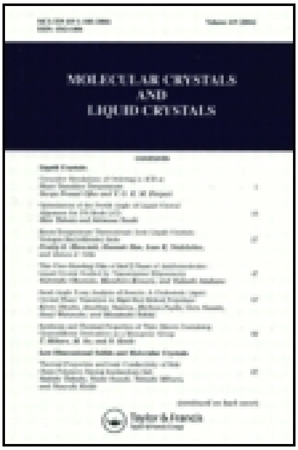

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Chemical Transformation of Amphiphilic Ru Complexes Containing 2,6-Pyridinedicarboxylate at the Air-Water Interface

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A novel amphiphilic Ru complex, [Ru(L18)(pdc)], was synthesized, where L18= 2,6-bis(2'-(1'-octadecylbenzimidazolyl))pyridine and pdc = 2,6-pyridinedicarboxylate. When this complex was spread on the air-water interface as a Langmuir-Blodgett (LB) monolayer, the chemical reaction at the interface with water occurred. The resulting product at the interface could be transferred on glass or indium-tin oxide (ITO) substrate as a stable LB film. The in-situ UV spectra indicates the MLCT band at 500 nm was shifted to a longer wavelength (680 nm). The ν(CO) stretching of [Ru(L18)(pdc)] was changed from 1646 cm^{-1} to 1735 cm^{-1}. These results strongly suggest that the coordinated carboxylate groups were protonated at the air-water interface to obtain the $[Ru(L18)(py(COOH)_2)(OH)_2]$.

Keywords: amphiphilic Ru complex; chemical transformation at interface; LB film

INTRODUCTION

The Langmuir-Blodgett (LB) 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

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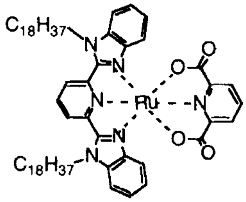
including sensors, nonlinear optical and electronic devices. We have been pursuing the possibility of metal coordination reaction at the air-water. Metal complexes can provide us diversity for the molecular design and the selection of functionality such as the electrochemical, optical, and magnetical properties by selecting the metal ions and the ligands. Recently, we reported the validity of "metal complex as a ligand" strategy. [1] The chemical reaction such as metal coordination plays an important role for the self assembling in two dimensional environments. The desolvation from metal ion is one of the important factors to induce the metal coordination to an amphiphilic ligand at the interface. Once the metal assembly was formed at the air-water interface, the LB transfer can be achieved.[2] In the course of systematic studies of auxiliary ligand effect on [Ru(L18)(X)], we found the chemical reaction of [Ru(L18)(pdc)] at the air-water interface.

EXPERIMENTAL

Materials

The amphiphilic ligand, 2,6-bis(N-octadecylbenzimidazol-2-yl)pyridine(L18) was prepared in the previous literature.[1] All other supplied chemicals were of standard reagent grade quality.



Scheme 1. The structure of Ru complex, [Ru(L18)(pdc)]

Synthesis of amphiphilic ruthenium complex, [Ru(L18)(pdc)]. A mixture of [Ru(L18)Cl_3] (0.18 g, 0.18 mmol), 2,6-pyridinedicarboxylic acid (0.035 g, 0.20 mmol), and NaOH (0.014 g, 0.035 mmol) were refluxed in methanol (40 ml) for 10 h, during which time the color of the solution changed from brown to violet. After being cooled to room temperature, the precipitate was formed, which was collected. Further purification was done by a recycling HPLC column chromatography (JAI Co.) with $CHCl_3$. The desired complex was eluted as a second violet band. The eluate was evaporated to dryness to give the crude product, which was recrystallized from $CHCl_3$/ether. Yield, 0.15g (79 %). Anal. Calcd for $C_{62}H_{88}N_6O_4Ru$. C 68.79; H, 8.19; N, 7.76. Found: C, 68.29; H, 8.41; N, 7.30 %.

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 subphase 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 Hitachi 4000 UV spectrophotometer. *In-situ* UV-vis spectra of monolayers on subphase were recorded on a UV-vis spectrophotometer (UNISOKU Ltd.) with a Hamamatsu R2949 photomultiplier and a Y type quartz optical fiber. Electrochemical measurements were made by BAS 100B electrochemical analyzer, using three-electrode system.

RESULTS AND DISCUSSION

Fig. 1 shows a π-A isotherm of Ru complex, [Ru(L18)(pdc)], which reveals a liquid-expanded state at an area/molecule of 1.4 $nm^2molecule^{-1}$. Increasing the compression, the isotherm becomes steeper and the collapse of monolayer was observed at 42 mNm^{-1}.

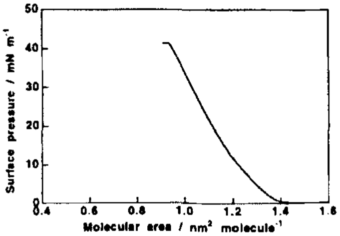


FIGURE 1. π-A isotherm of [Ru(L18)(pdc)]at 20 °C.

The limiting molecular area is 1.3 $nm^2molecule^{-1}$. Considering the molecular size of the Ru complex, the molecular C_2 axis along with Ru ion is oriented perpendicular to the air-water interface with the alkyl chains sticking out of the surface. The Ru complex in $CHCl_3$ solution exhibits absorption maximum for MLCT transition at 500 nm, and for intraligand π–π*

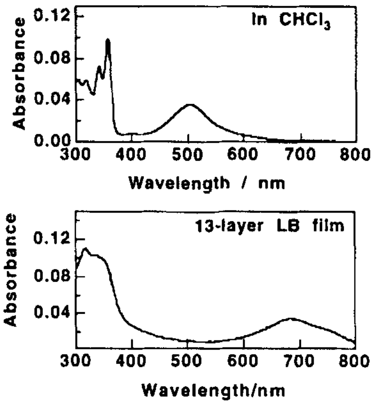


FIGURE 2. The UV spectra of [Ru(L18)(pdc)] in $CHCl_3$ and on a hydrophilic glass plate.

transitions at 361 and 319 nm.(Fig.2) The present Ru 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 Fig.3. The broadening of intraligand π–π* bands indicates the existence of intermolecular interaction in the LB films. The plot of absorbance vs the number of layers has a curvature with increasing number of layers. However, the absorption spectrum showed a dramatic change after a LB transfer on the substrate; the MLCT band of the Ru complex is shifted to 680 nm compared to that in $CHCl_3$ solution (500 nm). (Fig 2 and 3) The dissolution of LB film into $CHCl_3$ revealed the MLCT band at 680 nm, which indicates that this spectral change does not arise from the specific interaction between the Ru complex and solid substrate, but arises from the molecular transformation of the Ru complex. In order to shed light on this transformation, *in situ* UV spectra was measured, which is shown in Fig.4.

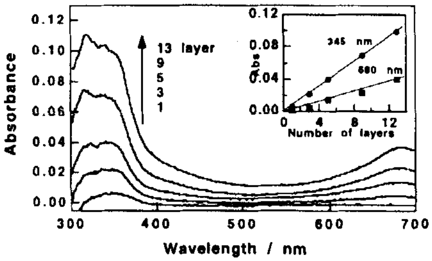


FIGURE 3 The UV spectral change for [Ru(L18)(pdc)] LB transfer process on a hydrophilic glass plate

The absorption band at 680 nm was clearly observed in the UV spectra, which strongly indicates that the transformation of [Ru(L18)(pdc)] complex proceeded at the air-water interface when the CHCl$_3$ solution of the Ru complex was spread on the air-water interface. Furthermore, The ν(CO) stretching of [Ru(L18)(pdc)] was changed from 1646 cm^{-1} to 1735 cm^{-1}. This change of carbonyl stretching frequency reveals the change on metal coordination mode of carboxylate groups in the [Ru(L18)(pdc)] complex. Considering the longer wavelength shift of MLCT band on UV spectra, an electron-donating group may be substituted on the Ru coordination sphere.

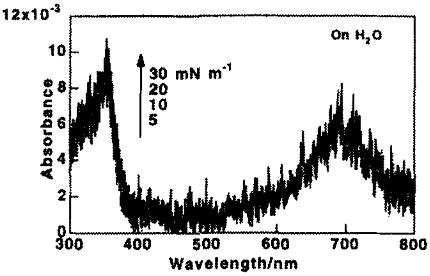
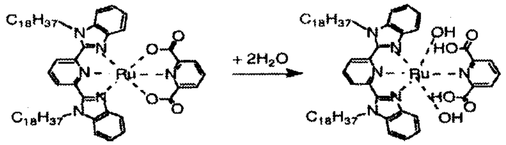


FIGURE 4. *in situ* UV spectra of [Ru(L18)(pdc)] at the air-water interface at different surface pressure(20 °C).



(1)

We propose that the coordinated carboxylate groups will be transformed into [Ru(L18)(py(COOH)$_2$)(OH)$_2$] at the air-water interface, as shown in eq. 1.

The cyclic voltammogram of the monolayer LB film on ITO coated glass shows a broad oxidation wave at +560 mV vs SCE, which corresponds to the Ru(II)/Ru(III) process (Fig. 5). The peak current for each wave shows a linear dependence on scan rates, indicating the complex was immobilized on the ITO surface. There oxidation potential of [Ru(L18)(py(COOH)$_2$)(OH)^2] is

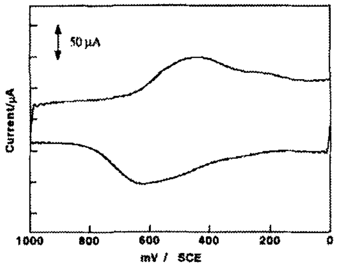


FIGURE 5. Cyclic voltammogram of [Ru(L18)(pdc)] LB monolayer transferred on ITO eletrode: Scan rate = 500 mVs^{-1}

lower than that of $[Ru(L18)(tppz)]^{2+}$($E_{1/2}$ = + 1.17 V vs SCE), where tppz = 2,3,5,6-tetrakis(2'-pyridyl)pyradine. The oxidation wave is relatively broad, indicating the strong intermolecular interaction exists.

Acknowledgments

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References

[1] (a) M. Haga, N. Kato, H. Monjushiro, K. Z. Wang and M. D. Hossain, *Supramol. Sci.*, **5**, 337 (1998). (b) M. Haga, K. Wang, N. Kato, and H. Monjushiro, *Mol. Crys. Liq. Crys.*, in press (1999).

[2] A. Ulman, *An Introduction to Ultrathin Organic Films From Langmuir-Blodgett to Self-Assembly* (Academic Press, San Diego, 1991), p101.