

ELECTROCHEMISTRY OF MULTILAYERED Ru COMPLEXES WITH TETRAPOD ANCHORED GROUPS ASSEMBLED BY LAYER-BY-LAYER METHOD

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The construction of programmed nanostructures on the surface has been paid much attention in connection with the molecular based nanoelectronics. As a “bottom-up” method, the combination of self-assembly on solid surface with the layer-by-layer growth by metal complexation has the potential to provide well-defined nanostructures. In the present study, new rod-shaped Ru complex modules with tetra pod free-standing phosphonate ligand (LP), complexes **1** and **2** in Fig 1, have been synthesized in order to fabricate the nanometer-size multilayer films on the surface. Four phosphonate groups of LP ligand in the Ru complexes were self-assembled to an ITO electrode. The multilayer films were fabricated by the alternate immersion of an ITO electrode into the complex and zirconium ion solutions. The layer-by-layer growth of the complexes **1** and **2** with the assistance of zirconium (IV) ion was confirmed by a linear increase of the UV absorbance. A typical plot of the absorbance at 504 nm vs. the number of layers for **1** is shown in Fig 2. The self-assembled monolayer on ITO electrode exhibits a reversible one-electron wave at $E = +0.63$ V ($\Delta E_p = 250$ mV) for **1**, and a reversible two-electron wave at $E = +0.93$ V vs. Ag/AgCl ($\Delta E_p = 194$ mV) for **2**, respectively. The surface coverages for **1** and **2** are 5.5×10^{-11} and 5.2×10^{-11} mol/cm², respectively. Considering the molecular area of free-standing complex **1** and **2** obtained from a molecular modeling (2.88 nm²/molecule), the complexes are oriented perpendicular to the surface normal. When the modules have different oxidation potentials, the selection and ordering of modules in multilayer films brings about potential gradients in any order on the surface. Two different ordered three layered films were prepared: i.e., ITO|complex **2**|complex **2**|complex **1**| (film **A**) and ITO|complex **1**|complex **1**|complex **2**| (film **B**). In film **A**, oxidation peak of **1** was observed, but the corresponding reduction peak was small. In film **B**, the reduction peak of **2** was observed, but no oxidation peak was observed. These voltammograms strongly indicate that inner layer acts as a redox mediator for charge-transfer process of superficial layer, and the blocking of electron transfer by potential gradient in layers. Therefore, we can control the direction of electron flow by changing the order of modules, which results in the potential gradient.

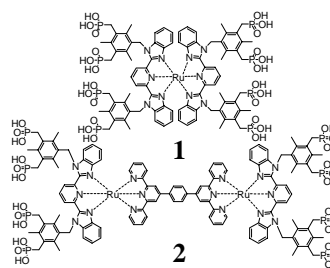


Fig. 1. Structures for the complexes **1** and **2**.

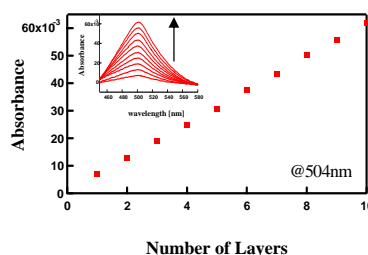


Fig. 2. Plot of the absorbance at 504 nm vs. the number of layers. The inset shows UV spectra with different number of layers.

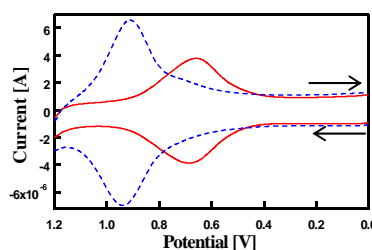


Fig. 3 Cyclic voltammograms of monolayer film **1**(solid line) and **2**(dotted line) on ITO electrode in 0.1M NaClO₄ solution. Scan rate 0.1V/s.

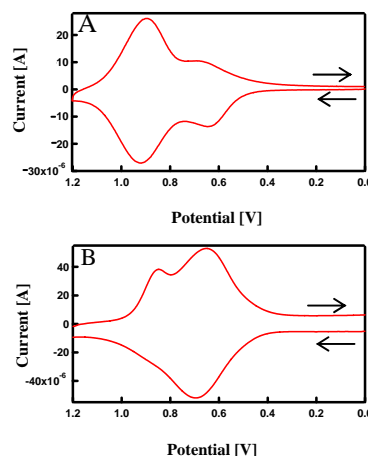


Fig. 4. Cyclic voltammograms of three-layered films on ITO.
A. ITO|Complex **2**|Complex **2**|Complex **1**|. Scan rate, 0.4V/s
B. ITO|Complex **1**|Complex **1**|Complex **2**|. Scan rate, 1.0V/s