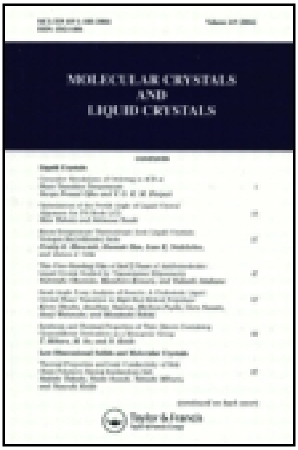

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Monolayer Properties of a Dipyridyl Coordinated Ruthenium Compound

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Version of record first published: 24 Sep 2006

To cite this article: Ji-Young Kim, Yunghee Oh, Eun Mi Son, Jin Un Kim & Burm-Jong Lee (2001): Monolayer Properties of a Dipyridyl Coordinated Ruthenium Compound, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 371:1, 63-66

To link to this article: http://dx.doi.org/10.1080/10587250108024688

Mol. Cryst. and Liq. Cryst., 2001, Vol. 371, pp. 63-66

Monolayer Properties of a Dipyridyl Coordinated Ruthenium Compound

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A ligand exchange of trichloro-2,2'-dipyridylstearylamine ruthenium(III) (Ru(dps)Cl_3) monolayer was investigated at the air-water interface and in the LB film. The optical image of the monolayer was monitored by Brewster angle microscopy. When the monolayer was spread on alkaline subphase (pH 11), the surface pressure spontaneously increased up to 15 mN/m. The λ_{max} around 550 nm of UV-Vis absorption spectra of Ru(dps)Cl_3 in chloroform was shifted to around 670 nm in the LB film. The FT-IR spectra of the LB films also supported the two-dimensional ligand exchange of chloride to water or hydroxide ions.

Keywords: ruthenium(III); coordinated complex; monolayer; BAM; ligand exchange

INTRODUCTION

The Ru-complexes have been investigated for their potential applications to advanced materials such as photosensitizer, molecular electronics, and molecular switch[1]. Langmuir-Blodgett (LB) technique provides featured ultrathin films of nm-sized thickness and ordered molecular structure. The photochemical and electrochemical properties of Ru-containing LB films were

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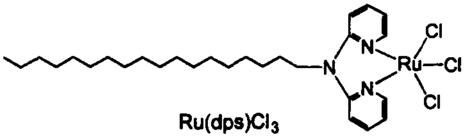
recently investigated[2,3]. However, LB films of amphiphilic Ru-complexes have been seldom examined because of their synthetic difficulty and structural instability[4]. In this paper, we report the monolayer properties of an amphiphilic Ru-complex, trichloro-2,2'-dipyridylstearylamine ruthenium(III) (Ru(dps)Cl_3), at the air-water interface and in the LB film. The optical image of the monolayer was monitored by Brewster angle microscopy. Specifically, the ligand exchange of chloride to water or hydroxide ions at the air-water interface was characterized from surface pressure-area isotherms, UV-Vis, and FT-IR spectra.

EXPERIMENTAL

Ru(dps)Cl_3 was synthesized from substitution reaction of stearyl chloride with dipyridylamine followed by coordination of the ligand with Ru(III) chloride. The chemical structure was determined from FT-IR, ^{1}H-NMR, EPR, HR FAB-MS, and elemental analysis.



Ru(dps)Cl_3

A film balance system NLE-LB200-MWC (Nippon Laser and Electronics) was used for measuring surface pressure as a function of molecular area and for LB transfer of monolayer by the vertical mode (trough surface size, 80x585 mm^2). BAM images were obtained from Mini BAM (Nanofilm Technologie GmbH). The employed substrates were quartz plates for UV-Vis, and calcium fluoride plates for FT-IR spectroscopy.

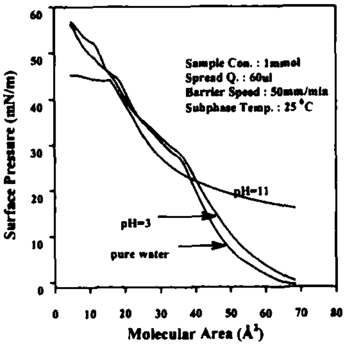


FIGURE 1 Surface pressure-area isotherms of Ru(dps)Cl_3.

RESULTS AND DISCUSSION

The surface pressure-area isotherms showed that Ru(dps)Cl_3 monolayer was stable up to ca. 25 mN/m of surface pressure and slowly collapsed by further barrier compression (Fig. 1). The optical image of the monolayer was monitored by Brewster angle microscopy (BAM). Any noticeable structure was not detected until the surface pressure reached at the collapse point. Parallel white lines were observed as collapsed aggregate images during the further compression.

When the monolayer was spread on alkaline subphase (pH 11), the surface pressure spontaneously increased up to 15 mN/m within 30 min. The spontaneous increase of surface pressure was not observed on both neutral and acidic (pH 3) subphases. This phenomenon was understood as related to ligand exchange from chloride to hydroxide, which was also evidenced from followed characterization of the LB films by UV-Vis and FT-IR spectroscopy.

The UV-Vis spectra showed very different absorption peaks in the states of chloroform solution and LB film as shown in Fig. 2. The λ_{max} around 550 nm of UV-Vis absorption spectra of Ru(dps)Cl_3 in chloroform was shifted to around 670 nm in the LB film. The FT-IR spectra of the LB films revealed the noticeable increase of stretching band due to hydroxyl group. Together with the large red shift of the λ_{max} in UV-Vis spectra, it was also supposed to be related with the ligand exchange. The quantitative analysis on the extent of ligand exchange and the ratio of exchanged ligand species is in progress.

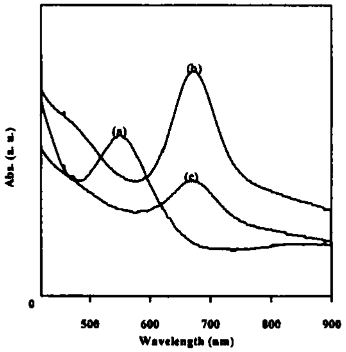


FIGURE 2 UV absorption spectra of Ru(dps)Cl_3 (a) in chloroform solution, (b) in LB film (pure water), and (c) in LB film (pH 11).

Acknowledgments.
This work was supported by BK21 program of Ministry of Education, Korea (D-0024).

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