of crystallographic software.[16] Difference Fourier maps based on these atomic positions yielded other non-hydrogen atoms. The final structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically.

The entry of CCDC-800555 contains the supplementary crystallographic data for $[(MQ)ZnBr_3]$. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. Fax: (Internet) +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk.

Synthesis of $[(MQ)ZnCl_3]$ (1). Compound **1** was synthesized by a hydrothermal method in the literature.[15d] In this work, it was obtained via a solution method by reaction of $ZnCl_2$ (424 mg, 3 mmol) and $MQCl\cdot H_2O$ (700 mg, 3 mmol) in 20 mL of water in the ratio of 1:1. The phase purity of its crystalline sample was checked by PXRD (Figure S1, Supporting Information) and an elemental analysis. Calcd (%) for compound **1**: C, 38.52; H, 3.23; N, 8.17. Found (%): C, 38.46; H, 3.19; N, 8.13.

Synthesis and Crystal Structure of $[(MQ)ZnBr_3]$ (2). Typically, the reaction of $MQCl\cdot H_2O$ (45 mg, 0.2 mmol) and $ZnBr_2$ (45 mg, 0.2 mmol) in 6 mL of water yielded a clear yellow solution, which was filtered and allowed to stand in the dark for several days to produce yellow-brown block crystals of **2** (ca. 56% yield based on Zn). Compound **2** is isostructural to compound **1** (Figure S2, Supporting Information). The phase purity of its crystalline sample was checked by PXRD (Figure S3, Supporting Information) and an elemental analysis. Calcd (%) for compound **2**: C, 27.74; H, 2.33; N, 5.88. Found (%): C, 27.87; H, 2.44; N, 5.90.

Synthesis of $[(MQ)ZnI_3]$ (3). Compound **3** has been reported in the literature.[15e] In this work, it was obtained via a solution method by reaction of ZnI_2 (64 mg, 0.2 mmol) and $MQI\cdot H_2O$ (63.1 mg, 0.2 mmol) in 6 mL of water in the ratio of 1:1. The phase purity of its crystalline sample was checked by a PXRD analysis (Figure S3, Supporting Information).

Synthesis of $[(MQ)ZnCl_{1.53}I_{1.47}]_2[(MQ)ZnCl_{1.68}I_{1.32}]$ (4). Compound **4** has been reported in the literature.[15e] It was obtained via a solution method by reaction of ZnI_2 (956 mg, 3 mmol) and $MQCl\cdot H_2O$ (702 mg, 3 mmol) in 20 mL of water in the ratio of 1:1 in this paper. The phase purity of its crystalline sample was checked by a PXRD analysis (Figure S3, Supporting Information).

RESULTS AND DISCUSSION

Compounds **1**−**4** have similar discrete molecular structures (Figure 1). Thermogravimetric analyses reveal that there is no weight loss in the temperature range of 30−200 °C (Figure S4, Supporting Information). PXRD patterns (Figures S1 and S3, Supporting Information) and IR spectra (Figures S5 and S6, Supporting Information) of **1**−**4** annealed at 200 °C for 2 h correspond well with those of the obtained products, indicating that there are no obvious structural changes after heat treatment and that compounds **1**−**4** are thermally stable at least within 200 °C. In addition, compounds **1**−**4** show good physicochemical stability compared with $MQX\cdot H_2O$, which are highly deliquescent in the air.

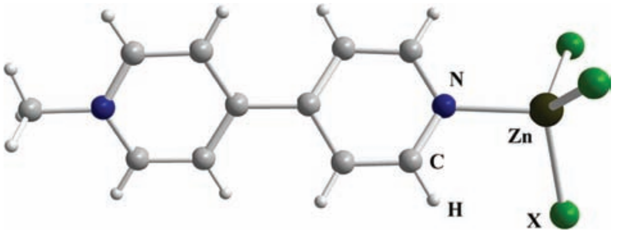

Figure 1. Molecular structures of **1**−**4**: X = Cl (**1**), Br (**2**), I (**3**), Cl/I (**4**).

UV−vis light-induced photochromic studies of **1**−**4** were performed in the air at room temperature (Figure 2). Upon UV−vis light irradiation, yellow compound **1** and yellow-brown compound **2** become bluish green and pale green, respectively. Meanwhile, they generate two new absorption bands centered at ~400 and 615 nm, respectively, after irradiation for 2 h. The photoproducts of **1** and **2** (hereafter named as **1A** and **2A**) can be kept in the dark for several weeks, but easily decolor after annealing at 140 and 120 °C for 2 h in the air, respectively. The new emerging absorption peaks vanish after decoloration (Figure 2). The decolored samples can also display color changes after irradiation again, which indicates reversible photochromism of **1** and **2**. The recognizable photochromic response of **1** and **2** indicates that they generate long-lived charge separation states after UV−vis irradiation. Oppositely, compound **3** with an orange color shows no photochromic behavior since it has neither recognizable color variations nor changes in the UV−vis reflection spectra after irradiation even for 3 h. This may be correlated to the very fast charge recombination of excited species due to the so-called heavy-metal effect of I atoms.[17]

The coloration of **1** and **2** all tends to be saturated after illumination for 30 min by a 500 W Hg lamp (Figure S7, Supporting Information), but the absorption intensity of **1A** is larger than that of **2A**. Therefore, the light sensitivity of **1**−**3**, with Cl, Br, and I atoms, respectively, is in the order of **1** > **2** > **3**. The influence of different coordinated halogen atoms on the photochromic behaviors accords with that of halogen ions in some halide salts.[11b,18] Although compound **3** with I atoms is nonphotochromic, fractional substitution of I atoms with Cl atoms can result in the occurrence of photochromism, as exemplified by compound **4**. Figure 2 shows that compound **4** also has no recognizable color changes, but displays a slight absorption band centered at ~719 nm upon UV−vis light irradiation. This absorption band disappears after heating at 100 °C for 2 h in the air, indicative of a typical photochromic characteristic. It should be noted that the decolored temper-

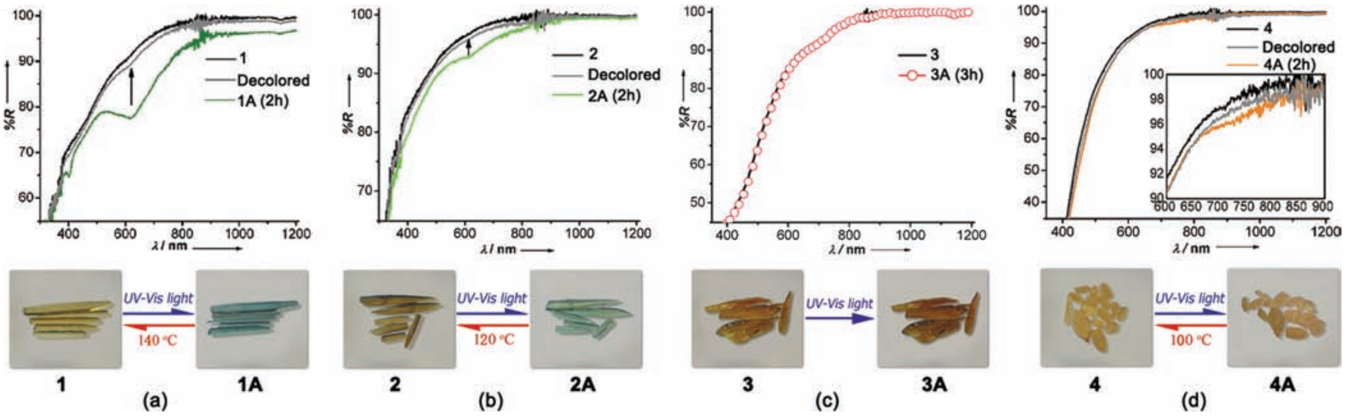

Figure 2. Diffuse reflectance spectra and photographs showing the photochromic behavior of **1**–**4** (a–d). The decolored curves were recorded on samples of **1A**, **2A**, and **4A** annealed at 140, 120, and 100 °C for 2 h, respectively.

atures of **1A**, **2A**, and **4A** (photoproduct of **4**) reduce gradually, which is opposite to the order of their color intensity. The quite obvious coloration and the relatively stable photoproduct show that compound **1** may be a more suitable photochromic material than the others in this work.

ESR studies show that compounds **1**, **2**, and **4** exhibit no ESR signals before irradiation but present single line signals with g = 1.9949, 1.9968, and 2.0014 after irradiation, respectively (Figure 3a,b,d). The Zn(II) 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 close to that of a free electron (2.0023), suggesting that the paramagnetic centers of **1A**, **2A**, and **4A** should be radicals. It should be noted that the single line ESR signals of **1A**, **2A**, and **4A** are very similar to those of some reported photochromic biradical species.[11a,b,19] Compound **3** shows no ESR signals after irradiation (Figure 3c), which evidences again the silence of its photochromism.

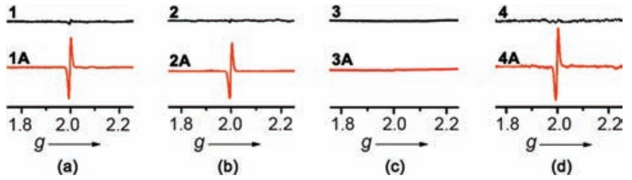

Figure 3. ESR spectra for **1** (a), **2** (b), **3** (c), and **4** (d) before and after irradiation.

XPS measurements were performed to probe the origin of the radicals in **1A**, **2A**, and **4A**. Here, we take compound **1**, for example, since **1**–**4** have similar molecular structures. The N 1s core-level spectrum of **1** reveals the existence of two components at the binding energy of ~398.6 and 400.6 eV, attributable to the pyridine nitrogen atom and the positively charged nitrogen atom, respectively (Figure 4a).[19b,20] After illumination, a new weak peak appears at a low binding energy of ~396.9 eV (Figure 4b), which should be assigned to the nitrogen pyridyl radical[11f] and also indicates that MQ^+ ligands receive electrons. Meanwhile, the Cl 2p core-level spectrum changes obviously after irradiation (Figures 4c,d). Before illumination, the Cl 2p core-level spectrum should be resolved into only one pair of spin–orbit-split doublets Cl $2p_{3/2}$ and Cl $2p_{1/2}$ because three Cl atoms with the same coordination sphere are equivalent. Indeed, we observed only one major pair of Cl $2p_{3/2}$ and Cl $2p_{1/2}$ peaks of the Cl atom, lying at ~196.9 and 198.6 eV, respectively. After irradiation, a new pair of prominent peaks centered at ~199.8 and 201.3 eV, respectively, appears in the Cl 2p core-level spectrum (Figure 4d), suggesting that the Cl atoms lose electrons.[11f] It should be mentioned that a very weak pair of peaks, centered at the same position, also appears before irradiation. This is possibly caused by the effect of unexpected light during sample handling and XPS measurements. The $ZnCl_2$ salt is not photochromic-active upon UV–vis light irradiation. In addition, the Zn 2p and C 1s core-level spectra of **1** have no clear changes after irradiation (Figure 5). Thus, the radicals should originate from Cl → MQ^+ electron transfer. PXRD patterns (Figure S1, Supporting Information) and IR (Figure S5, Supporting Information) spectra of **1** before and after UV–vis light irradiation coincide well, showing that the photochromism is not caused by isomerization or dissociation. It is reasonable to think that the photochromism of **1** is based on an electron-transfer mechanism. The same conclusion also applies to **2** and **4**.

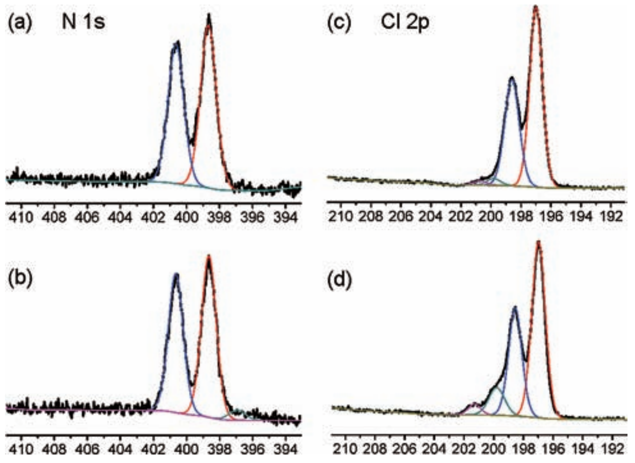

Figure 4. N 1s (a, b) and Cl 2p (c, d) XPS core-level spectra of **1** before and after irradiation. The horizontal axis represents binding energy (eV).

■ CONCLUSIONS

In summary, we have first found the photochromism of MQ^+ compounds, as exampled by a series of MQ^+ coordinated halozinc complexes with similar molecular structures of $[(MQ)ZnX_3]$ (X = halogen atoms). These compounds with good physicochemical stability exhibit different photochromic behaviors. The X → MQ^+ electron-transfer mechanism,

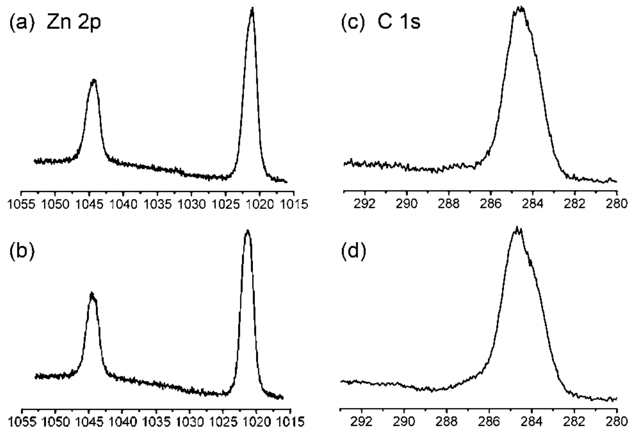

Figure 5. Zn 2p (a, b) and C 1s (c, d) XPS core-level spectra of **1** before and after irradiation. The horizontal axis represents binding energy (eV).

manifested by ESR and XPS measurements, is proposed to elucidate the photochromism. Our work also shows that the Cl atom may be a more suitable electron-donating ligand than Br and I atoms to design redox photochromic metal complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data for complex **2** in CIF format, PXRD patterns, X-ray structure of compound **2**, TGA curves, FT-IR spectra, and diffuse reflectance spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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