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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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Near-IR Electrochromism in Electropolymerized Films of a Biscyclometalated Ruthenium Complex Bridged by 1,2,4,5-Tetra(2-pyridyl)benzene

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Supporting Information

ABSTRACT: Reductive electropolymerization of the biscyclometalated ruthenium complex $[(vtpy)Ru(tpb)Ru(vtpy)]^{2+}$ [vtpy = 4′-vinyl-2,2′:6′,2″-terpyridine; tpb = 1,2,4,5-tetra(2-pyridyl)benzene] proceeded smoothly on electrode surfaces. Thanks to the strong electron coupling between the ruthenium centers of the individual monomeric units and strong intervalence charge-transfer absorption in the mixed valence state, the produced adherent metallopolymeric films exhibited near-IR electrochromism with tricolor switching, good contrast ratio (40% at 1165 nm), short response time, low-switching voltage, and long memory time.

Electrochromism refers to reversible changes in electronic absorption bands caused by switching between two or more redox states using an external electric field.[1] Electrochromic materials with long-term stability, good contrast ratio and coloration efficiency, low switching potential, and quick response time are useful for practical applications such as information storage, optical memory, smart windows, and color displays.[2] In some particular applications, materials with a long memory time and multicolor changes are desirable. The most frequently studied electrochromic candidates are organic conducting polymers[3] and metal oxides.[4] These compounds usually exhibit distinctly different absorption bands in the visible region in different redox states. However, materials that display electrochromism in the near-IR (NIR) region (800−2000 nm) are much less well known,[5] although they are of great importance in many military and civilian uses.[6]

Another set of materials that are promising candidates for electrochromism are coordination metallopolymers,[7] which are characterized by intense metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) transitions in the visible region whose energies and absorptivities are largely dependent on the redox states of the metals and ligands. By employing theses features, Abruña[8] and Higuchi and Kurth[9] successfully realized efficient electrochromism of indium tin oxide (ITO) films coated with metallopolymers. Van der Boom recently reported electrochromic behaviors of self-propagating assembly films of polypyridyl Os^{II} complexes.[10] In principle, coordination polymers with mixed-valent dimetallic units can be used to extend the electrochromic window into the NIR region by manipulating the intervalence charge transfer (IVCT) transitions.[11] However, this concept has met with limited success to date.[12] We recently reported the biscyclometalated ruthenium complex $\mathbf{1}^{2+}$ bridged by 1,2,4,5-tetra(2-pyridyl)benzene (tpb) (Figure 1).[13] This complex could be oxidized stepwise to $\mathbf{1}^{3+}$ and $\mathbf{1}^{4+}$ at considerably low potentials (+0.12 and +0.55 V vs Ag/AgCl) and with an impressively wide potential separation (430 mV). Complex $\mathbf{1}^{3+}$ was determined to be a Robin−Day class-III mixed-valent system[14] and displayed intense NIR transitions due to strong electronic delocalization that were not present in $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$. We conjectured that these features would make complex $\mathbf{1}^{2+}$ an appealing NIR electrochromic material if it could be incorporated into polymers and adhesively deposited on electrode surfaces. In this regard, we disclose herein the electropolymerization of complex $\mathbf{2}^{2+}$ with a vinyl group at each end and the NIR electrochromic behavior of the resulting polymeric films.

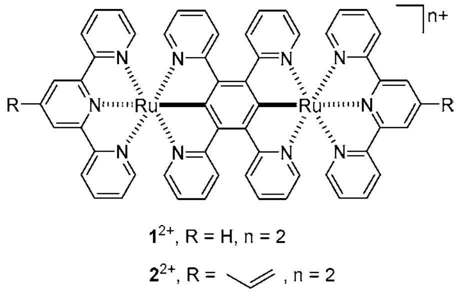

Figure 1. Dimetallic complexes **1** and **2**.

It is well-known that vinyl-substituted polypyridine complexes can be readily and controllably electropolymerized by reduction of ligands[15] to produce electrodes coated with adhesive and redox-active polymeric films. These films are very stable upon redox cycling and have excellent counterion transport ability. We note that Meyer and co-workers previously used this method to prepare electrochromic films with a monometallic ruthenium complex.[16] However, electrochromic films with mixed-valent dimetallic components prepared by reductive electropolymerization have not been documented.

Received: October 12, 2011
Published: December 1, 2011

The synthesis of complex $\mathbf{2}^{2+}$ is shown in the Supporting Information (SI). We first carried out the electropolymerization experiments at a homemade Pt disk electrode (d = 2 mm). When a clean Pt electrode was placed in a solution of $\mathbf{2}^{2+}$ in acetonitrile containing 0.1 M Bu_4NClO_4 as the supporting electrolyte and the potential was scanned repeatedly between −0.8 and −1.7 V vs Ag/AgCl, reductive electropolymerization proceeded smoothly, as evidenced by the continuous and gradual growth of the current in the cyclic voltammogram (CV) (Figure 2a). The produced polymeric film exhibited two distinct consecutive redox couples at +0.14 and +0.54 V in a clean supporting electrolyte solution (Figure 2b). This indicates that the degree of electron delocalization of the polymeric film is quite similar to that of $\mathbf{1}^{2+}$ and that there is no significant electronic interaction between individual monomeric units. The potential separation between the anodic and cathodic wave of each redox couple was less than 59 mV (23 mV at 100 mV/s and 50 mV at 2000 mV/s). Both the anodic and cathodic currents were linearly dependent on the scan rate up to 2000 mV/s (Figure 2c), which is characteristic of redox events confined on an electrode surface. The surface coverage of deposited polymers could be readily adjusted by varying the number of potential cycles during electropolymerization. For instance, Figure 2d shows CVs at the same scan rate for three polymeric films obtained after scanning the potential between −0.8 and −1.7 V for 10, 20, and 40 electropolymerization cycles of $\mathbf{2}^{2+}$ (0.6 mM) in acetonitrile, which gave surface coverages of 5.7×10^{-10}, 16×10^{-10}, and 30×10^{-10} mol/cm^2, respectively (Figures S1−S3 in the SI). It should be noted that complex $\mathbf{1}^{2+}$ lacking vinyl groups did not undergo similar electropolymerization at all.

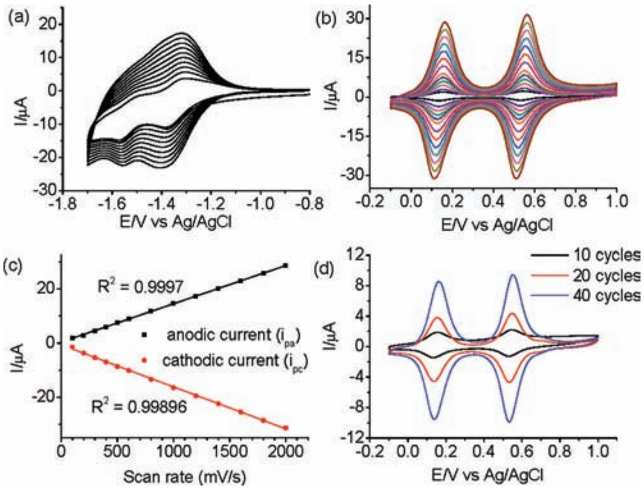

Figure 2. (a) Reductive electropolymerization of $\mathbf{2}^{2+}$ (0.6 mM in acetonitrile) on a Pt disk electrode (d = 2 mm) by 10 repeated potential scan cycles at 100 mV/s. (b) CVs of the polymeric films obtained in (a) at different scan rates (100, 200, 300, 400, 500, 600, 800, 1000, 1200, 1400, 1600, 1800, and 2000 mV/s, respectively). (c) Linear dependence of the peak currents in (b) as a function of scan rate. (d) CV profiles of polymeric films obtained after 10, 20, and 40 electropolymerization cycles. The scan rate was 100 mV/s.

The electropolymerization of $\mathbf{2}^{2+}$ proceeded equally well on an ITO glass electrode (Figures S4−S7) to afford adherent metallopolymeric films with a typical geometrical dimensions of 20 mm × 8 mm. Figure 3a shows CV profiles of a polymeric film (surface coverage = 5.5×10^{-9} mol/cm^2) at different scan rates, which exhibit two consecutive redox couples as found in Figure 2. The peak separation between the anodic and cathodic wave of each redox couple was 45 mV at 10 mV/s. However, the separation became as wide as 200 mV when the scan rate was increased to 100 mV/s. This is possibly caused by the nonohmic contact between the polymer and the ITO surface. These films exhibited good electrochemical stability. Well-defined redox couples were retained when the potential was scanned for over 1000 cycles, with the peak current dropping to 76% of its original state (Figure 3b). X-ray photoelectron spectroscopy (XPS) of the above film showed bands of N 1s (399.6 eV), O 1s (531.9 eV), Ru $3p_3$ (461.6 eV), and Cl 2p (207.1 eV) (Figure S8).

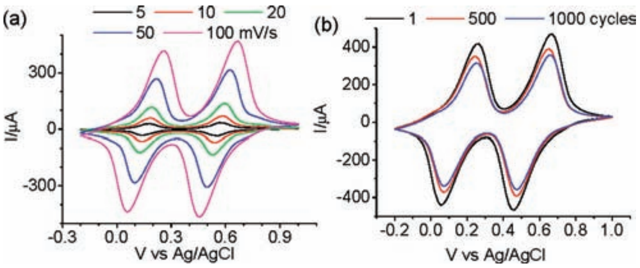

Figure 3. (a) CV profiles of a polymeric film of $\mathbf{2}^{2+}$ on ITO glass (surface coverage = 5.5×10^{-9} mol/cm^2) at different scan rates. (b) CV profiles of the same film used in (a) after 500 and 1000 potential cycles at 100 mV/s.

The UV/vis/NIR spectral changes of a representative polymeric film on ITO glass upon application of various potentials from +0.01 to +1.0 V vs Ag/AgCl are shown in Figure 4. When the potential was gradually increased to +0.4 V to induce one-electron oxidation of the dimetallic unit, MLCT transitions at 600 nm decreased. Concomitantly, broad transitions in the NIR region (centered at 1165 nm) ascribed to IVCT transitions (better termed as charge resonance bands) for Robin−Day class-III systems evolved, and the deep-blue color of the original film changed to pink. When the potential was further increased to +1.0 V, the intensity of the NIR band at 1165 nm decreased, and two new MLCT bands at 480 and 610 nm appeared. As a result, the color of the film changed from pink to green. It should be noted that the tricolor change (blue → pink → green) was fully reversible when the applied potential was reversed. Similar color changes were also observable in the cyclic potential scans in Figure 3.

The electrochromic behavior of the polymeric film of $\mathbf{2}^{2+}$ was further studied by double-potential-step chronoamperometry (Figure 5). The percent transmittance (T%) changes at 1165 nm were recorded as a function of time when the potential was switched stepwise between two potentials. In the first one-electron oxidation step (−0.2 to +0.4 V vs Ag/AgCl; Figure 5a−c) of a film with a surface coverage of 1×10^{-8} mol/cm^2, a contrast ratio (ΔT%) of 40% was achieved.[17] The coloration efficiency (CE) at 1165 nm for this process was determined to be 250 cm^2/C according to the equations $CE(\lambda) = \Delta OD/Q_d$ and $\Delta OD = \log(T_b/T_c)$, where OD is the optical density, Q_d is the injected/ejected charge density (C/cm^2), and T_b and T_c are the transmittances in the bleached and colored states at the indicated wavelength. The response time for the contrast ratio to reach over 90% of its maximum was 6 s for the oxidation process and 5 s for the reverse reduction process. In the second one-electron oxidation step (+0.4 to +1.0 V; Figure 5d−f), a comparable contrast ratio (37%) was achieved. The response

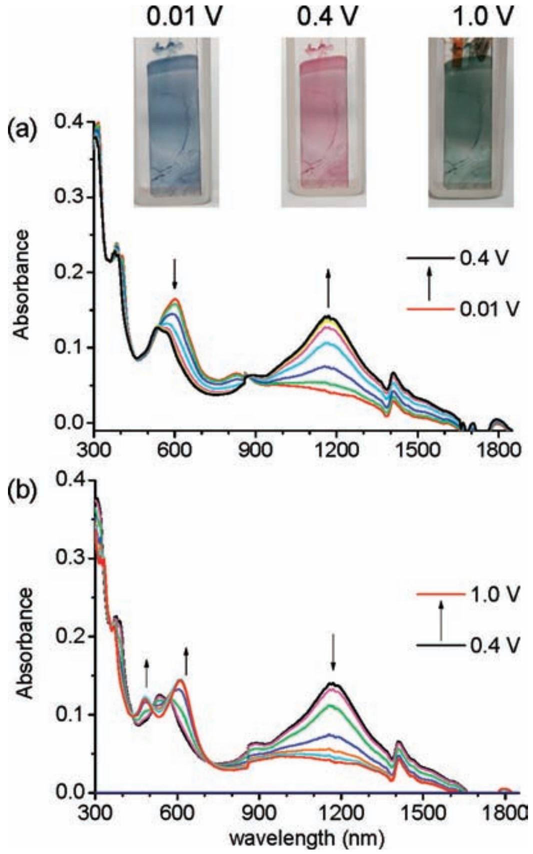

Figure 4. UV/vis/NIR absorption spectral changes of a polymeric film of 2^{2+} on ITO glass (surface coverage = 5.5×10^{-9} mol/cm^2) upon stepwise application of potentials from (a) +0.01 to +0.4 V and (b) +0.4 to +1.0 V vs Ag/AgCl. The inset in (a) shows films at different potential with different colors.

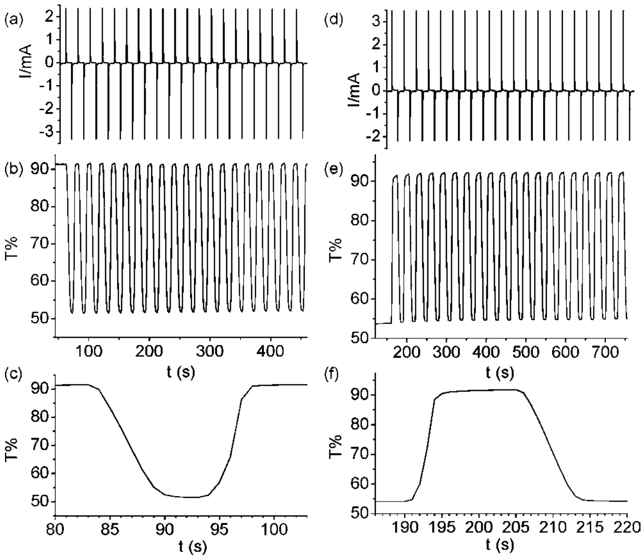

Figure 5. Electrochromic switching of a polymeric film of 2^{2+} on ITO glass (surface coverage = 1×10^{-8} mol/cm^2) between (a–c) −0.2 and +0.4 V and (d–f) +0.4 and +1.0 V vs Ag/AgCl in 0.1 M Bu_4NClO_4/CH_3CN. The intervals were 20 s for (a–c) and 30 s for (d–e). (a, d): Current assumption. (b, c) and (e, f): Transmittance changes monitored at λ = 1165 nm as a function of time.

times for the oxidation and reverse reduction processes were 4 and 8 s, respectively.

Finally, the optical memory effect (the ability to retain the T% value after the applied potential is turned off) of the above films was investigated. We note that the pink color of films of polymerized $\mathbf{2}^{2+}$ after one-electron oxidation lasted at least for several days. This was supported by the fact that the transmittance of a typical film remained close to its original state during the period examined (6 h) after an applied potential of +0.4 V vs Ag/AgCl was released (Figure 6a). However, the memory time after an applied potential of +1.0 V was turned off was within 50 min (Figure 6b).

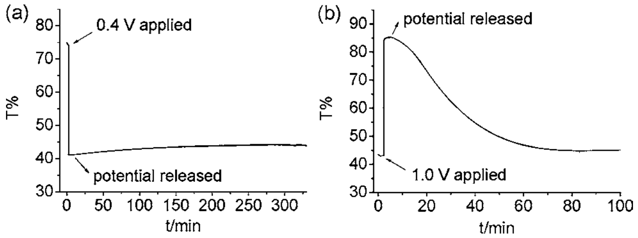

Figure 6. Optical memory effect of a polymeric film of $\mathbf{2}^{2+}$ on ITO glass (surface coverage = 1.3×10^{-8} mol/cm^2) after the potential at (a) +0.4 or (b) +1.0 V vs Ag/AgCl was released.

In conclusion, reductive electropolymerization was successfully used to prepare adherent metallopolymeric films of the biscyclometalated ruthenium complex $\mathbf{2}^{2+}$ with two appended vinyl groups. The produced films exhibited NIR electrochromism with acceptable contrast ratio (40%) and coloration efficiency (250 cm^2/C) at 1165 nm as a result of switching of the IVCT band and MLCT transitions of individual mixed-valent dimetallic units. The electrochromic switching can be operated at rather low voltages thanks to the strong metal–ligand orbital mixing and readily oxidizable nature of cyclometalated ruthenium complexes.[18] Interestingly, these materials display multicolor electrochromism and long memory time, which may make them useful in applications such as smart windows.[19] The performance of electrochromism of these films will be susceptible to improvement by changing the conducting glass electrode and electrolyte used. Applications of other mixed-valent systems[20] as electrochromic materials are currently being investigated in this laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, characterization, and CV profiles during electropolymerization of $\mathbf{2}[PF_6]_2$; XPS spectrum of a polymeric film on ITO glass. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

We thank the National Basic Research 973 Program of China (2011CB932301), the National Natural Science Foundation of China (21002104), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry of China, and Institute of Chemistry, Chinese Academy of Sciences ("100 Talent" Program) for funding support.

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