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PREPARATION OF SURFACTANT RUTHENIUM COMPLEXES CONTAINING 6,6'-BIS(*N*-ALKYLBENZIMIDAZOLYL)-2,2'-BIPYRIDINE WITH LONG ALKYL CHAINS

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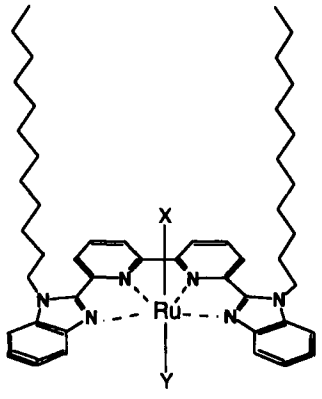
Abstract New surfactant ruthenium complexes, $[Ru(X)(Y)(L8 \text{ or } 12)]^{n+}$, were synthesized by the reaction of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ with L8 or 12 in methanol or DMSO, where L8 or 12 stands for tetradentate 6,6'-bis(*N*-octyl- or laurylbenzimidazolyl)-2,2'-bipyridine. The complexes formed stable monolayer films on the Langmuir trough at the air-water interface and were transferred to a glass plate. The π-A isotherms indicate the phase transition between expanded liquid state and the solid state at around 14 mNm^{-1}, and monolayer collapses at a pressure of 45 mNm^{-1}. This phase transition may be interpreted in terms of a change of molecular orientation. The structure of the LB films on glass were discussed.

INTRODUCTION

The design and molecular architecture of self-organizing metal complexes is of great interest from the viewpoint of energy conversion and information-processing devices. In order to control the molecular ordering or molecular architecture in two dimensions, Langmuir-Blodgett(LB) technique has been widely used in the last two decades, and a significant amount of data have been compiled, particularly for organic amphiphilic functional molecules.[1] On the other hand, reports concerning amphiphilic inorganic complexes are relatively limited for the planar metal complexes such as porphyrins and phathalocyanines.[2] Our aim is to construct the desired ordered multilayers organized

by metal coordination in the LB monolayer on the air-water interface. Ruthenium complexes have redox- and photo-active properties, which are suitable to be the building blocks for the construction of molecular devices.[3] In order to study controlled ordering of the ruthenium complex in two dimensions, we have synthesized surfactant ruthenium complexes containing 6,6'-bis(*N*-octyl- or laurylbenz-imidazolyl)-2,2'-bipyridine (L8 or 12) as shown in Scheme 1, where the number in the ligand abbreviation corresponds to the number of carbon atom in alkyl chains.

SCHEME 1.



$[Ru(X)(Y)(L8 \text{ or } 12)]^{n+}$
n= 0; X=Y=Cl or CN
n= 1; X=Cl, Y=DMSO

EXPERIMENTAL

Preparation of Ru Complexes. The complexes, $[RuCl_2(L8 \text{ or } 12)]$ were synthesized by the reaction of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ with L8 or 12 in ethanol. The metathesis of $[RuCl_2(L8 \text{ or } 12)]$ with the cyanide anion gave the dicyano complex, $[Ru(CN)_2(L8 \text{ or } 12)]$. These complexes were characterized by elemental analysis, MS, IR, NMR, and CV measurements. Anal. $[Ru(CN)_2(L12)]$. Calcd for $C_{50}H_{64}N_8Ru$: C,68.39; H, 7.35; N,12.76% Found; C, 67.98; H, 7.23; N, 12.66%. $[Ru(CN)_2(L8)]$. Calcd for $C_{42}H_{48}N_8Ru$: C, 65.86; H, 6.32; N,14.63%. Found; C, 65.25; H, 6.36; N, 14.37%. Both complexes show a ν(CN) vibration at 2084 cm^{-1}.

Physical Measurements: The measurements of π-A isotherms and the automated deposition of LB films were carried out by using the computer-controlled film balance system FSD-300(USI System, Co., Fukuoka). The trough surface and the moving barrier were coated with Teflon. The subphase was pure water purified by ELGASTAT UHQ-PS system, with temperature controlled at 20°C. The Ru complexes were dissolved in chloroform and spread on pure water. The measurements were carried out several times to check the reproducibility of the π-A isotherms. The monolayer was transferred to a precleaned hydrophilic glass plate by using a conventional vertical dipping method. The UV spectra were recorded using a Simadzu 3200 UV spectrophotometer. XPS measurements were carried out with a VG Scientific ESCALAB MK II X-ray photoelectron spectrometer. Molecular modeling was carried out using Chem3D Pro software, Cambridge, Mass. USA.

RESULTS AND DISCUSSION

π–A isotherms. Figure 1 shows a π-A isotherm of Ru complex, $[Ru(CN)_2(L12)]$, spread on pure water at 20°C. The isotherm indicates the complex begins to pack into the liquid-expanded state at an area/molecule of approximately 1.26 nm^2/molecule. As compression continues, a plateau region occurs at 14.0 mNm^{-1}. The isotherm then becomes steeper with a limiting molecular area of about 0.91 nm^2/molecule and a collapse pressure of 44 mNm^{-1}. Considering the molecular size of $[Ru(CN)_2(L12)]$ from molecular modeling, this behavior suggests that at low surface pressure the plane of the complex is lying flat on the surface with the alkyl chains protruding away from the surface. At higher pressure, the complex is more densely packed, and this is accompanied by a change in molecular ordering, probably the plane of complex is now oriented almost perpendicular to the air/water surface. This behavior is reminiscent of the change in molecular orientation of metal-free 2,9,16,23-tetra-*t*-butyl tetrabenzotriazaporphine occurring as a function of the mole fraction of this species in its mixture with stearic acid.[4] Features in the π-A isotherm of $[RuCl_2(L12)]$ are almost the same, except that the significant relaxation was observed at 21.2 mNm^{-1}. In the case of $[Ru(CN)_2(L8)]$, the surface pressure gradually increases without any drastic transition, indicating that this complex is not stable enough to form a monolayer because of the short alkyl chain length.

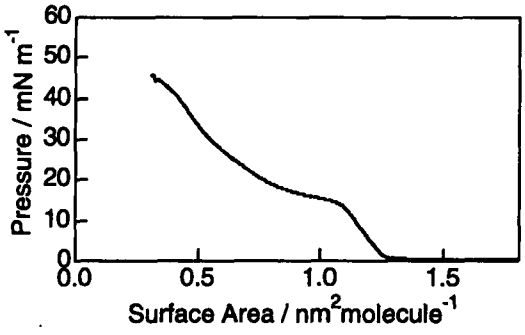


FIGURE 1. π-A isotherm of $[Ru(CN)_2(L12)]$ on pure water at 20°C.

UV spectra of monolayer on glass plate. The complex, $[Ru(CN)_2(L12)]$, dissolved in chloroform exhibits absorption maxima for Ru-to-ligand charge transfer transition(MLCT) at 530 and 420 nm, and for intraligand π–π* transitions at 365, 348, and 319 nm. When this dicyano complex was transferred to a glass plate as a monolayer, the MLCT band shifted to shorter wavelength. As described below, this shift is attributed to the specific interaction between one of the cyano groups in the complex and the -OH group on the glass plate. A similar hypsochromic effect was observed when a metal ion or proton was attached to the cyano group in the cyano complexes.[5]

XPS measurements. The XPS C1s, $Ru3d_{5/2}$ and N1s spectra of $[Ru(CN)_2(L12)]$

were measured for both the powder sample and the monolayer on the glass surface transferred by LB method. The XPS C1s and $Ru3d_{5/2}$ signals were observed at 285.0 and 281.0 eV, respectively, with no difference between the powder and LB monolayer films. However, a distinct spectral difference was observed for the XPS N1s spectra.

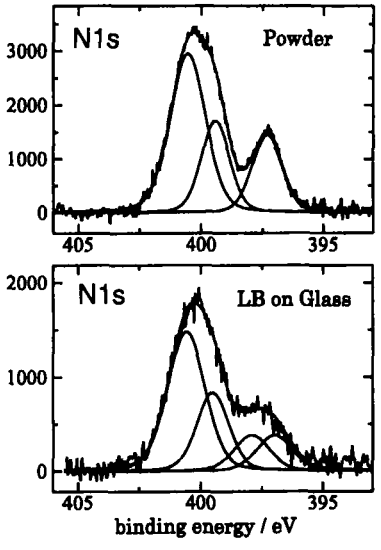
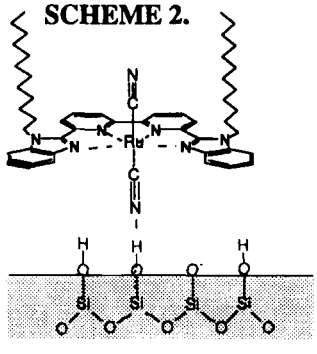


FIGURE 2. XPS N1s spectra of $[Ru(CN)_2(L12)]$ complex for both the powders and LB films on glass plate.

The N1s spectrum of the powder sample consists of three components, which can be assigned as two pyridyl C=N (400.5 eV), imino-type C-N (399.4 eV) and cyano CN(397.3 eV) groups present in the $[Ru(CN)_2(L12)]$ complex. On the other hand, the N1s spectrum of the LB monolayer films on the glass surface shows two broad peaks, one of which appears as a shoulder besides the large main N1s peak. Curve fitting of the XPS N1s spectra for both the powders and LB monolayer films of $[Ru(CN)_2(L12)]$ gave the results shown in Figure 2. In the LB monolayer films, the signals for the cyano groups are split into two components with equal height at 397.0 and 397.9 eV, which is distinct from those for the powder sample, where even the N1s peaks on the tetradentate ligand remain identical. This spectral difference may indicate that the two cyano groups possess different chemical environments; most likely explainable by one of the axial cyano groups weakly interacting with the surface, probably to the hydroxy group on the glass surface through hydrogen bonding(Scheme 2). These XPS results are consistent with the hypsochromic spectral shift on the UV spectra.

SCHEME 2.



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