Substituent-Induced Intermolecular Interaction in Organic Crystals Revealed by Precise Band-Dispersion Measurements

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We reveal quite small but different intermolecular valence band dispersions of sub-100-meV scale in crystalline films of Zn and Mn phthalocyanine (ZnPc and MnPc) and fluorinated ZnPc (F16ZnPc). The intermolecular transfer integrals are found to be reasonably dependent on the intermolecular distance with the $75 \pm 5$ meV/Å relation. Furthermore, the angle-resolved photoemission spectra show anomalous dispersive behaviors such as phase flips and local-dimerization-derived periodicities, which originate from the site-specific intermolecular interaction induced by substituents.

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Organic semiconductors have attracted considerable interest for (opto)electronics based on the degree of freedom of molecules. Solid-state functionalities of such organic semiconductors are dominated not only by individual molecular properties but also by their intermolecular interactions. This concerted interplay governs a key process of the electric conduction in organic electronics, which consists of the charge injection at interfaces near the Fermi level ($E_F$) [1–3] and the charge transport in organic solids [4]. The coherence of the charge transport is dominated by the intermolecular coupling of individual molecular orbitals, depending on various conformations. In this Letter, we discuss the electronic band dispersion, i.e., energy versus wave vector [$E(k)$], of organic solids with high experimental accuracy, which can assess charge transport properties and related phenomena.

The intermolecular $E(k)$ relation, originating from the periodicity of the molecular stacking structure, is in general difficult to observe precisely. This is because a very small bandwidth due to the weak intermolecular interaction is easily obscured by structural and thermal energy broadenings. Therefore, the intermolecular $E(k)$ relation has been mainly reported for high hole-mobility ($\mu_{hh}$) materials with relatively large bandwidths ($\geq 0.2$ eV) [5–10]. Even in these cases, however, the intermolecular $E(k)$ relation is dominated by charge transport properties of the target molecules themselves. Precise and systematic study on the intermolecular $E(k)$ relation has not yet been established as a universal role in organic semiconductors. Thus, the fundamental knowledge on the intermolecular interaction is still insufficient.

In the present work, by using angle-resolved photoemission spectroscopy (ARPES) with synchrotron radiation, we shed light on quite small intermolecular $E(k)$ relations of sub-100-meV scale in crystalline films of metal phthalocyanine (MPC, $M =$ metal). Even though MPC molecules are archetypal hole-transport materials in organic photovoltaics, their (opto)electronic properties have not yet been fully understood in relation to the intermolecular interaction because of the small $E(k)$ relation, which is easily buried by energetic disorders. Such a small $E(k)$ relation has not yet attracted much attention due to the lack of credible experimental data; however, present precise $E(k)$ measurements on MPC with different terminal groups and central metals are found to be sensitive and essential to characterize the intermolecular interaction in terms of the intermolecular distance, the conformational geometry, and the orbital character. Such a systematic approach provides deeper insights into the nature of the intermolecular interaction, which further represents the importance of the site specificity in the intermolecular interaction as a possible origin of unique molecular electronic properties.

A precise measurement of the small intermolecular $E(k)$ relation was carried out for MPC crystalline films on Au(111). Since the interaction between the physisorbed molecule and Au(111) is relatively weak [11,12], the self-assembling behavior by the intermolecular interaction plays a crucial role in the film crystallinity and its morphology from the initial stage of the film growth.

MPC crystalline films were prepared by vacuum deposition of purified MPC powders at 2 Å/min onto the clean Au(111) surface at 300 K. The Au(111) substrate was cleaned by repeated cycles of Ar$^+$ sputtering and annealing at 700 K, as confirmed by a core-level and a Shockley-state photoemission, and LEED. For molecular films, the photoemission peaks show the thickness-dependent energy shift, originating from the photohole relaxation by surrounding mediums [13,14]. Thus, the MPC deposition was continued until the MPC-derived peaks were stabilized in energy with respect to the deposition amount. The deposited MPC films were subsequently annealed at 350–360 K, which is the optimized temperature for the fabrication of MPC-based photovoltaic cells [15]. This annealing induces the enhancement of the Au 4f photoemission peak as the result of the molecular aggregation by further crystallization. The sample crystallinity was characterized by $N$ $K$-edge x-ray absorption spectroscopy (XAS), LEED, and ex situ CuKα x-ray diffraction (XRD) (see the Supplemental...
Material [16]). The ARPES and XAS experiments were performed at a high-brilliant vacuum ultraviolet and soft x-ray in-vacuum linear-polarized undulator beam line 6U of UVSOR-III at the Institute for Molecular Science. The ARPES spectra were obtained by using a micro-channel-plate detector of a hemispherical electron energy analyzer (A1, MB Scientific). The total energy resolution of 13 meV and the angular resolution of 0.2° were used in the present work. In order to avoid the radiation damage of the sample, by incident photons during the ARPES measurements, we chose a different fresh sample position after every measurement.

The ZnPc molecules on Au(111) form a flat-lying crystalline film with the intermolecular distance along the surface normal (a⊥) of 3.326 Å in a Stranski-Krastanov growth mode (see the Supplemental Material [16]). In order to investigate the $E(k)$ relation in the π-π stacking direction, the normal-emission ARPES spectra as a function of the photon energy ($h\nu$) were measured for the ZnPc crystalline film at the specimen temperature ($T$) of 15 K [Fig. 1(a)]. Because of the growth mode of the ZnPc molecule on Au(111), the small remanent substrate appears and is utilized for the energy calibration for the ARPES measurements, the resultant hole effective mass ($m_h^*$) of 15.0$m_0$, where $m_0$ is the free-electron mass. The observed $m_h^*$ gives the ideal $\mu_h^*$ of 26.6 cm$^2$ V$^{-1}$ s$^{-1}$ for the HOMO of α-ZnPc crystals at 15 K from $\mu_h^* > 20(m_0/m_h^*)300/T$ [5].

In α-ZnPc crystals, two nonequivalent molecules in the unit cell should induce the HOMO-band splitting, as

![Figure 1](image-url)  
**FIG. 1** (color online). Intermolecular $E(k)$ relation in the ZnPc crystalline film on Au(111). (a) $h\nu$-dependent normal-emission ARPES spectra at 15 K ($h\nu$ step = 4 eV). The experimental geometry, wide valence-band spectrum at $h\nu$ = 45 eV, and the linear combination of atomic orbitals (LCAO) pattern of the HOMO of ZnPc are also shown. (b) $E(k_{\perp})$ map obtained from the second derivative of the ARPES spectra ($-d^2I/dE_h^2$), with the tight-binding fitting (white curve). Sum of the $-d^2I/dE_h^2$ spectra is shown in the right side of the $E(k_{\perp})$ map. (c) $T$ dependence of the HOMO band at the Γ and Y points, measured at $h\nu = 60$ and 90 eV, respectively. The HOMO-band dispersion is illustrated in the inset.

After converting to $k_{\perp}$ from $h\nu$ in the second derivative of the ARPES spectra, the $E(k_{\perp})$ map for the ZnPc crystalline film at 15 K is obtained [Fig. 1(b)]. For the $k_{\perp}$ conversion, we used an inner potential of −1.0 eV, based on the low-energy electron transmission experiment on α-CuPc [17]. The weak shoulder structure in the ARPES spectra around $E_h = 2.2$ eV is resolved in the $E(k_{\perp})$ map as labeled HOMO-1 and is derived from a Zn 3d, $\pi^-$ orbital with the $b_{1g}$ symmetry [18]. In the $E(k_{\perp})$ map, the HOMO, HOMO-1, and $\pi$ peaks show the dispersion with the same $k_{\perp}$ periodicity. The inflection points in the periodic dispersion correspond to the Γ and Y points in the Brillouin zone of the ZnPc crystalline film, as determined from $a_{\perp} = 3.326$ Å by XRD. This agreement proves that the observed periodic dispersion is ascribed to the delocalized band formation due to the weak intermolecular van der Waals (vdW) interaction. The one-dimensional tight-binding fitting, $E(k_{\perp}) = E_0^h - 2t_1 \cos(a_{\perp}k_{\perp})$, as shown by white curves in the $E(k_{\perp})$ map, to the HOMO-band dispersion at 15 K gives the dispersion center $(E_0^h)$ of 1.388 eV, the transfer integral $(t_1)$ of 23 meV, and the resultant hole effective mass $(m_h^*)$ of 15.0$m_0$, where $m_0$ is the free-electron mass. The observed $m_h^*$ gives the ideal $\mu_h^*$ of 26.6 cm$^2$ V$^{-1}$ s$^{-1}$ for the HOMO of α-ZnPc crystals at 15 K from $\mu_h^* > 20(m_0/m_h^*)300/T$ [5].
observed for pentacene and rubrene with the split energy of \(-0.4\) eV by relatively strong intermolecular interaction [7–9]. In the present case of ZnPc, however, the HOMO-band splitting is not resolved by the weak intermolecular interaction. It might be reflected in the \(T\)-dependent width and energy of the HOMO peak according to the small polaron theory based on the electron-phonon (\(e\)-\(ph\)) coupling [19,20]. Figure 1(c) shows the \(T\)-dependent HOMO peak at the \(\Gamma\) and \(Y\) points, measured at \(h\nu = 60\) and \(90\) eV, respectively. The \(\Gamma\)-point HOMO shifts to the lower \(E_b\) side with increasing \(T\), while the \(Y\)-point HOMO does not shift, indicating the narrowing of the bandwidth at higher \(T\). Furthermore, only the \(\Gamma\)-point HOMO shows a peak width narrowing with increasing \(T\) (435 meV at 15 K and 380 meV at 300 K), which is the opposite trend of the thermal broadening in the remanent substrate \(E_F\). This evidence indicates that the \(\Gamma\)-point HOMO is weakly split at 15 K. Here, the bandwidth (4\(\Delta\)) of 92 meV at 15 K is of the same order as the reorganization energy for local phonons in CuPc [21]. It is considered that the \(T\)-dependent transition between the incoherent hopping transport by the local \(e\)-\(ph\) coupling and the coherent band-like transport by the nonlocal \(e\)-\(ph\) coupling exists within the energy scale of 100 meV in \(\alpha\)-ZnPc crystals.

Since functionalities of MPC can be modified by the chemical substitution of terminal groups and central metals in the molecule, the present precise \(E(k)\) observation for ZnPc is considered to be a starting system in carrying out a systematic study on the dependence of the intermolecular interaction. In this context, we prepared crystalline films of fluorinated ZnPc (F\(_{16}\)ZnPc) and MnPc on Au(111), obtained by the same sample preparation procedure for ZnPc. It is confirmed by XAS and XRD that the molecules form the \(\beta\)-bilayer (\(\beta_{bl}\))-crystalline phase [22,23] with \(a_\perp = 3.236\) Å for F\(_{16}\)ZnPc and the \(\alpha\)-crystalline phase with \(a_\perp = 3.273\) Å for MnPc (see the Supplemental Material [16]).

As shown in the inset of Fig. 2(a), the HOMO of F\(_{16}\)ZnPc is derived from the C 2\(p\) and F 2\(p\) orbitals with \(a_{1u}\) symmetry. Different intermolecular interaction between F\(_{16}\)ZnPc and ZnPc is expected due to the F 2\(p\) orbital and the different \(a_\perp\). The \(h\nu\) dependence of the normal-emission ARCES spectra for the F\(_{16}\)ZnPc crystalline film on Au(111) at 15 K is shown in Fig. 2(a). The HOMO peak shows a clear dispersive behavior with \(h\nu\). Figure 2(b) shows the \(E(k_\perp)\) map in the HOMO-band region of F\(_{16}\)ZnPc, in comparison with that of ZnPc. We found that the HOMO bandwidth of F\(_{16}\)ZnPc (120 meV) is larger than that of ZnPc (92 meV), which is reasonably explained by a shorter intermolecular distance \(a_\perp = 3.236\) Å for F\(_{16}\)ZnPc than \(a_\perp = 3.326\) Å for ZnPc.

A more important result in Fig. 2(b) is the difference in the HOMO dispersion phase between ZnPc and F\(_{16}\)ZnPc crystalline films. From the \(\Gamma\) to \(Y\) point, the HOMO band of ZnPc disperses to the lower \(E_b\) side, in agreement with the calculated band structure of \(\alpha\)-CuPc [24]. On the other hand, the HOMO dispersion direction of F\(_{16}\)ZnPc is flipped from that of ZnPc. The observed \(E(k)\)-phase flip may originate from the modification of the intermolecular HOMO overlap between ZnPc and F\(_{16}\)ZnPc due to the different conformational structure and an intermolecular interaction between Pc \(\pi\) and F 2\(p\).

The next modification is on the central metal, MnPc. The HOMO of MnPc is derived from the half filled Mn 3\(d\) orbital with \(e_\pi\) symmetry, and the HOMO-1 of MnPc corresponds to the HOMO of ZnPc [25–27]. The half filled HOMO of MnPc induces the crystallinity-dependent magnetic properties [28]. Figure 3(a) shows the \(h\nu\) dependence of the normal-emission ARCES spectra for the MnPc crystalline film on Au(111) at 15 K. The relative intensity between the HOMO (Mn 3\(d\)) and HOMO-1 (C 2\(p\)) peaks changes with \(h\nu\) due to different ionization cross sections. The Mn 3\(d\) and C 2\(p\) peaks show a clear dispersive behavior with \(h\nu\). Moreover, the Mn 3\(d\) peak consists of two components, indicating the relatively strong interaction at the Mn site. Figure 3(b) shows the \(E(k_\perp)\) map for the MnPc crystalline film on Au(111) at 15 K, wherein the \(\Gamma\) and \(Y\) points are estimated from \(a_\perp = 3.273\) Å (see the Supplemental Material [16]). The agreement between the periodicity of the C 2\(p\) dispersion and the Brillouin zone indicates that the observed C 2\(p\) dispersion is ascribed to the intermolecular vdW interaction. From the tight-binding fitting, we found that the bandwidth for the C
ZnPc and HOMO of MnPc are also shown. (b) $h/C_23\text{ band spectrum at } 15\text{ K.}$ The experimental geometry, wide valence-band spectrum at $h\nu = 45\text{ eV, and the LCAO pattern of the HOMO of MnPc are also shown.}$ (b) $E(k)$ map obtained from the second derivative of the ARPES spectra, with the tight-binding fitting (white curve).

The $2p$ band of MnPc (104 meV) is between ZnPc (92 meV) and $F_{16}\text{ZnPc}$ (120 meV), which is consistent with $a_\perp = 3.273\text{ Å}$ for MnPc between $a_\perp = 3.326\text{ Å}$ for ZnPc and $a_\perp = 3.236\text{ Å}$ for $F_{16}\text{ZnPc}$.

For the Mn 3$d$ peak, the peak splitting and its dispersion are resolved in the $E(k)$ map. The $k_\perp$ periodicity of the Mn 3$d$ dispersion is 1/2 times that of the C 2$p$ dispersion as labeled $Y_{2}\alpha$ and is simply thought to originate from the local dimerization and the resultant double-$a_\perp$-periodicity modulation at the Mn site. Such evidence is not observable for the full-filled Co 3$d$ peak of the CoPc crystalline film (see the Supplemental Material [16]), suggesting the importance of the half filled orbital character. This is an indication of the strong electron correlation at the Mn site, which induces the smaller $m^*_h$ of 3.6$m_0$ for the topmost Mn 3$d$ band as well as the antiferromagnetism found for the MnPc crystalline film [28].

### Table I.

<table>
<thead>
<tr>
<th>$a_\perp$</th>
<th>$E^0_\parallel$ (meV)</th>
<th>$t_\perp$ (meV)</th>
<th>$m^*_h$ (eV cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_\parallel$ (eV cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnPc</td>
<td>3.326</td>
<td>1.388</td>
<td>23</td>
<td>15.0$m_0$</td>
</tr>
<tr>
<td>MnPc</td>
<td>3.273</td>
<td>1.274</td>
<td>26</td>
<td>13.7$m_0$</td>
</tr>
<tr>
<td>$F_{16}\text{ZnPc}$</td>
<td>3.236</td>
<td>1.251</td>
<td>30</td>
<td>12.2$m_0$</td>
</tr>
</tbody>
</table>
As demonstrated above, precise and systematic intermolecular \( E(k) \) measurements on various organometallic complexes enable us to reveal different intermolecular interactions quantitatively and to obtain a quantitative guiding principle for the design of functional molecular systems and their theoretical considerations from the viewpoint of the intermolecular interaction in addition to the individual molecular property, as a critical tool for organic electronics.

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