

Novel photo- and/or hydrochromic organometallics derived from methyl viologen cations

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ABSTRACT

By the reaction of $\text{TM}(\text{NO}_3)_2$ (TM = Co, Ni, Cd) with 1,1'-bis(methyl)-4,4'-bipyridinium dibromide (MV-2Br) and 1,4-benzenedicarboxylic acid (*p*-H₂BDC), three novel organometallic compounds have been obtained, (MV)[Co(H₂O)₆](*p*-BDC)₂·4H₂O (1), (MV)[Ni(H₂O)₆](*p*-BDC)₂·4H₂O (2), {(MV)[Cd(*p*-BDC)(Br)₂]}_n (3). Compounds 1 and 2 are isostructural ionic salts made up of one MV²⁺ cation, one [TM(H₂O)₆]²⁺ cation, two uncoordinated *p*-BDC²⁻ anions, and four crystallization water molecules, and linked by extensive hydrogen bonds to afford the 3D networks; Compound 3 is constituted by MV²⁺ cations and zigzag chains of Cd(II) ions bridged by the deprotonated *p*-BDC²⁻ species through four carboxylate oxygen atoms to form a 1D coordination polymer. Compound 3 exhibits electron-transfer photochromism similar to other viologen-based materials, while 1 and 2 are photoinert. However, the thermal stimulation not only makes compounds 1 and 2 exhibit hydrochromic behaviors by means of dehydration and rehydration of the crystals, but also can induce a phase transition from photochemically inert to active states, demonstrating a positive role in improving photoinduced electron transfer.

1. Introduction

Recently, stimuli responsive materials have attracted increasing interest from both private and commercial sectors due to a series of applications in diverse areas, such as energy harvesting, waste remediation and drug delivery [1]. Chromism has proved to be a very promising domain for a variety of present and potential applications not only in our daily life but also in various high-tech areas [2]. Color changes can be caused by photo-irradiation, heat, compression, or solvent effects; the phenomena are correspondingly named photochromism, thermochromism, piezochromism, and solvatochromism [3]. Burgeoning interest has been focused on these chromic materials due to their fascinating applications in protection, optical switching, memory and display [4]. A commonly used strategy to construct these chromic materials is to incorporate the stimuli responsive units as linkers in the framework (see Scheme 1).

It is well known that as functional organic ligands, bipyridinium derivatives have fascinating chromic properties due to their electron-accepting ability and redox activity, and have attracted increasing attention in recent years [5]. Viologens, namely, 1,1-disubstituted-4,4-bipyridinium dications, have been widely studied as chromic materials in modern chemistry for decades [6]. In the solid state, materials incorporating viologen units can undergo a direct electron-transfer

process, and have also been considered for various applications such as photochromic displays, molecular electronics, phytotoxic agents, and so on [7]. More interestingly, because of the photocatalyzed electron transfer from the counter-anion to the methyl viologen cation (MV²⁺), most MV²⁺ has potential photochromic behaviors which promises MV-containing materials more potential applications [8].

The research of organometallics has been of particular importance in the field of crystal engineering because the resulting structures will play an important role in determining the properties of the crystalline solid [9]. A few attractive organometallics constructed by the use of viologens with various structural features and chromic properties have been reported [10]. Nevertheless, reversible solid-state hydrochromism related to dehydration-rehydration has long been known in transition metal compounds, which has also been observed in viologens [11]. However, As far as we know, the reports on the both photo- and hydrochromic behaviors of the viologens are relatively rare [12]. Therefore, the synthesis of new multifunctional chromic properties of viologen materials is of great challenge. In this work, a cationic viologen derivative, 1,1'-bis(methyl)-4,4'-bipyridinium dibromide (MV-2Br) has been select to construct new chromic materials. By varying different transition metals, three photo- and/or hydroresponsive organometallic compounds (MV)[TM(H₂O)₆](*p*-BDC)₂·4H₂O (TM = Co (1), Ni (2)) and {(MV)[Cd(*p*-BDC)(Br)₂]}_n with methyl viologen dications as the guest

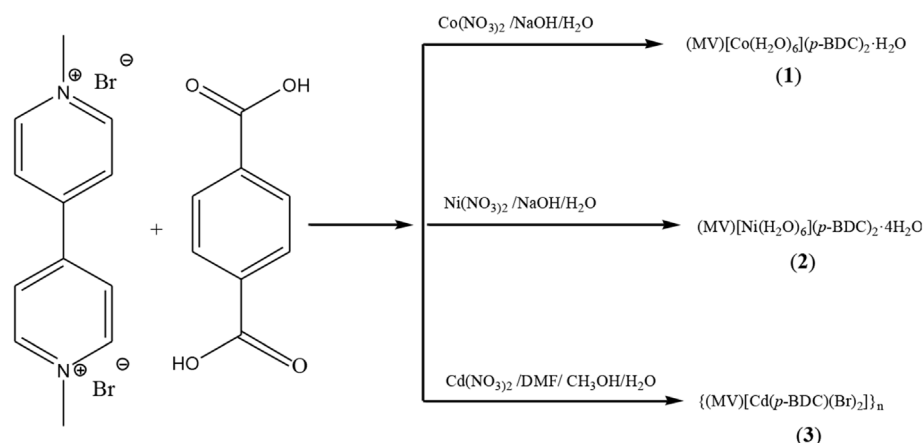
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Scheme 1. Preparation of compounds 1–3.

templating-block and TM-carboxylate anionic framework as the host unit (MV = methyl viologen, *p*-BDC = 1,4-benzenedicarboxylate) have been obtained. Interestingly, compounds **1** and **2** show different changes in color upon removal and reabsorption of water molecules by the thermal stimulation. Notably, thermal dehydration not only can induce a visible color change of **1** and **2** but also lead to new phases accompanying the structural transformation and regain photochromism in the solid state. Compound **3** exhibits photochromism similar to other viologen-based materials.

2. Experimental section

2.1. Materials and methods

All chemicals, obtained from commercial sources, are of reagent grade quality and used without further purification. 1,1'-bis(methyl)-4,4'-bipyridinium dibromide was synthesized according to literature method [13]. X-ray powder diffraction (PXRD) patterns were collected using a Rigaku Ultima IV-185 diffractometer. Elemental analysis of C, H and N was performed on a Vario EL III CHNOS elemental analyzer. FT-IR spectra (4000–500 cm^{-1}) were obtained with a Nicolet 5DX spectrometer by use of KBr pellets. UV–vis diffuse reflectance spectrum was performed on a Varian Cary 5000 UV–vis spectrophotometer at room temperature. Thermogravimetric (TG) experiments were carried out using a HTG-3 equipment in the range 30–800 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ in air. Electron paramagnetic resonance (EPR) spectrum was recorded on a Bruker A300-10/12 spectrometer at room temperature.

2.2. Synthesis

(MV)[Co(H₂O)₆](p-BDC)₂·4H₂O: Co(NO₃)₂·6H₂O (29 mg, 0.1 mmol) was added into a 5 mL aqueous solution of MV·2Br (35 mg, 0.1 mmol) and then stirred for 5 min. 1,4-Benzenedicarboxylic acid (33 mg, 0.2 mmol) and NaOH (16 mg, 0.4 mmol) was dissolved in 10 mL water at heated conditions and filtrated. Then the two kinds of solution were mixed together and filtrated after stirring for another 5 min. After the reaction, the filtrate was left for slow evaporation at room temperature. Some yellow block crystals were obtained within a week in 31.2% yield (based on MV·2Br). Elemental analysis: Anal. Calcd for C₂₈H₄₀CoN₂O₁₈: C, 44.71; H, 5.32; N, 3.72%. Found: C, 44.98; H, 5.52; N, 3.86%. IR (KBr, cm^{-1}): 3411, 2360, 1637, 1565, 1369, 1149, 1129, 1020, 826, 745, 570, 517.

(MV)[Ni(H₂O)₆](p-BDC)₂·4H₂O: The procedure was similar to the synthesis of compound **1**, except Ni(NO₃)₂·6H₂O (29 mg, 0.1 mmol) was replaced by Co(NO₃)₂·6H₂O (29 mg, 0.1 mmol). Light green block crystals were obtained within a week in 28.4% yield (based on MV·2Br). Elemental analysis: Anal. Calcd for C₂₈H₄₀NiN₂O₁₈: C, 44.72; H, 5.32;

N, 3.72%. Found: C, 44.23; H, 5.68; N, 4.12%. IR (KBr, cm^{-1}): 3412, 2359, 1637, 1537, 1369, 1149, 1110, 1020, 826, 751, 576, 517.

{(MV)[Cd(p-BDC)(Br)₂]}_n: A 7 mL DMF/CH₃OH (V 5:2) solution of 1,4-Benzenedicarboxylic acid (17 mg, 0.1 mmol) was added to a 5 mL aqueous solution containing MV·2Br (35 mg, 0.1 mmol) and Cd(NO₃)₂·4H₂O (31 mg, 0.1 mmol). After mixed and heated until the solution became clear. The filtrate was left for slow evaporation at room temperature. Yellow block crystals were obtained within three weeks in 21.2% yield (based on MV·2Br). Elemental analysis: Anal. Calcd for C₂₀H₁₈Br₂CdN₂O₄: C, 38.55; H, 2.39; N, 4.50%. Found: C, 38.23; H, 2.51; N, 4.32%. IR (KBr, cm^{-1}): 3466, 3116, 3044, 2547, 2360, 1947, 1639, 1561, 1499, 1447, 1382, 1267, 1184, 1087, 1012, 885, 834, 747, 616, 525.

The purities of compounds **1–3** have been investigated by PXRD. The diffraction peaks of experimental and simulated X-ray powder diffraction pattern agree well in position, confirming that the as-synthesized samples have high phase purities (Fig. 6c, Fig. 7c and Fig. S1).

2.3. X-ray crystallography

Crystallographic data were recorded at 293 K for **1–3** on an Oxford Gemini diffractometer using graphite monochromated Mo–K α ($\lambda = 0.71073 \text{ \AA}$). An empirical absorption correction with spherical harmonics was carried out by SCALE3 ABSPACK scaling algorithm [14]. Three structures were solved by direct method and refined by full-matrix least-squares techniques on F^2 performed with SHELXTL-97 program [15]. All non-hydrogen atoms were refined anisotropically. The crystallographic data of **1–3** are listed in Table 1, and selected bond lengths and bond angles are listed in Table S1 of the Supporting Information.

3. Results and discussion

3.1. Structural description

(MV)[Co(H₂O)₆](p-BDC)₂·4H₂O: Compounds **1** and **2** are isomorphous and isostructural, **1** is discussed in detail. Compound **1** crystallizes in the monoclinic space group $I 2/m$ and contains one MV²⁺ cation, one [Co(H₂O)₆]²⁺ cation, two *p*-BDC²⁻ anions and four crystallization water molecules (Fig. 1). Each cobalt ion locates at a crystallographic special position and is six-coordinated by six water molecules forming the octahedral coordination geometry, with two Co–O bond lengths of 2.1116 Å and 2.0851 Å (Ni–O, 2.0697 Å and 2.0623 Å for **2**). There exists numerous hydrogen-bonding interactions among four crystallization water molecules, six coordinated waters in [Co(H₂O)₆]²⁺ cations and oxygen atoms of carboxylate groups (Table S2), which plays a key role in stabilizing the crystal structure and

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