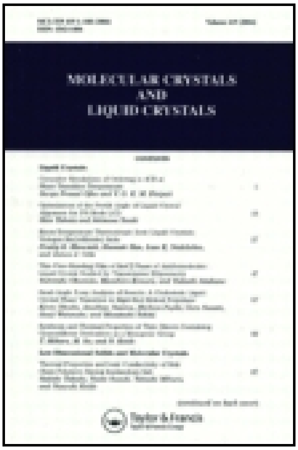

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Highly Ordered LB Films of a Novel Ferric Schiff Base Complex

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Highly Ordered LB Films of a Novel Ferric Schiff Base Complex

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An amphiphlic ferric Schiff base complex, FeLCl•$2H_2O$ (L = N,N'-bis-(1-phenyl-3-methyl-4-octadecylidene-pyrazone-5-one)ethylenediamine), is newly synthesized and characterized. Surface pressure-area isotherm on pure water subphase of the complex shows stable Langmuir film-formation. UV-visible spectroscopy and low-angle x-ray diffraction indicate that LB films transferred on hydrophilic glass are of highly ordered structure.

Keywords: Langmuir-Blodgett film; ferric Schiff base complex

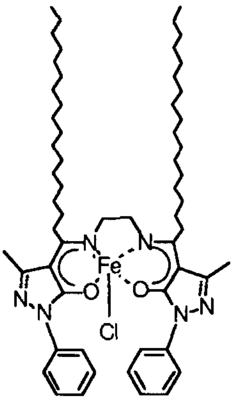
INTRODUCTION

Langmuir-Blodgett films based on metal complexes have been shown to exhibit more fascinating and tunable optical, electronic and magnetic properties compared to their organic counterparts. Without doubt, judicious design of amphiphilic functional complexes which can form highly ordered and anisotropic supramolecular architectures would be great challenge for LB work of metal complexes[1]. On the other hand, bistable switching characteristic is one of the most attractive goals pursued for future molecular electronic devices. Some metal complexes are well recognized to exhibit spin transition under external stimulus. Thus introduction of metal complexes of this kind into LB films is of particular interest to make ultrathin magnetic bistable switching and memory devices of molecular dimension[2]. Herein, we reported a novel ferric Schiff base complex for LB films with potential spin transition property.

EXPERIMENTAL

The Fe(III) complex, Fe(L)Cl (L = N,N'-bis(1-phenyl-3-methyl-4-octadecylidene-pyrazone-5-one)-ethylenediamine) with its chemical structure shown in Scheme 1, was synthesized according to minor modification of literature method[3]. Anal. Fe(L)Cl·2H_2O Calcd for $C_{58}H_{94}N_6O_4FeCl$: C, 67.63; H, 9.13; N, 8.16%. Found: C, 67.90; H, 9.90; N, 8.32 %. Positive MS-FAB: 995 ($[Fe(L)Cl]^+$). IR (KBr): 2921(vs); 2851(s);1592 (s); 1590 (m); 1519(m); 1486(m); 1397(w);1117(w);756 cm^{-1} (w). Instrumentations for physical measurements were the same as before[1].

SCHEME 1



Fe(L)Cl

RESULTS AND DISCUSSION

Surface Pressure-Area Isotherm on Pure Water Subphase

As shown in Fig.1, the first short solid condensed region appears at a molecular area of 1.1 $nm^2 molecule^{-1}$ and the second one is present at a limiting molecular area nearly one-half of the first phase. This behaviour is characteristic of the change of molecular orientation for planar complexes. Final very steep phase is probably associated with multilayer formation.

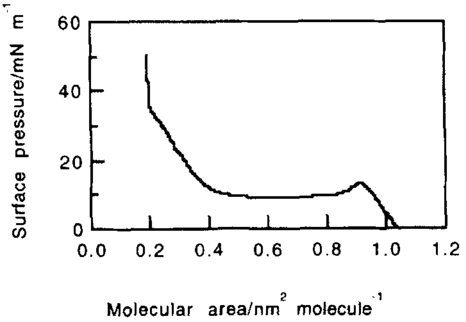


FIGURE 1 Surface pressure-area isotherm of Fe(L)Cl complex at 20°C on pure water subphase

Ultraviolet-Visible (UV-vis) Spectroscopy

The complex in $CHCl_3$ shows one broad band centered at 500 nm in the visible region and nearly structureless absorption in the UV region. The LB film transferred at 5 mN m^{-1} shows an ill-defined shoulder at 360 nm. This difference is due to the fact that the chloride in the complex was replaced by water molecule during the film transfers, as revealed by x-ray photoelectron spectroscopy of the film. Uniform film transfers at 5 mN m^{-1} were achieved, as evidenced by linear increase in the absorbance of the film at 363 nm vs number of layers (9, 19 and 27 layers) deposited. The films transferred at 20 and 40 mN m^{-1} show a more defined peak at 360 nm compared to the film prepared at 5 mN m^{-1} and that transfer ratios fell as the layer number deposited exceeds 5 layers.

Low Angle X-ray Diffraction

Low angle x-ray diffraction pattern for 23-layer Y-type LB film prepared at 5 mNm^{-1} is shown in Fig.2. Three sharp regular diffraction peaks are observed at *2θ* = 3.52, 7.08 and 10.62° which are assigned to (001), (002) and (003) Bragg diffractions, demonstrating highly orientional ordering of the film. Mean bilayer spacing between two adjacent Fe layers was derived to be 2.5 nm which compare well with the value (2.6 nm) obtained based on molecular modeling for interdigitated structure, given that two long alkyl chain and the coordination plan both orientate perpendicularly to the surface of the glass substrate. A 16-layer film prepared at 20 mN m^{-1} and 4-layer film prepared at 40 mN m^{-1} both give almost the same x-ray diffraction patterns as Fig. 2, although the phases of monolayer are significantly different for these three surface pressures, judging from π-A isotherm in Fig. 1 .

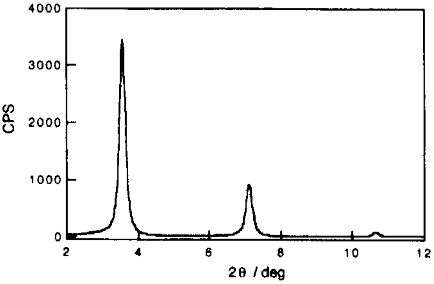


FIGURE 2 X-ray diffraction pattern of a 23-layer LB film prepared at 5 mN • m^{-1}.

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