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Observation of Molecular Alignments and Dimer Formation of Bis(5-alkylsalicylidene)ethylenediaminatonickel(II) in a Monolayer

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A monolayer of bis(5-butylsalicylidene)ethylenediaminatonickel(II), prepared on highly oriented pyrolytic graphite by the Langmuir–Blodgett method, was observed by scanning tunnelling microscopy. The image revealed that one of the monolayers was comprised dimers of complexes, similar to that observed in the crystalline phase. The π–A isotherms of the analogues of various alkyl chain lengths were measured, and the critical area of the monolayer was found to decrease by 20% when the alkyl chain length decreased from 3 (propyl) to 2 (ethyl). This decrease of the critical area is explained by the presence of CH–π interactions between the π conjugated system of the salen moiety, and α- and γ-methylenes of the alkyl side chain.

Metal-complex monolayers on the solid substrates, especially on the electrodes, are becoming the major concern of researchers working in the field of molecular devices. In order to attain good electronic properties as molecular devices, control of the monolayer structure or, moreover, the surface morphology of the metal-complex monolayer on electrode surface, as well as the molecular structure, is the key technology that should be established. The Langmuir–Blodgett (L–B) method, used to produce monolayers of surface-active compounds at an air-water interface, is one of the useful methods used to control the aggregating structure of the complexes.[1]

A scanning tunnelling microscope (STM),[2] having atom-resolving capability is now widely used to investigate the surface morphologies of adsorbed molecules, such as surfactants,[3] metallophthalocyanines,[4] etc. Since STM can directly resolve the molecular arrangements, it is being successfully used in investigations of interactions between the molecular species or between the surface and the adsorbed molecules.

In a previous paper, we reported on the aggregating properties of the nickel(II) complexes of salen[5] substituted with two alkyl (C_nH_{2n+1}) groups ([Ni(C*n*-salen)]).[6] The dodecyl- and hexyl-substituted analogues were reported to change upon heating from the crystalline state (K) into the smectic E (S_E) liquid-crystalline phase, and then to the smectic A (S_A) phase, and finally to the isotropic liquid (IL) phase.[7] A high-temperature powder diffraction study revealed that the S_E phase comprises dimers of complexes, while S_A phase is of monomers.[8] A single-crystal X-ray analysis, performed on the butyl-substituted analogue, also suggested the formation of dimers in the crystalline phase. Figures 1(a) and 1(b) show the molecular structure of [Ni(C4-salen)] and the structure of its dimer in the crystalline state, respectively. Figure 1(b) shows that the dimeric structure is formed by π–π stacking and CH–π interactions.[9] We have also reported on the formation of monolayers at the air–water interface with the [Ni(C12-salen)], the dodecyl substituted analogue,[10] but we could not determine the aggregating structure of the complex in the monolayers.

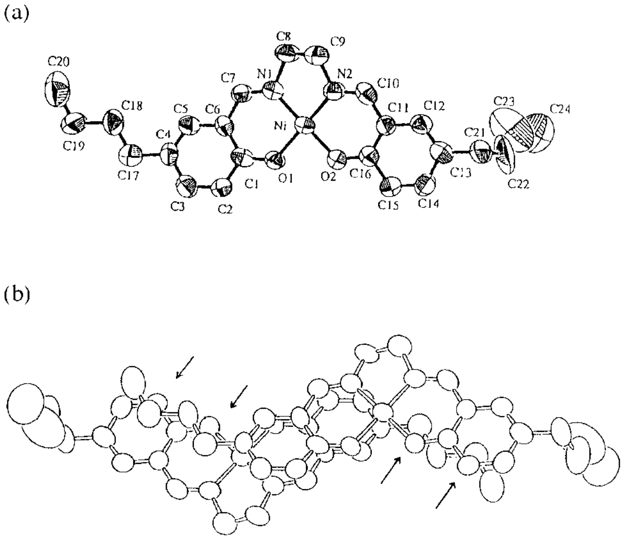

Fig. 1. (a) Molecular structure of [Ni(C4-salen)], and (b) that of a dimer of [Ni(C4-salen)]. Arrows in (b) indicates the CH–π interactions between alkyl chains and the salen moieties. The same figures are in the Ref. 9, but are given here for clarity.

Here, we report on detailed discussions concerning monolayer formation of the complex [Ni(C*n*-salen)] by the L–B method, and on observation of the aggregating structure of [Ni(C4-salen)] in the monolayer state using STM.

Experimental

The nickel(II) complexes of salen substituted with two alkyl chains (C_nH_{2n+1}, n = 1,2,3,4,6,7,8,10,12) [Ni(C*n*-salen)] were synthesized according to a reported method.[6] They were all recrystallized using a chloroform–methanol mixed solution before use in the following measurements. The results of elemental analyses were given in a previous paper,[11] and the formation of the complexes was confirmed by ^{1}H NMR. The fact that the UV-vis spectra for these complexes were identical, indicates that the electronic state of the complexes does not depend on the length of the substituted alkyl chains.

Surface Pressure–Area (π–A) Isotherm Measurements. The π–A isotherms of [Ni(C*n*-salen)] with different alkyl groups were measured with HBM-AP of Kyowa Interface Science Co. by spreading their chloroform solution on an air–water interface of 940 cm^2 and compressed at 7.0 $cm^2\,min^{-1}$. The subphase was distilled water and its temperature was maintained at 25±1 °C using a thermostat throughout the π–A isotherm measurement and the sampling procedure for STM measurement. At least three independent measurements were carried out for each complex and the averaged values were used as the measured data.

STM Measurements. The monolayer of [Ni(C4-salen)] was scooped onto a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG) at a surface pressure of 4.0 and 22.5 $mN\,m^{-1}$, and then allowed to be dried up before a measurement with STM. This procedure was very difficult and only a small number of samples gave sufficient STM images. The STM measurements were carried out using a Nanoscope I (Digital Instruments) unit with an originally developed control system.[12] All STM images were obtained with the constant-current mode at ambient condition.

Results and Discussion

Not all, but not a few, of the metal complexes substituted with long alkyl chains form stable monolayers at the air–water interface. Figure 2 shows the π–A isotherm of the butyl-substituted analogue, [Ni(C4-salen)]. Such an isotherm is not unusual,and has already been reported for other metal complex.[13] Although the π–A isotherms of [Ni(C*n*-salen)] with alkyl chains longer than the ethyl group exhibited a similar π–A isotherm, the methyl substituted analogue did not form stable monolayers. Upon decreasing the surface area, the surface pressure of [Ni(C1-salen)] did not increase at all. Thus, it can be said that the methyl group is too short to form stable monolayer structures. Two parts, A and B, indicated in Fig. 2, correspond to different aggregation states. The critical areas extrapolated to 0 $mN\,m^{-1}$ for A and B are approximately 75 and 25 Å^2, respectively. The data show that the molecules in B are so closely packed that they should be standing perpendicular to the surface and jam-packed, while in A the molecules are relatively expanded and should be lying on the surface. Thus, the aggregation states, A and B, are named the expanded phase and the condensed phase, respectively.

Figure 3 shows the alkyl chain-length dependence of the critical areas of both the expanded and condensed phases. Upon increasing the length of the alkyl chains, the critical areas of both phases tended to decrease at a rate of 1.0 and 1.5 Å^2 per methylene for the expanded and condensed phases, respectively. However, the critical area of the expanded phase was found to decrease by approx. 20% from n = 3 (propyl) to n = 2 (ethyl). It should be reminded that [Ni(C*n*-salen)] were completely neutral in charge, and that their solubilization towards water used as a subphase could be neglected. Therefore, this fact indicates that the γ-methylene occupies the water surface in the monolayer state, while the methylenes further from the benzene ring than the δ-methylenes do not. The γ-methylene is reported to form a CH–π interaction in the crystal of [Ni(C4-salen)].[9] This fact strongly implies the presence of a CH–π interaction in the monolayer state as well as in the crystalline state, because the absence of γ-CH in the ethyl (n = 2) substituted analogue should cause a structural change of the aggregates.

Figures 4(a) and 4(b) show two successively obtained STM images of a sample prepared at an expanded phase (4.0 $mN\,m^{-1}$), observed at a different scale. The image was taken by the constant-current mode of 0.2 nA at a bias voltage of 800 mV. Complex molecules can be distinguished as bright rods aligned regularly over the region of 80 Å. Furthermore, the images show that there are two types of molecules, relatively bright and dark ones, aligned alternatively. The bright and dark molecules were displaced against each other

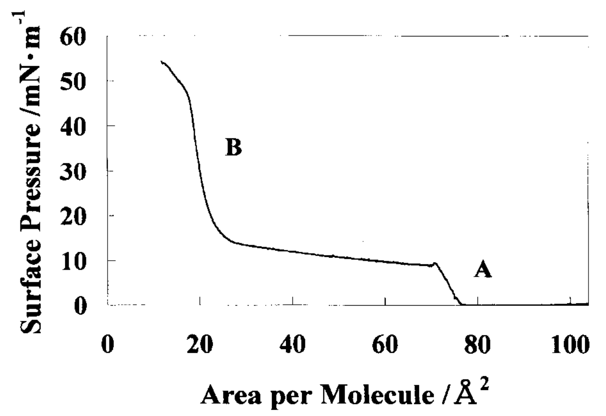

Fig. 2. π–A Isotherm of [Ni(C4-salen)]. A: Expanded phase, B: Condensed phase.

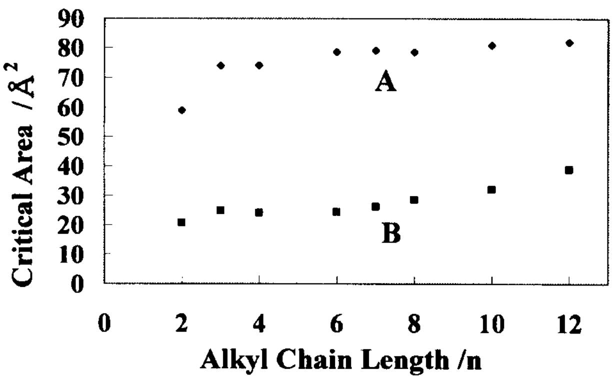

Fig. 3. Alkyl chain length dependence of critical area. A: Expanded phase, B: Condensed phase.

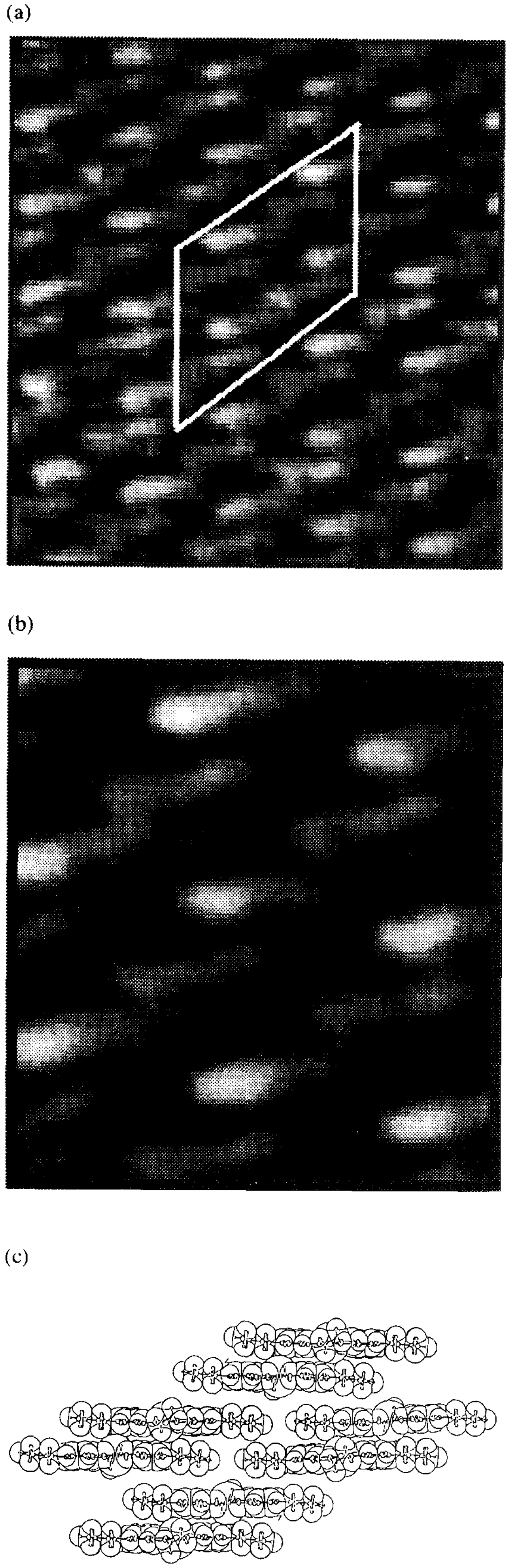

Fig. 4. Successively obtained STM images of monolayer of [Ni(C4-salen)] prepared at 4 mN m^{-1}. (a) 80×80 Å, (b) 40×40 Å, (c) proposed molecular alignment for the area indicated by a white parallelogram in (a).

in the direction of the molecular axis by 5 Å, and the intermolecular distance was 3.5 Å. These distances agree well with the scales reported for the dimer structure in Fig. 1(b), analysed by an X-ray crystallographic study. This fact, together with the result of the alkyl chain-length dependence of the critical area, indicates that the monolayer of complexes [Ni(C*n*-salen)] in the expanded phase comprises dimers with CH–π and π–π interactions, as in the crystalline state. This is important because the presence of the CH–π interaction in the monolayer state is rather unusual. The molecules in the dimer, if their NiN_2O_2 planes are placed perpendicular to the substrate surface, should be distinguished in the STM image, because the orientations of the salen moieties are reversed for the two molecules in the dimer. This can explain the reason why the complexes are imaged as bright and dark images alternatively aligned. Figure 4(c) shows a packing model of complexes in the monolayer state surrounded by a parallelogram. The conformation of the alkyl groups is modified from the reported structure in the crystalline state so as to fit with the observed structure.

The mean length of the bright rods in Fig. 4(a) is 14 Å, which equals the length of the salen moiety. It should be pointed out that conjugated systems, such as the salen moiety, are usually observed as bright parts in STM images. We thus conclude that the salen moiety is observed brightly in the STM images. Although the butyl chains are not observed, we suppose from the fact that the molecules in the dimer are displaced by 5 Å, the butyl chains interact with the conjugated system of the salen moiety by the CH–π interaction as those in the dimer of [Ni(C4-salen)] (Fig. 1(b)). The average area per molecule, evaluated from Figs. 4(a) and 4(b) was 101 Å^2, which was much larger than 71±2 Å^2 estimated from the π–A isotherm.

The STM image of the condensed monolayer shown in Fig. 5(a), on the other hand, exhibits a periodic alignment of 7.0×3.1 Å units tilted by 120°, although the image is rather unclear compared to that of the expanded phase. The tunnel current of this sample in the STM measurement was very unstable, probably due to the increased thickness of the insulating monolayer of the condensed phase. In this case, the dimers are indistinguishable. Assuming that the unit is of a single molecule of [Ni(C4-salen)], the average area per molecule has been evaluated from an STM image to be 20.3 Å^2, which is almost in accord with that from the π–A isotherm (20.8±0.2 Å^2). We thus conclude that the condensed phase is constituted of complex molecules aligned as in Fig. 5(b). The molecules are estimated to be so closely packed that the molecular axis should be almost perpendicular to the HOPG surface. Such a morphology is usually the case in the condensed phase of molecules with long alkyl side chains.

Conclusion

Although the formation and observation of a monolayer of complexes was reported for porphyrins,[4] the observed structure showed that the interaction between the complex and the surface of the substrate was important in the mono-

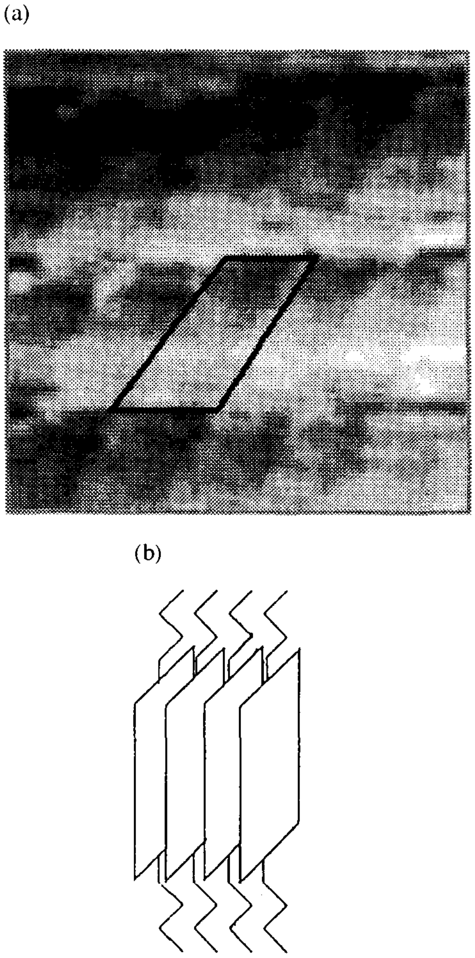

Fig. 5. STM image of monolayer of [Ni(C4-salen)] prepared at 22.5 mN m^{-1}. (a) 40×40 Å, (b) proposed molecular alignment. Black parallelogramic box in (a) corresponds to the complex moiety represented by a parallelogram in (b).

layer state of the porphyrins. The outstanding feature of the salen derivatives reported here is that they form dimers in the monolayer state, which should be the result of inter-monomer interactions, i.e. the inter-molecular interactions between the complexes play important roles in organizing the molecules into some structure. We have also obtained some strong evidence that the dimer in the monolayer state is also formed by CH–π interactions, as in the crystalline state. The fact that Figs. 4 and 5 exhibited totally different morphologies of [Ni(C4-salen)] indicates that a structural change at the air–water interface is induced by a change in the surface pressure. This means that the monolayer of [Ni(C4-salen)] has two aggregation forms, a dimeric expanded phase and a jam-packed condensed phase, which can be controlled by the surface pressure.

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