Fabrication and Characterization of Novel Mixed-valence Pentaamminechlororuthenium(III) Hexacyanoruthenate(II) Coordination Compound Self-assembled Film

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Functional self-assembled film of a class II mixed-valence coordination compound, pentaamminechlororuthenium(III) hexacyanoruthenate(II) $(Na[NH_3]_5Ru(III)\text{-}CN\text{-}Ru(II)(CN)_5)$, was fabricated and characterized by surface plasmon resonance (SPR), X-ray photoelectron spectroscopy (XPS) and phase modulation infrared reflection–absorption spectroscopy (PMIR-RAS).

Some charge transfer complexes, for example ruthenium bipyridyl complexes, are well known as one of the best candidates for dye sensitized solar cells and electrochromic devices,[1] because charge transfer absorptions usually not only have high absorption coefficients, but also appear as wide absorption bands. In our previous work, we have found that metal ions can play an important role in some photoinduced electron transfer (PET) systems.[2] From the basic point of view, it is quite reasonable that not only interfacial charge transfers, but also charge transfers inside the dye-molecule layer is a key for photocurrent generation.[3] Different from ruthenium bipyridyl complexes, in which charge transfer absorption is generated from metal-to-ligand charge transfer (MLCT), what we present here is metal-to-metal charge transfer (MMCT) complex. According to the classification of Robin and Day[4] which is based on the electronic interaction between two metal ions, we choose a typical class II compound. The reason is that class II compounds have strong interaction between metal ions, but charge is still localized. Self-assembled monolayer (SAM), especially thiol or disulfide derivatives on gold substrate,[5] has been used to fabricate highly organized stable monolayers and regarded as one of well-defined model systems. In this paper we presented an interesting func-
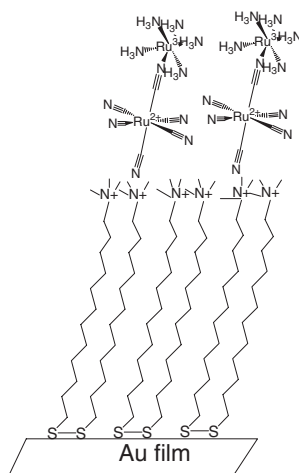
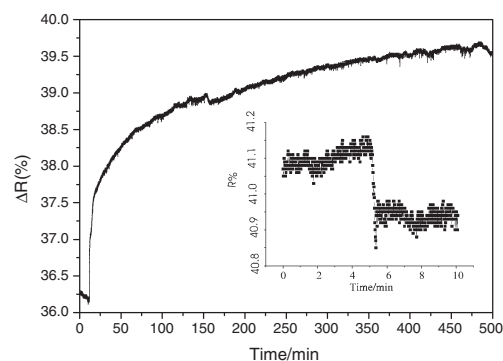**Scheme 1.** Supposed structure of self-assembled film.

Figure 1. Kinetic profile of $Na[NH_3]_5Ru(III)\text{-}CN\text{-}Ru(II)(CN)_5$ in 1 mM water solution absorbed onto positively charged QA-terminated SAM on gold substrate. Inset is kinetic profile of washing process of $Na[NH_3]_5Ru(III)\text{-}CN\text{-}Ru(II)(CN)_5$ SAM by deionized water at room temperature.

tional SA film of $Na[NH_3]_5Ru(III)\text{-}CN\text{-}Ru(II)(CN)_5$ as a result of combining these two interesting fields.

The synthesis of $Na[NH_3]_5Ru(III)\text{-}CN\text{-}Ru(II)(CN)_5$ was performed in water at $60\,°C$ and purified by passing through ion exchange resin and Bio-Gel P2 size exclusion column according to the references.[6] The CV spectra, provided as the supporting data, indicated our sample was free from electroactive contaminates. In order to immobilize our functional anion, a disulfide derivative with quaternary ammonium (QA) terminal group was synthesized and deposited on gold surface. The possible structure of SA film is shown in Scheme 1 (note: the scheme is only for the convenience of understanding, we have not quantitative evidence for the alignment of titled molecules). The surface plasmon resonance (SPR) investigation of the first layer showed that the optical thickness of the first layer is 2.6 ± 0.3 nm assuming its refractive index of 1.50. The formation of the first layer is discussed in detail elsewhere.[7]

SPR data of the adsorption of our charge transfer complex clearly indicated (as shown in Figure 1) that MMCT molecules, $Na[NH_3]_5Ru(III)\text{-}CN\text{-}Ru(II)(CN)_5$, adsorbed on this positively charged SAM-modified gold surface successfully and quite stable in deionized water implied from Figure 1 inset. The reflectivity only changed $\approx 0.2\%$ after washed by water, compared with increasing $\approx 3.5\%$ for film deposition. The thickness of the second layer was determined by curve fitting of the SPR angular-scan data.[8] It is not surprising that the optical thickness of charge transfer complex layer is 0.9 nm with the refractive index, $n = 1.5$, which is in good agreement with its theoretical molecular length of 1 nm calculated by MM+ method in Hyper Chem^{TM} molecular modeling system. The refractive index of 1.5 was ever used by both Mallouk[9] and Page[10] to get reasonable
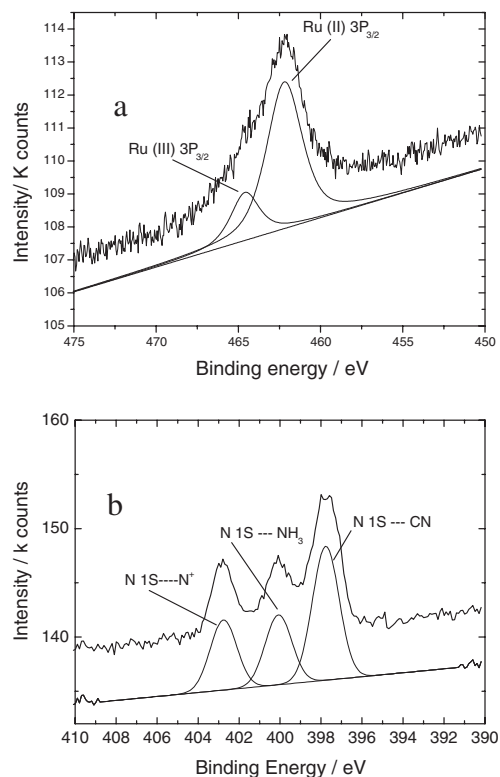
Figure 2. XPS spectra of SA film on gold with emphasis on: a. Ru 3P$_{3/2}$ peaks; b. N 1S peaks by a 200-W monochromatic X-ray source.

Figure 3. PMIRRAS of SA films on gold before and after adsorption of Na[NH$_3$]$_5$Ru(III)-CN-Ru(II)(CN)$_5$ on QA terminated SAM surface. Arrow in figure points the CN stretching mode.

by SPR, XPS, and PMIRRAS. Further investigations on the properties of related functional SA film are being carried out in our laboratory.

ellipsometry thicknesses for their SAMs of complexes.

X-ray photoelectron spectroscopy (XPS) data of the SA film were shown in Figure 2. The Ru (II) and Ru (III) peaks are separated by 2.5 eV in the 3p region (shown in Figure 2a) and 2.1 eV in the 3d region (provided as supporting data). As shown in Figure 2b, we also got three N 1s peaks at 397.7, 400.0 and 402.7 eV that are assigned to nitrogen in cyanide groups, in ammine groups and in quaternary ammonium groups, respectively. We did not quantitatively analyze XPS data of our SAM, because of the unstability of the charge transfer complex, especially peaks for Ru(III) ions under X-ray irradiation even with low power X-ray source.

Phase modulation infrared reflection–absorption spectroscopy (PMIRRAS) data of our functional SAM were shown in Figure 3. IR spectrum of bulk complex exhibits CN vibration peak at 2063 cm^{-1}. PMIRRAS of two layer film showed a peak at 2065 cm^{-1}, which was assigned as the CN stretch demonstrating the existence of the complex layer. In the frequency range of 2700–3100 cm^{-1}, the shoulder peak of the asymmetric methylene stretching modes at 2925 cm^{-1} disappeared after the adsorption of Na[NH$_3$]$_5$Ru(III)-CN-Ru(II)(CN)$_5$, indicating that the order of the QA layer was improved by the adsorption of the complex layer with electrostatic interaction. The relation between the vibrations and the order of the alkyl chains in SAM was proposed in the reference.[11]

To the best of our knowledge, this is the first effort to introduce metal-to-metal charge transfer complex into the functional self-assembled film. We not only successfully fabricated the SAM of charge tranfer complex, but also characterized the film
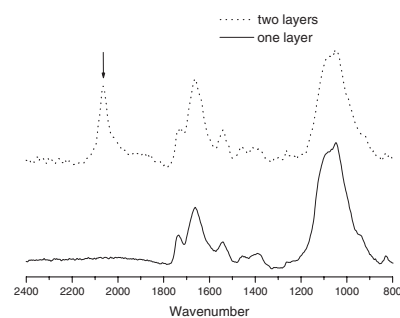
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12 Experimental: The details of the experimental set-up have been described in the paper; E. F. Aust, S. Ito, M. Sawodny, and W. Knoll, *Trends Polym. Sci.*, **9**, 313 (1994). Here we used high refractive index glass (LaSFN9, $n = 1.845$) slides and a 45° prism. A p-polarized HeNe-laser beam ($\lambda = 632.8$ nm) was used as the light source, which was mechanically chopped in conjunction with a lock-in amplifier before entry into the prism. The intensity of the beam reflected at the gold interface was detected by a photodiode detector and recorded as a function of the incidence angle for "angular-scan" measurements, or as a function of time at a fixed angle of incidence for "kinetic-scan" measurements. All sample cells and tubes were made of Teflon. The gold (50 nm) was deposited on LaSFN9 glass plates by thermal evaporation in a vacuum chamber (AUTO 306, Edwards, $\approx 1 \times 10^{-6}$ mbar).