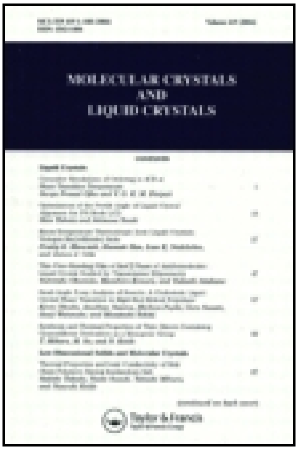

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Langmuir-Blodgett Films of Alkyl-Substituted Quinhydrone

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LANGMUIR-BLODGETT FILMS OF ALKYL-SUBSTITUTED QUINHYDRONE

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Abstract

The charge transfer (CT) properties were examined in the mixed and the alternate-layer Langmuir-Blodgett (LB) films of 2-methyl-5-octadecyl-1,4-dihydroxybenzene ($C_{18}HQ$) and 2-methyl-5-octadecyl-1,4-benzoquinone ($C_{18}Q$). Intermolecular CT took place in both types of LB films. The CT band between $C_{18}HQ$ and $C_{18}Q$ appeared at 590 nm suggested the neutral CT state as in the case of unsubstituted quinhydrone. The direction of CT was examined by the polarized spectra. The CT state was accompanied by hydrogen bonding, which was confirmed by the hydrogen bonded and non-hydrogen bonded C=O stretching bands appeared in the IR spectra.

INTRODUCTION

The control of intermolecular charge transfer (CT) interactions in the ordered thin films is one of the important steps to be accomplished towards the molecular level electronic and photonic devices exploiting organic CT complexes. Langmuir-Blodgett (LB) technique provides a molecular manipulation method at the nano-meter dimension and is widely used for constructing functional organic thin films.[1] Number of CT-complex LB films have been reported too, which are mainly fabricated from semi-amphiphilic molecules composed of an amphiphilic donor or an amphiphilic acceptor complexes with an unsubstituted counterpart.[2]

There are ideally two components which characterize the intermolecular CT interactions, that is, the direction of CT and its strength (or the degree of CT). Hence both of the components intimately relate with the functions emerging from films, a sophisticated technique will be needed to control each component of CT interactions in the LB films. One possible solution is to use the donors and acceptors with amphiphilic character, each of which can be incorporated at the desired sites of an LB multilayer, provided that each donor or acceptor forms a stable monolayer at the air-water interface and is transferred to the solid substrates by subsequent deposition process.[3-5]

Quinhydrone derivatives have been attracting much interest in recent years from the view point of cooperative proton-electron transfer phenomena arising from the CT state accompanied by hydrogen bonding.[6] In this paper, we will describe the mixed and the alternate-layer LB films of an alkyl substituted quinhydrone as a model system for the control of intermolecular CT interactions in the ordered thin films.[7]

EXPERIMENTAL

We synthesized 2-methyl-5-octadecyl-1,4-dihydroxybenzene ($C_{18}HQ$) and 2-methyl-5-octadecyl-1,4-benzoquinone ($C_{18}Q$) from 2-methyl-5-octadecyl-1,4-dimethoxybenzene. Mixed LB films were deposited with cadmium arachidate as a matrix. Each compound was dissolved in benzene at the concentration of 1×10^{-3} M and was mixed before spreading on a water surface containing 4×10^{-4} M $CdCl_2$ and buffered with $KHCO_3$. A mixing ratio of donor : acceptor : arachidic acid = 1 : 1 : 2 was adopted. The films were deposited in Y-type manner. The donor or the acceptor was mixed 1:1 with arachidic acid to form alternate-layer LB films. The $C_{18}HQ$ containing layer was first transferred (downward stroke) followed by $C_{18}Q$ containing layer (upward stroke).

RESULTS AND DISCUSSION

Figure 1 shows the UV-visible spectra of 16-layer mixed and alternate-layer LB films of $C_{18}HQ$ and $C_{18}Q$. The absorption bands observed at around 260 and 590 nm are the local excitation band of the quinone moiety and the intermolecular CT band, respectively. The position of the latter band is almost the same as that of the unsubstituted quinhydrone (600 nm), indicating that the HOMO-LUMO gap is not affected by the alkyl substitution and that the CT ratio should be around 0.2-0.3 in the amphiphilic quinhydrone as in the case of unsubstituted one in the crystalline form, provided the similar magnitude of Madelung energy between the crystal and the LB film.[8]

The CT band already appeared in the bilayer films and increased linearly with the layer number. The peak position did not change significantly with an increase in the number of layers or with the deposition manner (mixed or alternate-layer). On the other hand, the local excitation band of the quinone moiety appeared at 254 and 268 nm in the mixed and alternate-layer LB films, respectively. The band appeared almost the same position in the mixed LB films as that in solution and showed a red-shift in the alternate-layer LB films. These results suggest that the molecules form J-like aggregates in the alternate-layer LB films.

The direction of CT interactions can be estimated conveniently from the polarized spectra in the visible region. Should the transition dipole distributes in the film plane, the intensity of the peak become large at the light-incidence angle of 45° compared with the normal incidence by using s-polarized light (the electric vector is perpendicular to the plane of incidence). The CT band of the alternate-layer LB films showed a strong dichroism, indicating that the direction of CT is relatively parallel to the film plane. These phenomena are quite reasonable in the mixed LB films in which the donors and acceptors locate in the same layer. The CT direction in the alternate-layer LB films showed a tendency to align in the film plane, too. The CT interaction is supposed to be interlayer, or perpendicular to the film surface, in the case of the alternate-layer LB films, however. The results can be explained by assuming the interdigitated structure of the head groups at the layer interface in the alternate-layer LB film.

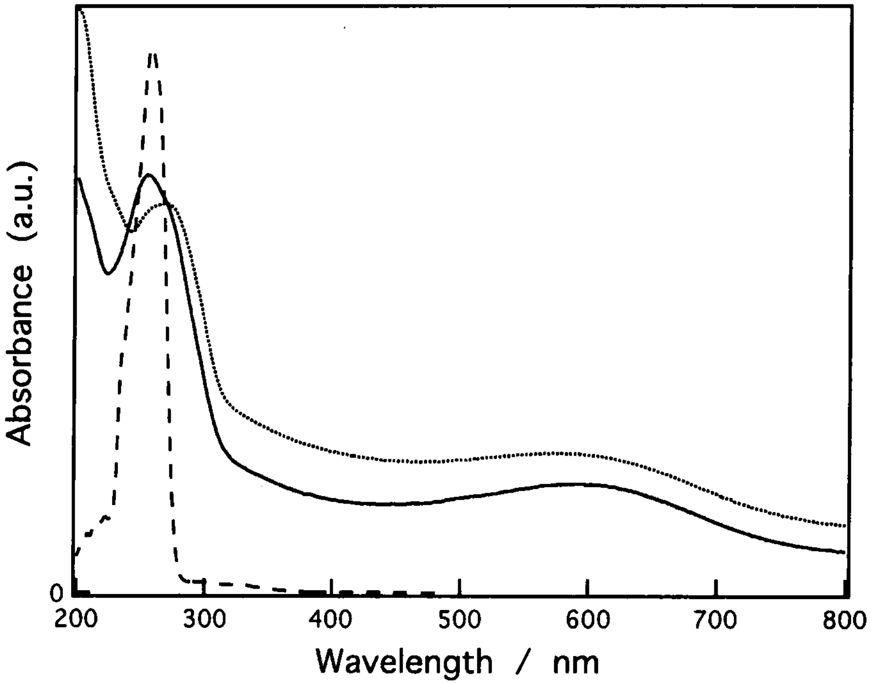

FIGURE 1. UV-visible spectra of 16-layer sample of the mixed (solid line) and the alternate-layer (dotted line) LB films of $C_{18}HQ$ and $C_{18}Q$, in addition to the spectrum of $C_{18}Q$ in chloroform solution (dashed line).

Hence the CT in quinhydrones is coupled with hydrogen bonding between the quinone and hydroquinone moiety, CT interactions can be examined from the hydrogen bonding character of each film. In IR spectra, two peaks at 1628 and 1657 cm^{-1} appeared, which may be assigned to the hydrogen bonded and non-hydrogen bonded

C=O stretching bands, respectively.[9] The intensity of the former peak was weak in the alternate-layer LB film, suggesting that a relatively large amount of free quinones exist in the film. In other words, the intermolecular CT is not complete in the alternate-layer LB film.

CONCLUSION

We have demonstrated the intermolecular CT phenomena which take place either intra- or interlayer in the LB films. From the application point of view, CT complexes in the interleaved LB films have a noncentrosymmetric structure which is favourable for the second harmonic generation (SHG). For this purpose, the sufficient interlayer CT interactions are essential. To accomplish the interlayer CT in the alternate-layer LB films, further investigations will be needed, eg. on the heat-treatment effects. The degree of CT is an important factor determining the magnitude of SHG effect too, which could be controlled by changing the donor- or acceptor-ability of each molecule forming interleaved LB films. Studies on this line are now in progress.

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