Layer-by-Layer Molecular Organization of Polypyridine Ruthenium(II) Complexes on Glass Plates

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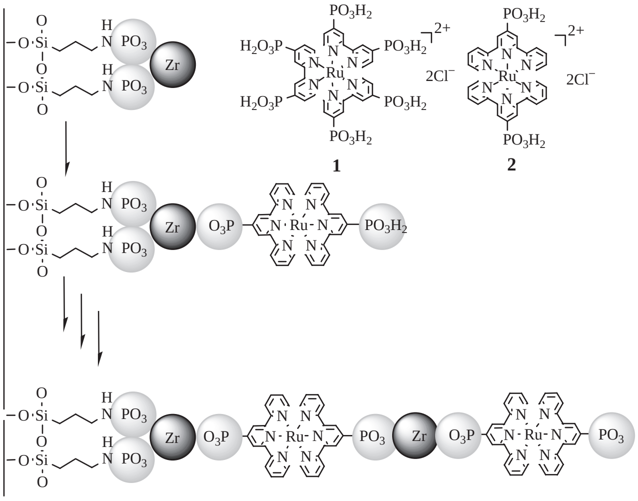
We have developed a methodology for the two-dimensional multilayer formation of polypyridine ruthenium complexes on solid surfaces under mild conditions. The alternate multilayers of the ruthenium complex and Zr were fabricated on pretreated glass plates using interlayer phosphonate–Zr linkages. The RuL$_n$ molecules in the films are electronically independent, with neither interchromophoric interactions nor electronic perturbations of the Zr^{IV} centers in the ground state.

Functionalized electrodes with redox-active and/or emissive transition-metal complexes are useful for devices such as solar cells, solid state LEDs, transistors, and sensors.[1] Such functional devices are based on solid films of metal complexes, which are usually fabricated by casting or coating methods for polymer-dispersed or neat solutions,[2] LB procedures for particular complexes containing amphiphilic substituents,[3] and SAM modifications of substrate surfaces with silyl, carboxyl, or thiol end group substituents on their polypyridine ligands, L.[4] Although casting/coating methods are both convenient and attractive practically, it is difficult to explore and control the functionalities of films using these techniques. On the other hand, LB methods are well known to be superior in the fabrication of molecular-ordered multilayers, but the chemical and mechanical fragility of LB films often causes serious difficulty in the construction and durability of devices. From the viewpoint of film stability, SAM modifications are attractive because of the chemical bonding between the monolayer and the substrate surface. However, the fabrication of chemically bonded multilayers is usually difficult since sequential chemical reactions on the two-dimensional film surface have to be controllable. Such reactions should proceed smoothly under mild conditions without the formation of significant defects in the resulting multilayers.[5]

During the course of our investigation into chemically bonded multilayers,[6] we succeeded in the fabrication of chemically bonded multilayers of the polypyridine ruthenium complex, RuL$_n$, utilizing the facile chemical reactions between the phosphonic acid substituents of the ligand and Zr(O)Cl$_2$.[7] In this paper, we report on the step-by-step preparation of two multilayered films: **1**, $Ru(L_1)_3{}^{2+}$, where L_1 = 2,2′-bipyridine-4,4′-diphosphonic acid;[8] and **2**, $Ru(L_2)_2{}^{2+}$, where L_2 = 2,2′:6′,2″-terpyridine-4′-phosphonic acid.[9] We also report on their photophysical properties.

RuL$_n$ was employed in our research because it exhibits long-lived transition-efficient phosphorescence from the metal-to-ligand charge-transfer (MLCT) triplet state. It also exhibits high photosensitization energy or electron-transfer capability, reversible redox behavior of the Ru^{III}/Ru^{II} couple in solution, and remarkable stability in its photochemical and electrochemical activation. These unique photophysical and electrochemical properties have been utilized in various fields of chemistry and biology.



Scheme 1. The chemical structures of the polypyridine ruthenium complexes and a schematic outline of the bottom-up fabrication process used for film preparation (in this case, indicating **2** as the polypyridine ruthenium complex).

Scheme 1 illustrates the procedures used to fabricate RuL$_n$ on quartz plates. Clean quartz plates were initially modified with (3-aminopropyl)trimethoxysilane (the plates were immersed in a 5 mM CH_3OH solution for a period of 3 h at 50 °C). They were then treated with $POCl_3$ solution in acetonitrile containing 2,6-lutidine (25 mM for a period of 1 h at room temperature). This treatment created a new surface covered with N–PO_3H_2-headed groups, which then reacted with the Zr(O)Cl$_2$. The pretreated substrates were sequentially immersed in an aqueous solution of Zr(O)Cl$_2$ (20 mM for a period of 1 h at room temperature) and a solution of **1** or **2** (pH = 4, 0.1 mM for a period of 5 h at 80 °C).[10] The facile chemical reaction of Zr(O)Cl$_2$ with the PO_3H_2 substituents of **1** ensured the deposition of **1** with a Zr^{IV}–RuL$_n$ linkage on the substrate surface. The immersion procedure was repeated to fabricate multilayer films of **1** with a three-dimensional network.

Figure 1A shows the UV–vis absorption spectra of the films of **1** after the deposition cycle. They show a continuous increase in absorbance in the 300–600 nm wavelength range with an increase in the number of deposition cycles. The inset of Figure 1A shows a plot of absorbance at $\lambda = 465$ nm (the MLCT band maximum) vs. the number of immersion cycles, which shows a linear dependence with a gradient of 0.015 absorbance units per deposition cycle. Assuming that the molar absorption coefficient of **1** ($\varepsilon = 2 \times 10^4$) remained unchanged in the multi-

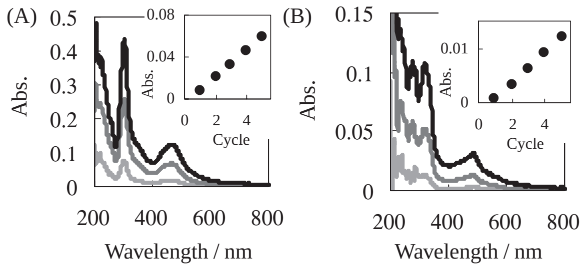


Figure 1. (A) Absorption spectra of 2 (gray), 6 (dark gray), and 10 (black) cycle films of **1**, and the inset shows the plots of absorbance at 465 nm vs. deposition cycle. (B) Absorption spectra of 2 (gray), 6 (dark gray), and 10 (black) cycle films of **2**, and the plots of absorbance at 480 nm vs. deposition cycle (inset).

layers, then the surface coverage of the Ru(bpy)$_3$ chromophore was estimated to be 3.8×10^{-10} mol·cm^{-2} per deposition cycle, which corresponds to an occupied area of 0.43 nm^2 for a single chromophore. This area is much smaller than the molecular size of **1** (1.91 nm^2) and considerably smaller than the size of the chromophore (1.1 nm^2) (excluding the phosphonic acid substituent). Therefore, it is strongly suggested that the Ru$^{\text{II}}$ chromophores are densely packed into a three-dimensional network. On the other hand, the surface coverage of the Ru(tpy)$_2$ chromophore was estimated to be 1.6×10^{-10} mol·cm^{-2} per deposition cycle in the case of **2**, which corresponds to an occupied area of 1.0 nm^2 for a single chromophore.[11]

It should be noted that the spectral features of the solid films remain unaffected with an increasing number of deposition cycles accompanied by a zero shift in the ligand π–π^* and MLCT band maxima. These were essentially identical with those observed in a dilute aqueous solution of RuL$_n$. Therefore, it is evident that the densely packed RuL$_n$ molecules in the films are electronically independent, with neither interchromophoric interactions nor electronic perturbations of the Zr$^{\text{IV}}$ centers in the ground state.

X-ray photoemission spectroscopy (XPS) measurements were carried out on the films of **1**, and the ratios of atoms in the films are shown in Table 1. The ratio of Zr atoms in the film increased after immersion in the Zr(O)Cl$_2$ solution, and the ratio of Si atoms decreased with an increase in the number of immersion cycles. The ratios of N, P, and Ru atoms increased after dipping in the solution of **1**. This observation indicates that a stepwise fabrication of the molecules occurred on the glass plate.

Table 1. Elemental ratios of the multilayer films (1, 3, and 5 layers) of **1**

No. of cycles	Type[a]	Elemental ratio[b]					
		N_{1s}	P_{2p}	$Ru_{3p3/2}$	Cl_{2p}	Zr_{3d}	Si_{2p}
1	A	0.058	0.039	0.011	0.006	0.012	0.26
	B	0.049	0.026	0.008	0.015	0.024	0.28
3	A	0.11	0.11	0.018	0.012	0.03	0.15
	B	0.085	0.094	0.019	0.022	0.06	0.13
5	A	0.13	0.15	0.023	0.022	0.041	0.071
	B	0.12	0.12	0.02	0.025	0.059	0.079

[a] A: meaured after immersing in the solution of **1**; B: measured after immersing in the solution of ZrOCl$_2$. [b] Area ratios of the XPS signals vs. the sum of N_{1s}, O_{1s}, P_{2p}, $Ru_{3p3/2}$, Cl_{2p}, Zr_{3d}, and Si_{2p} taken at the takeoff angle of 90°.

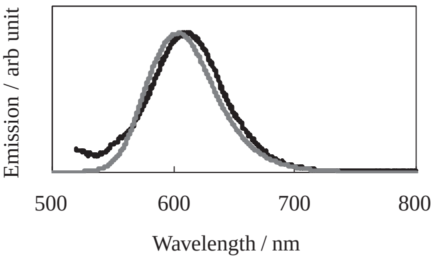


Figure 2. Emission spectra of a 17-cycle multilayer film of **1** (black) and **1** in an aqueous solution (gray).

Figure 2 shows the emission spectrum of a 17-cycle film compared with the emission spectrum of an aqueous solution of **1**. The spectrum of the film was essentially identical to that of the solution ($\lambda_{\text{max, film}} = 607$ nm and $\lambda_{\text{max, soln}} = 604$ nm). The Ru$^{\text{II}}$ chromophore in the MLCT triplet state should be electronically independent of the adjacent chromophores.

In conclusion, we have developed a methodology for the formation of molecular multilayers of polypyridine ruthenium complexes on solid surfaces under mild conditions. The multilayered films of **1** were emissive, making them useful in devices such as photocurrent conversion systems and biosensors. The thickness of the complex on substrates can be controllable. Furthermore, hetero-structured films composed of RuL$_n$ and other transition-metal complexes can be easily prepared using this layer-by-layer deposition method.

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10 The surface coverage of **1** or **2** increased with increasing immersion time, but the coverage was saturated within a period of 3 h. The rate of adsorption of the molecules onto the plate in a pH = 4 solution was faster than in a pH = 7 solution. No multilayered film formed in a pH = 10 solution. Multilayers were not obtained without dipping the plate in a Zr(O)Cl$_2$ solution.
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