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Electrochromic Behavior of a Self-Propagating Molecular-Based Assembly

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Electrochromic films undergo optical changes when exposed to an electric field.[1−3] This is an intriguing phenomenon for which there might be a wide range of applications, including color displays, smart windows, sensors, and memory elements. These materials can be prepared by various methods: spin coating, electropolymerization, Langmuir−Blodgett technology, and polyelectrolyte layer-by-layer assembly, just to name a few. Polymeric materials possessing a combination of very high coloration efficiency, contrast ratio, low-switching voltage (∼1 V), stability, and processability have generated much interest. Despite the great strides in this field,[4,5] the design of suitable electrochromic materials (e.g., metal oxide films, conductive polymers, and liquid crystals) remains a challenging task. Here we introduce an alternative approach for the preparation of highly effective electrochromic films by self-propagating molecular-based assembly. The recently reported molecular-based structure consists of polypyridyl osmium complexes (**1**) cross-linked via $PdCl_2$ (Figure 1).[6] The short linkage ensures a high chromophore density. Formation of this porous metal−organic network involves in- and outward diffusion of $PdCl_2$. This reservoir of $PdCl_2$ is used by the system to bind layers of complex **1** from solution to the film surface in an exponential manner.[6,7]

The electrochromic properties are reported here for ∼25 nm thick structures assembled on indium−tin oxide (ITO)-coated glass. Cyclic voltammetry (CV) measurements showed a reversible redox process characteristic of an $Os^{2+/3+}$ couple with a half-wave redox potential, $E_{1/2}$, of 0.89 V (vs Ag/AgCl) and a peak splitting of 130 mV at a scan rate of 50 mV s^{-1} (Figure 2A).[8] UV−vis spectroscopy in the transmission mode revealed the characteristic singlet and triplet metal-to-ligand-charge-transfer (MLCT) bands of the Os^{2+} structure at $\lambda = 510$ and 680 nm, respectively (Figure 2B). Applying a potential step between 0.4 and 1.2 V resulted in a significant reduction of the absorption intensities of both MLCT bands, along with the concurrent appearance of the Ligand-to-Metal-Charge-Transfer (LMCT) band at $\lambda = 385$ nm. Subsequent electrochemical reduction of the assembly regenerates the original spectrum. Complex **1** exhibits similar optical behavior in solution upon changing the metal oxidation state.

Monitoring the intense MLCT band of the multilayer at $\lambda = 510$ nm while applying different double-potential steps as a function of time revealed the following interesting properties (Figure 2C,D): (i) a low-switching voltage (1.2 V) resulting in fast modulation of the absorbance (0.5 and 0.35 s for 95% oxidation and reduction, respectively), (ii) stepwise control over the transmission by the formation of intermediate assemblies having both Os^{2+} and Os^{3+} complexes, and (iii) a contrast ratio, ΔT, of 35% between the transmittance of the colored (Os^{2+}) and bleached (Os^{3+}) states. The contrast ratio is relatively low in comparison with other systems.[9−12] For instance, poly(3,4-ethylenedioxythiophene), PEDOT, has a contrast ratio of 54%.[12] However, the electric field-induced modulation between the two metal oxidation states ($Os^{2+/3+}$) is clearly visible by the naked eye as the redox-active film reversibly changes color from bordeaux red (Os^{2+}) to light yellow (Os^{3+}) (inset Figure 2B). The oxidized structure is transparent and also being reduced under open circuit conditions (= no electric field) at a much slower rate, as judged by UV spectroscopy. Full reduction was observed after 6 min under ambient conditions, whereas under nitrogen this process takes about twice as long to go to completion. The overall process is more than 3 orders of magnitude slower than the electrochemically induced reduction and might be caused by adventitious water. Indeed, washing an oxidized assembly with water for several minutes also restores the initial UV−vis spectrum of the Os^{2+} system. Monolayers of surface-confined osmium−polypyridyl complexes can be used to detect and quantify ppm levels of water in organic solvents.[13] Our self-propagating assembly can be oxidized chemically with a solution of $(NH_4)_2[Ce(NO_3)_6]$ (1 mM, 3 min) in dry acetonitrile, as observed by UV−vis spectroscopy. The possibility of reversibly addressing the optical output of this system, both chemically and electrochemically, might be of much value for molecular Boolean logic operations.[14]

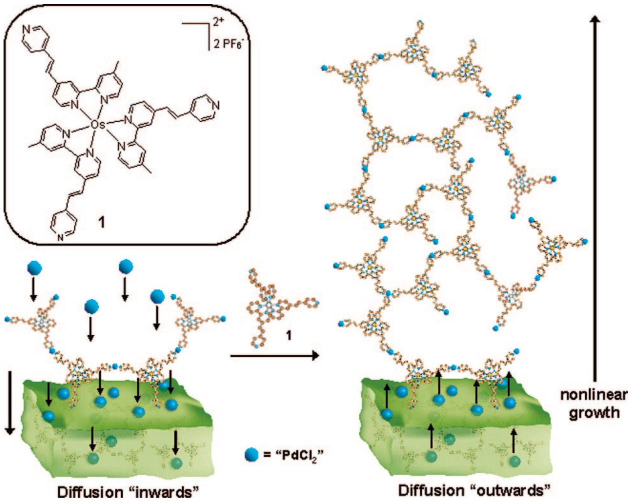

Figure 1. Solution-based self-propagating assembly. The films were formed on ITO-coated glass by iterative deposition of complex **1** (inset) and $(PhCN)_2PdCl_2$ using identical procedures described in ref 6.

The long-term stability of the film was determined by measuring the contrast ratio as a function of the number of switching cycles. The assembly was subjected to repetitive double-potential step chronoamperometry (0.4−1.2 V) with intervals of 3 s (Figure 3A). The transmittance changes of the assembly at $\lambda = 510$ nm were recorded simultaneously as a function of time (Figure 3B; black). Only 5% loss was observed in the contrast ratio after 1000 redox cycles (Figure 3B; red). UV−vis analysis and mass spectrometry of the electrolyte solution showed some desorption of complex **1**, but no decomposition. This suggests that the material stability might be enhanced by applying a different linker between the chromophores.

The efficient color changes in response to applied charge were calculated according to a standard equation from the ratio between

10.1021/ja900507c CCC: $40.75

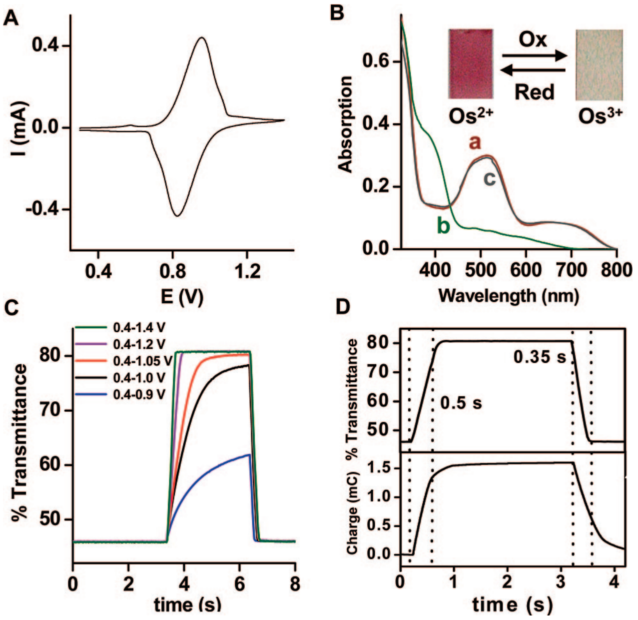

Figure 2. Electrochemical measurements of **1**-based films (23 layers, ~25 nm thick) on ITO-coated glass (surface area = 0.7 cm × 3 cm). (A) Cyclic voltammogram with a scan rate of 50 mV s^{-1}. (B) Spectroelectrochemistry using double-potential steps between 0.4 and 1.2 V: (a) reduced (Os^{2+}), (b) oxidized (Os^{3+}), and (c) reduced (Os^{2+}) states. Inset: photographs showing the colored (Os^{2+}) and the bleached (Os^{3+}) states. (C) Transmittance changes at $\lambda = 510$ nm vs time as a function of different potential steps. (D) Simultaneous chronoabsorptometry (top; $\lambda = 510$ nm) and chronocoulometry experiment (bottom; 0.4−1.2 V). The dotted lines indicate the response times at 95% oxidation (left) and reduction (right). All experiments were carried out at room temperature in 0.1 M TBABF$_4$/CH$_3$CN. ITO-coated glass, Pt wire, and Ag/AgCl were used as working, counter, and reference electrodes, respectively.

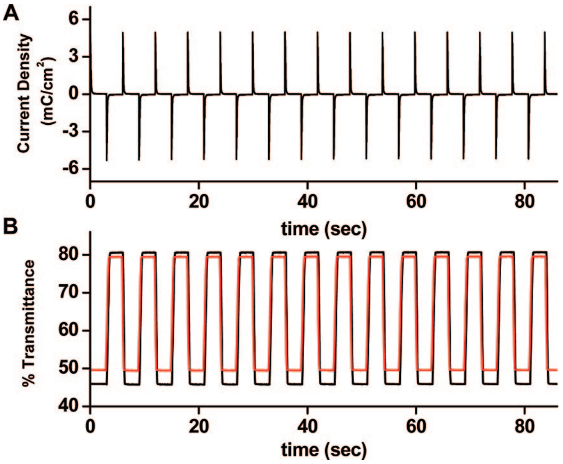

Figure 3. Multiple double-potential chronoamperometric experiment using TBABF$_4$ (0.1 M) in propylene carbonate with real-time monitoring of both (A) switching current (0.4−1.2 V) and (B) in situ transmittance at $\lambda = 510$ nm with 3 s intervals. The red trace is the % transmittance after 1000 redox cycles.

the optical contrast and the charge density used for coloration/bleaching of the assembly.[15] For our film, a maximum CE of 350 cm^2/C was obtained at $\lambda = 510$ nm with a charge density of 1.4 mC/cm^2. Interestingly, this CE is higher than the efficiencies observed for inorganic materials (e.g., IrO$_2$, WO$_3$)[16] and for conjugated polymers such as PEDOT (183 cm^2/C).[12] It is comparable to the CE of other polythiophene systems.[10] The electrochromic properties of the multilayer assembly are highly dependent on the film thickness. For instance, the response time, contrast ratio, and CE values for a much thinner structure (9 vs 25 nm) at $\lambda =$ 510 nm are 0.3 s, 17%, and 260 cm^2/C, respectively. Apparently, redox-active assemblies can be generated with designed and controllable electrochromic behavior as a function of the number of deposition cycles.

We have introduced here a new molecular-based material that exhibits a better CE than many inorganic films and a CE and switching time comparable to those of industrially important conducting polymers such as PEDOT and derivatives.[10,12] Recently, thiophene- and selenophene-based polymers have been reported with CE values as high as 680 and 773 cm^2/C by Wudl and Bendikov,[10,11] respectively. Nevertheless, the combination of a redox-active and stable film prepared via a self-propagating process might provide a useful new entry into this rapidly evolving area. The large variety of chromophores that might be used will offer ample opportunities to generate new electrochromic materials. Furthermore, the charge-storage capability of the assembly may make it an interesting candidate for battery, memory, and related technologies with an optical readout.[4,5,14,17]

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Supporting Information Available: A movie showing the real-time electrochemical switching of the multilayer assembly. This material is available free of charge via the Internet at http://pubs.acs.org.

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