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**Photostability, Electrochemistry, and
Monolayers of
[M(bpy)₂(*trans*-1,2-bis(4-pyridyl)ethylene)L]⁺
(M = Ru, Os; L = Cl, H₂O)**

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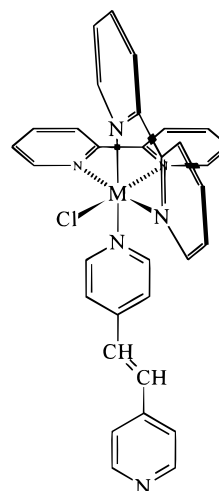
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Introduction

Success in areas of molecular electronics, such as, solar energy conversion, artificial photosynthesis, and enzyme mimics demands not only the ability to control the physical structure of a molecular assembly but also the ability to direct energy and electron transfer in well-defined directions. This prerequisite for vectorial electron and energy transfer has led to the design of molecular assemblies where the individual components have desirable electro- and photochemical properties. In this regard osmium and ruthenium polypyridyl complexes are especially attractive building blocks because of their facile, reversible electrochemical responses, their ability to act as multielectron reservoirs, and their rich photochemistry.^{1–5} However, for assemblies of these molecules to perform a particular function, it must be possible to probe, and preferably control, the properties of the individual components. When development of redox active systems is sought, a powerful approach is to eliminate the need for the components to diffuse through solution by forming films on electrode surfaces. Initial work in this area focused on investigations into electrode surfaces modified with electroactive polymers,⁶ and our recent interest has focused on the formation and characterization of ordered structures produced by self-assembly or spontaneous adsorption of transition metal complexes.^{7–11}

In this contribution, we present an investigation into the electrochemical and photochemical properties of [M(bpy)₂bpe Cl]⁺ (M = Ru, Os; bpy = 2,2'-bipyridyl; bpe = *trans*-1,2-bis(4-pyridyl)ethylene) complexes both in solution and as spontaneously adsorbed monolayers. The generic complex is illustrated in Chart 1 and for simplicity the two systems are denoted as Ru-bpe and Os-bpe, respectively. Our long range-goal in this area is to assemble monolayers in which a vacant coordination site can be

Chart 1



created photochemically that acts as a docking site for the assembly of a second monolayer. In this way, complicated supramolecular assemblies can be assembled sequentially in a highly controllable manner. Here, we report on the photostability of osmium and ruthenium complexes that have attractive features for realizing this objective.

Experimental Section

Materials. [RuCl₃·H₂O] (Oxkem Ltd.), K₂[OsCl₆] (99.5%) (Johnson Matthey), and 2,2'-bipyridine and *trans*-1,2-bis(4-pyridyl)ethylene (Aldrich) were used as received without further purification. All water used was deionized using a Millipore purification system.

The complexes were synthesized using methods similar to those published previously.¹² Elemental analysis and NMR, HPLC, and UV-vis characterization indicate that both compounds are obtained in the form [M(bpy)₂(bpeH)Cl](PF₆)₂, where the free pyridine group is protonated. That the unbound pyridine moiety of the 1,2-bis(4-pyridyl)ethylene ligand is protonated arises because the synthesis was carried out in dry methanol. This protonation does not persist in aqueous media and it will therefore not affect the electrochemical experiments or the formation of spontaneously adsorbed monolayers.

Procedures. *Spectroscopy and HPLC.* UV-vis spectra were recorded using a Shimadzu 3100 UV/VIS/NIR double beam spectrophotometer interfaced with an Elonex PC-433. High-performance liquid chromatography was performed on a Waters 990 Photodiode Array HPLC system in conjunction with a PC, a Waters HPLC pump model 501, a 20 μL injector loop, and a cation exchange column.

Photochemistry. Samples and coating solutions were irradiated using a 100 W slide projector. A water-filled cell was placed between the source and the sample to avoid thermal reactions.

Electrochemistry. Cyclic voltammetry was performed using a CH Instruments model 660 electrochemical workstation and a conventional three-electrode cell with a BAS Ag/AgCl electrode as reference (all quoted potentials are quoted with respect to this reference). Microelectrodes were fabricated from platinum and gold microwires (Goodfellow Metals Ltd.) of radii between 1 and 25 μm by sealing them into soft glass using a procedure described previously.⁵ Microdisk electrodes were pretreated before monolayer formation as described in earlier papers.¹²

Preparation of Monolayers. Spontaneously adsorbed monolayers were typically formed by placing a freshly polished and electrochemically cleaned electrode in a 2 mM solution of the metal complex in aqueous acetone containing 0.1 M LiClO₄ as

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Table 1. Absorption Maxima of the Ruthenium Complex Dissolved in Different Solvents with and without Light Exposure

solvent	λ_{\max} (nm)/complex present	λ_{\max} (nm)/model complex ^a
acetonitrile (sample kept in the dark)	493/[Ru(bpy) ₂ (bpe)Cl] ⁺	494/[Ru(bpy) ₂ (py)Cl] ⁺
acetonitrile (sample exposed to light)	481/[Ru(bpy) ₂ (CH ₃ CN)Cl] ⁺	480/[Ru-N ₄ -CH ₃ CN-Cl]
acetone (sample kept in the dark)	495/[Ru(bpy) ₂ (bpe)Cl] ⁺	494/[Ru(bpy) ₂ (py)Cl] ⁺
acetone (sample exposed to light)	512/[Ru(bpy) ₂ (Acetone)Cl] ⁺	
water/1 M HClO ₄ (sample exposed to light)	468/[Ru(bpy) ₂ (bpe)H ₂ O] ²⁺	470/[Ru(bpy) ₂ (py)H ₂ O] ²⁺

^a Values for the model complexes are taken from ref 16; py is pyridine.

supporting electrolyte. The electrode was poised at 0.1 V vs Ag/AgCl during the 30 min deposition cycle. Prior to deposition, all solutions were degassed for at least 15 min using nitrogen, and a blanket of nitrogen was maintained over the solution during all experiments.

Results and Discussion

General Photochemical Properties. In seeking to use [M(bpy)₂bpeCl]⁺ complexes as supramolecular "building blocks", one important consideration is their photostability. For example, photolabile materials have the disadvantage that the chemical composition of the resulting monolayers may be ill-defined. Also for practical applications, e.g., dye sensitization of semiconductors for solar energy conversion, it is important to identify differences in the reactivity of solution phase vs adsorbed species.¹⁰

The UV-vis spectra of osmium and ruthenium polypyridyl complexes are sensitive to the nature of the ligands within the coordination sphere. For example, a clear indication that the synthetic procedure yields [Ru(bpy)₂bpeCl]⁺ is obtained from the close agreement of the absorption maximum of 493 nm observed in acetonitrile and acetone with the value of 494 nm observed previously for [Ru(bpy)₂pyCl]⁺.¹³ In principle, the two monodentate ligands Cl⁻ and bpe can both be photochemically displaced. Previous investigations on related systems indicate that loss of chloride, rather than the monodentate pyridine ligand, is favored in water.¹⁴ In contrast, loss of the bpe ligand is expected following irradiation in organic solvents such as acetonitrile or acetone.¹⁵ As shown in Table 1, irradiation of the Ru-bpe complex in acetonitrile results in a product with a λ_{\max} of 481 nm, which is in good agreement with the literature value of 480 nm found for [Ru(bpy)₂(CH₃CN)Cl]⁺ and indicates loss of bpe. In aqueous acetone, irradiation produces a species with an absorption maximum of 512 nm, indicative of [Ru(bpy)₂(solvent)Cl]⁺, where solvent is acetone or water.¹⁵

These ligand substitution reactions can also be conveniently monitored using cyclic voltammetry. For example, irradiation in acetonitrile causes the formal potential, E° , of the Ru^{2+/3+} couple to shift from 0.74 to 0.80 V. The initial potential observed agrees with that found for [Ru(bpy)₂(pyridine)Cl]⁺ under similar conditions. Consistent with the replacement of the bpe ligand by acetonitrile, the shift in a positive potential direction of E° indicates that it is thermodynamically more difficult to oxidize the photoproduct and that the electron density on the metal center is lower.

In a later section, we discuss the formation of spontaneously adsorbed monolayers from essentially aqueous solutions of the complexes. Therefore, it is important to study the photostability of the complexes in aqueous solution. In these experiments, [Ru(bpy)₂bpeCl]⁺ was

suspended in water. Following irradiation with visible light, these dilute suspensions form solutions that exhibit an absorption maximum of 468 nm, which agrees closely with the value reported by Meyer^{16,17} for [Ru(bpy)₂pyH₂O]²⁺ (470 nm). Similar changes are observed if the suspensions are allowed to stand under normal laboratory light for several hours. These results clearly indicate that the ruthenium complex is photochemically unstable in both organic and aqueous media. However, irradiation in organic media triggers loss of the bpe ligand creating the nonsurface active [Ru(bpy)₂(Solvent)Cl]⁺ complex, while in aqueous solutions the chloride is replaced by water and the surface active bpe ligand is retained. This observation has important implications for the formation of monolayers using these complexes. For example, the rapid loss of chloride in aqueous solution, that is triggered by even low intensity visible light, means that monolayers of [Ru(bpy)₂bpeCl]⁺ can only be prepared by rigorously avoiding exposure of the deposition solution to ambient light. In contrast, irradiation represents a convenient method of preparing [Ru(bpy)₂(bpe)H₂O]²⁺ in situ in which the metal-based electrochemistry is expected to involve coupled electron and proton transfer at some pH values. Moreover, the aquo ligand is expected to be a good leaving group opening up the possibility of "layer-upon-layer" assembly.

In sharp contrast to the high lability of the ligands within the ruthenium complex, no photosubstitution reactions were observed for the Os-bpe complex. This behavior is consistent with the higher energy of the triplet metal centered excited state of osmium polypyridyl complexes compared to their ruthenium analogues.

General Electrochemical Properties. Figure 1 shows typical cyclic voltammograms for spontaneously adsorbed monolayers of [Ru(bpy)₂(bpe)H₂O]²⁺ and [Os(bpy)₂(bpe)Cl]⁺ on a 5 μ m platinum microelectrode at a scan rate, ν , of 1 V s⁻¹. The formal potential for the osmium monolayer is 0.28 V, which agrees closely with that found for this complex by Abruña^{2,3} and with values reported for other similar compounds such as [Os(bpy)₂(p2p)Cl]⁺ (p2p = 1,2-bis(4-pyridyl)ethane)^{5,7,9} (E° = 0.31 V) and [Os(bpy)₂(PVP)Cl]⁺ (PVP = poly(4-vinylpyridine))¹⁸ (E° = 0.25 V). For the osmium-containing monolayer, at this relatively high scan rate, the peak to peak separation between the anodic and the cathodic potentials, ΔE_p , is approximately 100 mV. However, at slower scan rates more ideal behavior is observed with ΔE_p being less than 20 mV for 20 $\leq \nu \leq$ 500 mV s⁻¹. This scan rate dependence of ΔE_p is consistent with heterogeneous electron transfer influencing the voltammetric response in fast scan experiments.¹⁹

In contrast to the osmium voltammetry, the response for the ruthenium-containing monolayer is more complex and, as illustrated in Figure 1, two peaks are observed at

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Table 2. Redox Potentials of [Ru(bpy)₂(bpe)H₂O]²⁺ in Aqueous Solutions with Different Proton Concentrations^a

solution	<i>E</i> _{1/2} (V) Ru(II)/Ru(III)	<i>E</i> _{1/2} (V) Ru(III)/Ru(IV)
1 M HClO ₄ (pH 0)	0.81 (0.82)	1.00 (1.03)
0.1 M HClO ₄ (pH 1.03)	0.83	0.94
0.1 M LiClO ₄ (pH 5.7)	0.64 (0.46 at pH 7)	0.77 (0.57 at pH 7)

^a Values in parentheses are taken from the work of Moyer and Meyer and for ease of comparison are corrected for differences in reference electrode potential.¹⁶

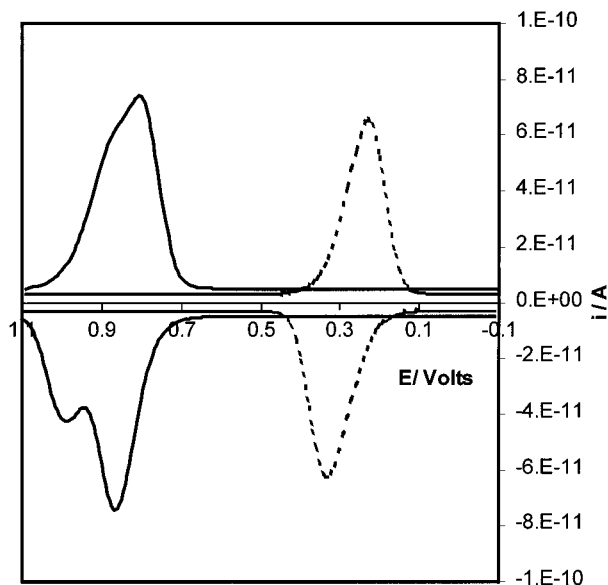
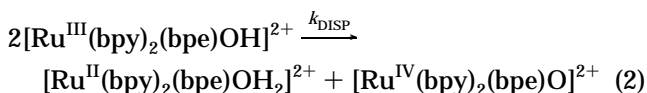
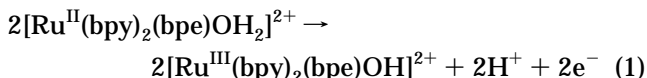


Figure 1. Cyclic voltammograms for spontaneously adsorbed [Ru(bpy)₂(bpe)H₂O]²⁺ (solid line) and [Os(bpy)₂(bpe)Cl]⁺ (dashed line) monolayers spontaneously adsorbed on a 5 μm platinum disk. The supporting electrolyte is 0.1 M HClO₄. The scan rate is 1.0 V s⁻¹.

formal potentials of approximately 0.83 and 0.94 V where the scan rate is 1 V s⁻¹. The ruthenium complex was not deliberately irradiated prior to monolayer formation, but no precautions were taken to exclude ambient light during the preparation and subsequent handling of the deposition solutions. Figure 2 illustrates the effect of changing the pH of the supporting electrolyte on the voltammetric response of the ruthenium complex in solution. The behavior is analogous to the coupled electron/proton transfer reactions reported by Meyer and co-workers^{16,17} for [Ru(bpy)₂(py)H₂O]²⁺ in solution or by Hillman and Vos for thin films of the metallopolymer [Ru(bpy)₂-(PVP)₁₀H₂O]²⁺, where PVP is poly-4-vinylpyridine.²⁰ The effect of electrolyte pH has also been investigated for monolayers, and the results are summarized in Table 2. The general electrochemical properties are retained on surface confinement. Therefore, we assign the two peaks to the Ru^{2+/3+} and Ru^{3+/4+} couples and the voltammetric response observed for 2 ≤ pH ≤ 7 can be described by eqs 1 and 2 in which the Ru³⁺ species initially formed undergoes a disproportionation reaction.



As reported previously for the [Ru^{II}(bpy)₂(py)OH₂]²⁺ complex,⁹ the two redox couples are observed only at low

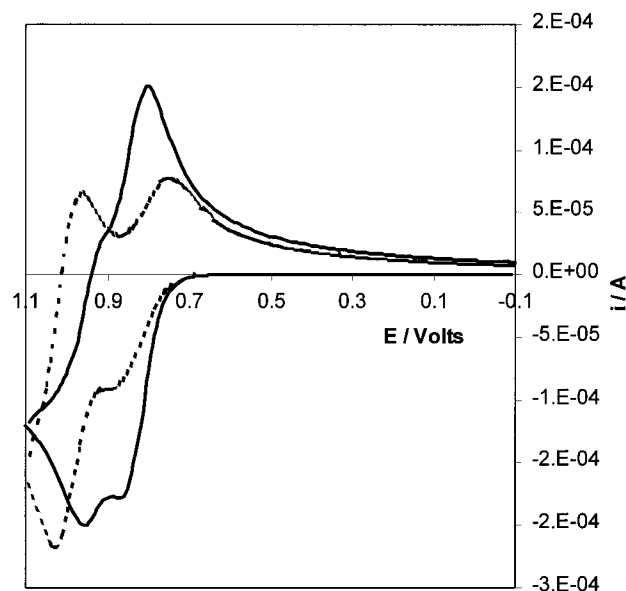


Figure 2. Cyclic voltammogram for a 5 mM solution of [Ru(bpy)₂(bpe)H₂O]²⁺ in 0.1 M NaClO₄ solutions adjusted to pH 1.05 (solid line) and 0.5 (dashed line) by the addition of concentrated HClO₄. The working electrode was a 2 mm glassy carbon electrode. The scan rate is 0.1 V s⁻¹.

scan rates (<200 mV s⁻¹). This behavior suggests that relatively slow disproportionation represents the rate-determining step, at least for solution-phase reactants. In contrast, the voltammetric response of the monolayer exhibits two peaks even at scan rates as high as 100 V s⁻¹. This observation indicates that disproportionation occurs within the monolayer even at short time scales. Given that disproportionation is a bimolecular process, it is likely that the absence of diffusional mass transport and controlled orientation of the reactants in the monolayer both favor a higher reaction rate. Future reports will address the issue of the dynamics of surface confined vs solution-phase chemical reactions using double potential step chronoamperometry.

Charge Effects on Adsorption. In contrast to self-assembled monolayers, the formation of spontaneously adsorbed monolayers is frequently assumed to be driven by the interaction of the surface-active ligand with the electrode surface. While the osmium and ruthenium complexes considered here possess the same bridging ligand, their coordination spheres and overall charges are different. Therefore, these complexes are attractive for investigating how differences in solubility and charge affect the equilibrium surface coverage and dynamics of monolayer formation. For example, when a two-component monolayer is deposited from a solution that contains 2.5 μM of both complexes, the surface coverage of the osmium centers is approximately 5 times larger than that found for ruthenium assuming a two-electron reaction for the ruthenium center. The combined surface coverage of both complexes at equilibrium is (7.0 ± 0.5) × 10⁻¹¹ mol cm⁻² and does not increase further by increasing the concentration of the complexes in solution or the deposition time. This saturation coverage is smaller than that found

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by Acevedo and Abruña for single-component monolayers of the same complexes but lies within the range measured by Forster and Faulkner for related systems.^{5,7,9,21} The striking difference in the limiting surface coverages found for the osmium and ruthenium complexes indicates that factors other than the nature of the bridging ligand influence the saturation coverage in systems of this type. In particular, it appears that the decreased hydrophobicity of the ruthenium complex because of its 2+ charge arising from replacement of the chloride ligand by water, causes the surface coverage of $[\text{Ru}(\text{bpy})_2\text{bpe} \cdot \text{H}_2\text{O}]^{2+}$ to be lower than that of $[\text{Os}(\text{bpy})_2\text{bpeCl}]^+$.

Conclusions

In contrast to the osmium systems, $[\text{Ru}(\text{bpy})_2(\text{bpe})\text{Cl}]^+$ complexes are highly photosensitive with either the bpe or chloride ligand being rapidly lost upon visible irradiation depending on the solvent. Monolayers of $[\text{Os}(\text{bpy})_2(\text{bpe})\text{Cl}]^+$ and $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$ have been formed and

their electrochemical properties investigated. While oxidation of the osmium centers proceeds as a simple one-electron-transfer reaction, the behavior of the ruthenium aquo complex is more complex and involves coupled proton and electron transfer for $2 \leq \text{pH} \leq 7$. The rate at which two Ru^{3+} centers disproportionate to form Ru^{2+} and Ru^{4+} is larger for the immobilized than solution phase reactants most likely reflecting the higher effective concentration and controlled orientation within the monolayer. Significantly, the equilibrium coverage for the osmium complex is approximately five times larger than that found for the ruthenium complex indicating that factors such as overall charge and hydrophobicity, as well as the interaction of the lone pair of the pyridine nitrogen with the electrode surface, influence adsorption in systems of this kind.

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