Electronic Structures of a Well-Defined Organic Hetero-Interface: C\textsubscript{60} on Pentacene Single Crystal* 

Masayuki Yamamoto  
Graduate School of Advanced Integration Science, Chiba University 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Yasuo Nakayama†  
Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan, and  
Faculty of Engineering, Chiba University, Japan

Yuki Uragami and Hiromi Kinjo  
Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Yuta Mizuno  
Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Kazuhiko Mase  
Institute for Materials Structure Science, High Energy Accelerator Research Organization (KEK), Japan, and  
Department of Materials Structure Science, The Graduate University of Advanced Studies, 1-1 Oho, Tsukuba 305-0801, Japan

Kaveenga Rasika Kosswattage  
Center for Frontier Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Hisao Ishii  
Center for Frontier Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan, and  
Graduate School of Advanced Integration Science and Faculty of Engineering, Chiba University, Japan  
(Received 24 December 2014; Accepted 9 February 2015; Published 28 February 2015)

Electronic structures of donor-acceptor hetero-interfaces are crucial for performance of organic solar cell devices. In the present study, a well-defined organic molecular interface of pentacene single crystal and C\textsubscript{60} overlayer is elucidated by x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and photoelectron yield spectroscopy (PYS). An energy level diagram at this hetero-molecular contact in the “head-on” orientation is derived, which reveals the vacuum level alignment and flat-band conditions. [DOI: 10.1380/ejssnt.2015.59]

Keywords: Photoelectron spectroscopy; Organic semiconductor; Pentacene; C\textsubscript{60} buckminsterfullerene; Photoelectron yield spectroscopy

I. INTRODUCTION

Hetero-interfaces between organic materials have crucial importance for functionalities of organic electronic devices. In the case of organic photovoltaics (OPVs), practical solar cell performance had not been realized until innovation of donor-acceptor bi-layer structures [1]. Generally, engineering of these interfaces has been one of the most essential issues for designing high-performance devices.

So far, number of studies by photoemission have addressed the electronic structures of organic hetero-interfaces [2-7]. However, most of the conventional works were conducted on structurally un-defined interfaces built onto amorphous or polycrystalline organic thin films, and thus disordered natures of the interfaces have hindered one from accessing unambiguous insights into electronic properties of the inter-molecular contact. One paradigm to resolve this question will be usage of organic single crystals instead of thin films for construction of uniform and well-defined hetero-interfaces. Nevertheless, photoemission measurements on micrometer-thick organic single crystal samples have been problematic because of sample charging caused by insufficient electric conductivity of organic semiconductor materials.

Our group has succeeded in overcoming this problem to demonstrate the highest occupied states, valence band dispersion, and core levels of organic semiconductor single crystals by means of photoelectron yield spectroscopy (PYS) and laser-assisted photoelectron spectroscopy techniques [8-10]. These methodologies exploited possibilities for approaching the electronic natures at the inter-molecular contacts through the established surface science paradigm. Actually, the electronic structures of an ordered interface between an organic single crystal and overlayer of an organic dielectric material were successfully revealed by these techniques [11].

In the present work, the electronic structures of a well-defined organic donor-acceptor hetero-interface consisting of the single crystal of pentacene and overlayer of...
C₆₀ buckminsterfullerene were elucidated by means of x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and PYS. Each target material, pentacene and C₆₀, is respectively a representative p- and n-type organic semiconductor, and a combination of these is known to constitute one of the most proto-typical organic solar cell devices [12]. Interface formation of this couple is interesting also in terms of their distinct molecular symmetries, namely pentacene has a molecular shape of a uniaxial elongation whereas C₆₀ is of the spherical symmetry [13]. A number of experimental and theoretical studies so far addressed energetics and dynamics of the inter-molecular contact of these two materials [14-20]. Since calculations have predicted that the electronic energy levels and intermixing tendency strongly depend on the contact orientation i.e. which face of the pentacene the C₆₀ molecule touches [17,19]. In this context, the present system will disclose the interface electronic structures of a specific molecular orientation at the topical molecular contact (so-called “head-on”, see Fig. 1) owing to uniformity and rigidity of the pentacene single crystal surface as a substrate.

II. EXPERIMENTAL

Pentacene single crystals (Pen-SCs) of a few millimeters-square wide and several micrometer-thick were produced by a horizontal physical vapor transport technique [21] in purified nitrogen stream. After production, the crystals were bounded onto gold-coated Si plates with silver paste in air for XPS and UPS experiments, while they were fixed by a tiny piece of conductive carbon tape onto bare Si substrates for PYS. Detailed description on the sample preparation scheme can be found elsewhere [22,23]. It should be noted that the Pen-SC samples were used without any surface treatment and thus the surface may not be the “clean surface” but a few percent of oxidized species existed at the surface [10].

C₆₀ (99.98%) was purchased from Advanced Technology Research and was used as received. It was deposited onto the Pen-SC surface from a graphite crucible at the rate of 0.1 - 1.5 nm/min which was monitored by a quartz microbalance and was calibrated by using a step profilometer afterwards. The surface morphology of this interface system was checked with atomic-force microscopy (AFM) in air. A typical topography is shown in Fig. 1. It was revealed that the C₆₀ overlayer grows in the Volmer-Weber (VW) mode on the Pen-SC surface to aggregate into table-shaped islands of 2 – 6 nm-high. Details in structural evolution of the topical interface are beyond the scope of this study.

XPS and UPS measurements were carried out at BL-13A [24] or 13B of Photon Factory (PF), KEK, by means of concentric hemispherical analyzer SES-200 of Gamma-data Scienta, while PYS was conducted by a home-built system equipped with an energy-tunable UV light source, hemispherical total electron collector, and precise ammeter (Keithley 6430) to measure the photoelectron emission amount as a function of excitation photon energy [23]. XPS and UPS spectra were obtained at the photon energy (hv) of 820 and 30 eV where the electron pass energy through the analyzer was set at 75 and 10 eV, respectively. In order to cancel photoemission-induced sample charging (“charge-up”), Pen-SC was illuminated by continuous-wave laser light (405 nm; 3.06 eV) to boost photoconductivity during XPS and UPS measurements [9]. In the case of XPS, a positive sample bias (\(V_s\)) of +100 V was applied to the sample for the sake of suppressing secondary electron emission to reduce total photoemission amount [10]. Along with each UPS measurement, the vacuum level position (i.e. work function) of the sample was determined from the secondary electron cutoff (SECO) taken under a negative sample bias (\(V_s = -5\) V). All the photoemission spectra are displayed in the binding energy (BE) scale with respect to the Fermi level where the energy standard was calibrated based on the Au 4f/7/2 peak (BE = 83.95 eV [25]) and Fermi edge for XPS and UPS, respectively. All measurements were conducted at room temperature.

III. RESULTS AND DISCUSSIONS

Figure 2(a) shows evolution of C 1s XPS spectra of a Pen-SC sample on step-by-step deposition of C₆₀. The C 1s peak of the Pen-SC appearing in the range of BE = 283 – 284.5 eV exhibited a left-weighted asymmetric profile and can be separated into two components (C1 and C2). This characteristic is consistent with a report for the gas phase pentacene molecules [26] as well as our results on the Pen-SC [10]. C₆₀ deposition yielded a new peak at BE ~ 285 eV, whose shape was symmetric and it can satisfactorily be reproduced by a single component. The new peak, attributed to the C 1s level of the C₆₀ overlayer, can be clearly separated from that of the Pen-SC. It should be mentioned that some extent (~ 0.1 V) of uncertainty in \(V_s\) has to be taken into account for the present XPS data, which may result in random fluctuation of each peak position. Meanwhile, the photoemission intensity is capable of accurate quantitative analyses. In the inset viewgraph, relative signal strengths of Pen-SC and C₆₀ to the total C
FIG. 2. (a) C 1s XPS, (b) UPS, and (c) SECO spectra of (o) a pentacene single crystal and that covered with (i) 0.16, (ii) 0.41, (iii) 0.82, (iv) 1.6, (v) 4.1, and (vi) 8.2 nm-thick C$_{60}$. For the XPS and UPS spectra (except the inset spectrum of b), the Shirley-type background was subtracted. The SECO spectra were normalized by respective maximum intensities. (Inset of a) Relative C 1s peak intensity of the pentacene (red marks) and C$_{60}$ (blue) to the total (Pen + C$_{60}$) intensity plotted as a function of the C$_{60}$ thickness. (Inset of b) Extended spectra of (v) in a region of the pentacene HOMO.

1s intensity are plotted as a function of the C$_{60}$ thickness. In the smaller-half thickness region, the Pen-SC and C$_{60}$-derived signals exhibited linear attenuation and increase, respectively, to the C$_{60}$ thickness. This is consistent with the VW-type growth mode where C$_{60}$ islands, which were sufficiently thick to overwhelm the photoemission signal from the underlying Pen-SC, gradually encroached upon the surface area as the overlayer growth. The trends of the C 1s intensity variation imply that the whole surface was covered with the C$_{60}$ islands at around 5 nm of the C$_{60}$ thickness. This value is also reasonable to the height of the C$_{60}$ islands observed by AFM.

UPS spectra taken on the identical samples to the XPS measurements are shown in Fig. 2(b). Note that the measurements were conducted in an “angle-integrated” condition and thus momentum-integrated density-of-states are represented in the obtained spectra [11,23]. The highest occupied molecular orbital (HOMO)-derived peak of pentacene appeared in the range of BE = 0.5 - 1.3 eV. This feature can be separated into two spectral components (H1 and H2) of dissimilar height and width which phenomenologically approximate the upper and lower valence bands, respectively, of the Pen-SC [23,27]. Here we only discuss the low BE component (H1) which predominantly play a role of a hole conduction state. The onset energy of the HOMO of the Pen-SC before C$_{60}$ deposition is determined to be BE = 0.52 eV by linear fitting of the peak slope. This position was substantially unchanged until complete disappearance of this peak. On the other hand, the HOMO of C$_{60}$ emerged at around BE = 2.5 eV, which overlapped to the next-HOMO feature of pentacene and became visible above 1 nm thickness. No apparent energy shift during growth of the C$_{60}$ overlayer was observed for the C$_{60}$ HOMO level within the accuracy of the present analysis. The onset energy of the C$_{60}$ HOMO is determined to be 1.94 eV for the thickest C$_{60}$ overlayer. Therefore, the HOMO level offset between donor and acceptor molecules of the present system is estimated to be 1.4(±0.1) eV from the present UPS results.

The vacuum level position of the sample is represented by the SECO energy. As shown in Fig. 2(c), the SECO position was preserved at BE = 25.53(±0.04) eV which corresponds the sample work function (WF) value of 4.47 eV. Accordingly, the ionization energies of the Pen-SC and C$_{60}$ overlayer are settled to be 4.99 eV and 6.41 eV, respectively. These values agree well with our previous results [6,23].

The aforementioned photoemission results are summarized into Fig. 3, in which the work function and binding energy of the HOMO onset, HOMO peak, and C 1s peak(s) of the Pen-SC and C$_{60}$ are plotted as a function of the C$_{60}$ thickness. The results obtained on different Pen-SC samples are also shown in the graph. This suggests that the vacuum level shift and band bending are negligibly small if any within an energetic accuracy (∼0.1 eV) of the present work, in other words the vacuum level alignment and flat band condition are fulfilled, in the present donor-acceptor hetero-interface.

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
The energetics of the HOMO states of the present system were cross-checked by PYS. This method mainly provides direct information about the HOMO onset position for organic materials with respect to the vacuum level, instead of the Fermi level, without any unreliability caused by the sample charging [28]. Figure 4(a) shows the PYS spectra of a Pen-SC and C$_{60}$ overlayers of various thicknesses. The photoelectron yield caused by the excitation photon smaller than 6.4 eV was exclusively from the Pen-SC because of energy shortage for accessing the deeply-lying C$_{60}$ HOMO. Declination of the photoelectron yield in the energy range of 5 – 6.5 eV was caused by coverage of the Pen-SC surface with the C$_{60}$ overlayer. In Fig. 4(b), the PYS spectra of the photoemission threshold region of the Pen-SC are plotted in an extended scale. Because of higher sensitivity and longer probing depth of the PYS method in comparison to the conventional UPS [29], photoelectron yield from the Pen-SC was detected even beyond the C$_{60}$ thickness of completion of the overlayer (~5 nm). It is empirically known that the photoelectron yield $Y$ can be expressed by the following power law as a function of the photon energy $h\nu$ [30];

$$Y(h\nu) = Y_0(h\nu - I_{th})^n \cdot S(h\nu - I_{th}),$$

where $I_{th}$ is the threshold ionization energy of the sample, $Y_0$ is a constant corresponding to the total photoemission strength, $S(x)$ is an adequate step function that switches from 0 to 1 when $x$ becomes negative to positive, and $n = 3$ is often adopted empirically for organic materials [31]. Note that this formula is applicable only when $(h\nu - I_{th})$ is small. By fitting each PYS curve with this equation, the ionization energy value $I_{th}$ of the Pen-SC is determined for each C$_{60}$ thickness. The $I_{th}$ of the C$_{60}$ overlayer can be obtained after subtracting the photoelectron contribution of the Pen-SC from the total $Y$ (spectra not shown). The $I_{th}$ values of the Pen-SC and C$_{60}$ derived from the PYS results are plotted as a function of the C$_{60}$ thickness in the inset graph of Fig. 4(b). As seen in this figure, the PYS results are fairly consistent with the aforementioned UPS ones. The energy offset of the HOMO level threshold is estimated to be 1.7(±0.2) eV from the present PYS results.

From the above, the energy level diagram at this well-defined organic hetero-interface can be illustrated as Fig. 4(c). Here, some extent of mismatch in the HOMO offset between the UPS and PYS results is taken into consideration equally. Since the energy gap width between the HOMO and lowest unoccupied molecular orbital (LUMO) of C$_{60}$ was reported to be 2.3 eV [32], the “photo-voltaic gap” $\Delta_{DA}$ between the Pen-HOMO and C$_{60}$-LUMO of 0.75(±0.25) eV is expected to be built within this hetero-interface in the case of the “head-on” molecular orientation.

One of the leading factors dominating the performance of OPVs, the open circuit voltage $V_{oc}$, is regulated by this $\Delta_{DA}$ magnitude [33]; namely, the largest available $V_{oc}$ is restricted at the energy gap between the donor-HOMO and acceptor-LUMO minus the binding energy of geminate electron-hole pairs at the hetero-interface [34]. As the present molecular combination consists one of the most protoypical OPV devices [12], several works have been addressed the interface electronic structures of pentacene and C$_{60}$ so far. Kang et al. reported an interface energy diagram between the C$_{60}$ overlayer and pentacene film formed onto the clean Au surface based on their UPS and XPS results [14]. They proposed $\Delta_{DA}$ of 1.56 eV and an upward vacuum level shift of 0.36 eV toward the C$_{60}$ side. Salzmann and co-workers studied this bi-molecular systems on a conductive polymer film to find the gap width of 1.15 eV and an absence of the vacuum level shift [15]. However, since reported $V_{oc}$ values for this molecular combination is less than 0.5 eV [35], even if an energy conversion loss of 0.3 – 0.5 eV [36,37] due to the binding energy of the electron-hole pairs is taken into account, the $\Delta_{DA}$ values of these previous works may be overestimated to explain the practical systems. In contrast, more practical $\Delta_{DA}$ was derived from this work, even though the interface itself was built onto the single crystal surface and thus much simplified in comparison to realistic devices. Slight reduction of the present $\Delta_{DA}$ than expected might be ascribed to oxidation of pentacene due to pre-exposure to air, which is also known to degrade $V_{oc}$ of practical OPV devices [38].

The substance of the carrier generation in OPV devices is nothing but charge transfer reactions between donor and acceptor molecules, and therefore molecular orientation at the hetero-interfaces is generally a crucial factor to regulate the device performance through modification of inter-molecular coupling [39]. As mentioned above, theoretical calculations have predicted that the energetics at the pentacene-C$_{60}$ hetero-interfaces will depend on the molecular orientation at the contact [17,18,20]. A general trend can be derived from these predictions that the inter-molecular interaction is weakened and the vacuum level shift changes from positive to negative or nearly zero when the contact orientation transforms from “flat-on” (where a pentacene molecule contacts to C$_{60}$ at its $\pi$-
conjugated face) to “head-on” (pentacene touches C\textsubscript{60} at its either end of the benzene rings, see Fig. 1). Since the Pen-SC surface exposes the end of the pentacene molecules at its surface, the present molecular interface is of exclusively “head-on” orientation. Accordingly, the present findings of the absence of the vacuum level shift and band bending are consistent with the theoretical predictions. Taking into consideration that the “head-on” orientation is thought to be dominant in the pilot OPV devices with a planar pentacene-C\textsubscript{60} heterojunction [40], which was reported to yield rather better power conversion efficiency than mixed heterojunction OPVs consisting of this materials’ combination [15], the present results obtained at a structurally well-defined molecular hetero-interface provide realistic insights into electron energetics in the pentacene-C\textsubscript{60} OPV devices.

In conclusion, the electronic structures of a well-defined pentacene-C\textsubscript{60} hetero-interface were elucidated by means of XPS, UPS, and PYS. No apparent energy shift of the C 1s nor HOMO levels of pentacene and C\textsubscript{60} was revealed by XPS and UPS. Attenuation of the photoemission signal from the Pen-SC substrate corresponded to the VW growth mode of the C\textsubscript{60} islands to complete the overlayer at the total thickness of ca. 5 nm. By means of PYS, photoelectron yield from the Pen-SC underneath the C\textsubscript{60} overlayer was detected and its HOMO onset energy with respect to the vacuum level was successfully determined. Neither the work function nor any electronic levels of the Pen-SC and C\textsubscript{60} exhibited detectable energy shift during growth of the C\textsubscript{60} overlayer within an accuracy of the present study (~0.1 eV). The energy level diagram at the pentacene-C\textsubscript{60} interface in the “head-on” contact orientation was derived from the present results, which suggests the vacuum level alignment and flat band condition. The energy gap between the donor (Pen-SC) HOMO and acceptor (C\textsubscript{60}) LUMO was estimated to be 0.75(±0.25) eV.

Acknowledgments

Financial supports from JSPS-KAKENHI (23750209), TEPCO Memorial Foundation, Yazaki Memorial Foundation for Science and Technology, and JGC-S Scholarship Foundation are gratefully acknowledged. The XPS and UPS experiments were conducted under approval of the KEK-PF Program Advisory Committee (2011G151 and 2013G135). This work has been also partially supported by JSPS-KAKENHI (21245042 and 25288144), G-COE (Advanced School for Organic Electronics; G-3) and TAKUETSU Programs of Chiba University, FIRST Program of Kyushu University, Izumi Science and Technology Foundation, and Casio Science Promotion Foundation.

[1] C. W. Tang, Appl. Phys. Lett. 48, 183 (1986).
[2] I. G. Hill, D. Milliron, J. Schwartz, and A. Kahn, Appl. Surf. Sci. 166, 354 (2000).
[3] N. R. Armstrong, W. Wang, D. M. Alloway, D. Placencia, E. Ratcliff, and M. Brumberg, Macromol. Rapid Commun. 30, 717 (2009).
[4] J. Wagner, M. Gruber, A. Wilke, Y. Tanaka, K. Topczak, A. Steindamm, U. Hörmann, A. Opitz, Y. Nakayama, H. Ishii, J. Pflaum, N. Koch, and W. Brütting, J. Appl. Phys. 111, 054509 (2012).
[5] Y. Nakayama, S. Machida, Y. Miyazaki, T. Nishi, Y. Noguchi, and H. Ishii, Org. Electron. 13, 2850 (2012).

[6] Y. Nakayama, T. L. Nguyen, Y. Ozawa, S. Machida, T. Sato, H. Takaizumi, Y. Noguchi, and H. Ishii, Adv. Energy Mater. 4, 1301354 (2014).

[7] U. Hörmann, C. Lorch, A. Hinderhofer, A. Gerlach, M. Gruber, J. Kraus, B. Sykora, S. Grob, T. Linderl, A. Wilke, A. Opitz, R. Hansson, A. S. Anselmo, Y. Ozawa, Y. Nakayama, H. Ishii, N. Koch, E. Moons, F. Schreiber, and W. Brütting, J. Phys. Chem. C 118, 26462 (2014).

[8] Y. Nakayama, S. Machida, T. Minari, K. Tsukagoshi, Y. Noguchi, and H. Ishii, Appl. Phys. Lett. 93, 173305 (2008).

[9] S. Machida, Y. Nakayama, S. Duhm, Q. Xin, A. Fujinakoshi, N. Ogawa, S. Kera, N. Ueno, and H. Ishii, Phys. Rev. Lett. 104, 156401 (2010).

[10] Y. Nakayama, Y. Uragami, M. Yamamoto, K. Yonezawa, K. Mase, S. Kera, H. Ishii, and N. Ueno, Submitted (n.d.).

[11] Y. Nakayama, J. Niederhausen, S. Machida, Y. Uragami, H. Kinjo, A. Vollmer, J. P. Rabe, N. Koch, and H. Ishii, Org. Electron. 14, 1825 (2013).

[12] S. Yoo, B. Domercq, and B. Kippelen, Appl. Phys. Lett. 85, 5427 (2004).

[13] A. Hinderhofer and F. Schreiber, Chemphyschem 13, 628 (2012).

[14] S. J. Kang, Y. Yi, C. Y. Kim, S. W. Cho, M. Noh, K. Jeong, and C. N. Whang, Synth. Met. 156, 32 (2006).

[15] I. Salzmann, S. Duhm, R. Opitz, R. L. Johnson, J. P. Rabe, and N. Koch, J. Appl. Phys. 104, 114518 (2008).

[16] T. Breuer and G. Witte, ACS Appl. Mater. Interfaces 5, 9740 (2013).

[17] S. Verlaak, D. Beljonne, D. Cheyns, C. Rolin, M. Linares, F. Castet, J. Cornil, and P. Heremans, Adv. Funct. Mater. 19, 3809 (2009).

[18] M. Linares, D. Beljonne, J. Cornil, K. Lancaster, J.-L. Brédas, S. Verlaak, A. Mityashin, P. Heremans, A. Fuchs, C. Lennartiz, J. Idé, R. Mérreau, P. Aurel, L. Ducasse, and F. Castet, J. Phys. Chem. C 114, 3215 (2010).

[19] Y.-T. Fu, C. Risko, and J.-L. Brédas, Adv. Mater. 25, 878 (2013).

[20] J. Beltrán, F. Flores, and J. Ortega, Phys. Chem. Chem. Phys. 16, 4208 (2014).

[21] R. Laudise, C. Kloc, and P. Simpkins, J. Cryst. Growth 187, 449 (1998).

[22] Y. Nakayama, Y. Uragami, S. Machida, K. R. Koswattage, D. Yoshimura, H. Setoyama, T. Okajima, K. Mase, and H. Ishii, Appl. Phys. Express 5, 111601 (2012).

[23] Y. Nakayama, Y. Uragami, M. Yamamoto, S. Machida, H. Kinjo, K. Mase, K. R. Koswattage, and H. Ishii, Jpn. J. Appl. Phys. 53, 01AD03 (2014).

[24] A. Toyoshima, T. Kikuchi, H. Tanaka, K. Mase, K. Amemiya, and K. Ozawa, J. Phys. Conf. Ser. 425, 152019 (2011).

[25] M. Seki, H. Gilmore, and G. Bannier, Surf. Interface Anal. 649, 642 (1998).

[26] A. Alagia, C. Baldacchini, M. G. Betti, F. Bussolotti, V. Carravetta, U. Ekström, C. Mariani, and S. Stanges, J. Chem. Phys. 122, 124305 (2005).

[27] H. Yoshida and N. Sato, Phys. Rev. B 77, 235205 (2008).

[28] Y. Nakayama, S. Machida, D. Tsunami, Y. Kimura, M. Niwano, Y. Noguchi, and H. Ishii, Appl. Phys. Lett. 92, 153306 (2008).

[29] Y. Ozawa, Y. Nakayama, S. Machida, H. Kinjo, and H. Ishii, J. Electron Spectrosc. Relat. Phenom. 197, 17 (2014).

[30] E. O. Kane, Phys. Rev. 127, 131 (1962).

[31] M. Kochi, Y. Harada, T. Hirooka, and H. Inokuchi, Bull. Chem. Soc. Jpn. 43, 2590 (1970).

[32] R. W. Lof, M. A. van Veenendaal, B. Koopmans, H. T. Jonkman, and G. A. Sawatzky, Phys. Rev. Lett. 68, 3924 (1992).

[33] C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, and J. C. Hummelen, Adv. Funct. Mater. 11, 374 (2001).

[34] B. Rand, D. Burk, and S. Forrest, Phys. Rev. B 75, 115327 (2007).

[35] A. C. Mayer, M. T. Lloyd, D. J. Herman, T. G. Kasen, and G. G. Malliaras, Appl. Phys. Lett. 85, 6272 (2004).

[36] M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldau, A. J. Heeger, and C. J. Brabec, Adv. Mater. 18, 789 (2006).

[37] X. Zhu, Q. Yang, and M. Muntwiler, Acc. Chem. Res. 42, 1779 (2009).

[38] P. Sullivan and T. S. Jones, Org. Electron. 9, 656 (2008).

[39] D. Beljonne, J. Cornil, L. Muccioli, C. Zannoni, J.-L. Brédas, and F. Castet, Chem. Mater. 23, 591 (2011).

[40] Y. Yi, V. Coropceanu, and J.-L. Brédas, J. Am. Chem. Soc. 131, 15777 (2009).