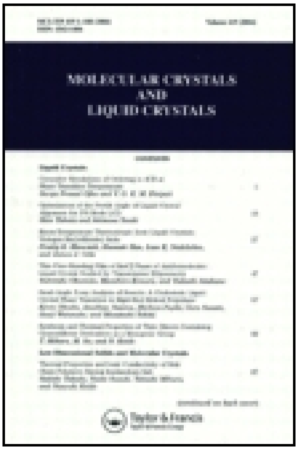

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Monolayer and LB Films of Amphiphilic 8-Hydroxyquinoline Derivatives

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Monolayer and LB Films of Amphiphilic 8-Hydroxyquinoline Derivatives

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The surface pressure-area isotherms of the monolayers of three kinds of amphiphilic derivatives of 8-hydroxyquinoline, N-hexadecyl-8-hydroxy-2-quinolinecarboxamide (**1**), 2-hexadecyloxycarbonyl-8-hydroxyquinoline (**2**) and 8-hexadecyloxy-2-quinaldinic acid (**3**) at an air-water interface on subphases with and without metal ion were investigated and compared with each other. Some information regarding the packing density and phase transition under different experimental conditions has been obtained. At the air-water interface **1**, **2** and **3** can form metal complexes with Cu^{2+} ion present in the aqueous phase. The formation of complexes leads to changes in the area per molecule and the collapse pressure of the monolayer. X-ray photoelectron spectroscopy analysis reveals Cu-ligand ratios in the LB films to be *ca.* 1:1 for **1** and **2** and 1:2 for **3**. Low-angle X-ray diffraction measurements showed the LB films of **1**, **2** and **3** deposited from $CuCl_2$ subsolution had good homogeneity and were Y-type bilayer films.

Keywords: Monolayer; LB films; 8-hydroxyquinoline amphiphilic ligand

1. INTRODUCTION

Tang et al.[1,2] found that an 8-hydroxyquinoline aluminum (Alq_3) complex be used as an emitting element in electroluminescent (EL) devices. In the EL diode they designed, high external quantum efficiency and brightness are achievable at a driving voltage below 10 V. After that, many other 8-hydroxyquinoline complexes, such as Znq_2, Beq_2, Mgq_2, $Zn(mq)_2$, $Be(mq)_2$, and $Al(prq)_3$ (mq and prq are 2-methyl-8-hydroxyquinoline and 7-propyl-8-hydroxyquinoline, respectively), were also used as emitting elements[3].

LB film technique makes it possible to prepare organic functional ultrathin films with a controlled thickness at a molecular size and with-defined molecular

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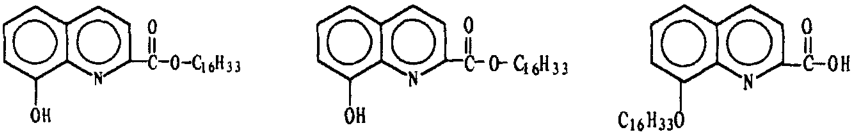
orientation, therefore, if some amphiphilic complexes with 8-hydroxyquinoline can be synthesized and further be incorporated in LB films, these LB films may be used as the emitting layer of EL devices. This kind of emitting layer can be fabricated more conveniently than the general vacuum deposited technique. With this in mind, we designed and synthesized three amphiphilic long alkyl chain derivatives of 8-hydroxyquinoline. Their molecular structures are shown in Scheme 1. In this study, the monolayer and Langmuir-Blodgett films of these amphiphilic derivatives have been investigated and compared with each other.



1 **2** **3**

SCHEME 1 Molecular structure of the amphiphilc ligands derivated from 8-hydroxyquinoline

2. METHODS AND EXPERIMENTS

8-Hydroxyquinaldine, n-hexadecylamine and n-hexadecanol are from Fluka Chemical Co. All the other reagents were of A.R. grade. The amphiphilic derivatives of 8-hydroxyquinoline, N-hexadecyl-8-hydroxy-2-quinoline carboxamide (**1**), was synthesized by a previously reported method[4]. 2-Hexadecyloxycarbonyl-8-hydroxyquinoline (**2**) and 8-hexadecyloxy-2-quinaldinic acid (**3**) were synthesized following classical procedures, involving the preparation of 8-hydroxyquinaldic acid[5] and subsequent reaction with long chain alkyl alcohol[6]. Formation of air-water monolayers and the deposition of the LB films have been outlined in another paper[7].

3. RESULTS AND DISCUSSION

3.1. Formation of Monolayer on Aqueous Subphase

All the three amphiphilic ligands **1**, **2** and **3** can form stable monolayers with collapse pressures of *ca.* 37, 40 and 44 $\mathrm{mN\ m^{-1}}$ on pure water subphase (pH 5.6, Figure 1). Compound **3** showed a expanded and condensed regions at different surface pressure. The limiting area per molecule **3** was *ca.* 0.30 $\mathrm{nm^2}$. In contrast, the isotherms of **1** and **2** display expanded, coexistence, and condensed regions at different surface pressures. The plateau might indicate a phase change or a change in orientation of the head group fragment (quinoline ring) that occurs when the surface pressure reaches 11 and 15 mN m^{-1} for **1** and **2**[8]. By extrapolating the surface pressure to zero in the region below and above the plateau, limiting areas of *ca.* 0.65 or 0.63 nm^2 and 0.26 or 0.34 nm^2 per molecule of **1** or **2** can be obtained, respectively (Table I).

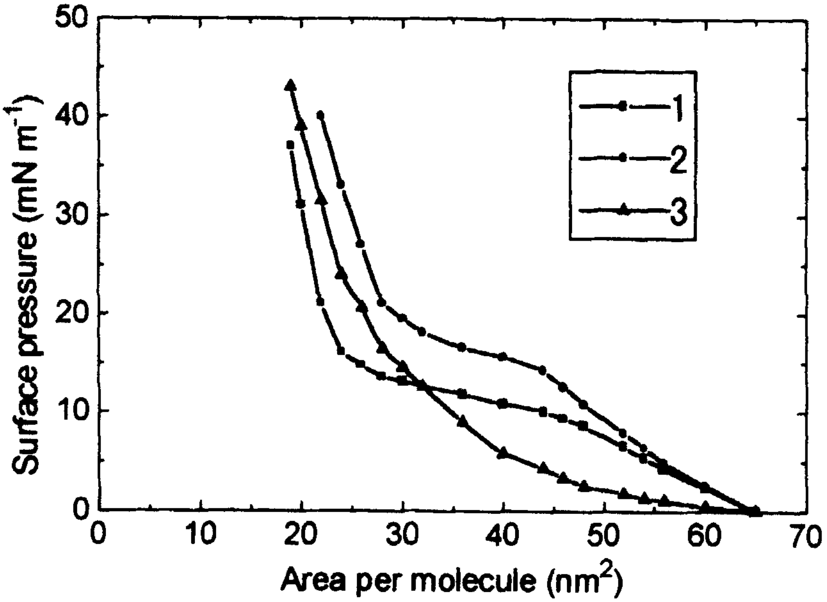


FIGURE 1 π -A isotherms of **1**, **2** and **3** on pure water subphase

TABLE I Limiting areas and collapse pressure of amphiphilic ligands before and after coordination

	Ligands			*Complex*		
	1	*2*	*3*	*1-Cu*	*2-Cu*	*3-Cu*
A_{01} (nm^2)	0.65	0.63				0.72
A_{02} (nm^2)	0.26	0.34	0.30	0.28	0.33	0.30
π_{max}(mN m^{-1})	37	40	44	48	49	54

According to a space-filling molecular (CPK) model, the 8-quinolinol ring can be approximated as a rectangular block with dimensions of about 0.84 × 0.74 × 0.36 nm^2[4]. Therefore, the area values of 0.65 or 0.63 nm^2 per molecule of **1** or **2** at the start of the plateau correspond to the face area (0.84 × 0.74 nm^2) and 0.26 or 0.34 nm^2 per molecule at the end of the plateau and 0.30 nm^2 per molecule **3** correspond to the side area (0.84 × 0.36 nm^2) of the 8-quinolinol ring. That is, the shape of the pH 5.6 isotherm for **1** and **2** might thus be seen as originating in a conformational transition of the chromophores upon compression, in which **1** or **2** turns from lying flat to an 'edge-on' position.

3.2. Metal Ions Complexation at Air-Water Interface

The metal ions, including the alkaline earth metal (such as $Ca^{2+}$and Mg^{2+}) and transitional metal ions (such as Cu^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+}) contained in subphases have a striking effect on the monolayer behavior of all the three amphiphilic compounds **1**, **2** and **3**. Different ligand or different metal ion shows different characters. The π-A isotherms of **1**, **2** and **3** monolayers in subphases containing 0.001 mol/L Cu^{2+}ion are shown in Fig. 2. Compared with pure water subphase, both the shape of the figures and the values of limiting areas of **1**, **2** and **3** changed in varying degrees (Table I). It indicated that the coordination between the ligands and Cu^{2+} ions have occurred at the air-water interface.

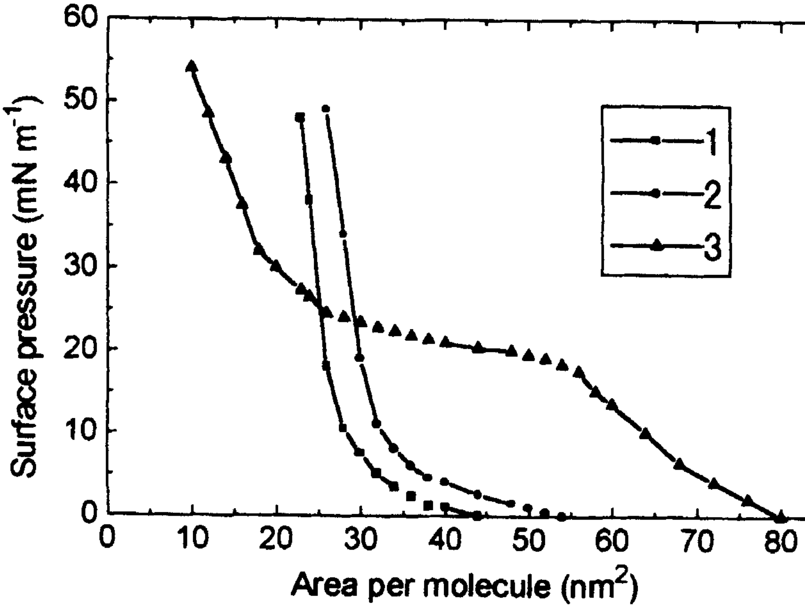


FIGURE 2 Surface pressure-area isotherms of **1**, **2** and **3** on subphase containing Cu^{2+} ion

It is interesting that after complexation, the plateaux of **1** and **2** disappear. On the contrary, the isotherm of **3** on aqueous Cu^{2+} subphase appears a plateau and is more expanded than that of **3** on pure water. It indicates that a formational change of the amphiphiles occurred after complexation

The areas per **1** and **2** molecular unit on Cu^{2+} ion subphase are 0.28 and 0.33 nm^2, respectively, which just enough correspond to the side area of 8-hydroxyquinoline (0.84×0.36 nm^2). The areas per **3** molecule below and above the plateau are 0.72 and 0.30 nm^2. The former area corresponds to the face area of 8-hydroxyquinoline (0.84×0.74 nm^2) and the latter is still consistent with the side area of quinaldic acid (0.74×0.36 nm^2).

3.3. X-Ray Photoelectron Spectroscopy (XPS)

In order to investigate the complexation of the amphiphilic ligands with Cu^{2+} ion containing subphases and any special characteristics of Cu^{2+}-ligand binding, the composition of the built-up LB films of amphiphilic ligand of **1, 2** and **3** deposited from subphases with and without Cu^{2+} ion were measured by means of XPS.

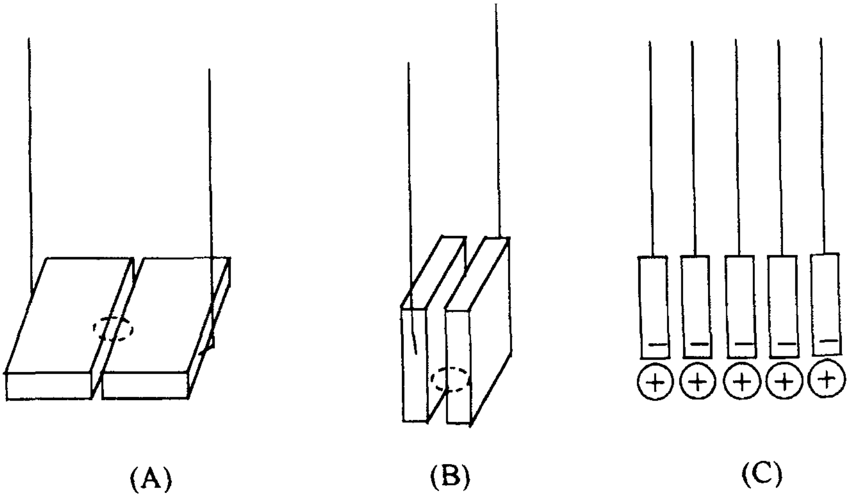


FIGURE 3 Stacking modes of amphiphiles in the air-water monolayer. The dashed circles represent Cu^{2+} ions

The XPS spectra present the core level peaks of carbon, oxygen, and nitrogen as well as metal copper containing subphase. Compared with the binding energy of N1s and O1s (Table II) in ligands, both N1s and O1s increased in the complexes **1**-Cu, **2**-Cu, and **3**-Cu LB films, respectively. N1s increases *ca.* 0.3~ 0.7 eV, O1s increases *ca.* 0.8~1.9 eV. It is clear that the lone pair electrons from the nitrogen and oxygen atoms were shifted into the metal atom and thereby a strong complexation was formed. That is, all the **1, 2** and **3** are coordinated to copper ion in subphase through the phenolic O atom and the heterocyclic N atom. The charge-transfer from the N, O atoms of the ligands to metal ions led to a decrease of charge density and an increase of binding energy of N, O atoms. Therefore, the orientation of the complexation can be described as that: the hydrophobic aliphatic chain of amphiphilic ligand is located above the air-water interface while the hydrophilic coordinating head groups (phenolic OH or carboxylic and tertiary N group) are in contact with the aqueous phase. The Cu^{2+} ions present in the subphase diffuse to the monolayer-water interface and form complexes with the head groups of the amphiphilic ligand.

The molar ratios of Cu^{2+} to C, N and O components estimated from the relative signal strength of the XPS peaks are shown in Table III. The elemental C/Cu ratios for **1** and **2** amount to *ca.* 26.0, indicating 1:1 complexes of Cu^{2+} ion with **1** or **2** are formed at the monolayer-water interface (Fig. 3, Mode C). However, the C/Cu ratio for **3** is 46.5. It shows that ligand **3** has a different coordination character comparing with **1** and **2**. Every Cu^{2+}ion may coordinate with two **3** molecules (Fig. 3, Mode A or B). This stiochoimetry ratio can be explain the results obtained from the molecular limiting area of **3**-Cu monolayer above. That is, upon compression, the orientation of **3** in the monolayer on aqueous $CuCl_2$ solution changed from Mode A to Mode B in Figure 3 accompanying with a decrease of limiting areas from 0.72 to 0.30 nm^2.

TABLE II Changes of binding energy of N1s and O1s of **1**, **2** and **3** before and after coordination (eV)

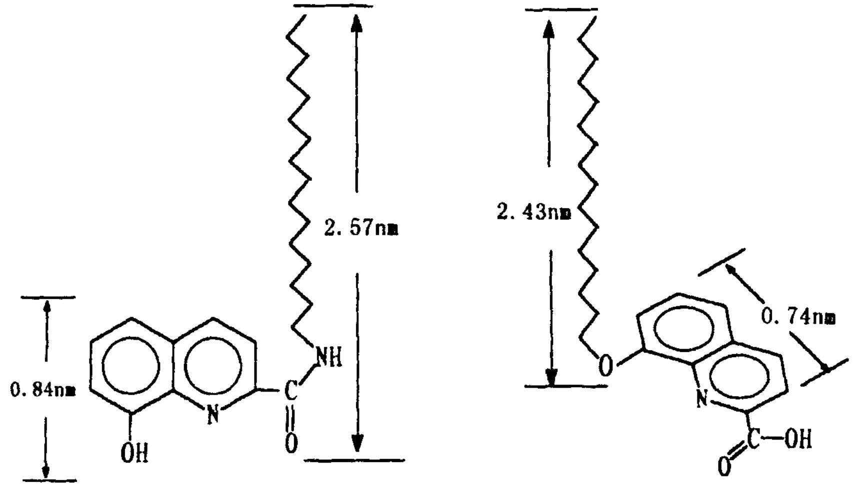
LB films	*Ligands*			*Complex*		
	1	*2*	*3*	*1-Cu*	*2-Cu*	*3-Cu*
N1s	399.6	399.8	399.7	400.1	400.5	401.0
O1s	531.0	531.3	531.5	532.9	532.2	532.3

TABLE III Relative intensities of the observed lines in XPS spectra of ligand-M LB films

LB Films	*Atomic ratio*^{a}			
	M	*C*	*N*	*O*
1-Cu	1.00 (1.00)	27.1 (26.0)	1.78 (2.00)	3.12(2.00)
2-Cu	1.00 (1.00)	25.1 (26.0)	1.85 (2.00)	2.85 (2.00)
3-Cu	1.00 (1.00)	46.5 (52.0)	3.15 (4.00)	5.19 (4.00)

a. The values in parenthesis are theoretical values.

In these LB films the observed oxygen signal is greatly enhanced over the theoretical values, which may be explained by the interference of the oxygen of SiO_2 in substrate. At the same time, the oxygen in the air may also affect the measurement.



1 **3**

FIGURE 4 Schematic representation of the arrangement of **1** and **3** in a compressed film at the air-water interface. The aliphatic chains have been represented in their extended form, but of course some degree of curling up may occur

3.4. Low-Angle X-ray Diffraction

Low-angle X-ray diffraction measurements were used to obtain some useful structure information on the films organization. The Bragg peaks of 21-layer LB films of **1**, **2** and **3** deposited from subphases containing 0.001 mol/L $CuCl_2$ are 1.730, 1.747 and 2.071°, respectively. These peaks indicates that the deposited LB films have good layered structure. The derived bilayer spacings are about 5.11, 5.06 and 4.26 nm, respectively. It can be seen that the latter (4.26 nm) is much smaller than the former (5.11 and 5.06 nm). This difference in thickness was caused by the difference of the structure between **1**, **2** and **3**. A schematic representation of the orientation of **1** and **3** in LB films is shown in Fig. 4. The length of $C_{16}H_{33}$ is *ca. 2.4* nm[9], the height of 8-hydroxyquinoline (Hq) is *ca.* 0.84 nm. For the LB films of **1** and **2**, the height of Hq is included in the height of $C_{16}H_{33}$ chain. However, only about half of the height of Hq is included in the height of $C_{16}H_{33}$ chain in compound **3**. So the heights of **1**-Cu and **2**-Cu in LB films are larger than that of **3**-Cu.These d values are near the double thickness of the long side-chain $C_{16}H_{33}$. It indicated that a Y-type bilayer structure was formed during the deposition process of **1, 2** and **3** from subphases containing Cu^{2+} ion.

The metal complex forming properties of **1, 2** and **3** should serve as the basis for the development of metal ion sensors and their complexes could be used as the emitting material of electroluminescent devices[10].

Acknowledgements

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