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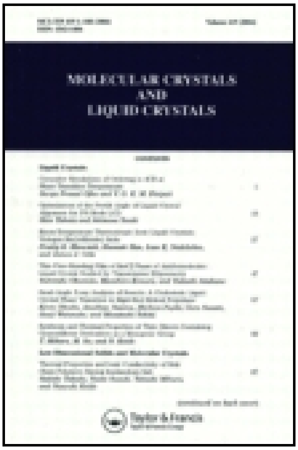

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The ESR Study on Langmuir-Blodgett Films Layered with Ammontum-TCNQ Anion Radical Salts

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THE ESR STUDY ON LANGMUIR-BLODGETT FILMS LAYERED WITH AMMONIUM-TCNQ ANION RADICAL SALTS

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Abstract Ammonium TCNQ anion radicals are formed with a TCNQ anion radical and an ammonium halide. Octadecylviologen-$(TCNQ)_2$ shows a very interesting UV-visible spectrum in chloroform-acetonitrile mixture and in Langmuir-Blodgett films. The ESR characteristics of the N-docosylquinolinium-TCNQ films and octadecylviologen-$(TCNQ)_2$ powder and films were studied to understand conducting mechanism and structure of LB films. The ESR spectra infer that the N-docosylquinolinium-TCNQ LB films exhibit anisotropic property. In other words, the LB films show angular dependence. Rotating the LB films around magnetic field results in a minimum band width at an angle close to the magic angle 54°. This results was due to the dipole-dipole interaction. The ESR spectra of octadecylviologen-$(TCNQ)_2$ powders exhibit a narrow line at g=2 together with symmetrical structure of a triplet state arising from a dimeric species. genetic species. The LB films and powder do not show angular dependence. In the course of temperature increase from 350 to 450K, the ESR signal of LB films becomes sharp. But powder octadecylviologen-$(TCNQ^-)_2$ does not have angular dependence.

INTRODUCTION

Conducting organic films are proven to be very difficult to make. The first successful example was the N-docosylpyridinium-TCNQ LB films doped with iodine vapor. This process gives rise to a ternary conducting compound located in the polar plane of the LB assembly. The conductivity of this phase has been found to be about 10^{-1} S/cm, from dc as well as microwave measurements.[3] Nakamura *et al.* and Barraud *et al.* published other kinds of conducting LB films involving TCNQ.[4-7] IR spectrum provides information about room temperature conductivity of films. The conductivity estimated from IR spectrum was 20-50 S/cm.[6,7] However, DC measurements generate values at least ten times lower than the estimated one. The behavior is attributed to polycrystalline nature, especially cracks, of the film. We have been investigated electrical conductivity of quinolinium-TCNQ$^-$ LB film, which clearly show insulating behavior.[8,9]

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Octadecylviologen-$(TCNQ^{-})_2$ was synthesized and investigated.[10] Viologen-$(TCNQ^{-})_2$ naturally generated $TCNQ^{-}$ dimers, due to the dicationic nature of viologen. Electron transfer from TCNQ anion radical to viologen moiety can generate a quaternary conducting layer. The viologen cation radical generated by an electron transfer can also be able to generate conducting layer($TCNQ^{-}$, $TCNQ^{0}$, viologen, viologen cation radical). The molecular orientations and temperature characteristics of viologen-$(TCNQ^{-})_2$ were investigated from the UV- visible and ESR spectra.

EXPERIMENTALS

The water used as a subphase was purified with distillation followed by deionization with Elgastat Spectrum C^{TM}. The resistivity of the purified water was higher than 18MΩ-cm. The quinolinium-$TCNQ^{-}$ LB films were deposited using the moving wall type deposition apparatus(NL-LB-240S-MWA) and the quinolinium-$TCNQ^{-}$ dissolved in $CHCl_3$ (10^{-3}mol/l) was spread on the water subphase. The surface pressure for the LB film deposition of quinolinium-$TCNQ^{-}$ was 30mN/m. The UV-visible absorption spectra of quinolinium-$TCNQ^{-}$ were obtained from the diode array type spectrophotometer (Hewlett-Packard, HP8452A). Synthesis of octadecylviologen-$(TCNQ^{-})_2$,was describing in elsewhere.[9] The OV-$(TCNQ^{-})_2$ turned green by addition of strong base, such as NaOH. The green color is characteristic color for viologen cation radical, which is generated by reduction of viologen dication. Y-type LB film was layered with KSV-3000 trough. The barrier was compressed from 300Å^2/molecule on water subphase at 15°C. At the surface pressure of 25mN/m, the lifting speed of substrate was 5mm/min. and submerging speed was 10mm/min. Aluminum layer was deposited up to 100Å thickness by vacuum evaporation method at 10^{-5} torr. The glass substrate was cleaned with sulfuric acid and potassium dichromate solution for more than 12 hours, and washed many times with clean water. UV-visible-near IR spectra of OV-$(TCNQ^{-})_2$ was obtained from Shimadzu(U/V-3103PC). ESR spectra was obtained from Brucker ESR spectrometer(EST300S). The powder sample was prepared in the cell, and LB film sample was cut to fit in the probe. The angle was set by a goniometer, which can rotate external magnet of spectrometer.

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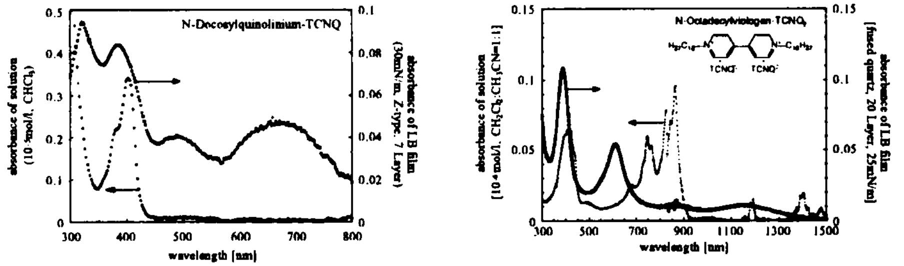
RESULTS AND DISCUSSION

The UV-visible absorption spectra of LB films obtained from OV-$(TCNQ^-)_2$ and quinolinium-$TCNQ^-$ at normal incidence are shown in FIGURE 1.



a) Quinolinium-$TCNQ^-$ b) Octadecylviologen-$(TCNQ^-)_2$

FIGURE 1 UV-vis. spectrum of quinolinium-$TCNQ^-$, (a) and octadecylviologen-$(TCNQ^-)_2$, (b).

The striking difference in between these spectra is that the $TCNQ^0$ and DCTC which is hydrolyzed product of $TCNQ^-$ with water are not observed in OV-$(TCNQ^-)_2$ film. The OV-$(TCNQ^-)_2$ shows fairly distinct localized excitation in $(TCNQ^-)_2$ dimers, and does not exhibit monomeric absorption of $TCNQ^-$, which is distinct feature observed in quinolinium-TCNQ and pyridinium-$TCNQ^-$ spectra. The very weak and broad band beyond 900nm is classically attributed charge transfer (CT) interactions in the $(TCNQ^-)_2$ dimers. The band is generally labeled as Torrances B band. Since the CT interaction is not discrete, the maximum transition energy varies from compound to compound. It is interesting that the dimer absorption maximum is fairly shifted to blue wavelength, 600 nm and the band is sharper than quinolinium-$TCNQ^-$ LB films. The sharp peak indicates that the aggregates is more regular and structured. The hypsochromic shift resulted from the H-aggregation of TCNQ.

The ESR spectra clearly exhibit a narrow line at g=2. The symmetrical structure indicates a triplet state arising from a dimeric species. Both quinolinium-$TCNQ^-$ and OV-$(TCNQ^-)_2$ LB films contain dimeric species. To investigate the molecular orientation of dimeric species, the spectra are recorded for different orientations of the sample in the magnet, corresponding to different values of the angle between the normal to the film and the permanent magnetic field. The spectra obtained from the quinolinium-$TCNQ^-$ LB film depend strongly on the orientation of the sample in the magnet field. This behavior evidences a high order of organization.

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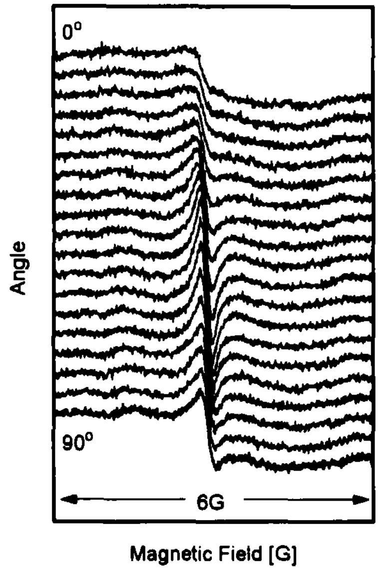

FIGURE 2 Angular dependence of quinolinium-TCNQ$^-$ LB film.

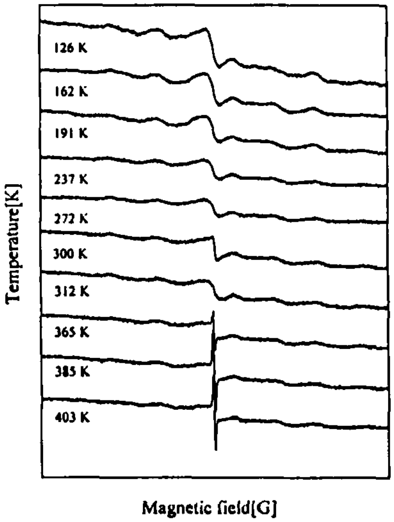

FIGURE 3 Temperature dependence of octadecylviologen-(TCNQ$^-$)$_2$ LB film.

However, the spectra of OV-(TCNQ$^-$)$_2$ LB film and powder sample do not show angular dependence. Since the viologen moiety and (TCNQ$^-$) dimers are too big to be packed nicely on the water surface, OV-(TCNQ$^-$)$_2$ LB film are rather randomly oriented. The spin resonance half-amplitude linewidth $\Delta H_{1/2}$ has a minimum around

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54o.(FIGURE 5.) The minimum band width are due to the dipole-dipole interaction. The value is slightly than pyridinium-TCNQ$^-$, which has a minimum around 50o.[11]

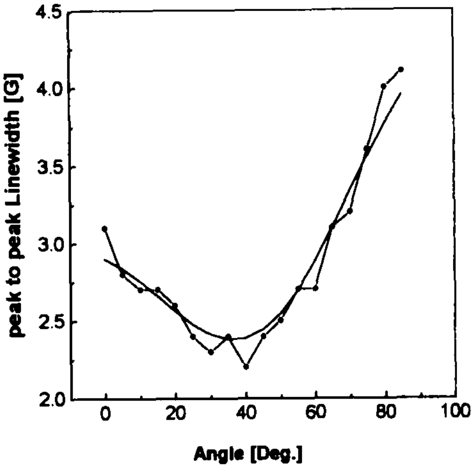

FIGURE 4 Angular dependence of ESR linewidth of quinolinium-TCNQ$^-$ LB film.

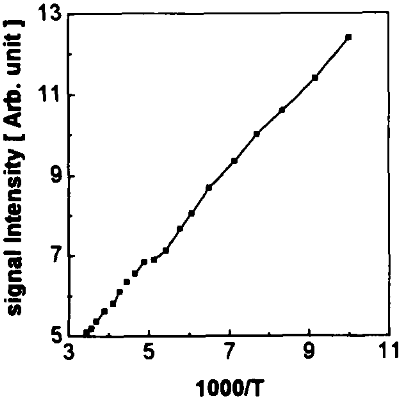

FIGURE 5 ESR signal intensity of quinolinium-TCNQ$^-$ LB film as a function of 1000/T.

The peak-to-peak linewidth decreases linearly as the temperature increase from 100K to 298K, for quinolinium-TCNQ$^-$. Interesting feature of ESR spectra of OV-(TCNQ$^-$)$_2$ as a function of temperature is a different type of ESR signal appeared at above 365K. The new ESR signal may be due to viologen cation radicals, which can be generated by electron transfer from TCNQ anion radicals to viologen moiety at the elevated temperature. We are trying to investigate the new chemical species generated at the elevated temperature by UV-visible and IR spectroscopy. Finally, double integration of ESR signal demonstrated that the spin susceptibility was roughly proportional to T^{-1}. This clearly corresponds to isolated paramagnetic species.(FIGURE 6)

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