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A series of donors and acceptors are synthesized and, by combing these molecules, Langmuir-Blodgett (LB) films of the charge transfer (CT) complexes are prepared. Ionic CT complexes with partial CT state exhibit high conductivity in the form of LB films. The second nonlinear optical properties of the films are examined using electro-apsorption method.

Keywords: Langmuir-Blodgett technique; electrical conductivity; second nonlinear optical property; electro-apsorption spectroscopy

INTRODUCTION

The charge transfer interaction between donor (D) and acceptor (A) molecules is described by the resonance between the neutral (D•A) and ionic ($D^+ \bullet A^-$) state of the D-A pair[1],

$$\psi \cong a\varphi(D \bullet A) + b\varphi(D^+ \bullet A^-) \qquad (1)$$

In ordinary molecular pairs, the coefficient b in ground state is relatively small and the contribution from charge-transferred structure is negligible, accordingly. However, when the ionization potential (Ip) of a D molecule is small and the electron affinity (EA) of an A molecule is large, the $D^+ \bullet A^-$ structure become predominant even in the ground state. The charge transfer (CT) complexes thus obtained have potentials for the application of the future electronic and

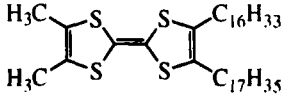
photonic devices[2]. In this paper, we will describe the Langmuir-Blodgett (LB) films of CT complexes, the degree of CT (δ) of which are controlled. The films show intriguing electrical and nonlinear optical properties.

RESULTS AND DISCUSSION

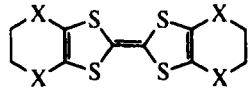
Degree of Charge Transfer

The difference between the Ip of D and the EA of A molecule is one of the main factors for determining δ from D to A molecule. The difference can be estimated conveniently from the difference between the first half wave oxidation ($E^{1}_{1/2}$(D)) and the reduction ($E^{1}_{1/2}$(A)) potentials, ΔE (= $E^{1}_{1/2}$(D) - $E^{1}_{1/2}$(A))[3]. The ionic partial charge transferred state, which is one of the necessary condition for high electrical conductivity of the CT-complex solids, is usually achieved when -0.02 $\leq \Delta E \leq$ 0.34 V

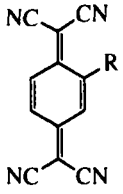
We have synthesized several D and A molecules with different $E^{1}_{1/2}$(D) or ($E^{1}_{1/2}$(A) (Scheme 1). By combing these molecules, we could obtain a variety of CT complexes which are summarized in Table 1 together with the composition, the CN or CO stretching-band position of A molecule and the charge on each molecule determined from IR and UV-vis spectra.



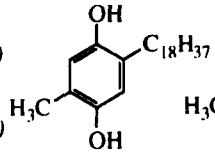
$C_{17}C_{16}$DMTTF



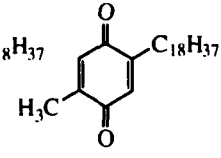
X=CH_2 *(OMTTF)*
=O *(BEDO-TTF)*



R=$C_{10}H_{21}$ *(C_{10}TCNQ)*
=$C_{14}H_{29}$ *(C_{10}TCNQ)*
=$C_{18}H_{37}$ *(C_{18}TCNQ)*
=CF_3 *(CF_3TCNQ)*



C_{18}HQ



C_{18}Q

SCHEME 1. Molecules used in this study

TABLE 1. CT complexes forming LB films

	Composition	$\nu_{CN}(\nu_{CO})$ / cm^{-1}	Charge on D	Charge on A
a	$(BEDOTTF)_{0.4}$ $(C_{10}TCNQ)$	2179	+0.4	-1
b	$(BEDOTTF)_{0.5}$ (CF_3TCNQ)	2188	+0.5	-1
c	(OMTTF) $(C_{10}TCNQ)$	2214	+0.2	-0.2
d	(OMTTF) $(C_{14}TCNQ)$	2214	+0.2	-0.2
e	(OMTTF) $(C_{18}TCNQ)$	2214	+0.2	-0.2
f	$C_{16}C_{17}DMTTF - C_{18}TCNQ$	2179	+1	-1
g	$C_{16}C_{17}DMTTF - C_{18}Q$	1700	~0	~0
h	$(C_{18}HQ)$ $(C_{18}Q)$	1657	+ 0.2	- 0.2

Electrical Properties

The LB films were prepared using the horizontal lifting method. We have already reported the high conductivity in LB films of **a**[4]. The LB film of **b** is also promising due to the ionic partial CT state of BEDO-TTF. We have found that the LB films of **b** mixed 2:1 with arachidic acid exhibit a conductivity of 3.7 S/cm at room temperature[5]. On the other hand, the complexes **c** - **e** are in the neutral CT states. The LB films should consist of mixed stacks of D and A molecules and the conductivity of these films is expected to be low, accordingly[6]. The fully CT state in the LB films of **f** leads to an insulating behaviour due to the large electron correlation (on-site Coulomb repulsion energy is larger than band-width)[7].

Nonlinear Optical Properties

Since we fabricated the LB films by the horizontal lifting method, the films have a non-centrosymmetric structure and hence have a second nonlinear optical activity. The second order molecular hyperpolarizability is related to the δ as,

$$\beta^{(2)} \propto \Delta\mu_{gr} f_{gr} \propto e^3 d^3 \delta(1-\delta)|2\delta - 1| \qquad (2)$$

where d is the average distance between D and A, $\Delta\mu_{ge}$ is the difference of the permanent dipole moment of the grand and excited state, and f_{ge} is the transition oscillator strength[8].

We evaluated the second nonlinear susceptibility $\chi^{(2)}(-\omega;\omega,0)$ by electro-apsorption spectroscopy. The modulation signal $\Delta\alpha$ is converted to the nonlinear susceptibility as,

$$I_m\chi^{(2)}(-\omega;\omega,0) = \frac{\lambda}{2\pi}\frac{1}{E}(n\Delta\alpha / l) \qquad (3)$$

where l is the film thickness. The second nonlinear susceptibility was 0.5 and 0.7 pmV^{-1} for the LB films of **a** and **c**, respectively. Quantitative analysis of the relationship between δ and $\chi^{(2)}$ is now in progress.

Acknowledgments

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