Preparation and characterization of Langmuir–Blodgett films of *N*-hexadecyl-8-hydroxy-2-quinolinecarboxamide and its lanthanum complex

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A new amphiphilic ligand, *N*-hexadecyl-8-hydroxy-2-quinolinecarboxamide (HHQ), and its lanthanum complex La(HHQ)$_2$, were synthesized and characterized by elemental analysis, IR and ^{1}H NMR spectroscopy. The characteristics of the monolayer, Langmuir–Blodgett (LB) films and cast films of HHQ and La(HHQ)$_2$ were investigated by different physical methods, including surface pressure–area isotherms, absorption and fluorescence spectra and low-angle X-ray diffraction analysis. The LB film of La(HHQ)$_2$ has good vertical homogeneity and the in-plane conductivity parallel to the compression direction is found to be 3.85×10^{-5} S m^{-1}.

8-Hydroxyquinoline and its derivatives readily form insoluble precipitates with many metal ions, and are available in the laboratory as analytical reagents and for the extraction of many metal ions;[1,2] for example, some alkylated 8-hydroxyquinolines, Kelex 100 and LIX26, have been widely used to extract lanthanides, palladium, thorium, uranium and zirconium.[3,4]

Tang *et al.*[5,6] found that an 8-hydroxyquinoline aluminium (Alq$_3$) complex can be used as an emitting element in electroluminescent (EL) devices. In the EL diode they designed, high external quantum efficiency, luminous efficiency and brightness are achievable at a driving voltage <10 V. Since 8-hydroxyquinoline chelates have unusual optical, electrical, magnetic and other physical properties, and the LB film technique makes it possible to prepare organic functional ultrathin films with a controlled thickness at a molecular size and with well defined molecular orientation, if 8-hydroxyquinoline or its derivatives can be incorporated in LB films, these films may have potential applications in molecular electronic devices.[7,8] Nevertheless, so far organized molecular films of long-chain derivatives of 8-hydroxyquinoline have not been studied. In this paper we report the synthesis of a new amphiphilic derivative of 8-hydroxyquinolines, (HHQ), the formation of highly ordered layers of La(HHQ)$_2$ and the utility of various physical methods for studying the molecular orientation and aggregation state of the chromophores as well as any interactions of the chromophores with species in the subphase.

Experimental

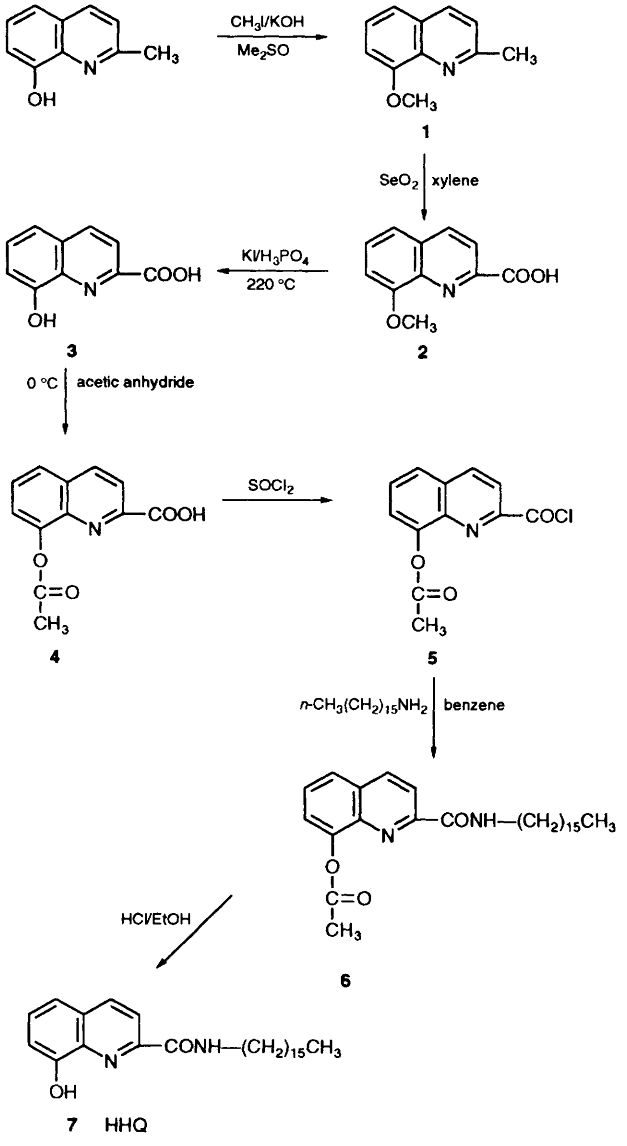
Materials

8-Hydroxyquinaldine (General Chemical and Pharmaceutical Co., Sudbury, Middlesex) and hexadecylamine (Fluka Chemical Co.) were used without any further purification. All solvents were purified by standard procedures. LaCl$_3$·7H$_2$O was of A.R. grade, purchased from Shanghai Chemical Reagents Co.

Synthesis

The synthesis procedure for the amphiphilic ligand, *N*-hexadecyl-8-hydroxy-2-quinolinecarboxamide (HHQ) is illustrated in Scheme 1. This route involves the preparation of 8-hydroxyquinadic acid **3**,[7] and subsequent reaction with long chain alkylamine; details of this procedure will be reported elsewhere.

The product HHQ is a light grey powder, mp 50–51.5 °C (Elemental analysis: Found: C, 72.8; H, 9.88; N, 6.24. Calc. for $C_{26}H_{40}N_2O_2 \cdot H_2O$: C, 72.6; H, 9.77; N, 6.51%). FTIR (KBr) ν/cm^{-1}: 3306 (OH), 2925, 2856 (CH$_2$, CH$_3$), 1650 (C=O), 1600 (C=C), 1550 (C=N), 1503 (C=C), 1462, 1300, 1162



Scheme 1 Synthesis of the amphiphilic molecule HHQ

(Ar—H), 1091, 1044, 1000, 850 (ring vibration), 723 [$(CH_2)_n$], 650. UV–VIS ($CHCl_3$) λ/nm 254, 307, 350. ^1H NMR ($CDCl_3$) δ 10.00 (0.15 H, OH), 8.35 (1 H, COOH), 8.00 (1 H, Ar—H), 7.92 (1 H, Ar—H), 7.55 (1 H, Ar—H), 7.43 (1 H, Ar—H), 7.32 (1 H, Ar—H), 3.54 (2 H, N—CH_2), 3.50–2.88 (2 H, H_2O), 1.64 (4 H, N—C—CH_2—CH_2), 1.45–0.98 (24 H, CH_2), 0.86 (3 H, CH_3).

The complex, bis[*N*-hexadecyl-8-hydroxy-2-quinolinecarboxamide]lanthanum, La(HHQ)$_2$ as its chloride salt, was prepared by coordinating $LaCl_3 \cdot 7H_2O$ with HHQ in boiling methanol. After washing with hot methanol several times, the complex La(HHQ)$_2$ gave satisfactory analytical results (Elemental analysis. Found: C, 58.16; H, 8.20; N, 5.32. Calc. for $C_{52}H_{78}N_4O_4ClLa \cdot 4H_2O$: C, 58.39; H, 8.10; N, 5.24%). FTIR (KBr) ν/cm^{-1} 2927, 2853 (CH_2, CH_3), 1622 (C=O), 1598 (C=C), 1565 (C=N), 1499 (C=C), 1458, 1297, 1155 (Ar—H), 1106, 1040, 892 (H_2O), 851, 724 (CH_2), 486 (La—O). The content of lanthanum was determined by titration against EDTA after La(HHQ)$_2$ was dissolved in HNO_3. Found: 13.40, Calc.: 13.00%.

Apparatus

C, H, N analyses of HHQ and its complex were performed using a Perkin-Elmer Model 240C elemental analyser. ^1H NMR spectra were obtained using a Bruker Am-500 NMR spectrometer with tetramethylsilane as an internal reference. IR spectra were recorded on a Nicolet Model 170 SX FTIR spectrometer. Electronic spectra were measured with a Shimadzu Model 3100 UV–VIS–NIR recording spectrophotometer, and fluorescence spectra were measured with a Hitachi 850 spectrofluorophotometer. Low-angle X-ray diffraction results were recorded on a D/max-γA X-ray diffractometer (Japan), using Ni-filtered Cu-Kα radiation and a scanning rate of 2° min^{-1}. The divergence and scattering slit was set at 1° for $1° < 2\theta < 6°$.

Isotherm measurement and fabrication of LB films

The dilute [*ca.* 1×10^{-3} mol dm^{-3} for HHQ, 4×10^{-3} mol dm^{-3} for La(HHQ)$_2$] chloroform solution was applied dropwise to the clean subphase surface by syringe. Generally 15 min was allowed for chloroform evaporation, and the monolayer was then compressed by two movable Teflon barriers at a rate of *ca.* 2 Å^2 molecule^{-1} min^{-1}, and a surface pressure (π) *vs.* area per molecule (A) isotherm was recorded with a WM-1 Langmuir trough system, which is a fully computerized and programmable apparatus.

The monolayer was transferred onto a clean substrate after *ca.* 30 min of self-organization by lifting–dipping cycles of the substrate through the air–water interface at 3 mm min^{-1} at a surface pressure of around 30 mN m^{-1}. For deposition of LB films on a hydrophilic slide, the slide was first immersed in the subphase and the monolayer was then formed and compressed to a certain surface pressure. The speed of substrate movement for the first layer was kept at 1 mm min^{-1}. All work was carried out in a dust-free box at 25 °C.

Quartz slides for deposition of monolayers were cleaned by washing with dichloromethane, heating at 110 °C for 2 h in concentrated chromic acid, rinsing repeatedly in doubly distilled water from a quartz distiller, and soaking in 1×10^{-3} mol dm^{-3} NaOH solution for 5 min. The slides were then rinsed repeatedly with purified water and kept in the final rinse until used, yielding a hydrophilic surface. The surface of an ITO electrode (SnO_2 film-coated glass slides) was always hydrophilic and was used without further treatment except for repeated rinsing with purified water.

Results and Discussion

Confirmation of the structures of HHQ and La(HHQ)$_2$

In the IR spectrum of HHQ, some major bands at 1600, 1503, 1300, 1162, 1000 and 850 cm^{-1} are assigned to be the absorption of the quinoline ring and aromatic C—H bonds. An intense broad band at 3306 cm^{-1} is characteristic of OH groups. This band is bathochromically shifted by *ca.* 200 cm^{-1} compared with that of free phenolic OH group. This may be the result of intramolecular hydrogen bonding and/or hydrogen bonding by water molecules. In fact, elemental analysis also indicated the presence of a water molecule in HHQ. Since the absorption position (1650 cm^{-1}) of the aromatic amide group ($\nu_{C=O}$) is consistent with the literature value, characteristic of a free aromatic amide group, this water molecule promotes the formation of hydrogen bonding with the OH group in the C-8 position rather than with the amide group in the C-2 position of the quinoline ring.

In the ^1H NMR spectrum of HHQ, a weak peak at low field (δ 10.00), integrated for 0.15 protons, is ascribed to the proton of the OH group. Since the hydrogen in the OH group is very active, it can be easily dissociated and substituted by deuterium in $CDCl_3$ solution, which makes the absorption of this proton partially, sometimes entirely, unobserved. The integrated value of 0.15 protons indicated that six-sevenths of the OH group protons in HHQ were substituted by deuterium. A signal at δ 8.35 is assigned to the proton of the amide group (CONH) in the C-2 position. A very broad and low peak at δ *ca.* 2.88–3.50 integrated for two protons can be assigned to water, and it differs from usual proton peaks (very narrow and sharp). Five proton signals appearing at δ 8.00, 7.92, 7.55, 7.43 and 7.32 are ascribed to the protons of the quinoline ring. Since the proton at the C-7 position of the quinoline ring (H^7) is adjacent to the phenolic OH group, an electron-donating group, H^7 appears at high field (δ 7.32). In contrast, the alkylcarbamoyl substituent in the C-2 position shields the meta-proton (H^4) the most and the H^4 absorption appears at the lowest field. (For other assignments, see Experimental.) From the results above and the elemental analysis, the structure of HHQ can be confirmed as in Scheme 1.

Comparing the IR spectrum of the complex [La(HHQ)$_2$] with that of the ligand (HHQ), the ν(OH) band observed at 3306 cm^{-1} in the HHQ spectrum is absent from the spectrum of La(HHQ)$_2$, indicating the deprotonation of HHQ and coordination through the oxygen atom. The disappearance of the band at 650 cm^{-1}, due to the out-of-plane bending of OH, also supports this observation. It is well known that coordination *via* the lone pair of electrons of the pyridine nitrogen can shift the C=N vibration to higher frequency. The blue shift of the C=N vibration from 1550 cm^{-1} (in HHQ) to 1565 cm^{-1} [in La(HHQ)$_2$] may be due to the participation of the ring nitrogen atom in bonding. A new peak at 486 cm^{-1} may be assigned to the vibration absorption of the La—O bond. Strong evidence for water coordination is given by the appearance of a broad band at 892 cm^{-1} due to the rocking vibration of H_2O.

Surface pressure–molecular area isotherm

Fig. 1 shows the surface pressure–area (π–A) isotherms of an HHQ monolayer on pure water and on an aqueous subphase containing La^{3+}. The isotherm of HHQ on pure water has expanded, plateau and condensed regions at different surface pressures and is more expanded than that on an aqueous subphase containing metal ions at low surface pressure. By extrapolating the surface pressure to zero for the expanded region, a limiting area of *ca.* 62 Å^2 per molecule is obtained which is in good agreement with the cross-section of 8-hydroxyquinoline approximated by a rectangular block with dimensions of $8.4 \times 7.4 \times 3.6$ Å^3 according to a space-filling molecular (CPK) model. However, with an increase of surface pressure an area per molecule of 26 Å^2 is obtained in the condensed region, this value is nearly consistent with the stacking of quinolinol ring of HHQ perpendicular to the water surface (8.4×3.6 Å^2). This suggests that the molecular planes

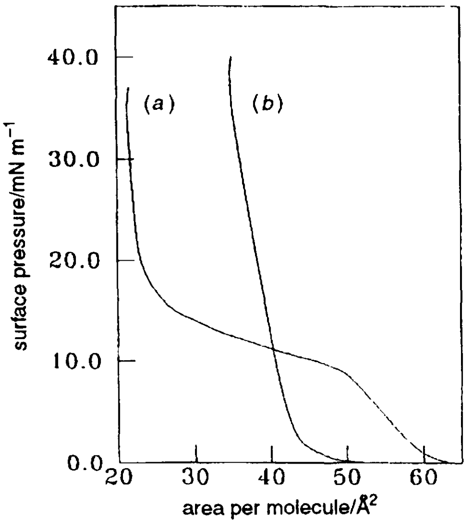


Fig. 1 π–A isotherms of HHQ on (*a*) pure water, and (*b*) a subphase containing 10^{-3} mol dm^{-3} LaCl$_3$

of HHQ lie almost flat on the surface at low surface pressures, and the orientation of the quinolinol ring of HHQ in the monolayer changes from a 'flat' to an 'edge-on' structure upon compression.

When La^{3+} ions were added to the subphase, the characteristics of the HHQ monolayer were changed remarkably. The limiting area per molecule on the La^{3+}-containing subphase is 50 Å^2 at a surface pressure of 30 mN m^{-1} (A_{30}). It is shown that La^{3+} ion was able to modify the construction of the HHQ film greatly, and the orientation of HHQ in the monolayer was different and the isotherm of La(HHQ)$_2$ on a water surface was significantly different from that of HHQ. Fig. 2 gives a typical π–A curve of this complex with a high collapse surface pressure of *ca.* 50 mN m^{-1}, indicating that La(HHQ)$_2$ can form a stable and dense monolayer at the air–water interface. As a result of the change of the molecular packing, the isotherm consists of two segments, (*a*) and (*b*), and two limiting areas, 125 and 70 Å^2 per La(HHQ)$_2$ molecule, can be obtained by extrapolating (*a*) and (*b*) to zero surface pressure. Since the 'face' area and 'side-on' area of 8-hydroxyquinoline are about 62 and 30 Å^2, respectively (approximated by the CPK model) we can deduce that there are three orientation modes of La(HHQ)$_2$ in the monolayer. Fig. 3 shows a schematic diagram of the proposed orientations of the HHQ chromophores. Mode I is a preferable mode since it is in a minimum energy state, the two long alkyl chains of La(HHQ)$_2$ extend fully and separately from both edges of the 8-hydroxyquinoline rings of the La(HHQ)$_2$ molecule. In contrast with mode I, mode II is in a higher energy state and is unstable. In modes I and II, the expected areas of the La(HHQ)$_2$ molecule are *ca.* 125 and 60 Å^2, respectively. The former is in good agreement with the area (125 Å^2) obtained from segment (*a*) of the π–A isotherm in Fig. 2, but the latter is smaller than the area (70 Å^2) obtained from segment (*b*). This suggests that the La(HHQ)$_2$ molecules in the monolayer orient in according to mode I at lower surface pressure (<14 mN m^{-1}), and they change from mode I to mode III upon further compression. Actually, when an La^{3+} ion coordinates with the N and O atoms of HHQ, the atomic orbitals of lanthanum are blended together to give hybrid orbitals. The spatial orientation requirements of the hybrid orbitals and the steric hindrance of the long alkyl chain in the C-2 position of the quinoline ring make the La(HHQ)$_2$ monolayer orient according to mode III.

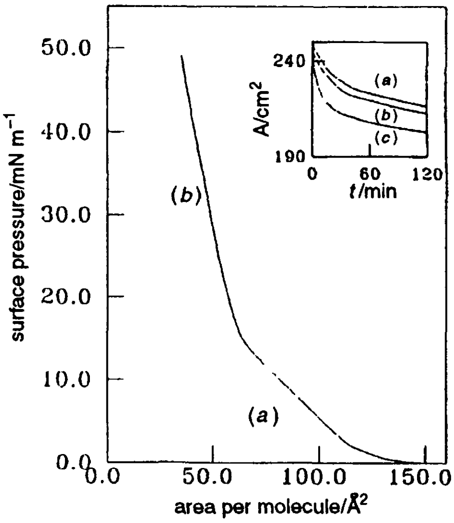


Fig. 2 π–A isotherm of La(HHQ)$_2$ at an air/water interface. The inset shows the decay of area with time of for (*a*) an La(HHQ)$_2$ monolayer; and HHQ monolayer with (*b*) and without (c) La ions in the subphase. The surface pressure is held at 30 mN m^{-1}.

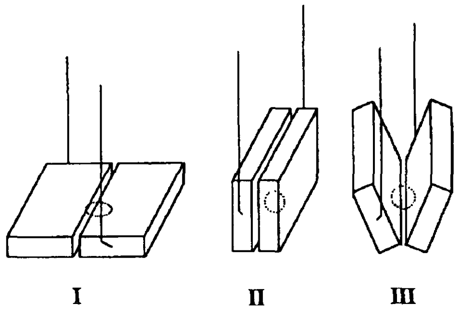


Fig. 3 Stacking modes of La(HHQ)$_2$ in a monolayer. The rectangular blocks represent the ligand HHQ, the metal ions are inserted in the middle below the blocks.

UV–VIS spectra

Since strong molecular area relaxations were observed at constant surface pressure (*cf.* the inset in Fig. 2), which are most probably due to the steepness of the isotherms, the deposition of monolayers onto substrates was carried out after *ca.* 30 min of self-organization. Fig. 4 shows the UV–VIS spectra of the LB film, cast film (made by evaporating the dilute La(HHQ)$_2$–acetonitrile solution slowly on a quartz glass) and of La(HHQ)$_2$ in chloroform. Compared with that of the ligand HHQ (Table 1), that of the ^1L_a band[10] of

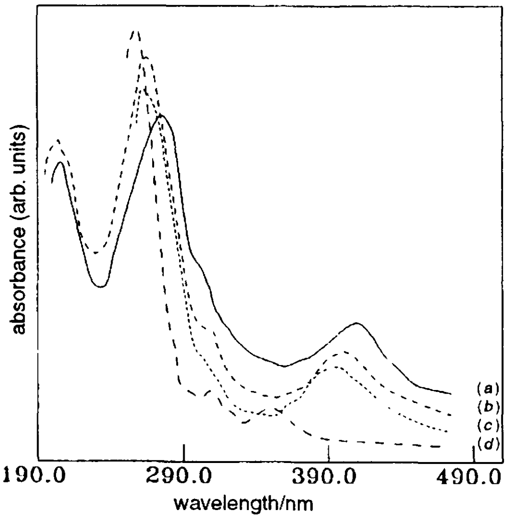


Fig. 4 UV–VIS absorption spectra of La(HHQ)$_2$ as (*a*) LB film, (*b*) cast film, (*c*) in chloroform solution and (*d*) that of HHQ in chloroform

Table 1 Absorption spectra (nm) of HHQ and La(HHQ)$_2$

	HHQ				La(HHQ)$_2$			
	^1L_a	^1L_b	^1B_b	n–σ*	^1L_a	^1L_b	^1B_b	n–σ*
chloroform	350	308	256		398	310	262	
cast film	356	307	261	200	400	310	262	202
LB film	370	320	260	200	410	310	274	205

La(HHQ)$_2$ in chloroform is bathochromically shifted from 350 to 398 nm, and that of the ^1B_b band is also bathochromically shifted from 256 to 262 nm These red shifts were attributed to a larger resonating path of electrons in the complex than in the ligand itself[11] However, the ^1L_b band of the ligand became weaker in the complex Similarly, compared with the absorption of the La(HHQ)$_2$ solution, cast film and LB film [curves (*a*), (*b*), (*c*) respectively in Fig 4], red shifts of *ca* 12 nm at the ^1L_a (from 398 to 410 nm) and ^1B_b (from 262 to 274 nm) bands were observed, which indicated a strong interaction between the molecules of the LB film

Fluorescence spectra

In general, under normal conditions, 8-hydroxyquinoline exhibits no fluorescence, while many of its metal chelates, such as the chelates of Cu, Ni, Co and Fe, do [12] [13] However, La(HHQ)$_2$ exhibits intense fluorescence Fig 5 shows the fluorescence emission spectra of La(HHQ)$_2$ in chloroform solution, cast film and LB film The fluorescence peak for La(HHQ)$_2$ in $CHCl_3$ (520 nm) was shifted to 524 nm in the cast film and to 540 nm in the LB film This red shift is in agreement with that obtained from UV–VIS spectra As we know, J-aggregates are characterized by an intense narrow absorption band with a bathochromic shift relative to the monomeric band,[14] hence, the red-shifted intense absorption of La(HHQ)$_2$ in LB films may be attributed to tilted chromophore orientation, and a strong interaction between La(HHQ)$_2$ molecules in the LB films[15] and J-aggregates are proposed for La(HHQ)$_2$ in LB films

Obvious fluorescence emissions, even with only one layer of La(HHQ)$_2$, could be detected One of the probable reasons for the strong fluorescence is that microcrystals of this complex are generated at the substrate–film interface Plotting the fluorescence intensity *vs* the number of layers (1–29) deposited, we obtain a linear relationship through the origin, which implies that the monolayer of La(HHQ)$_2$ at the air–water interface is uniform, the monolayer deposition is reproducible and the films have vertical homogeneity

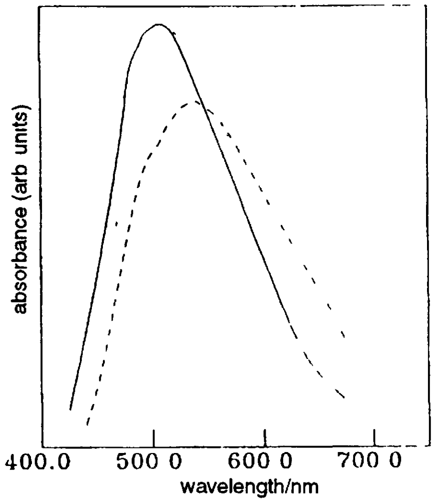


Fig. 5 Emission spectra of La(HHQ)$_2$ in solution (—), as a cast film ( ) and an LB film (--)

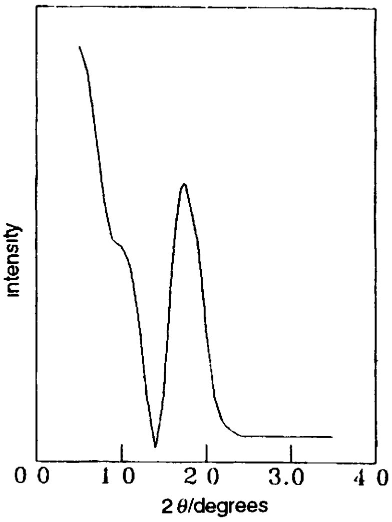


Fig. 6 X-Ray diffraction pattern of a 21-layer LB film of La(HHQ)$_2$ built up at 30 mN m ^{1}

Low-angle X-ray diffraction

Recently it was demonstrated that LB films of most amphiphiles maintain the bilayer characteristic Low-angle X-ray diffraction can be used to obtain useful structural information about the LB films[16] Fig 6 shows some low-angle X-ray diffraction profiles of a 21-layer LB film of La(HHQ)$_2$, only one broad Bragg peak ($2\theta = 1$ 749°) is observed The derived bilayer spacing is 50 5 Å, which is near the double thickness of the long side chain,[17] indicating Y-type bilayer formation during the La(HHQ)$_2$ deposition process Since the estimated thicknesses of a monolayer of La(HHQ)$_2$ (according to the CPK model) are 23 0 Å and 25 5 Å in modes I and II respectively in Fig 3, the former is smaller than the single-layer thickness (25 25 Å) derived from the bilayer spacing, while the latter is larger than this derived value, so we can deduce that the orientation of the La(HHQ)$_2$ molecules in LB films is mode III in Fig 3, *i e* the long alkyl chains of La(HHQ)$_2$ orient perpendicularly to the subphase surface, while the head-group fragments (quinolinol rings) are tilted at an angle with respect to the normal to the interface This result is in agreement with that deduced from the molecular limiting area of La(HHQ)$_2$

Conductivity

In recent years, the interest in electroactive LB films exhibiting specific electronic functions such as electrical conduction and redox activity has increased considerably Conductive LB films have been studied extensively [18] [20] Characterized as one-dimensional systems, these conductive films are sensitive to defects and disorders The conductivity of LB films of La(HHQ)$_2$ on a quartz substrate has been determined by a four-probe method,[21] using silver paste electrodes which were formed on the film surface with a length of 1 cm and a gap width of 0 5 cm A small current from a constant current source was passed through the outer two probes and the voltage was measured between the inner two probes The conductivity along the stacking direction of La(HHQ)$_2$ molecules ($\sigma_{\parallel}$) is defined in terms of a measured resistance ($R_{\parallel}$) and a cross-sectional area of film (*A*)[22] Usually, the conductivity is increased dramatically in the film state The molecules of the film are arranged in close spatial proximity and in similar crystallographic and electronic environments Although the resistances of 21- and 29-layer LB films of La(HHQ)$_2$ are different ($3\,0 \times 10^{11}$ and $2\,1 \times 10^{11}$ Ω, respectively), the calculated $\sigma_{\parallel}$ values of both LB films are same [($3\,85 \pm 0\,10) \times 10^{-5}$ S m ^{1}], which further implies the vertical homogeneity of the $La(HHQ)_2$ LB film.

In conclusion the characterization of $La(HHQ)_2$ films described above show that fairly stable uniform LB films are fabricated and they have good fluorescence and conductivity properties, which may be used in organic electroluminescent devices in the future.

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