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Conductive Langmuir-Blodgett Films of Dialkyldimethylammonium-$Ni(dmit)_2$ Complexes

Takayoshi NAKAMURA,* Hideaki TANAKA,† Mutsuyoshi MATSUMOTO,
Hiroaki TACHIBANA, Eiichiro MANDA, and Yasujiro KAWABATA
National Chemical Laboratory for Industry, Higashi, Tsukuba,
Ibaraki 305

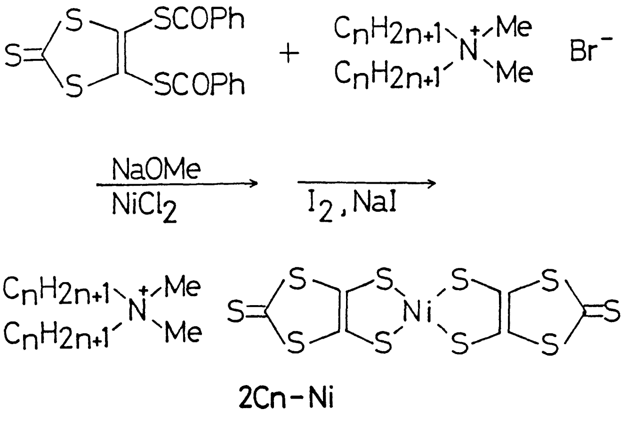
Conductive LB films of dialkyldimethylammonium-$Ni(dmit)_2$ complexes are described. The precursor 1:1 complexes were transferred onto substrates and converted into conductors by the bromine oxidation. The bulk conductivities of the films were 10^{-3} to 10^{-1} S/cm, depending on the length of alkyl chain. The spectral changes during the oxidation was also examined.

Langmuir-Blodgett (LB) technique has been applied in preparing organic thin films where functional moieties are assembled in ordered states.1) Extensive studies have been made on the construction of the electrical devices, and there are more than ten different conductive LB films reported so far.2-8) They are characterized as one-dimensional system, which is sensitive to defects and disorders and has intrinsic instability as one-dimensional conductors.9) To suppress these instabilities and accomplish the higher conductivities, one of the most important tasks in the next stage is to prepare conductive LB films of higher dimensionality.10)

Recently it has been reported11) that the mixed-valence complex of $(Et_2Me_2N)[Ni(dmit)_2]_2$ (H_2dmit = 4,5-dimercapto-1,3-dithiol-2-thione) is a two-dimensional conductor. Superconductor transition at 5 K (7 kbar) has been observed for an analogous complex, $(Me_4N)[Ni(dmit)_2]_2$.12)

We report here the synthesis, structural characterization and electrical conductivity studies of LB films of $(C_nH_{2n+1})_2Me_2N\text{-}Ni(dmit)_2$ (n=10, 12, 14, 16, 18, 22) (Scheme 1, hereafter referred to as 2Cn-Ni).

The complexes were prepared following the procedures described by Steimecke et al. (Scheme 1). The complexes 2Cn-Ni were insulating and further oxidation gave green to black



Scheme 1.

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† On leave of absence from Nippon Mektron, Ltd., Kukizaki, Ibaraki 300-12.

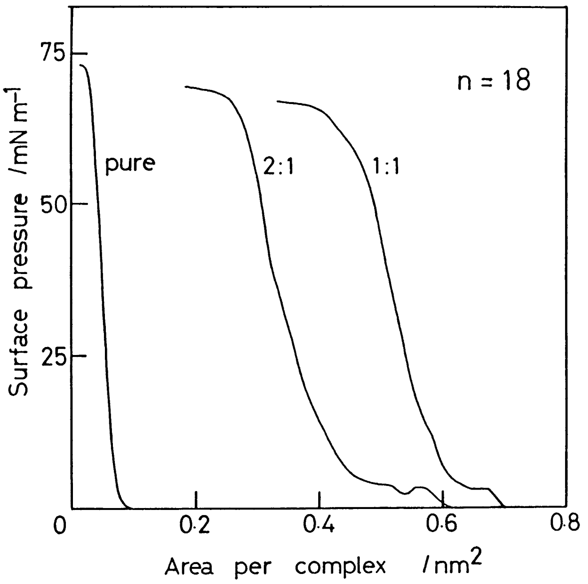

Fig. 1. π-A isotherms of pure and mixed monolayers of 2C18-Ni with icosanoic acid at 25 °C.

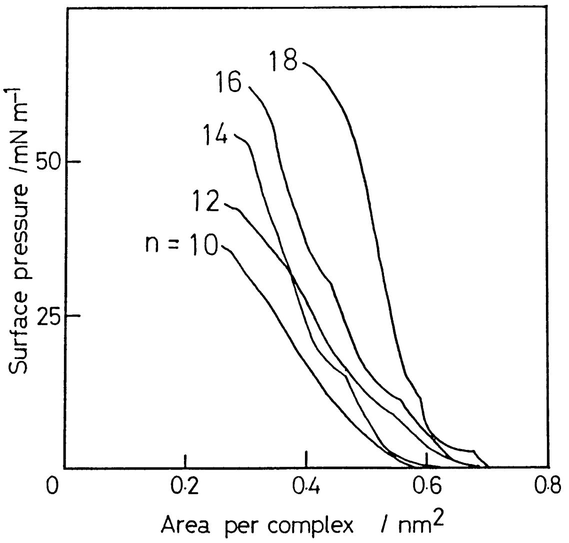

Fig. 2. π-A isotherms of 1:1 mixed monolayers of 2Cn-Ni and icosanoic acid at 25 °C.

solids. Although these solids were conductive, they are insoluble in common solvents at room temperature. Therefore, they are not appropriate for preparing LB films. As an alternative way to obtain a conductive LB film, we attempted the in situ oxidation method; precursor 1:1 complex is transferred onto a solid substrate, and then, the films are led to the conductors by "doping".$^{5)}$

Surface pressure-area (π-A) isotherms were measured using a Lauda film balance on pure water at 25 °C. Acetonitrile and benzene (1:1) was used as a spreading solvent. The monolayers were deposited onto glass, quartz and CaF_2 plates precoated with 5 monolayers of cadmium icosanoate for conductivity measurement, UV-visible spectroscopy and IR spectroscopy, respectively. Conductivities of LB films on a solid substrate were determined by DC two-probe method using gold paste as an electrode.

π-A isotherms of 2C18-Ni and the mixed monolayers with icosanoic acid are shown in Fig. 1. The abscissa is normalized to the number of $Ni(dmit)_2$ molecule. The pure 2C18-Ni formed a collapsed film. On the other hand, the 2:1 and 1:1 mixtures with icosanoic acid formed monolayers at the air-water interface.

Figure 2 shows the π-A isotherms of 1:1 mixture of 2Cn-Ni and icosanoic acid. As the carbon number of the alkyl chains increases, the slope of the condensed phase becomes steeper in these curves. This indicates that the longer alkyl chains are effective for the monolayer stability at the air-water interface. Indeed, the monolayer in a pure form is obtained for 2C22-Ni.

The monolayers of 1:1 mixture of 2Cn-Ni with icosanoic acid were transferred onto solid substrates by a usual vertical dipping method for n=16 to 22. The transfer of mixed monolayers of shorter alkyl chains (n=10 to 14) as well as pure 2C22-Ni was difficult due to the rigidity of the monolayers. These monolayers were transferred by a horizontal lifting method.

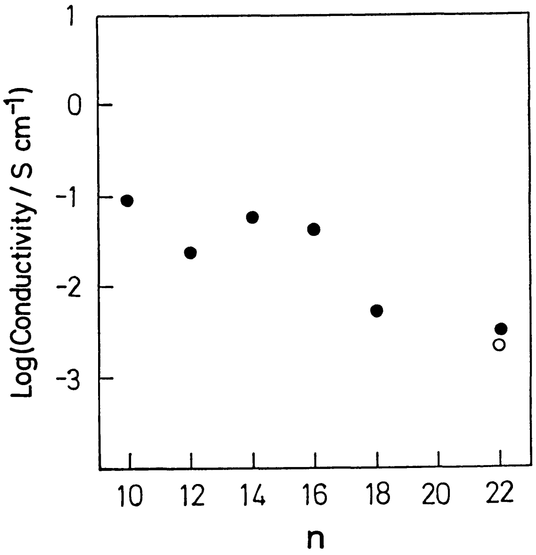

Fig. 3. Conductivity of oxidized 1:1 mixed LB films of 2Cn-Ni and icosanoic acid (●) and pure LB film of 2C22-Ni (○).

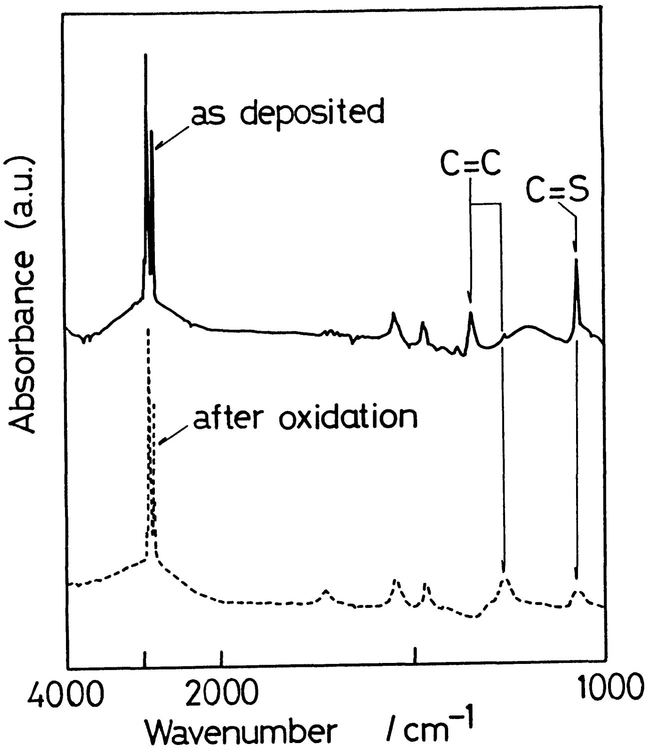

Fig. 4. IR spectra of 1:1 mixed LB film of 2C18-Ni and icosanoic acid.

The oxidation of LB films was performed by Br_2 gas diluted with N_2 gas. The amount of Br_2 gas was adjusted by monitoring the conductance of the films. The bulk conductivity of the oxidized films at room temperature is summarized in Fig. 3. These values were obtained by assuming a monolayer thickness of 3 nm, the thickness of matrix acid. As the carbon number of alkyl chains is smaller, the conductivity becomes larger. The value of 0.1 S/cm was obtained for 2C10-Ni, which is almost the same as that of TMTTF-octadecylTCNQ.3) The conductivity of the oxidized pure 2C22-Ni LB film was the same as that of the LB film of 1:1 mixture with icosanoic acid.

Although the color of the film changed from green to brownish green during the oxidation, there observed no significant change in UV-visible spectra of 1:1 mixed film of 2C18-Ni and icosanoic acid before and after oxidation. On the other hand, some shifts and broadening of the peaks are observed as indicated in IR-spectra shown in Fig. 4. The spectrum of the oxidized film is almost identical with that of a compound obtained by the bromine oxidation of $(Bu_4N)[Ni(dmit)_2]$.13) According to Steimecke et al, the signal near 1350 cm^{-1} of C=C is red-shifted to 1260 cm^{-1} and that near 1060 cm^{-1} of C=S is broadened by oxidation. This compound, although poorly characterized, showed a conductivity of ca. 1 S/cm in the form of compaction samples.14) The similar species can be predominant in the oxidized LB films. It is noted that the state of oxidation of this species, once regarded as $[Ni(dmit)_2]^0$,13) is not yet identified. Valade et al. pointed out that the oxidation process was not complete and the conductivity of neutral $[Ni(dmit)_2]^0$ obtained by the electrocrystallization was 3.5×10^{-3} S/cm even in the single crystalline form.$^{14)}$

To attain higher conductivities, the charge of Ni(dmit)$_2$ should be -0.5 as (Et_2Me_2)[Ni(dmit)$_2$]$_2$ (20-100 S/cm)$^{11)}$ and (Me_4N)[Ni(dmit)$_2$]$_2$ (60 S/cm).$^{12)}$ For this purpose we can use, for example, electrooxidation at a constant potential,$^{15)}$ which will be shown elsewhere. The syntheses of ammonium-metal(dmit)$_2$ system are simple and we can readily change both counter cation and central metal cation. This system will be one of the most promising candidates of the LB films of larger conductivity and higher dimensionality.

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References

1) See, e.g., Thin Solid Films, 159-160.
2) T. Nakamura, M. Matsumoto, F. Takei, M. Tanaka, T. Sekiguchi, E. Manda, and Y. Kawabata, Chem. Lett., 1986, 709.
3) Y. Kawabata, T. Nakamura, M. Matsumoto, M. Tanaka, T. Sekiguchi, H. Komizu, E. Manda, and G. Saito, Synth. Met., 19, 663 (1987).
4) M. Matsumoto, T. Nakamura, E. Manda, Y. Kawabata, K. Ikegami, S. Kuroda, M. Sugi, and G. Saito, Thin Solid Films, 160, 61 (1988).
5) J. Richard, M. Vandevyver, P. Lesieur, A. Ruaudel-Teixier, A. Barraud, R. Bosio, and C. Pecile, J. Chem. Phys., 86, 2428 (1987).
6) M. Vandevyver, J. Richard, A. Barraud, A. Ruaudel-Teixier, M. Lequan, and R. M. Lequan, J. Chem. Phys., 87, 6754 (1987).
7) A. S. Dhindsa, M. R. Bryce, J. P. Lloyd, and M. C. Petty, Synth. Met., 22, 185 (1987).
8) T. Iyoda, M. Ando, T. Kaneko, A. Ohtani, T. Shimidzu, and K. Honda, Tetrahedron Lett., 27, 5633 (1986).
9) K. Ikegami, S. Kuroda, K. Saito, M. Saito, M. Sugi, T. Nakamura, M. Matsumoto, Y. Kawabata, and G. Saito, Synth. Met., in press.
10) G. Saito, Pure Appl. Chem., 59, 999 (1987).
11) R. Kato, H. Kobayashi, H. Kim, A. Kobayashi, Y. Sasaki, T. Mori, and H. Inokuchi, Chem. Lett., 1988, 865.
12) H. Kim, A. Kobayashi, Y. Sasaki, R. Kato, and H. Kobayashi, Chem. Lett., 1987, 1799.
13) G. Steimecke, H. J. Sieler, R. Kirmse, and E. Hoyer, Phosphorus and Sulfur, 7, 49 (1979).
14) L. Valade, J. P. Legros, M. Bousseau, P. Cassoux, M. Gabauskas, and L. V. Interrante, J. Chem. Soc., Dalton Trans., 1985, 783.
15) H. Yoneyama and M. Fujihira, International Congress on Membranes and Membrane Processes, Tokyo, 1987, Abstr., No. 12-P08.

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