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Masa-Aki Haga [a], Kezhi Wang [a], Noriaki Kato [a] & Hideaki Monjushiro [b]

[a] Department of Applied Chemistry, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo, 112-8551, JAPAN

[b] Graduate School of Science, Osaka University, Machikaneyama-cho, Toyonaka, Osaka, 560, JAPAN

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Electrochemical Properties of Dinuclear Ru Complex Langmuir-Blodgett Films towards Molecular Electronics

MASA-AKI HAGA[a*], KEZHI WANG[a], NORIAKI KATO[a] and HIDEAKI MONJUSHIRO[b]

[a]*Department of Applied Chemistry, Chuo University, 1–13–27 Kasuga, Bunkyo-ku, Tokyo 112–8551, JAPAN and* [b]*Graduate School of Science, Osaka University, Machikaneyama-cho, Toyonaka, Osaka 560, JAPAN*

A novel amphiphilic Ru dinuclear complex, $[(L18)Ru(tppz)Ru(L18)]^{4+}$, was synthesized and was introduced as a redox-active complex in Langmuir-Blodgett (LB) films, where L18= 2,6-bis(2'-(1'-octadecylbenzimidazolyl))pyridine and 2,3,5,6-tetrakis(2'-pyridyl)pyrazine (tppz). This Ru complex leads to a stable LB film formation and monolayers of this complex were transferred on glass and indium-tin oxide (ITO) substrates. The π-A isotherm indicates an orientation of the complex with Ru-Ru axis nearly parallel to the substrate surface. Two succesive one-electron oxidation processes were observed for the LB monolayer on ITO electrode.

Keywords: amphiphilic metal complex; dinuclear Ru complex; LB films

INTRODUCTION

The Langmuir-Blodgett technique has been used for the construction of highly organized assemblies with a lamellar architecture. Different kinds of functional molecules can be assembled for a variety of useful applications including sensors, nonlinear optical and electronic devices. Metal complexes can provide us diversity for the molecular design and the selection of functionality such as the electrochemical, optical, and

* Corresponding author: mhaga@apchem.chem.chuo-u.ac.jp

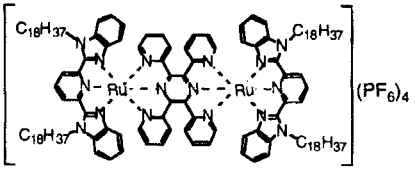
magnetical properties by selecting the metal ions and the ligands. However, the studies on amphiphilic metal complexes are relatively limited to phthalocyanine, porphyrin, ruthenium bipyridine complexes.[1] Therefore, we intend to synthesize new surface assembly of amphiphilic metal complexes through coordination bond.

EXPERIMENTALS

Materials

The amphiphilic ligand, 2,6-bis(N-octadecylbenzimidazol-2-yl)pyridine(L18) was preprared in the previous literature.[2] All other supplied chemicals were of standard reagent grade quality.

Synthesis of dinuclear amphiphilic ruthenium complex, [Ru(L18)(tppz)Ru(L18)](PF$_6$)$_4$. A mixture of [Ru(L18)Cl$_3$] (0.50 g, 0.5 mmol) and tppz (0.095 g, 0.25 mmol) was refluxed in ethylene glycol (40 ml) for 10 h, during which time the color of the solution changed from red-brown to blue green. After being cooled to room temperature, the solution was filtered and a saturated aqueous solution of NH_4PF_6 was added dropwise to the filtrate, leading to formation of a dark green precipitate. The precipitate was collected and recrystallized in CH_3OH. Further purification was done by a recycling HPLC column chromatography (JAI Co.) with $CHCl_3$. The desired dinuclear complex was eluted as a second blue-green band. The eluate was evaporated to dryness to give the crude product, which was recrystallized from $CHCl_3$/ether. Yield, 0.29 g (20 %). Anal. Calcd for $C_{134}H_{186}N_{16}Ru_2P_4F_{24}$. C, 57.45; H, 8.00; N, 6.64. Found: C, 56.98; H, 8.01; N, 6.78 %. FAB mass spectrum: m/z = 1257 (M -2PF$_6$), 790 (M - 3PF$_6$).



Scheme 1. The structure of Ru dinuclear complex, [Ru(L18)(tppz)Ru(L18)](PF$_6$)$_4$

Langmuir-Blodgett Technique.

The surface pressure-area isotherms were measured on a USI FSD-300

Langmuir trough with a Whilhelmy balance at 20°C with a compression speed of 30 cm^2min^{-1}. Monolayers were spread from chloroform solutions of concentration approximately (2 - 4) x 10^{-4} $molL^{-1}$ onto a water subpahse at (20 ± 0.2) °C. Monolayers were transferred to a indium-tin oxide coated (ITO) glass by the vertical dipping method at 20°C at a surface pressure of 30 mNm^{-1}. The UV spectra were recorded by Simadzu 3200 UV spectrophotometer. Electrochemical measurements were made by BAS 100B electrochemical analyzer, using three-electrode system.

RESULTS AND DISCUSSION

Figure 1 shows a π-A isotherm of dinuclear Ru complex which reveals a small phase transition from the liquid to the solid phase at the surface pressure of 15 mNm^{-1}. The limiting moleular area is 2.3 nm^2/molecule obtained from the extrapolation of the solid phase. Considering the molecuar size of Ru dinculear complex, the molecular axis along with two Ru ions is lying paralell to the air-water interface with the alkyl chains protruding away from the surface. The present Ru dinuclear complex was transferred onto a hydrophilic glass or ITO coated glass substrate as Y-type films. The transferred process was monitored by absorption spectra as shown in Figure 2. The plot of absorbance vs the number of layers has a curvature with increasing number of layers. The Ru dinuclear complex exhibits absorption maximum for Ru-to-tppz charge transfer(MLCT)

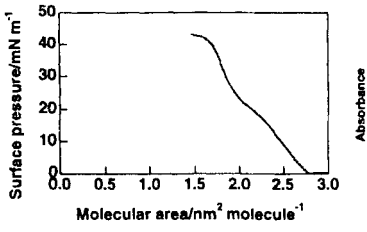


FIGURE 1 π-A isotherm of [Ru(L18)(tppz)Ru(L18)]$(PF_6)_4$ at 20°C

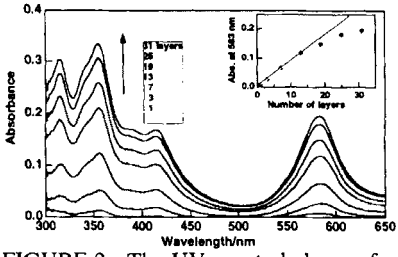


FIGURE 2 The UV spectral change for Ru dinuclear complex LB transfer process on a hydrophilic glass plate.

transition at 584 nm, and for intraligand π–π* tranisitions at 361 and 319 nm. The absorption spectra of LB film is coincident with that in solution. The MLCT band of Ru dinuclear complex is shifted to a longer wavelength significantly compared to that of mononuclear complex, $[Ru(L18)(tppz)]^{2+}$(490 nm).

The cyclic voltammogram of the monolayer LB fim on ITO coated glass shows two succesive oxidation weves at +1090 and +1260 mV vs SCE (Figure 3). The peak current for each wave shows a linear dependence on scan rates, indicating the complex was immobilized on the ITO surface. The oxidation processes can be considered as a stepwise one-electron oxidation as shown in the following equation:

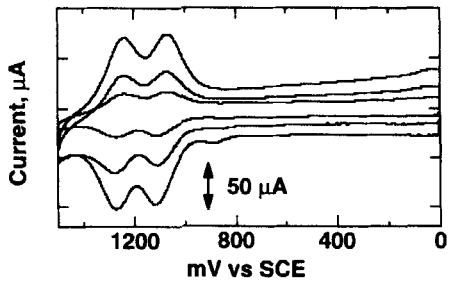


FIGURE 3 Cyclic voltammograms of Ru dinuclear complex monolayer LB film in 0.1 M $HClO_4$: Scan rate = 200, 100, 50 mVs^{-1}.

$$[Ru(II)(tppz)Ru(II)]^{4+} \rightleftharpoons [Ru(II)(tppz)Ru(III)]^{5+} + e^-$$

$$[Ru(II)(tppz)Ru(III)]^{5+} \rightleftharpoons [Ru(III)(tppz)Ru(III)]^{6+} + e^-$$

The mixed-valence $[Ru(II)(L18)(tppz)Ru(III)(L18)]^{5+}$ complex was formed after the one-electron oxidation on the ITO electrode.

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