Structural Change of a Cast Film of Amphiphilic Ruthenium(II) Cyano Complex Caused by Electrochemical Oxidation

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An amphiphilic ruthenium(II) cyano complex, $(\mathrm{N(C_2H_5)_4})_2$-$[\mathrm{Ru(dc18bpy)(CN)_4}]$ (dc18bpy = 4,4'-dioctadecyl-2,2'-bipyridine), was prepared by photo-induced ligand exchange. The X-ray diffraction patterns were compared before and after the electrochemical oxidation of the cast film on an ITO electrode. The film had a layered structure, whose interlayer distance changed irreversibly from 4.60 nm to 4.01 nm when the central Ru(II) ion was oxidized to Ru(III).

Design and investigation of new molecular films have been a central subject in the recent investigations on nano-structured composite materials. A main attention has been focused on the careful control of the arrangement and orientation of unit molecules in a film. Among molecules used as functional units, transition metal ions take a unique position because of their electronic and magnetic properties that are not realized in organic compounds. In this respect, cyano complexes are attracting a number of researchers due to their properties of formation of bridged complexes.[1–5] Such properties are utilized to form a film of metal complexes assembled through cyano groups.

In the present report, we have prepared a novel amphiphilic ruthenium(II) cyano complex, $(\mathrm{N(C_2H_5)_4})_2[\mathrm{Ru\ (dc18bpy)(CN)_4}]$ (dc18bpy = 4,4'-dioctadecyl-2,2'-bipyridine) (Figure 1, inset), which is capable of forming a layered film simply by being cast on a solid substrate. The present attempt is sharply contrasted with a number of previous reports on the films of cyano complexes in which the films are prepared by the hybridization with amphiphilic organic compounds such as positively charged lipids or amphiphilic ammonium cations.[6–8] In this respect, the present work is the initial success of preparing an ordered film of *pure* cyano complex simply by casting.

$(\mathrm{N(C_2H_5)_4})_2[\mathrm{Ru(dc18bpy)(CN)_4}]$ was synthesized according to the modified method of preparing $\mathrm{K_2[Ru\ (2,2'\text{-}bipyridine)(CN)_4]}$.[9] $\mathrm{K_4[Ru(CN)_6]}$ (Aldrich) was changed into $(\mathrm{N(C_2H_5)_4})_2[\mathrm{Ru(CN)_6}]$ by use of cation-exchange resin. $(\mathrm{N(C_2H_5)_4})_2[\mathrm{Ru(CN)_6}]$ (10 mg) was dissolved in a methanol solution containing 15 mg of dc18bpy (Wako Pure Chem. Ind.). The mixture in a quartz cell was irradiated by Xe-lamp (500 W) for 3 h. The color of the mixture changed from colorless to pale yellow. After drying the solution in vacuum, the residue was dissolved in acetone and recrystallized. Elemental analyses: Calcd for $\mathrm{C_{66}H_{132}O_6N_8Ru_1}$: C, 64.19, H, 10.77, N, 9.07%. Found: C, 65.33; H, 10.24; N, 8.40%. The ruthenium content of $(\mathrm{N(C_2H_5)_4})_2[\mathrm{Ru(dc18bpy)(CN)_4}]$ was determined by ICP measurements after the compound was decomposed by concentrated nitric acid and 31% hydrogen peroxide, and dissolved in water. The compound was identified with ^{1}H NMR in $\mathrm{CDCl_3}$: δ = 0.87 (t, 6H, bpy–$\mathrm{CH_3}$), 1.2–1.3 (68H, bpy–$\mathrm{CH_2}$), 1.4 (t, 24H, $\mathrm{N^+}$–$\mathrm{CH_3}$), 3.4 (16H, $\mathrm{N^+}$–$\mathrm{CH_2}$), 7.02 (d, 2H, bpy–5,5'), 7.70 (s, 2H, bpy–3,3') and 8.35 (d, 2H, bpy–6,6'). The infra-red spectrum of KBr disk of the compound showed the broad peak at 2056 $\mathrm{cm^{-1}}$ due to the stretching of CN ligands and three peaks around 3000 $\mathrm{cm^{-1}}$ due to methyl and methylene groups. The molar absorption coefficient at 435 nm in methanol was determined to be 9700 $\mathrm{M^{-1}cm^{-1}}$ (1 M = 1 mol $\mathrm{dm^{-3}}$).

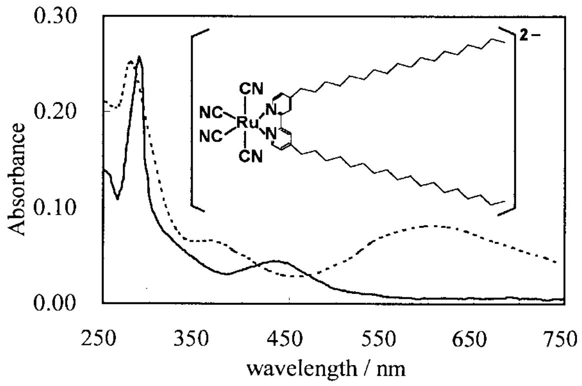

Figure 1. Molecurar structure (inset) and absorption spectra of $(\mathrm{N(C_2H_5)_4})_2[\mathrm{Ru(dc18bpy)(CN)_4}]$ in methanol (solid line) and addition of $\mathrm{Fe(ClO_4)_3}$ (dotted line).

Figure 1 shows the effects of cations on the absorption spectrum of a methanol solution of $(\mathrm{N(C_2H_5)_4})_2[\mathrm{Ru(dc18bpy)\ (CN)_4}]$. In the absence of added electrolytes, the complex shows the sharp peak at 275 nm due to the π–π^* transition of dc18bpy ligand and the broad peak at 440 nm due to the metal-to-ligand charge transfer (solid line). The addition of $\mathrm{N(C_2H_5)_4ClO_4}$ caused little effect on both of the peaks at 275 nm and 450 nm except for the slight increase of the former peak (not shown). When $\mathrm{Fe(ClO_4)_3}$ was added, however, the new peak appeared around 600 nm, resulting in the blue coloration of the solution (dotted line). The peak was assigned to the intermetallic charge transfer from Ru(II) to Fe(III) or it was an evidence for the formation of Ru(II)–CN–Fe(III) type bridged multinuclear complexes. When the titration of the reaction was made by plotting the absorbance at 600 nm against the added amount of $\mathrm{Fe(ClO_4)_3}$, it was concluded that one Ru(II) complex bound with 1.2 Fe(III) ions, assisting the formation of a linear chain of Ru(II)–CN–Fe(III). The blue compound was little soluble in methanol and precipitated after about 12 h.

The electrochemical properties of the complex were studied. When the cyclic voltammogram of a methanol solution of $(\mathrm{N(C_2H_5)_4})_2[\mathrm{Ru(dc18bpy)(CN)_4}]$ was measured in the presence of $\mathrm{N(C_2H_5)_4ClO_4}$, the reversible oxidation and reduction peaks were obtained at 780 mV and 640 mV (vs SCE) (not shown). This was due to the following redox reaction:

$$[\mathrm{Ru\ (dc18bpy)(CN)_4}]^{2-} \Leftrightarrow [\mathrm{Ru(dc18bpy)(CN)_4}]^{-} + e^{-} \quad (1)$$

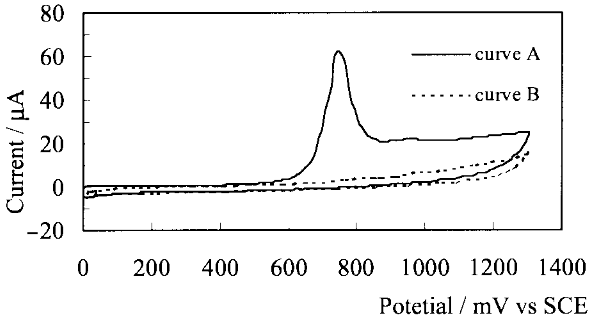

Figure 2. Cyclic voltammogram of cast films of $(N(C_2H_5)_4)_2[Ru(dc18bpy)(CN)_4]$ on an ITO electrode. Curves A and B represent the first and second scans, respectively.

A modified electrode was prepared by casting 30 mL of chloroform solution of $(N(C_2H_5)_4)_2[Ru(dc18bpy)(CN)_4]$ (0.10 mM) onto an ITO electrode (0.30 cm × 0.50 cm) and drying it under air. The thickness of the film was estimated to be 0.4 mm on the assumption that one molecule occupies 1 nm^2 and is 2.8 nm high on the basis of the molecular model. Figure 2 shows the results of the cyclic voltammogram. The first oxidation scan showed the peak at 720 mV with no peaks in the reduction scan (curve A). The succeeding second scan showed no peak in both scans (curve B). From the area of the oxidation peak of curve A, about 29.8% of Ru(II) complexes were estimated to be oxidized during the first scan. The results implied that a part of Ru(II) ions in a film were oxidized electrochemically but not reduced any more.

The upper and lower curves in Figure 3 show the X-ray diffraction patterns of the cast film on the electrode before and after the electrochemical measurements, respectively. The peaks on both spectra were assigned to (00l) diffraction with l = 1–4. The d-spacing was calculated to be 4.60 nm and 4.01 nm before and after the electrochemical oxidation, respectively. Thus the cast film maintained a layered structure and its interlayer distance decreased by 0.59 nm when Ru(II) ions were oxidized. If the height of $[Ru(dc18bpy)(CN)_4]^{2-}$ is estimated to be 2.8 nm as stated above, one layer was considered to be a double molecular layer containing cations. Based on this model, the change of the interlayer distance was interpreted by assuming the elimination of $N(C_2H_5)_4^+$ cations from the film to compensate the excess positive charge. The situations are schematically shown in Figure 4. Therefore the irreversibility of the electrochemical reaction means that the cations were unable to enter the double-molecular layers once the facing layers of metal complexes became closer after the elimination. The effect of the film thickness on the electrochemical oxidation was investigated by changing the cast volume of a metal complex solution from 30 mL to 100 mL. The fraction of oxidized metal complexes was found to remain nearly the same value.

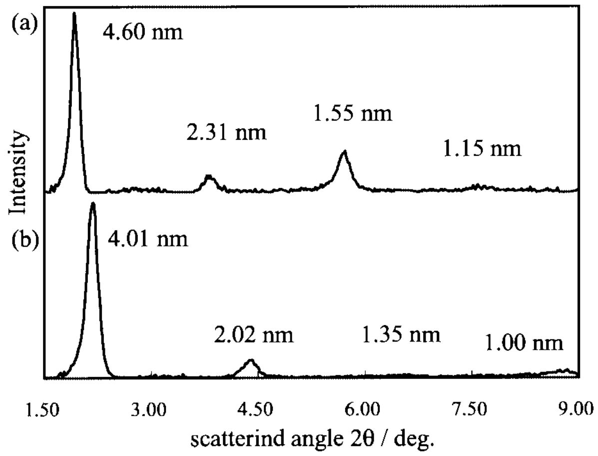

Figure 3. X-ray diffraction patterns of a cast film of $(N(C_2H_5)_4)_2[Ru(dc18bpy)(CN)_4]$ on an ITO electrode. The upper (a) and lower (b) curves are the results before and after electrochemical oxidation, respectively.

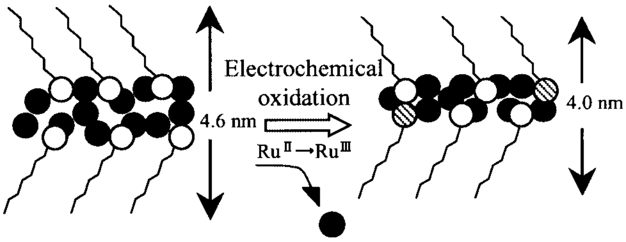

Figure 4. The schematic drawing of the irreversible structural change of a cast film of $(N(C_2H_5)_4)_2[Ru(dc18bpy)(CN)_4]$. Cations (denoted by filled circles) are eliminated when Ru(II) is oxidized to Ru(III).

The present observation is the first attempt of preparing an ordered cast film of cyano complex with no additive and may open a way to a functional electrode based on the self-assembling properties of cyano complex such as a cation-sensitive electrode.

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