

## Nano-Electrostatic phenomena at metal-Phthalocyanine film interface

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At the metal-organic film nano-interface, electrostatic phenomena are observed, due to the displacement of excess charges from metal to the films as well as alignment of polar dipoles. With the Kelvin-probe surface potential method, surface potential of evaporated phthalocyanine (Pc) and Alq3 films on metal electrode is examined. Fluorine substituted ZnPc (ZnPcF16) was charged more negatively than unsubstituted ZnPc film, indicating that HOMO and LUMO levels of ZnPcF16 are lower than those of ZnPc. These results well agree with our theoretical prediction based on the molecular orbital (MO) calculation. For evaporated Alq3 on metal electrodes, anomalous increase in surface potential was observed with increase of the deposited film thickness, indicating that the contribution of alignment of dipoles is significant. Based on these experimental evidence, the issue on "alignment of surface Fermi level" is discussed.

Key words: surface potential, surface Fermi level, Alq3

### 1. INTRODUCTION

The study of electrostatic interfacial phenomena occurring at organic film/metal interfaces is obviously important to the fields of electronics and electrical insulation engineering [1], and it has been a continuous research topic since the discovery of contact electrification [2]. It is known that interfacial electrostatic charges make a significant contribution to carrier injection, electrical transport, carrier generation, and other related electronic processes [3]. From contact-charge exchange experiments using thick polymer films, it has been revealed that excess charges are injected from a metal into a film, and a space charge layer of micrometer thickness is formed at the interface due to the existence of electronic states contiguous to the Fermi energies of contacting metals [4]. Duke, Fabish and other researchers carried out many experiments for elucidating the interfacial electrostatic charge phenomena in polymer films, and many interesting and important models of surface states, e.g., acceptor states model, have been proposed [5]. All of these studies made a significant contribution to the development of electrical insulation engineering. Recently, organic semiconductors have attracted much attention in electronics along with the successful preparation of films with high mobility and high electrical conductivity [6]. Organic solar cells, organic electroluminescent (EL) devices, and organic field-effect transistors (OFETs) have been fabricated. In these devices, carrier injection, carrier separation at organic film/metal interfaces, and carrier transport in the films are key processes [7]. Therefore, in the field of organic electronics, the understanding of nano-interfacial electrostatic phenomena is of great importance. However, our understanding is far way. "Fermi-level alignment" is one of the most important and fundamental issues concerning the organic materials electronics. There are many possible origins of the formation of an interfacial dipole layer at the organic film/metal interface, e.g., chemical bond formation, image charge effect and

permanent dipoles. Thus discussion on "the surface Fermi level alignment" is not easy, and the origins mentioned earlier work to break the so-called Fermi level alignment. Therefore, it is now a urgent task to elucidate the energetic states at film-metal nano-interfaces. In this paper, we examined the nano-interface electrostatic phenomena at metal-phthalocyanine (Pc) film interface and metal-tris-8-quinolinol-aluminum (Alq3) film interface by Kelvin-probe surface potential method, and then discussed the issue on the "Fermi-level alignment". It is known that the Alq3 is used as an electron transporting materials in organic EL devices in which process of carrier injection plays an important role.

### 2. Experiments

The molecules used here were unsubstituted,

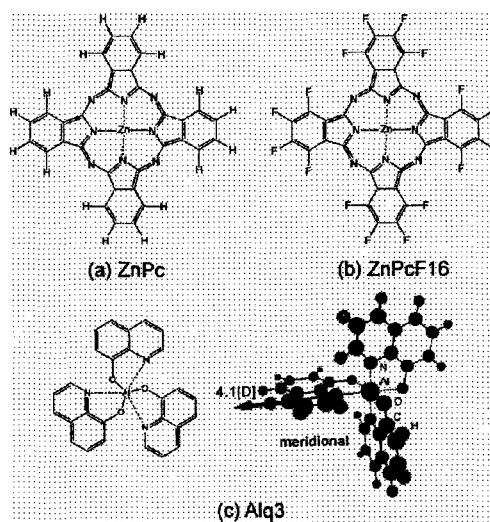


Fig.1(a) Chemical structures of ZnPc (b) ZnPcF16 and (c) Alq3. The dipolemoment of Alq3 (meridional) is indicated

fluorine-substituted zinc Pc, and Alq<sub>3</sub>, abbreviated ZnPc, ZnPcF<sub>16</sub>, and Alq<sub>3</sub>, respectively. These chemical structures are shown in Fig. 1. These molecules were purchased from Sigma-Aldrich Co. and used without further purification. For ZnPcF<sub>16</sub> molecule, sixteen fluorine atoms are attaching to the Pc ring. As the structure of ZnPc and ZnPcF<sub>16</sub> is symmetric, it is not supposed that permanent dipole moment is a main contribution to the surface potentials of ZnPc and ZnPcF<sub>16</sub> films on metal electrodes. Further it should be noted that ZnPcF<sub>16</sub> shows n-type semiconducting property, whereas ZnPc shows p-type semiconducting property [8,9]. On the other hand, Alq<sub>3</sub> has the polarity and possesses permanent dipole moment as shown in the figure. It is thus supposed that permanent dipole moment make a significant contribution to the surface potential if these dipoles align unidirectionally. All materials were deposited on Al and Au electrode by vacuum evaporation. During evaporation, process pressure was  $9 \times 10^{-7}$  torr and deposition rate monitored by quartz crystal microbalances (QCM) was controlled to be about 1 nm/min.

Fig. 2 shows schematically an image of the experimental setup for Kelvin probe measurement. The plate detector (vibrating top electrode) is placed parallel to the sample and it is vibrated vertically to the substrate during the measurement (Fig. 2). The surface potential is determined with respect to the potential of bare metal surface. At organic/metal interface, there are excess charges displaced from metal electrodes. Furthermore, dipolar molecules align in the films. It is supposed that the permanent dipole makes a significant contribution to Alq<sub>3</sub>, but not to ZnPc and ZnPcF<sub>16</sub> films.

The surface potential  $V_s$  built across organic films is the sum of the surface potential due to excess charges and that due to alignment dipolar molecules.  $V_s$  is given by

$$V_s = \frac{1}{\epsilon_r \epsilon_0} \int_0^d x \rho(x) dx + \frac{1}{\epsilon_r \epsilon_0} P_0$$

Here  $\rho(x)$  is the space charge density at position  $x$  from the film/metal interface,  $\epsilon_r$  is the dielectric constant of organic films, and  $d$  is the film thickness.  $P_0$  is the polarization due to dipolar molecules, and it is proportional to the orientational order parameter  $S_1 = \langle \cos \theta \rangle$ .  $\theta$  is an orientational angle from the normal direction to the substrate.

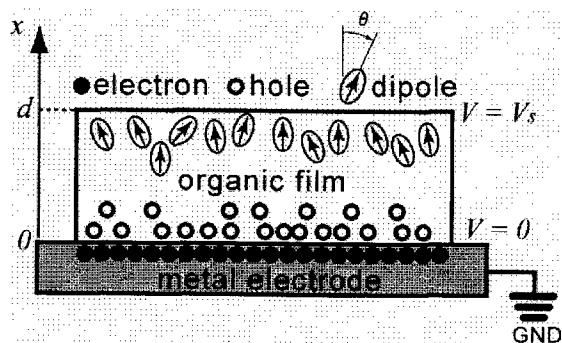


Fig. 2 Schematic image of the surface potential of organic films.

### 3. Results and Discussion

#### 3.1. ZnPc and ZnPcF<sub>16</sub>

Figure 3 shows the results of the surface potential measurement for the vacuum evaporated ZnPc and ZnPcF<sub>16</sub> films with various thickness deposited on Al and Au electrode. As figure shows, magnitude of the surface potential increases with the film thickness, and seems to saturate at thick region (thickness > 20nm). This tendency is coincident with the results reported previously for the CuttbPc LB films [10,11]. For the all samples except for ZnPc/Au structure, negative surface potential was clearly observed. It is also found that Al electrode generates more negative potential for ZnPc and ZnPcF<sub>16</sub> samples in comparison with the Au electrode. These results can be explained by the difference of the work function of metals, i.e., the work function of Au is larger than that of Al. On the other hand, compared with the unsubstituted Pc films, fluorine-substituted Pc films generate more negative potential. This can be assigned to the difference of the Fermi level between ZnPc and ZnPcF<sub>16</sub> molecules.

For further clarifying the details, electronic states calculation based on the molecular orbital (MO) theory was employed. Fig.4 shows the orbital energy of the ZnPc and ZnPcF<sub>16</sub> single molecule. For this calculation, a commercial based MO program (DGauss) based on the density functional theory (DFT) was used. At first, atomic coordinates of the molecule were optimized and the MO energies were calculated using the Dirac exchange and the Vosko-Wilk-Nusair correlation energy functions, and double-zeta valence basis functions. As shown in the figure, orbital energies of the HOMO (highest occupied molecular orbital), LUMO (lowest occupied molecular orbital) and other MOs simultaneously are deepened with electron accepting fluorine substitution in comparison with unsubstituted Pcs. As a result, Pc ring comes to accept electrons from other molecules and then fluorine-substituted Pc become to be covered with excess  $\pi$ -electrons. Thus fluorine-substituted Pc tends to have electron-acceptor property.

The Fermi levels of ZnPc and ZnPcF<sub>16</sub> are assumed roughly to locate at the center of the HOMO and LUMO level. In actual system, since the Fermi level is strongly

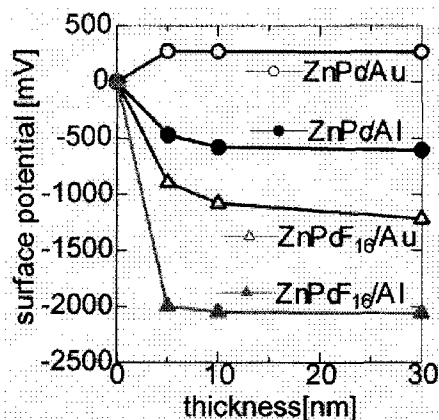


Fig.3 Surface potentials of ZnPcF<sub>16</sub> and ZnPc on Au and Al electrodes.

influenced on some trapping levels due to the impurities and defect of lattice, location of the Fermi level cannot be determined exactly. Thus, in this paper, the Fermi level of the phthalocyanine was reasonably treated as like an insulator due to the weak interaction between the molecules, for simplicity. According to the MO calculation, the Fermi levels are located at -4.48 eV and -5.24 eV for ZnPc and ZnPcF16, respectively, with reference to the vacuum level. Work functions of metal electrodes were obtained 4.2 eV and 4.8 eV for Al and Au [12], respectively. Thus the Fermi level of ZnPcF16 molecule is located deeply in comparison with those of Al and Au electrodes. On the other hand, the Fermi level of ZnPc molecule is located shallowly compared with that of Au electrodes. These predictions support the experimental results obtained for the surface potential measurements shown in Fig.3, where electrons are displaced from materials with high Fermi level to materials with low Fermi level. Taking into account these, we may consider that electron transfer happened at the nano-interface between metals and ZnPc and ZnPcF16 films, and surface Fermi level of PC films and Fermi level of metals coincide each other at the interface.

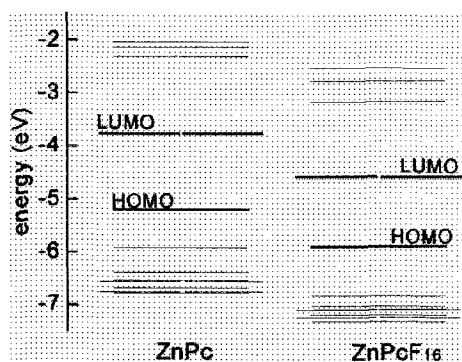


Fig.4 Orbital energy of the ZnPc and ZnPcF16 molecules calculated by MO method.

### 3.2. Alq3

Figure 5 shows the surface potential of vacuum evaporated Alq3 films with various thickness, that were deposited on Al and Au electrode. As shown in the figure, the surface potentials of as-deposited Alq3 (without photo irradiation) increase steeply and linearly with the film thickness. Surprisingly, the magnitude is quite large and reaches several volts in a manner similar to that reported by Ito et al [13]. The establishment of such large voltage across Alq3 films cannot be explained by only assuming the electron transfer at film-Alq3 interface, indicating that coincidence of Fermi level between Alq3 and Au (and Al) electrode is difficult. It is supposed that the orientational alignment of dipole moment of Alq3 makes a significant contribution. Taking into account the magnitude of dipole moment of Alq3 molecules (meridional form, 4.1 D) indicated in Fig.1, the orientational order parameter defined by  $S_1$  is calculated to be 0.07 and 0.04, for Alq3 films on Au and Al electrodes, respectively. The values of calculated order parameter  $S_1$  are small, but not zero. Similarly if

we assume that Alq3 is in facial form (7.1 D),  $S_1$  is calculated to be 0.04 and 0.02, for Alq3 films on Au and Al electrodes, respectively. As the order parameter  $S_1$  represents the average angle of dipolar molecules, Alq3 molecules are tilting and nearly facing to the substrate. However, this situation changes when the deposited Alq3 films were irradiated. As shown in the figure, the surface potential decreased drastically and only the potentials of the order of several hundred milli-volts remained, indicating that the spontaneous polarization due to the alignment dipoles disappeared. In other words, order parameters  $S_1$  for Alq3 films on Au and Al electrodes were changed to almost zero after photoirradiation. Interestingly, remained small surface potential is dependent on metal electrodes Au and Al, and Alq3 films on Al electrode are more negatively charged than Alq3 films on Au electrodes. Therefore, we expect at the interface, some excess charges are displaced from metal to Alq3 films, in a manner to that seen for ZnPc and ZnPcF16 films. Taking into account these, we expect that electron transfer happens at the nano-interface between metals and Alq3 films even before photoirradiation, but this effect is very small compared with the effect of the alignment of dipoles. On the other hand, after photoirradiation, the surface Fermi level of Alq3 films and Fermi level of metals come to close each other. However, further detailed study is required to judge the Fermi level alignment at the interface after photoirradiation.

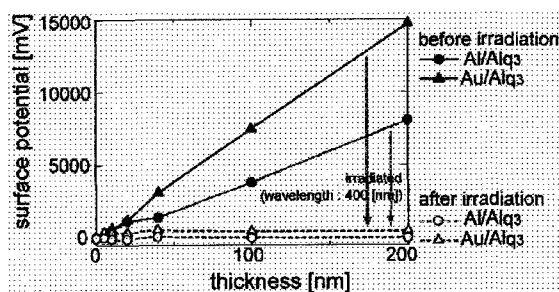


Fig.5 Surface potential of Alq3 films on Au and Al electrodes. Solid lines for as-deposited films, and broken lines for photoirradiated films.

### 4. Conclusion

At the interface, electron transfer and alignment of dipoles are two main contributions to the establishment of surface potential. For ZnPc and ZnPcF16 films on metal electrodes, the main contribution was found to be electron transfer. On the other hand, for as-deposited Alq3 films, the both two contributions were indicated, where the ordering of dipoles was the main. However, after photoirradiation, the contribution of the electron transfer was significant.

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