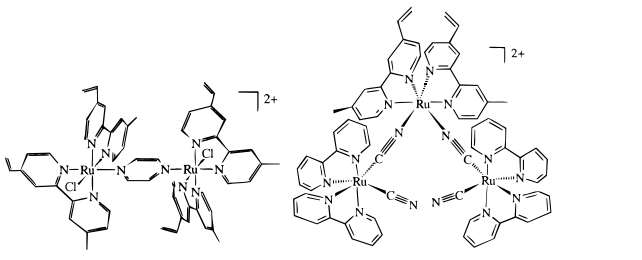
# Electropolymerization of Molecular Assemblies

**John A. Moss,[†] Roberto Argazzi,[‡] Carlo A. Bignozzi,*[,‡] and Thomas J. Meyer*[,†]**

Department of Chemistry, The University of North Carolina, CB#3290, Chapel Hill, North Carolina 27599-3290, and Dipartimento di Chimica, Universitá di Ferrara, Via L Borsari 46, 44100 Ferrara, Italy

*Received July 26, 1996*

Electropolymerization of appropriately derivatized metal complexes on conducting substrates leads to electroactive thin films.[1,2] One approach is reduction of vinyl-containing polypyridyl complexes such as $Ru(vbpy)_3^{2+}$ (vbpy is 4-methyl-4′-vinyl-2,2′-bipyridine).[3] Imaging and the creation of active microstructures have been demonstrated in the resulting films.[4] We report here that this chemistry can be extended to the electropolymerization of ligand-bridged molecular assemblies **1** and **2** and that they retain their mixed-valence[5] and photochemical properties[6] in the film environment.



$[(vbpy)_2(Cl)Ru(pz)Ru(Cl)(vbpy)_2]^{2+}$ $[(bpy)_2(CN)Ru(CN)Ru(vbpy)_2(NC)Ru(CN)(bpy)_2]^{2+}$

**1** **2**

Electrochemical reduction of **1** in 0.1 M $[N(C_4H_9)_4]PF_6$ (TBAH) in $CH_3CN$ at 5 °C through the first ligand reduction at −1.29 V by scanning from −0.4 to −1.4 V vs. SSCE at a tin doped indium oxide (ITO) electrode results in formation of poly-*cis*,*cis*-$[(vbpy)_2(Cl)Ru(pz)Ru(Cl)(vbpy)_2](PF_6)_2$ (**3**).[7] In cyclic voltammograms of the resulting film, Figure 1a, there are oxidative waves for the couples in eq 1 with $E_{1/2}(1) = 0.83$ V and $E_{1/2}(2) = 0.95$ V versus SSCE in $CH_3CN$ 0.1 M in TBAH. They appear at $E_{1/2}(1) = 0.82$ V and $E_{1/2}(2) = 0.94$ V for the unpolymerized complex in solution.

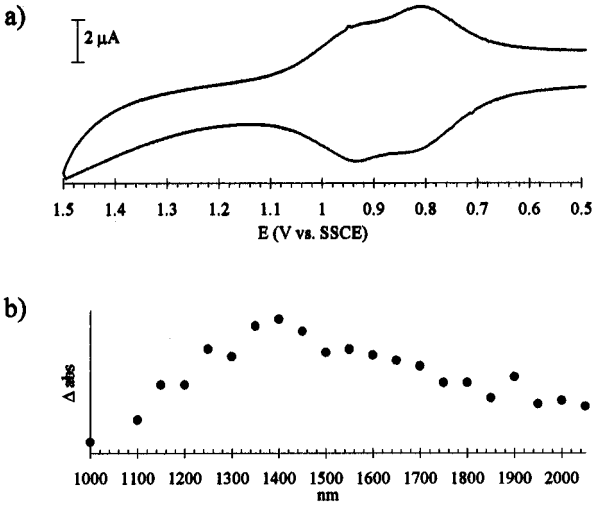



**Figure 1.** (a) Cyclic voltammogram of poly-*cis*,*cis*-$[(vbpy)_2(Cl)Ru(pz)Ru(Cl)(vbpy)_2](PF_6)_2$ on a 4 mm diameter Pt disk electrode in $CH_3CN$ 0.1 M in TBAH vs Ag/0.01 M $AgNO_3$ and corrected to SSCE. (b) Near-infrared absorption spectrum of poly-*cis*,*cis*-$[(vbpy)_2(Cl)Ru^{III}(pz)Ru^{II}(Cl)(vbpy)_2](PF_6)_3$ on ITO at surface coverage $\Gamma = 1 \times 10^{-8}$ mol/cm$^2$ in $CD_3CN$ containing 0.1 M TBAH. The spectrum shows the maximum absorbance change relative to that at $E_{app} = 400$ mV, $\Delta A_{max}$, as the potential was increased from 400 to 1000 mV (vs SSCE) at 10 mV/s (see Supporting Information).

$$\text{poly}[(vbpy)_2(Cl)Ru^{III}(pz)Ru^{III}(Cl)(vbpy)_2](PF_6)_4 + e^- \rightarrow \text{poly}[(vbpy)_2(Cl)Ru^{III}(pz)Ru^{II}(Cl)(vbpy)_2](PF_6)_3 + PF_6^- \quad \textbf{3} \qquad (1a)$$

$$\text{poly}[(vbpy)_2(Cl)Ru^{III}(pz)Ru^{II}(Cl)(vbpy)_2](PF_6)_3 + e^- \rightarrow \text{poly}[(vbpy)_2(Cl)Ru^{II}(pz)Ru^{II}(Cl)(vbpy)_2](PF_6)_2 + PF_6^- \qquad (1b)$$

The electrochemical experiment demonstrates that the mixed-valence character of **1** is retained in the electropolymerized assembly. The near-infrared (NIR) spectrum in Figure 1b shows that the intervalence transfer (IT) band characteristic of the mixed-valence form **3** is also retained, eq 2. From these measurements, $\lambda_{max} \sim 1400$ nm ($\epsilon \sim 270$ M$^{-1}$ cm$^{-1}$)[8] compared to 1300 nm ($\epsilon = 650$ M$^{-1}$ cm$^{-1}$) for *cis*,*cis*-$[(vbpy)_2(Cl)Ru(pz)Ru(Cl)(vbpy)_2]^{3+}$ in $CD_3CN$.

$$\text{poly}[(vbpy)_2(Cl)Ru^{III}(pz)Ru^{II}(Cl)(vbpy)_2](PF_6)_3 \xrightarrow{h\nu} \text{poly}[(vbpy)_2(Cl)Ru^{II}(pz)Ru^{III}(Cl)(vbpy)_2](PF_6)_3 \qquad (2)$$

The ligand-bridged assembly is unstable toward ligand loss in solution, a reactivity that is retained in the film in the presence

[†] The University of North Carolina.
[‡] Universitá di Ferrara.

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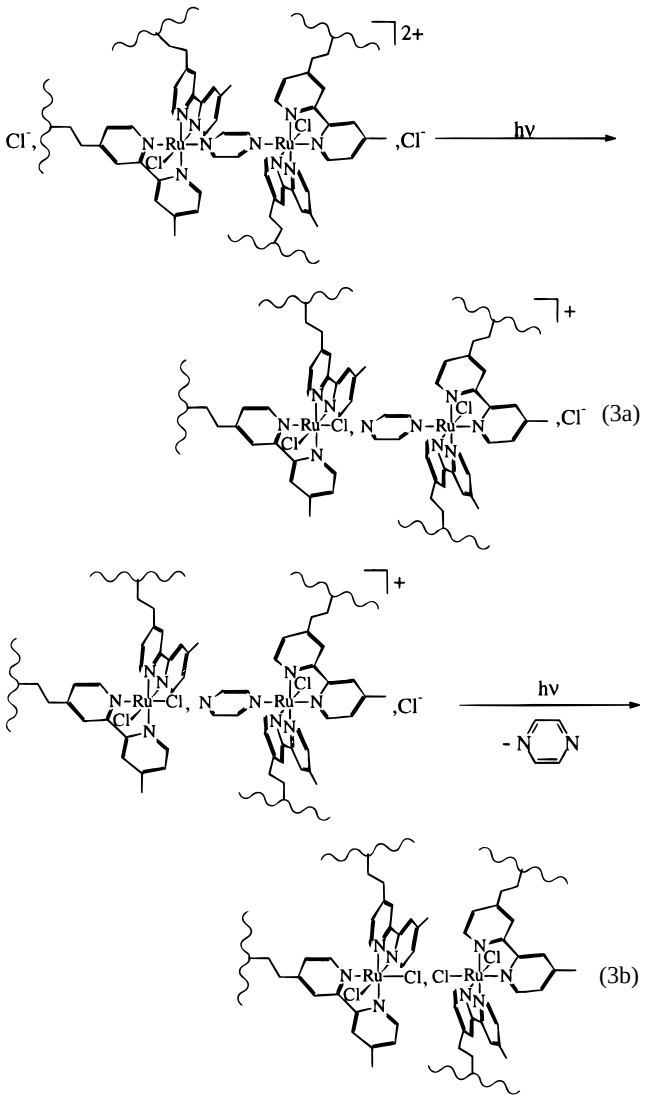
(7) Electropolymerization at more negative potentials and higher temperatures resulted in partial decomposition.
(8) Calculated from the surface coverage $\Gamma$ (in mol cm$^{-1}$) as $A = (10^{-3})\epsilon\Gamma$, with $\epsilon$ in M$^{-1}$ cm$^{-1}$.

S0020-1669(96)00902-0 CCC: $14.00 

of chloride, eq 3.[9] Visible photolysis of a film ($\Gamma = 5.0 \times 10^{-9}$ mol cm$^{-2}$) soaked in dichloromethane containing 0.1 M [N($n$-$C_4H_9$)$_4$]Cl for 30 min results in the disappearance of the waves at 0.83 and 0.94 V and the appearance of a single wave at 0.32 V for the dichloride complex. There was no evidence for an intermediate stage, and the quantum yield for ligand loss in eq 3b is greater than the quantum yield for eq 3a as for the bpy dimer in solution.[10] Photochemical pyrazine loss is notable because the photoproducts are formed in a fixed orientation relative to each other (eq 3b), which may be important in tuning film properties.




The electropolymerization of molecular assemblies is a general phenomenon as demonstrated by the formation of films based on **2**. The carboxylic acid derivative *cis,cis,cis*-[(bpy)$_2$(CN)Ru(CN)Ru(dcb)$_2$(NC)Ru(CN)(bpy)$_2$](PF$_6$)$_2$ (dcb is 4,4′-dicarboxy-2,2′-bipyridine) is known to be an effective photosensitizer of $TiO_2$ for photochemical energy conversion.[11] In this case, electropolymerization of **2** gives poly-*cis,cis,cis*-[(bpy)$_2$(CN)Ru(CN)Ru(vbpy)$_2$(NC)Ru(CN)(bpy)$_2$](PF$_6$)$_2$ (**4**), with stable films formed containing polymerizable vbpy ligands only on the central $Ru^{II}$. In cyclic voltammograms a reversible wave appears at 0.69 V for the $Ru^{III/II}$ couple of the central Ru and irreversible waves at $E_{p,a} = 1.30$ and 1.51 V for oxidation of the terminal Ru's.[12] The irreversibility is due to oxidative loss of the terminal $CN^-$ ligands at these high potentials.[13]

In the mixed-valence form poly-*cis,cis,cis*-[(bpy)$_2$(CN)$Ru^{II}$(CN)$Ru^{III}$(vbpy)$_2$(NC)$Ru^{II}$(CN)(bpy)$_2$](PF$_6$)$_2$, generated by electrolysis at $E_{app} = 0.9$ V, a broad IT band appears at 1230 nm with a high energy shoulder at 1000 nm. These features appear for *cis,cis,cis*-[(bpy)$_2$(CN)$Ru^{II}$(CN)$Ru^{III}$(vbpy)$_2$(NC)$Ru^{II}$(CN)(bpy)$_2$]$^{2+}$ in $CH_3CN$ at 1230 nm and 960 nm. **2** emits at room temperature in $CH_3CN$ at $\lambda_{em} = 780$ nm. Emission decay is exponential with $\tau = 61$ ns ($k = 1.6 \times 10^7$ s$^{-1}$, $\lambda_{ex} = 460$ nm).[14] In film **4** a weak emission appears at 740 nm. Decay is nonexponential but can be fit to the biexponential expression in eq 4a with $k_1 = 7.6 \times 10^7$ s$^{-1}$ ($A = 0.88$), $k_2 = 1.5 \times 10^7$ s$^{-1}$ and an average lifetime, $\langle\tau\rangle$, calculated from eq 4b, $\langle\tau\rangle = 19$ ns.

$$I = Ae^{-k_1 t} + (1 - A)e^{-k_2 t} \quad (4a)$$

$$\langle\tau\rangle = A\tau_1 + (1 - A)\tau_2 \quad (4b)$$

Our success in preparing these film-based molecular assemblies opens new vistas for the preparation of novel thin film structures. The retention of the often complex photochemical and mixed-valence properties of the electropolymerized assemblies demonstrates the feasibility of designing films based on structural units which themselves have controllable chemical and physical properties.

**Acknowledgments** for the support of the work at UNC are made to the Army Research Office under Grants No. DAAH04-95-1-0144 and No. DAAL03-92-G0198 and the National Science Foundation under Grant No. CHE-9503738. The work at Universitá di Ferrara was supported by MURST.

**Supporting Information Available:** Text giving the synthesis of [(vbpy)$_2$(Cl)Ru(pz)Ru(Cl)(vbpy)$_2$](PF$_6$)$_2$ and [(bpy)$_2$(CN)Ru(CN)Ru(vbpy)$_2$(NC)Ru(CN)(bpy)$_2$](PF$_6$)$_2$ and procedures for electropolymerization and near-infrared intervalence transfer absorption measurement and photolysis (2 pages). Ordering information is given on any current masthead page.

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(14) At 77K in an EtOH glass $\lambda_{em} = 710$ nm with a vibronic component at 765 nm and $\langle\tau\rangle = 1.0$ $\mu$s (eq 4b).