CHEMISTRY LETTERS, pp. 1715-1718, 1987.

ESR Study on the Regularity of the LB Films of Amphiphilic TCNQ Salts

Shigeru FUJITA, Kosaku SUGA,* Masamichi FUJIHIRA,*
Takayoshi NAKAMURA,† and Yasujiro KAWABATA†
Department of Chemical Engineering, Faculty of Engineering,
Tokyo Institute of Technology, Meguro-ku, Tokyo 152
†National Chemical Laboratory for Industry, Yatabe, Ibaraki 305

The ESR spectra of the LB films of N-docosyl- and N-octadecylpyridinium-$(TCNQ)_n$ (n=1,2) deposited on glass capillaries or glass slides were measured. The intensity of the ESR spectrum increased markedly with the number of layers. From this and other results, it was suggested that the ordering of the LB film was enhanced by cumulation of monolayers. The ESR spectrum of the LB film deposited on a glass slide showed marked dependence on the orientation of the film in the static magnetic field.

Recently, much attentions have been directed to functional Langmuir-Blodgett (LB) films, because of their feasibility of constructing micro-electronic devices. It is a current subject to find the characterization methods of microscopic structures of functional LB films. ESR specroscopy is expected to be a powerful tool for this purpose, since it offers informations concerning the electronic states, the dynamic properties, and the conformational structures of paramagnetic samples. Furthermore, it has a high sensitivity, which is indispensable to the characterization of LB films.

Since the first synthesis of tetracyanoquinodimethane (TCNQ), a number of investigations concerning the electric[1] and magnetic[2] properties of quasi-one-dimensional organic conductors consisting of TCNQ have been reported. Recently, conducting LB films of amphiphilic TCNQ salts were prepared, and their electric and magnetic properties were investigated.[3-5,9]

In this letter, we will report the ESR spectra of the LB films of amphiphilic TCNQ salts, and discuss the conformational and electronic structures of these LB films.

N-Octadecylpyridinium tetracyanoquinodimethane (TCNQ) salt (C_{18}Py-TCNQ), N-docosylpyridinium TCNQ salt (C_{22}Py-TCNQ), N-octadecylpyridinium $(TCNQ)_2$ salt (C_{18}Py-$(TCNQ)_2$), and N-docosylpyridinium $(TCNQ)_2$ salt (C_{22}Py-$(TCNQ)_2$) were synthesized by the method cited in the literature.[6] Samples of LB films of these salts for ESR measurements were prepared by transferring monolayer of these amphiphiles onto glass capillaries with 1.5 mm diameter or glass slides with 0.5 mm thickness. Two LB troughs from Kyowa Interface Science Co. were used in this experiments.

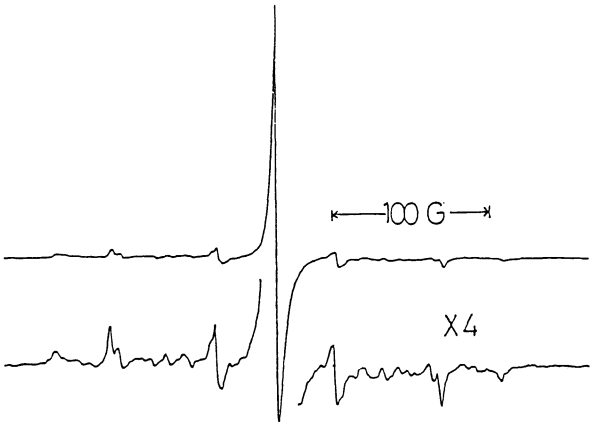

Fig. 1. ESR spectrum of the powder sample of C_{18}Py-TCNQ.

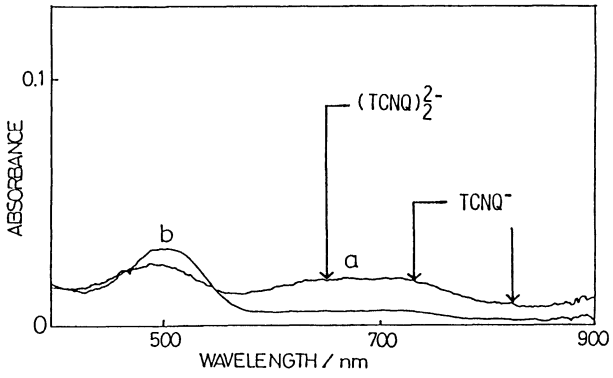

Fig. 2. Absorption spectra of the LB films of C_{18}Py-TCNQ (a) and C_{22}Py-$(TCNQ)_2$ (b).

Figure 1 shows the ESR spectrum of the powder sample of C_{18}Py-TCNQ. This spectrum has a strong sharp line with g value near the value of free electron and several side lines. These side lines may be due to triplet states of $(TCNQ)_2^{2-}$.[7] The ESR spectrum of the powder sample of C_{22}Py-TCNQ was very similar to that of C_{18}Py-TCNQ. On the other hand, both the ESR spectra of the powder samples of C_{18}Py-$(TCNQ)_2$ and C_{22}Py-$(TCNQ)_2$ have only single peak with g value near the value of free electron. These results may be attributed to the fact that the $TCNQ^-$ molecules in C_{18}Py-TCNQ and C_{22}Py-TCNQ are usually in the vicinity of other $TCNQ^-$ molecules, whereas the TCNQ molecules in C_{18}Py-$(TCNQ)_2$ and C_{22}Py-$(TCNQ)_2$ are situated between the $TCNQ^-$ molecules.

The absorption spectra of the LB films of C_{18}Py-TCNQ and C_{22}Py-$(TCNQ)_2$ are shown in Fig. 2.[8] Inzelt et al.[7] reported that the radical anion ($TCNQ^-$) bands at 735 nm and 830 nm and the dimer ($(TCNQ)_2^{2-}$) band at 655 nm were found in the film of the TCNQ oligomer, and no absorption band was found for the mixed valence species $(TCNQ)_2^-$. Therefore, the specra shown in Fig. 2 suggest that the the $TCNQ^-$ molecules in the LB film of C_{18}Py-TCNQ are in the forms of $(TCNQ)_2^{2-}$ and $TCNQ^-$, while the $TCNQ^-$ molecules in the LB film of C_{22}Py-$(TCNQ)_2$ are mostly in the form of $(TCNQ)_2^-$ and slightly in the forms of $(TCNQ)_2^{2-}$ and $TCNQ^-$.

The ESR spectra of the LB films of C_{22}Py-$(TCNQ)_2$ with 4, 8, and 18 layers deposited on the glass capillaies are shown in Fig. 3. The apparent peak to peak line width of each ESR spectrum of these LB films decreased from about 3 to 1.1 gauss with the increase in number of layers. It is also noteworthy that the ESR line of the LB film with 4 layers has broad lower slopes at both sides of the line which is not expected in the Lorentzian line shape. This finding suggests that this ESR spectrum consists of the superposition of many lines with varying line width. Table 1 lists the relative intensities and the line widths of the ESR spectra shown in Fig. 3. The relative intensity is defined here by the peak height multiplied by the square of the peak to peak line width, and is

corresponding to the area of the integrated ideal Lorentzian ESR line. From this Table, it is shown that the relative intensity is not proportional to the number of layers, but increased drastically with the increase in the number of layers.

ESR spectra of these LB films have only single peak, and have no hyperfine structures as well as the powder samples. This result shows that $TCNQ^-$ molecules in LB films interact with TCNQ molecules by electron exchange, or with other $TCNQ^-$ molecules by spin exchange. If the regularity of the ordered structure of an LB film is low, the interaction of $TCNQ^-$ in the film with each other or with TCNQ may be so weak that the narrowing of the ESR lines is not sufficient for our detection of the lines. Therefore, the results shown above suggest that the regularity of the ordered structure of the LB films of $C_{22}Py\text{-}(TCNQ)_2$ increased with the number of layers. In other words, the ordering of the LB film was enhanced by the cumulation of monolayers. This idea may be also supported by the following results: The intensity of the ESR spectrum of the LB films with 8 or 12 layers of $C_{22}Py\text{-}(TCNQ)_2$ was usually much larger than the double of the intensity of the ESR spectrum of the LB films with separately deposited 4 or 6 layers of $C_{22}Py(TCNQ)_2$. The intensity of the ESR spectrum of LB films with 4 or 6 layers of $C_{22}Py\text{-}(TCNQ)_2$ was markedly enhanced by the additional deposition of the several layers of an ESR-insensitive cadmium arachidate onto these samples. This indicates the overlay enhanced the regularity of the underlaid LB film.

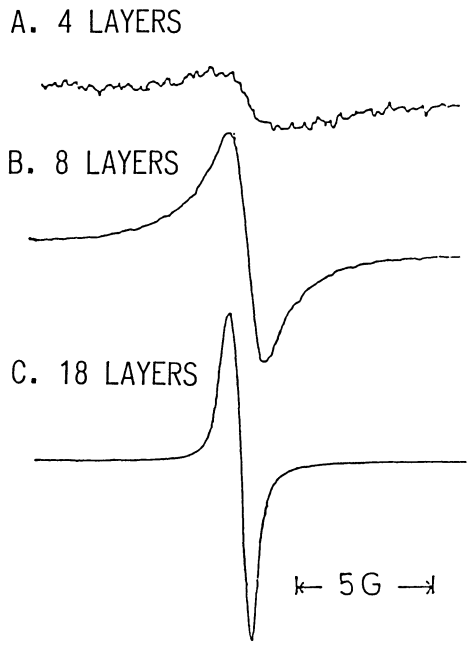

Fig. 3. ESR spectra of the LB films of $C_{22}Py\text{-}(TCNQ)_2$ with various number of layers.

Table 1. The dependence of the relative intensity and the line width, ΔH_{pp}, of the ESR spectrum for the LB film of $C_{22}Py\text{-}(TCNQ)_2$ on the number of layers

Sample	$S/A_3/T_4$ [a)]	$S/A_3/T_8$ [a)]	$S/A_3/T_{18}$ [a)]
Relative intensity	1.0	21	260
ΔH_{pp}/G	3	1.5	1.1

a) S: Substrate, A: Arachidic acid, T: $C_{22}Py\text{-}(TCNQ)_2$.

ESR spectrum of the LB film of $C_{22}Py\text{-}(TCNQ)_2$ deposited on a glass slide have shown marked dependence on the orientation of the film in the static magnetic field. Figure 4 shows the plots of the peak to peak line width (ΔH_{pp}) of

the LB film with 24 layers of $C_{22}Py$-$(TCNQ)_2$ versus the angle (θ) between the normal to the film plane and the static magnetic field at 20 °C and -130 °C. The behavior is similar to those of the ESR spectra of the I_2 doped and undoped LB films of $C_{18}Py$-TCNQ[4] and $C_{22}Py$-$(TCNQ)_2$.[9] However, the line width of the ESR spectrum at 20 °C in this experiment was slightly smaller than those reported by K. Ikegami et al.,[9] and scarecely increased even at -130 °C in contrast to their results. This disagreement also indicates that the structure of these LB films are affected by the preparation condition as described above.

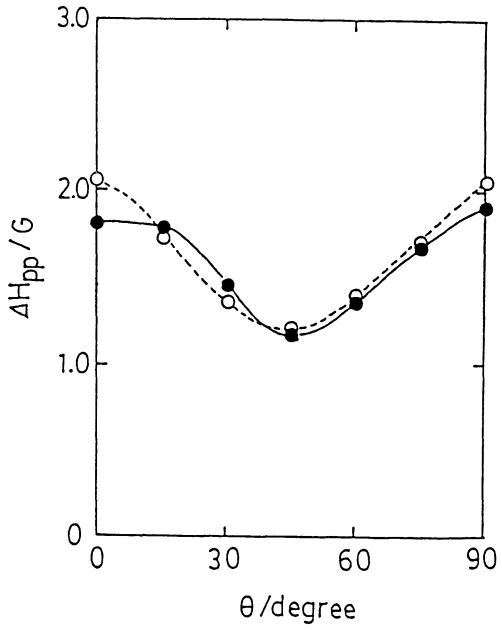

Fig. 4. Plots of the line width of the ESR spectra, ΔH_{pp}, vs. θ for the LB film of $C_{22}Py$-$(TCNQ)_2$ at 20 °C (●) and -130 °C (○).

We wish to thank Profs. Hiroshi Fukutomi and Hiroshi Tomiyasu for giving us facilities for ESR measurements at the Research Laboratory of Nuclear Reactor in Tokyo Institute of Technology.

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(Received May 28, 1987)