



Short communication

## Tetrazole-viologen based metal complex: Photochromism and reversible fluorescence modulation



Ya-Ping Zhao<sup>a,b</sup>, Yan Li<sup>c</sup>, Shuai-Hua Wang<sup>a,\*</sup>, Jian-Gang Xu<sup>a,b</sup>, Yong Yan<sup>a,b</sup>, Fa-Kun Zheng<sup>a,\*</sup>, Guo-Cong Guo<sup>a</sup>

<sup>a</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100039, PR China

<sup>c</sup> Department of Chemistry, East China University of Science and Technology, Shanghai 200237, PR China

## ARTICLE INFO

## Article history:

Received 28 March 2016

Received in revised form 10 April 2016

Accepted 13 April 2016

Available online 16 April 2016

## Keywords:

Tetrazole-viologen compound

Zinc(II) complex

Photochromism

Fluorescence modulation

## ABSTRACT

By UV–Vis spectroscopy, ESR study, X-ray photoelectron spectroscopy and theoretical calculation, a newly synthesized tetrazole-viologen based zinc(II) coordination compound,  $[\text{ZnCl}_2(3\text{-TzV})(\text{H}_2\text{O})]$  (3-TzV = *N*-(3-tetrazylbenzyl)-4,4'-bipyridinium), was found to exhibit electron-transfer photochromism. In addition to the commonly observed decrease in fluorescence intensity, the fluorescence color changes from green to blue during the coloration, and this change is reversible by altering UV–Vis irradiation and heating for at least seven cycles. The unprecedented photoswitching of fluorescence color for viologen-based photochromic compounds offers a good candidate for multicolor emitting display.

© 2016 Elsevier B.V. All rights reserved.

Recently, photochromic materials have attracted increasing interest owing to their potential applications in radiation protection, high-density memory, optical switch and many other high-tech areas [1]. With the structural diversity and synergetic interaction between the inorganic and organic components of metal complexes, coordination chemistry can serve as an efficient approach for the development of novel materials possessing improved fluorescence modulation based on photochromic reactions [2–4]. Electron-transfer photochromic metal complexes have potential applications in the modulation of fluorescent performance [5]. Among this system, pyridinium derivatives, such as viologens (*N*-monosubstituted or *N,N'*-disubstituted-bipyridinium), are typical electron acceptors and usually are used to prepare redox photochromic metal complexes [6]. Some substituents of carboxylate, carboxybenzyl or alkyl groups have been introduced as photochromic candidates for reversible fluorescence intensity switching [7–10]. For example, a Cd(II) complex based on 1,2-bis(4,4'-bipyridinium)ethane dibromine ligand was reported to show non-destructive readout luminescence switching [9]. By the introduction of viologen, the lanthanide(III) complex also exhibits excellent photo-modulated fluorescence intensity as a fluorescent switching with the non-destructive readout capability in the solid state [10]. However, the fluorescent color modulation study on metal complexes with coordinated pyridinium derivatives has been rarely reported [11]. If a luminescence chromophore is introduced into a photochromic viologen derivative to construct metal complexes, there will be a good chance

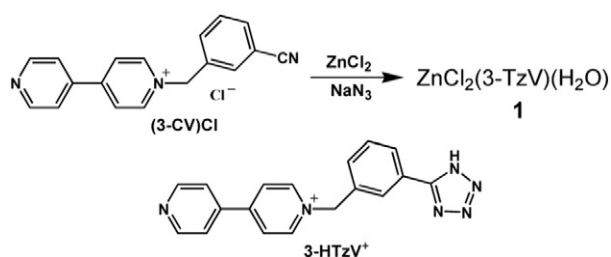
that new solid-state photo-switchable materials with fluorescence modulation during the photochromic process can be obtained.

Herein, tetrazole group was introduced into a viologen derivative to yield a photochromic metal complex  $[\text{ZnCl}_2(3\text{-TzV})(\text{H}_2\text{O})]$  **1** (Scheme 1) with fluorescence color modulation. The ligand *N*-(3-1H-tetrazylbenzyl)-4,4'-bipyridinium (3-HTzV<sup>+</sup>) was formed by the *in situ* [2 + 3] cycloaddition of cyano-precursor (*N*-(3-cyanobenzyl)-4,4'-bipyridinium chloride) and azide [12]. To the best of our knowledge, only a tetrazole-viologen based photochromic compound has been obtained [13]. Complex **1** is the first tetrazole-viologen based metal complex showing fluorescence color modulation based on photochromic reaction. The photochromic mechanism of **1** was proved by various characterization methods and theoretical calculation, followed by the investigation on the photoinduced fluorescence color modulation.

The *in situ* [2 + 3] cycloaddition of an azide to a nitrile has been successfully applied in the preparation of a series of tetrazole-based metal organic complexes by our group [14]. Along with the preparation of photochromic compound  $[\text{ZnCl}_2(3\text{-TzV})(\text{H}_2\text{O})]$  **1**, tetrazole group was introduced simultaneously into viologen to produce the tetrazole-viologen based ligand 3-TzV (Experimental section in ESI), which is a neutral inner salt and contains an electron-donating tetrazolate (Tz<sup>−</sup>) group and an electron-accepting 4,4'-bipyridinium (V<sup>+</sup>) group. In the IR spectra (Fig. S1), the peaks at ca. 1478 and 1380 cm<sup>−1</sup> are attributed to the tetrazolate group and the cyano peak at ca. 2240 cm<sup>−1</sup> for (3-CV)Cl disappears, indicating the formation of the ligand 3-TzV. The experimental powdered X-ray diffraction (PXRD) patterns of the bulk products are consistent with the calculated one based on the single-

\* Corresponding authors.

E-mail address: [zfk@fjirm.ac.cn](mailto:zfk@fjirm.ac.cn) (F.-K. Zheng).

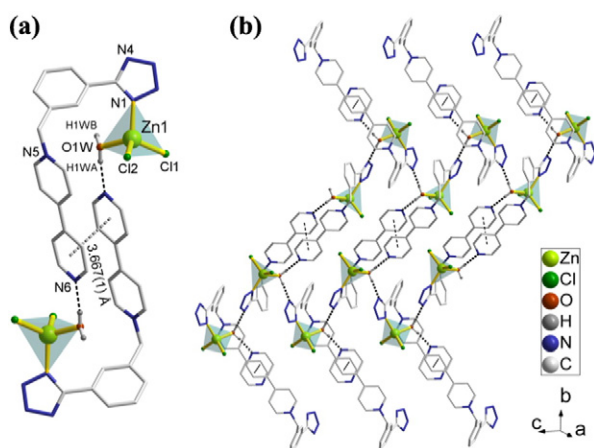


**Scheme 1.** Hydrothermal synthesis of  $\text{ZnCl}_2(3\text{-TzV})(\text{H}_2\text{O})$  **1**.

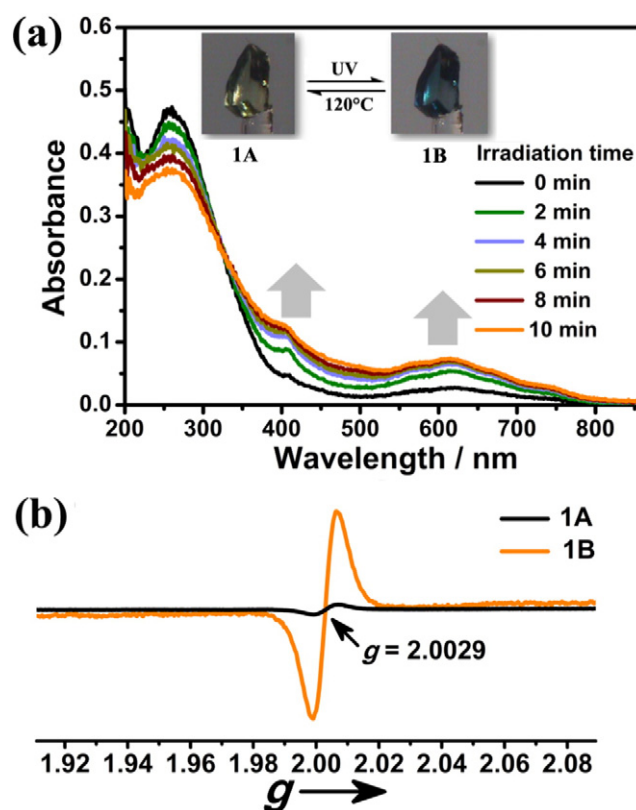
crystal data, indicating a pure phase of **1** (Fig. S2). Thermogravimetric analyses (TGA) curve (Fig. S3) shows that **1** has a weight loss of 4.10% up to 200 °C, in accordance with the release of one coordinated water molecule (calc. 4.15%). Then continuous heating led to the framework collapse presumably due to decomposition of organic ligand.

Single-crystal structural analysis (Experimental section in ESI and Table S1) reveals that complex **1** crystallizes in the  $P2_1/c$  space group. There exist one crystallographically independent Zn(II) atom, one 3-TzV ligand, two chloride atoms and one coordinated water molecule in an asymmetric unit. The Zn(II) atom is tetrahedrally coordinated by one nitrogen atom from the 3-TzV ligand, two chloride atoms and one water molecule (Fig. 1(a)). The bond lengths (Zn1–O1W, 1.992(4) Å; Zn1–N1, 2.001(5) Å; Zn1–Cl1, 2.320(2) Å; Zn1–Cl2, 2.279(3) Å) are in the rational range [13–15]. Each isolate mononuclear unit is linked together by O1W–H1WB⋯N4 hydrogen bonds (2.73 Å) to form a zigzag chain along the *c* axis. Such chains connect to each other through O1W–H1WA⋯N6 hydrogen bonds (2.76 Å) to yield a 2D supramolecular layer in the *bc* plane (Fig. 1(b), Table S2). Furthermore, there exist face-to-face  $\pi\cdots\pi$  interactions with the center-to-center distance of 3.667(1) Å in the layers, and the adjacent layers are further packed together *via*  $\pi\cdots\pi$  stacking interactions (the slipped packing with the center-to-center distance of 3.770(2) Å) to give a 3D supramolecular structure (Fig. S4) [16].

Photochromic studies of **1** were performed under ambient conditions. Complex **1** is very sensitive to light, showing slight adsorption at ~400 and ~620 nm before UV–Vis light irradiation (Fig. 2a), which are characteristic absorptions of viologen radicals [17]. Upon UV–Vis light irradiation, the intensity of absorption peaks at ~400 and ~620 nm both gradually increases with the extension of irradiation time and tends to be saturated until 10 min. Correspondingly, the color change of **1** from green-yellow to navy blue can be visualized by the naked eyes. The sample **1** before illumination is named as **1A**, and produced **1B** fully irradiated by the UV–Vis light. When exposed to atmospheric environments in the dark, **1B** remains rather stable for several weeks.



**Fig. 1.** (a) Hydrogen-bonded molecular framework in **1**. (b) 2D supramolecular framework in **1** by hydrogen bonds.



**Fig. 2.** (a) Time-dependent UV–Vis absorption spectra (irradiated by 300 W Xe lamp). The inset shows reversible color change between **1A** and **1B**. (b) ESR spectra for **1A** and **1B**.

Still, the photoproduct **1B** can be decolored easily when heated at 120 °C in the air for 10 mins.

The generation of radicals was confirmed by ESR studies. There is a tiny ESR signal before irradiation, proving the high sensitivity of **1A** as former mentioned, but a sharp resonance signal at  $g = 2.0029$  is observed with sufficient irradiation (Fig. 2b). This  $g$  value is close to that of a free electron (2.0023), suggesting that the generated radicals of **1** is derived from electron transfer during irradiation [18]. To elucidate the origin of the radicals, a density functional theory (DFT) calculation based on the 6–31 +  $g(d, p)$  basis set and B3LYP functional was performed. The calculated spin density of the  $[\text{ZnCl}_2(3\text{-TzV})(\text{H}_2\text{O})]$  molecule of **1** in the triplet ground state is shown in Fig. S5. It can be seen that the spins almost distribute in the bipyridinium and  $\text{Tz}^-$  ions, implying that the bipyridinium cations behave as electron acceptors and  $\text{Tz}^-$  anions as electron donors. X-ray photoelectron spectroscopy (XPS) measurements were performed to further demonstrate the above results. As shown in Fig. 3, the core-level spectrum of N 1 *s* changes remarkably after UV–Vis irradiation. In the N 1 *s* core-level spectrum of **1**, there are three components at the binding energy of 398.4, 399.5 and 401.6 eV, which can be ascribed to the tetrazolate nitrogen atom, pyridine nitrogen atom and electropositive pyridine ( $\text{V}^+$ ) nitrogen atom, respectively. After illumination, the intensity of peak at a higher binding energy 401.6 eV becomes weaker and partly shifts to a position with a lower binding energy of 401.3 eV. Therefore, the electropositive pyridine nitrogen atoms should be electron acceptors to produce pyridyl radicals. Meanwhile, a minor shift toward a higher binding energy position (398.6 eV) for tetrazolate nitrogen atoms should be assigned to the electron-donor group. In addition, the Zn 2 *p* and Cl 2 *p* core-level spectra of **1** have no clear changes after irradiation, similar to the situations of C and O elements (Fig. S6). Thus, the viologen radicals should originate from  $\text{Tz}^-$  to  $\text{V}^+$  electron transfer upon light irradiation. The PXRD pattern and IR spectrum of **1B** match well with those of **1A** (Figs. S1 and S2), indicating that their crystalline structures are almost

Download English Version:

<https://daneshyari.com/en/article/1305262>

Download Persian Version:

<https://daneshyari.com/article/1305262>

[Daneshyari.com](https://daneshyari.com)