# Intermolecular band dispersion in a self-assembled phthalocyanine derivative film: The case of tetrakis(thiadiazole)porhyrazine

Yusuke Tanaka,[1,*] Kouji Takahashi,[2] Takuya Kuzumaki,[3] Yuta Yamamoto,[3] Kunihiro Hotta,[3] Ayumi Harasawa,[4] Yasuhito Miyoshi,[2] Hirofumi Yoshikawa,[2] Yukio Ouchi,[1] Nobuo Ueno,[3] Kazuhiko Seki,[1] Kunio Awaga,[2] and Kazuyuki Sakamoto[3,†]

[1]*Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan*

[2]*Research Center for Materials Science and Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan*

[3]*Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522, Japan*

[4]*Institute for Solid State Physics, The University of Tokyo, Chiba 277-8581, Japan*

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The electronic band structure of a tetrakis(thiadiazole)porhyrazine ($H_2$TTDPz) thin film prepared on $SiO_2$, which is a system close to a real device one, was studied by photoelectron spectroscopy (PES). Although the film was grown on a bumpy surface, clear electronic band dispersion was observed along the surface-normal direction. The bandwidth of the highest occupied molecular orbital (HOMO) band was approximately 180 meV. By analyzing the PES result using the tight-binding method, the transfer integral for the $\pi$-$\pi$ interaction, the effective mass of the HOMO hole, and the hole mobility were estimated to be approximately $45 \pm 10$ meV, $1/m_h^* = (0.14 \pm 0.03)/m_0$, and $\mu_h = 8.2 \pm 1.8$ $cm^2/V$ s, respectively, at 100 K.

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## I. INTRODUCTION

Organic semiconductors have recently attracted much interest due to their potential application for organic devices such as light-emitting diodes, solar cells (SC), and field-effect transistors (FET). One of the key factors for the device performance is the charge-transport property between the coherent bandlike one and the incoherent hopping-related one. The charge-transport coherency strongly depends on the orientation and packing structure of organic molecules. Angle-resolved photoelectron spectroscopy (ARPES) performed using synchrotron radiation light is a powerful technique to measure the electronic band structure [binding energy ($E_B$) vs wave vector ($\vec{k}$)], and thus to obtain a proper understanding about the coherent electronic properties of solids.[1,2] However, so far, only a tiny number of studies report the intermolecular band dispersion of organic films, which originates from an adequate overlap of the $\pi$ orbitals of adjacent molecules and relates closely to the bandlike transport mechanism.[3–9] This is due to the small bandwidth that results from the weak intermolecular van der Waals interaction, and because of the difficulty to prepare a well-oriented sample that is necessary for doing ARPES measurements.

The band dispersion of organic films has been observed in systems where molecules are deposited on inert single-crystal substrates,[3–9] which are flat in atomic scale and have few defects, since such inert crystals are ideal substrates to grow well-ordered organic films. In contrast to these ideal cases, however, organic films are usually prepared on bumpy surfaces with quite a few defects in real devices. This means that in order to investigate a more realistic system, one has to form a well-ordered organic film on such a rough surface. Phthalocyanine (Pc) derivatives are one of the most studied prototypical conjugated organic molecules due to their potential applications in FET (Ref. 10) and SC.[11] Pc derivative crystals are known to consist of one-dimensional stacking column whose direction is perpendicular to the molecular plane in many cases, because of the strong $\pi$-$\pi$ intermolecular interaction and the weak intercolumn interaction that comes from the presence of hydrogen atoms terminating the benzo ring.[12,13] In contrast to most of such Pc derivatives, the tetrakis(thiadiazole)porphyrazine ($H_2$TTDPz) (Ref. 14) [Fig. 1(a)] was reported to have a strong intermolecular interactions and to show a two-dimensional hexagonal close-packing crystal structure [Fig. 1(b)].[15,16] The x-ray diffraction (XRD) patterns of 1000-Å-thick $H_2$TTDPz films grown on various substrates show that $H_2$TTDPz molecules orient with their molecular plane parallel to the substrate surface with an interlayer distance of 3.3 Å [Fig. 1(c)].[17,18] This suggests the possibility of growing a well-ordered $H_2$TTDPz film on a nonatomically controlled surface and to discuss the band dispersion and the bandlike charge-transport property of this film in a system similar to a real device.

In this Brief Report, we report the electronic band structure of a $H_2$TTDPz thin film (80 Å) grown on a native oxide $SiO_2$ substrate, a prototype system for organic FET. (A native oxide $SiO_2$ substrate is usually *not flat in atomic scale*.[19]) The band structure measured along the surface-normal direction shows that the dispersion width of the highest occupied molecular orbital (HOMO) is approximately 180 meV. By analyzing the band dispersion, we estimated the transfer integral to be approximately $45 \pm 10$ meV for the $\pi$-$\pi$ interaction, the effective mass of HOMO hole to be $1/m_h^* = (0.14 \pm 0.03)/m_0$, and the hole mobility as $\mu_h = 8.2 \pm 1.8$ $cm^2/V$ s at 100 K.

## II. EXPERIMENTAL DETAILS

The ARPES measurements were performed at beamline BL-18A at the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF), Tsukuba, Japan. The experiment was carried out in an ultrahigh vacuum system that consists of an analysis chamber and a preparation one. A hemispherical energy analyzer (Scienta SES-100) was used

 

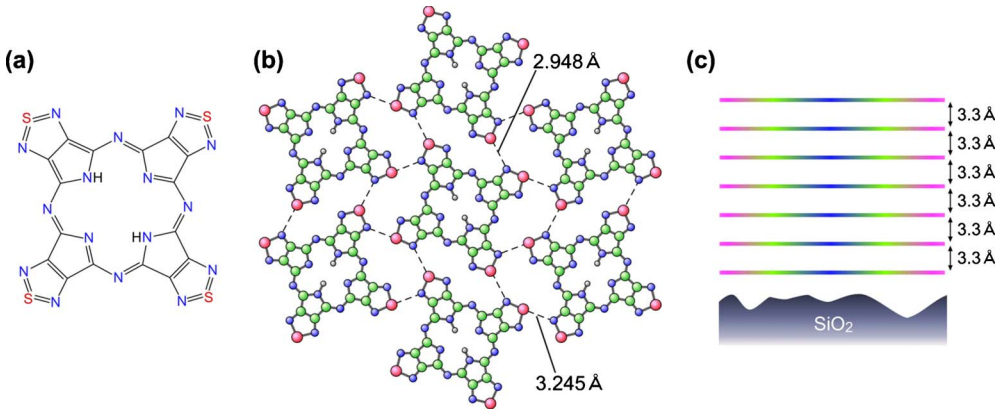


FIG. 1. (Color online) (a) Schematic illustration of the molecular structure of $H_2$TTDPz. (b) Top and (c) side views of the packing structure for $H_2$TTDPz film grown on a $SiO_2$ substrate.

in a condition of a total-energy resolution of approximately 100 meV at a photon energy ($h\nu$) of 25 eV and an angular acceptance of $\pm 2°$ for all ARPES measurements. The incidence $h\nu$-dependent PES spectra were measured with a photon incidence angle ($\theta_i$) of 45° and photoelectron emission angle of ($\theta_e$) of 0° (normal emission). All the PES measurements have been performed at a sample temperature of 100 K.

The $SiO_2$ substrate was first degreased using acetone before it was inserted into the vacuum system and then annealed at approximately 900 K for more than 1 h in the vacuum chamber. $H_2$TTDPz was first prepared by using the method described in Ref. 14 and then purified under a pressure of approximately $10^{-1}$ Pa with continuous $N_2$ gas flow (50 ml/min) at 800 K. After these procedures, the purified $H_2$TTDPz was loaded in a quartz crucible and then introduced into the preparation chamber. The $H_2$TTDPz was carefully out gassed below 500 K for over 2 h prior to evaporation. The film thickness and the deposition rate (~2 Å/min) were monitored with a quartz microbalance.

## III. RESULTS AND DISCUSSION

Figure 2(a) shows the PES spectrum of a 80-Å-thick $H_2$TTDPz film grown on a $SiO_2$ substrate measured with $h\nu=25$ eV, and $(\theta_i, \theta_e)=(45°, 0°)$. (The $H_2$TTDPz film is formed by islands whose widths are 200–500 Å, a length ten times longer than the terrace width of the $SiO_2$ substrate.[19]) Taking into account that a $SiO_2$ substrate shows a large peak at $E_B$ of approximately 7.5 eV and no structure at lower $E_B$ as shown in the inset of Fig. 2, all the structures observed at approximately 2.2, 4.3, 5.4, and 7.6 eV in Fig. 2(a) are assigned to the MOs of $H_2$TTDPz. ($E_B=0$ eV corresponds to the Fermi level.) Since no feature is observed at the lower $E_B$ side of the peak at approximately 2.2 eV, the corresponding peak, which is well separated from the other MOs, is the HOMO. Further, the negligible intensity at the Fermi level indicates that the electronic character of this molecule is semiconducting.

In Fig. 2(b), we show the energies of MOs calculated by a density-functional theory (DFT) method, in which an unrestricted open-shell wave function [B3LYP/6–31G(d,p)] was used. Electron correlation was taken into account using Becke's three-parameter exchange with Lee, Young, and Parr correlation function (B3LYP). The simulated spectrum was obtained by employing a Gaussian convolution with the full width at half maximum of 0.5 eV to the calculated MOs. As shown in Fig. 2, the simulated spectrum shows good agreement with the experimental one. The agreement indicates that the MOs of $H_2$TTDPz are hardly perturbed in the film phase. That is, although $H_2$TTDPz molecules form a graphenelike structure that results from a side-by-side intermolecular S-N contact [Fig. 1(b)], and the graphenelike $H_2$TTDPz layers are stacked owing to the $\pi$-$\pi$ interactions as in the graphite structure [Fig. 1(c)], these interactions are not strong enough to strongly perturb the electronic structure

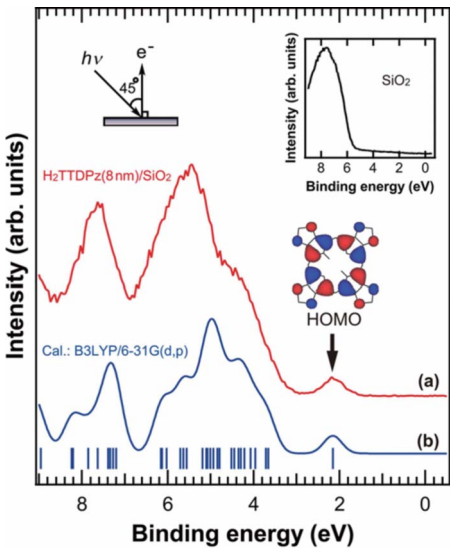


FIG. 2. (Color online) (a) PES spectrum of a 80-Å-thick $H_2$TTDPz film grown on $SiO_2$ and (b) simulated spectrum obtained by the MO energies calculated by a DFT [B3LYP/6–31G(d,p)] method that are displayed at the bottom of the simulated spectrum. The spectrum in (a) was measured by a $p$-polarized synchrotron radiation light with $h\nu=25$ eV, and $(\theta_i, \theta_e)=(45°, 0°)$. Inset shows the valence-band spectrum of the $SiO_2$ substrate. The symmetry of the HOMO of an isolated $H_2$TTDPz molecule and the measurement configuration are also shown.

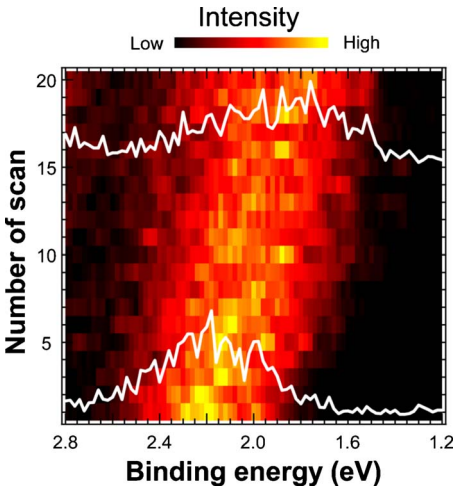


FIG. 3. (Color online) Intensity mapping of PES spectra for the HOMO band region as a function of number of scan, which corresponds to the photon irradiation time. The lower spectrum is obtained by the first scan, and the upper one corresponds to the twentieth scan. The intensity map and the spectra are obtained by using $h\nu$=80 eV.

of $H_2$TTDPz. By comparing the experimental and simulated spectra, we conclude that the HOMO, which consists of a single $\pi$ MO, is separated more than 1.4 eV from the second highest-occupied molecular orbital (HOMO-1) and therefore that the hole-transport property in $H_2$TTDPz film would mainly be determined by the HOMO band.

Since the damage induced by photon irradiation is a problem in many organic semiconductor films, we would like to mention the effect of photon to the HOMO of $H_2$TTDPz before starting the discussion on the electronic band structure. In order to investigate the photon-induced radiation damage, we have continuously measured the HOMO region at a fixed sample position using $h\nu$=80 eV. Figure 3 shows an intensity mapping of the PES spectra in the HOMO region as a function of scan number, and the PES spectra obtained by the first scan and by the twentieth one. As shown in the figure, the peak position and intensity of the HOMO change with increasing the number of scans. The $E_B$ of the HOMO shifted approximately 400 meV to the lower $E_B$ side from the first scan to the twentieth one, and the maximum intensity of the HOMO peak decreased by approximately 20% after the twentieth scan. This change is also recognized from the change in spectra, i.e., the $E_B$ of the HOMO of the twentieth scan is shifted from that of the first scan, the peak width becomes broader and the peak intensity becomes lower. These results indicate that the radiation damage cannot be ignored in the present study, and thus that one needs to decrease the photon flux and to measure the HOMO as quickly as possible to minimize the damage effects. (Here we note that the radiation damage at different $h\nu$ was smaller than that at $h\nu$=80 eV but large enough to be observable after several scans.) In the present study, we focused on the peak position of HOMO, measured a narrow $E_B$ range and used only the spectra obtained by the first scan to shorten the measuring time and thus to minimize the damage effects. We also changed the measurement positions on the sample after each scan.

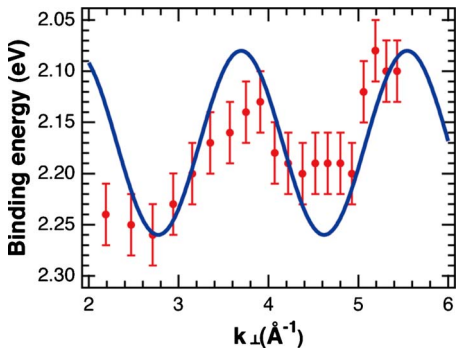


FIG. 4. (Color online) Dispersion of the HOMO band of the 80-Å-thick $H_2$TTDPz film grown on $SiO_2$, along the surface-normal direction. The solid curve is the dispersion obtained by analyzing the HOMO using a simple tight-binding model.

Figure 4 shows the band dispersion of the HOMO of the 80-Å-thick $H_2$TTDPz film grown on $SiO_2$ along the surface-normal direction obtained with $h\nu$=20–115 eV. The filled circles are the experimental result, which shows a dispersion width of approximately 180 meV, and the solid line is the dispersion obtained by analyzing the HOMO using a simple tight-binding model. (The experimental error bar, $\pm$0.03 eV, is estimated by measuring the HOMO at different sample positions using the same $h\nu$.) The use of a simple tight-binding model has been successfully used to explain the band dispersion of other organic materials.[3–6,20] According to the tight-binding model and assuming a free-electronlike final state, the energy-band dispersion along the surface normal is given by

$$E_B(k_\perp) = E_B^0 - 2t\cos(a_\perp k_\perp), \tag{1}$$

$$k_\perp = [2m_e^*(h\nu - E_B - V_0)]^{1/2}/\hbar, \tag{2}$$

where $E_B^0$, $t$, $a_\perp$, $k_\perp$, $m_e^*$, and $V_0$ are the energy of the band center, the transfer integral, the lattice spacing in the direction normal to the surface, the wave-vector component of photoexcited electron along surface normal, the effective mass of the photoelectron in the final continuum state, and the average inner potential in the solid for the final free-electronlike parabola, respectively.

The calculated dispersion was obtained by fitting the experimental data of the observed $E_B$ positions to a cosine curve in the tight-binding model.[4] Of the parameters, $E_B^0$ was found to be 2.17 eV from the experimental result. We used $V_0$=−5.1 eV, which was found appropriate for a number of other organic materials.[3,5,6] The other parameters, $t$ and $a_\perp$ were found to be $45\pm10$ meV and $3.4\pm0.1$ Å, respectively, from the fitting procedure. (The errors are obtained by considering the experimental data points at $k_\perp \sim 2.7$ and 5.3 Å$^{-1}$.) The obtained lattice spacing of $3.4\pm0.1$ Å agrees with the value 3.3 Å obtained from XRD measurements for $H_2$TTDPz thick films and $H_2$TTDPz crystals,[17] and therefore supports the validity of our analysis. The close spacing values also suggest that the packing structure of $H_2$TTDPz molecules are independent of the film thickness and the substrate roughness. By using the parameters obtained from the analy-

sis, the effective mass of the HOMO hole ($m_h^*$) is estimated to be $1/m_h^*=(0.14\pm0.03)/m_0$. Taking into account that the hole mobility ($\mu_h$) can be expressed as $\mu_h=e\tau/m_h>(e/m_h)(\hbar/W)$,[21,22] where $\tau$ and $W$ are the relaxation time due to scattering and the width of the HOMO band and can be simplify as $\mu_h>20(m_0/m_h^*)(300/T)$ in the case of $\tau>\hbar/k_BT$, the estimated value of $m_h^*$ leads to $\mu_h=8.2\pm1.8$ $cm^2/V$ s at the sample temperature used in the present study, 100 K. These values suggest that the bandlike transport would contribute to the entire charge-transport mechanism even in systems where thin films are grown on bumpy surfaces such as real device systems.

## IV. CONCLUSION

In conclusion, we have performed a PES study on an $H_2$TTDPz film grown on $SiO_2$, a prototype system for organic FET. By measuring the band structure along the surface-normal direction using different $h\nu$, we found that the HOMO show a band dispersion of approximately 180 meV *even on a film grown on a nonatomically flat surface*. The analysis performed using the tight-binding model leads to the estimation of the transfer integral of approximately $45\pm10$ meV for the $\pi$-$\pi$ interaction, the effective mass of the HOMO hole to be $1/m_h^*=(0.14\pm0.03)/m_0$, and the hole mobility as $\mu_h=8.2\pm1.8$ $cm^2/V$ s at 100 K. This result indicates that the bandlike transport along the surface-normal direction would play a role to the entire charge-transport mechanism in a real device system such as vertical-type static induction transistor.[23]

## ACKNOWLEDGMENTS

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*y_tanaka@mat.chem.nagoya-u.ac.jp
†kazuyuki_sakamoto@faculty.chiba-u.jp

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