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Preliminary note

Unexpected oxidative electropolymerization of ruthenium phenanthroline complexes of 4,4'-bipyridine- and bis(pyridyl)ethylene

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Electrochemically prepared metallopolymeric films represent important new materials in the world of chemically modified electrodes and interfacial redox chemistry [1]. The tremendous surge of interest in such materials stems from their unique fundamental characteristics (unusual transport properties, redox conductivity [2], microstructural effects [3], etc.) and from the vast possibilities in applications chemistry (sensors, electrochromics [4], macromolecular electronics [5], catalysis [6], energy conversion [7], etc.). Consistent with that interest, electrosynthetic routes now exist to nearly 100 different materials [8,9]. Unfortunately, nearly all these routes are based on reductive electrochemistry [8]. The invention of alternative *oxidative* synthetic methodologies [9] is clearly desirable for at least two reasons: (1) to provide routine access to n-type semiconductors as photochemically modifiable electrode substrate materials (typically in n-type materials the band edges are inappropriately located energetically to utilize existing reductive methodologies), and (2) to permit potentially useful, but reductively unstable, monomers like metal-chloro complexes [10], etc., to be fashioned into metallopolymers. We report here two unusual and unexpected examples of metallopolymer assembly based on oxidative electrochemistry, and suggest that these may presage the development of an important general strategy for oxidative film assembly.

Figure 1 shows consecutive cyclic voltammograms between 0.9 V and 1.7 V vs. SSCE, for a 1.2 mM solution of $\text{Ru}(\text{phen})_2(4,4'\text{-bpy})_2^{2+}$ in acetonitrile, with 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte. (Synthesis of the monomer followed literature procedures for the 2,2'-bipyridine analog [8k]; satisfactory elemental analyses were obtained.) The key observation is that the current due to the oxidation and reduction of the metal center increases with each consecutive

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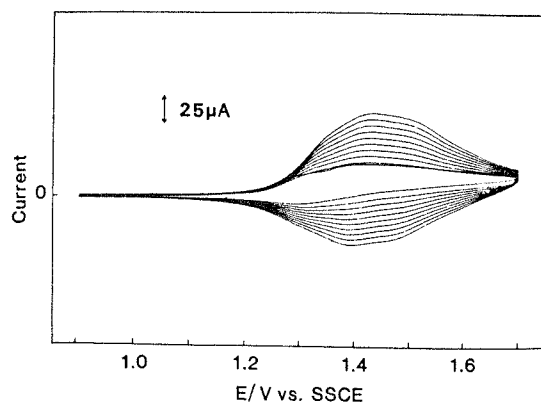


Fig. 1. Consecutive cyclic voltammograms recorded at 50 mV s^{-1} with $1.2 \text{ mM Ru(phen)}_2(4,4'\text{-bpy})_2^{2+}$ in acetonitrile containing 0.1 M TEAP . The electrode is a glassy carbon disk (area = 0.07 cm^2).

cycle. Subsequent emersion reveals the existence of a strongly adherent, bright orange film on the electrode surface. (The monomer solution is also orange.) If the electrode is re-introduced (after vigorous rinsing) into a fresh solution containing only acetonitrile and 0.1 M TEAP , the electrochemical response is still observed (with negligible peak separation at 10 mV/s), verifying that an immobilized, oxidatively assembled, electroactive coating exists. It should be noted that the current response is stable for many cycles and that the film retains its electroactivity even after storage for several days.

We have observed very similar behavior for $\text{Ru(phen)}_2(\text{BPE})_2^{2+}$ (BPE is bis(pyridyl) ethylene; $\text{N} \begin{array}{c} \diagup \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{---} \text{C}=\text{C} \text{---} \begin{array}{c} \diagup \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{N}$). The BPE complex is unusual in

that electroactive films can be grown by reductive electropolymerization as well (radical-anion olefin activation) [8k]. In fact, an extended electrochemical investigation of the reductive polymerization provided the basis for the serendipitous discovery of oxidative film growth. The observation of both film assembly pathways in a single complex provides a particularly direct mechanism for evaluating relative efficiencies for film growth. For the solution conditions described above, reductive cycling (50 mV/s , 10 cycles) between -0.7 and -1.7 V leads to an electroactive film coverage of $\Gamma = 8 \times 10^{-8} \text{ mol cm}^{-2}$ for $\text{Ru(phen)}_2(\text{BPE})_2^{2+}$. The corresponding oxidative experiment yields $\Gamma = 1.2 \times 10^{-7} \text{ mol cm}^{-2}$. For $\text{Ru(phen)}_2(4,4'\text{-bpy})_2^{2+}$, reductive electropolymerization is not observed, but oxidative cycling (Fig. 1) yields $\Gamma = 1.3 \times 10^{-7} \text{ mol cm}^{-2}$. It should be noted that in all three cases higher coverages are attainable based on longer cycling sequences.

Spectroelectrochemical experiments (Fig. 2) show that along with the metal-centered redox chemistry there exists a strong electrochromic effect. Films are orange in the reduced state and essentially transparent in the oxidized state. Our intent is to exploit this observation, together with spatially-selective photo-electro-

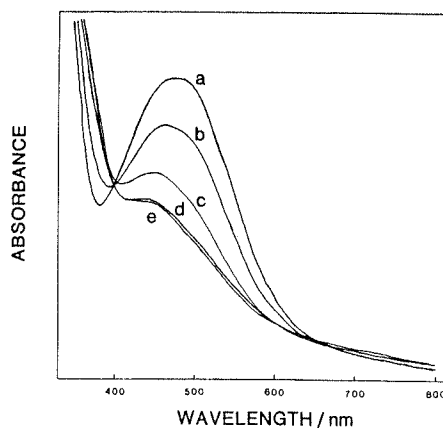


Fig. 2. Absorption spectra as a function of potential for a $\text{Ru}(\text{phen})_2(\text{BPE})_2^{2+}$ -based polymeric film on indium-tin oxide in acetonitrile containing 0.1 M TEAP. Key to potentials: (a) 0.5, (b) 1.4, (c) 1.5, (d) 1.7, and (e) 1.9 V.

polymerization [11], in the development of semiconductor-based electrochromic devices.

Our observations thus far have provided few clues concerning the detailed mechanism for oxidative film growth. We do know that an "exposed nitrogen" ligand like 4,4'-bpy or BPE is a prerequisite, and that replacement of 1,10-phenanthroline by 2,2'-bipyridine eliminates film formation. In those cases where films do form, the coverages are sufficiently high (ca. 1600 monolayer equivalents from just ten electrochemical cycles, based on 1.5 nm for the monomer diameter) that their formation cannot possibly be from simple adsorption effects. Instead, the weight of evidence suggests electrochemical polymer formation very strongly. One further observation that supports the idea of electropolymerization (as opposed to adsorption, surface precipitation, etc.) is the appearance of new redox waves upon film formation. The waves are reversible and occur at potentials that are several tenths of a volt positive of phenanthroline reduction. These last results are reminiscent of those of Guarr and Anson [8i] who also encountered "anomalous" reactivity in electrochemical studies of phenanthroline complexes. Our suspicion is that electropolymerization in our case involves attachment of a remote nitrogen from one monomer at an olefinic phenanthroline site on a second monomer, but the basis for oxidative activation is not obvious. In any case, we intend to screen a larger combination of ligands and metals, and to utilize additional spectral techniques, with the dual aim of gaining mechanistic information and ascertaining the degree of generality of the polymerization chemistry.

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