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Nonempirically Tuned Long-Range Corrected Density Functional Theory Study on Local and Charge-Transfer Excitation Energies in a Pentacene/C₆₀ Model Complex

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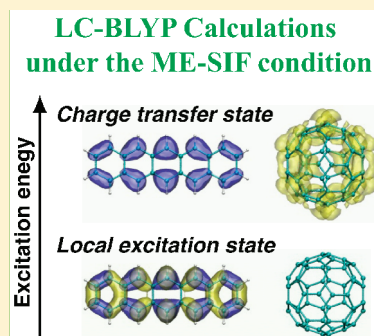
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 Supporting Information

ABSTRACT: The local and charge-transfer excitation energies in a pentacene/C₆₀ complex, which is prototypical of the minimal structural unit of the donor–acceptor heterojunction in pentacene/C₆₀ organic cells, are evaluated using the time-dependent long-range corrected density functional theory (TD-LC-BLYP) method in comparison with those estimated from the experimental data for pentacene and C₆₀. In the framework of the tuned range-separated hybrid (Livshits et al. *J. Phys. Chem. A* **2008**, *112*, 12789), we tune the range separating parameter (μ) of the LC-BLYP functional by imposing the many-electron self-interaction-free (ME-SIF) condition on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of pentacene and C₆₀. The TD-LC-BLYP method with $\mu = 0.20$ is found to succeed in the semiquantitative description of both the local and charge-transfer excitation energies in the pentacene/C₆₀ complex.

SECTION: Energy Conversion and Storage



Recently, organic photovoltaic cells (OPVs) have attracted a great deal of attention from the viewpoint of clean and renewable energy, which overcomes the inevitable end of fossil fuels, global warming, and other environmental problems.^{1–3} Although this type of solar cell has various advantageous features, including low-cost, flexibility, tunability, and lightness for solar energy conversion, their power conversion efficiencies are still at a low level.^{4–7} The light-to-electricity conversion process in OPVs is usually described via five main steps, namely (i) the optical absorption and exciton formation, (ii) the exciton migration to the donor/acceptor (D/A) interface, (iii) the exciton dissociation into charges resulting in a Coulomb bound electron–hole pair, (iv) the charge-carrier mobility, and (v) the charge collection at the electrodes.⁸ Further investigations on each of these steps are indispensable to gain clear view of the photo-conversion mechanism at the molecular level, and to establish novel guidelines for improvement of the OPVs performance.⁹ As reviewed recently, the theoretical description of the electronic processes occurring at organic/organic (O/O) interfaces is particularly challenging.¹⁰ More especially, the energetics in excited states is essential for discussing the exciton dissociation mechanisms at these interfaces. For example, in the case of pentacene/C₆₀, a typical D/A pair in organic solar cells,^{11,12} pentacene is excited by sun illumination, and then charge separation occurs at the pentacene/C₆₀ interface. This implies that the energy difference between the local excited state in pentacene and the charge-transfer (CT) excited state at the interface

determines the dynamics of charge separation process. Previous theoretical studies focusing on the excited state energies at O/O interfaces have demonstrated that the time-dependent density functional theory (TD-DFT) is practically applicable to the investigation of the excited states in such large systems, providing a good compromise between accuracy and computational cost.¹³ Nevertheless, the exchange–correlation (xc-) functional has to be carefully chosen since the CT excitation energies are known to significantly depend on the xc-functionals.¹⁴ Indeed, the long-range corrected DFT, LC-BLYP, with a range separating parameter (μ) [which tunes the Hartree–Fock (HF) exchange fraction in the short- and long-range region of interelectron distance], is found to improve CT excitation energies for small molecules,¹⁵ although it turns out to exhibit some range-separating parameter dependences of the relative energies of low-lying excited states in extended conjugated molecular systems.¹⁶ In this Letter, we therefore assess the reliability of various calculation methods for the lowest local and CT excited state energies of the pentacene/C₆₀ complex by comparing with the excitation energies estimated from experimental data. Especially, we propose a simple tuning scheme of the range-separating parameter μ in the TD-LC-BLYP method to reproduce reliably these two types of excitation energies. Since the theoretical approach is

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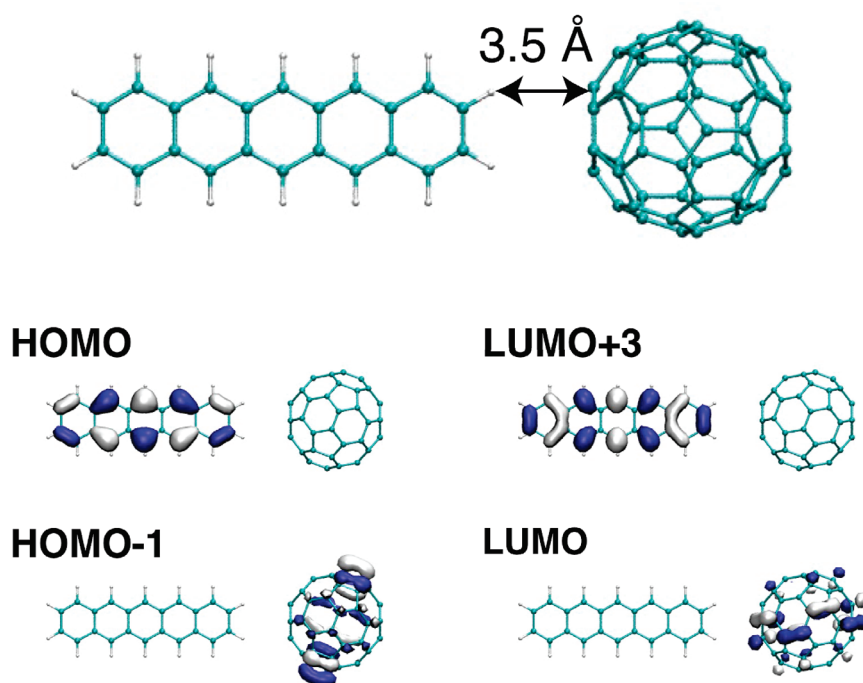


Figure 1. Structure (top) and representative frontier molecular orbitals (bottom) of the pentacene/ C_{60} complex. The strict localization of the orbitals on each molecule indicates negligible intermolecular interactions in the ground state of the complex (see Figure 1S and Table 1S in the Supporting Information for more details).

based on first principle, and since the TD-LC-BLYP method is based on the rigorous formalism of time-dependent generalized Kohn–Sham (TD-GKS) approach,¹⁷ it is notable that the present tuning scheme is nonempirical. Therefore, this scheme should be useful for a reliable prediction of both the local and CT excitation energies for arbitrary D/A molecules in organic solar cells.

We first provide a brief explanation of the pentacene/ C_{60} complex (Figure 1) and show how to estimate the local and CT excitation energies from the experimental data. The molecular geometries are optimized for isolated pentacene and C_{60} using the B3LYP/6-31G** method. The edge-to-edge relative configuration of the pentacene and C_{60} (Figure 1) is assumed to mimic the interface morphology observed in pentacene/ C_{60} bilayers formed by growing pentacene on top of a layer of C_{60} on a Ag(111) surface.¹⁸ We estimate the reference values for (i) the local excitation energy in pentacene and (ii) the CT excitation energy from experimental data in order to assess the reliability of calculated results. In this complex, the intermonomer interaction is expected to be sufficiently weak and then not to affect the excitation energy due to the negligible overlap of π -electrons between pentacene and C_{60} . It is indeed shown that the molecular orbitals are well localized on each molecule and that the orbital interaction energies between pentacene and C_{60} are less than ~ 0.05 eV (see Figure 1S and Table 1S in the Supporting Information). In addition, the lowest local excitation energy of pentacene in the complex (2.898 eV) is found to coincide with that of isolated pentacene at the level of configuration interaction singles (CIS)/6-31G* approximation. This justifies the means that employs the experimental excitation energy of isolated pentacene in gas phase¹⁹ for the local excitation energy of pentacene in the pentacene/ C_{60} complex ($\omega_{\text{pentacene}}^{\text{est}} = 2.312$ eV). As is well-known, when we can ignore the intermolecular orbital

interaction, the CT excitation energy can be predicted based on the Mulliken's theory,²⁰ that is, $\omega_{\text{CT}} = (\text{IP}_{\text{donor}} - \text{EA}_{\text{acceptor}}) + V_{\text{Coulomb}}$, where IP and EA represent the ionization potential and electron affinity, respectively, and V_{Coulomb} represents the Coulomb interaction between the electron (in the acceptor molecule) and the hole (in the donor molecule) in the CT excited state of the D/A complex. The IP of pentacene (donor) and EA of C_{60} (acceptor) are adopted from the experimental data in gas phases, the values of which are 6.589 eV²¹ and 2.683 eV,²² respectively. The Coulomb interaction between electron and hole is calculated by

$$V_{\text{Coulomb}} = \sum_{\substack{i \in \text{Pentacene} \\ j \in C_{60}}} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

where r_{ij} represents the electron–hole distance, and q_i and q_j represent the natural charges²³ on the i th atoms in pentacene and C_{60} in the CT excited state of the complex, respectively. This approximation is justified when the integer electron transfer occurs between pentacene and C_{60} to create the CT excited state. We ensure that this approximation is applicable to the present pentacene/ C_{60} complex, because it is found from the CIS/6-31G* results that molecular orbitals are localized on each molecule and the weight of the CT configuration amounts to about 98% in the lowest CT excited state (see Table 2S in the Supporting Information). The natural charges in the CT excited state are calculated using the CIS/6-31G* method. From these results, the value of the electron–hole interaction in the pentacene/ C_{60} complex is predicted to be $V_{\text{Coulomb}} = -1.427$ eV, and thus the CT excitation energy in the dimer is estimated to be $\omega_{\text{CT}}^{\text{est}} = 2.479$ eV. Moreover, the electron–hole interaction

Table 1. Excitation Energies [eV] in the Pentacene/C₆₀ Model Complex

method	μ^a	LXP ^b	CTX ^c	CTX ^c –LXP ^b
estimated value		2.312 ^d	2.479 ^e	0.167
CIS		2.898	4.192	1.294
TD-B3LYP		1.946	1.087	–0.859
TD-LC-BLYP	0.47	2.604	3.997	1.393
	0.33	2.500	3.668	1.168
	0.20	2.258	2.950	0.691
	0.10	1.903	1.724	–0.179
	0.00	1.662	0.390	–1.272

^a Range separating parameter (μ) of the LC-DFT method. ^b Local excitation in pentacene. ^c CT excitation from pentacene to C₆₀. ^d From ref 19. ^e Estimated from $IP_{\text{Pentacene}}^{21} - EA_{\text{C}_{60}}^{22} + V_{\text{Coulomb}}$, where the $IP_{\text{Pentacene}}$ and $EA_{\text{C}_{60}}$ are taken from the experimental values, and the Coulomb interaction between electron and hole, V_{Coulomb} , is calculated using the natural charges in the CT excited state calculated at the CIS/6-31G* level of approximation.

V_{Coulomb} has also been calculated using the quantum chemical valence-bond/Hartree–Fock (VB/HF) method at the AM1 level, in which the total net charge of each monomer is imposed during the SCF cycles via a fragment orbital formalism.²⁴ In this scheme, the electron–hole interaction is evaluated as $V_{\text{Coulomb}} = E^{\pm} - E^+ - E^-$, where E^{\pm} is the total energy of the pentacene/C₆₀ complex in the CT state, and E^+ and E^- are the total energies of the charged monomers. When using for the fragment orbitals the MOs of the isolated monomers, a value of –1.162 eV is obtained for V_{Coulomb} , while taking into account the orbital relaxation effects induced by the mutual polarization of the electronic clouds further decreases V_{Coulomb} to –1.386 eV, which is very similar to that at the CIS/6-31G* level of approximation.

Next, we investigate the calculation method dependences of the lowest excitation energies of the local and CT excited states in the pentacene/C₆₀ complex. All of the excited state calculations are performed with the frozen core approximation using the 6-31G* basis set (using the 1176 CI-active orbitals), and their results are compared with the references, that is, the estimated local and CT excitation energies ($\omega_{\text{pentacene}}^{\text{est}}$ and $\omega_{\text{CT}}^{\text{est}}$, respectively). Table 1 lists the local excitation energy of pentacene (LXP), the CT excitation energy (CTX) and its difference (CTX–LXP) calculated by the CIS, TD-B3LYP, and TD-LC-BLYP methods, as well as the various range separating parameters (μ) employed in the LC-BLYP calculations. The CTX–LXP difference is the crucial factor for determining the possibility and the rate of charge separation after light absorption in pentacene. Significant dependences of the LXP, CTX, and CTX–LXP on the calculation methods are observed.

Especially, it is noteworthy that the B3LYP method, which is known to well reproduce various experimental results concerning molecular structures, reactivities, and chemical-physical properties, significantly undershoots the CTX value by about 60% and then gives the opposite sign of CTX–LXP (–0.859 eV) to that of reference value (0.167 eV). On the other hand, the CIS method, which is often used for the calculation of excited states of large molecules, significantly (about eight times) overshoots the CTX–LXP (1.294 eV), which is caused by the lack of electron correlations. Even in the LC-BLYP method, which is known to efficiently include electron correlation effects via the xc-functional, the CTX–LXP is shown to nearly fall in with the CIS one

when we employ the default values of μ (0.33 in GAMESS²⁵ and 0.47 in GAUSSIAN09²⁶ program packages). Judging from the CIS, TD-B3LYP, and TD-BLYP [= LC-BLYP ($\mu = 0$)] results, the decrease of HF exchange fraction in hybrid xc-functionals tends to cause a more significant reduction in CTX than in LXP, which decreases the CTX–LXP difference and finally inverts its sign at the B3LYP and BLYP levels of approximation. Similarly, the decrease of μ in the LC-BLYP method, which reduces the HF exchange fraction even at a large interelectron distance, is found to decrease the CTX–LXP difference and to invert its sign around $\mu = 0.10$. As a result, only the LC-BLYP method with $\mu = 0.20$ is predicted to well reproduce the excitation energies of the pentacene/C₆₀ complex, though the CTX slightly overshoots the estimate value. From the viewpoint of examining a wide variety of D/A systems, however, such optimal μ values should be obtained without resorting to experimentally estimated values. We therefore perform a scheme for tuning μ based on a concrete theoretical condition, that is, the many-electron self-interaction-free (ME-SIF) condition,²⁷ and confirm the validity of the above μ value for the present system.

Before explaining our calculation scheme, we provide a brief explanation of the ME-SIF condition. It is well-known that conventional approximate xc-functional violates some of the conditions to be satisfied for an exact xc-functional.²⁸ In exact DFT, the total energy of the ground state with a fractional electron number δ ($0 \leq \delta \leq 1$) should be a linear average of the energies of systems with integer number N and $(N + 1)$ of electrons, that is, $E(N + \delta) = (1 - \delta)E(N) + \delta E(N + 1)$.²⁹ The deviation from this relationship is known as the many-electron self-interaction error (ME-SIE), which is also referred to as the “delocalization error”.²⁸ The ME-SIE can be evaluated with a dimer model ($R - R$) by an energy difference between a localized charged state ($R^{\pm} - R$) and a delocalized charged state ($R^{0.5\pm} - R^{0.5\pm}$) in the dissociation limit of a singly charged dimer system (R_2^{\pm}), that is, $\Delta E_{\text{ME-SIE}} = E(R^{0.5\pm} - R^{0.5\pm}) - E(R^{\pm} - R)$.²⁸

In our scheme, we first impose the ME-SIF condition, $\Delta E_{\text{ME-SIE}} = 0$, for R_2^+ and R_2^- , which correspond to its imposition on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of R , respectively. As shown below, we can tune the range-separating parameter in the LC-BLYP method so as to satisfy this condition for R_2^+ and R_2^- . This treatment is appropriate for the present study focusing on the excited states (LXP and CTX) contributing to the charge separation process characterized by the electron transfer between the HOMO of pentacene and the LUMO of C₆₀.

Then, we evaluate $\Delta E_{\text{ME-SIE}}$ for the singly charged face-to-face stacked dimer models, that is, (pentacene)₂[±] and (C₆₀)₂[±]. The structures of these charged species are taken from those of isolated monomer structures, optimized by the B3LYP/6-31G** method, together with the large intermolecular distance 100 Å, which represents the dissociation limit (see Table 3S–6S in the Supporting Information). Figure 2 shows the variation in $\Delta E_{\text{ME-SIE}}$ as the function of the range separating parameter (μ) used in LC-UBLYP/6-31G* calculations. We observe that the ME-SIF condition is satisfied around $\mu = 0.20$ both for the dimer models. In addition, in case of using this μ value, the HOMO and LUMO energies are found to agree with the vertical electron deattachment (of pentacene) and attachment (of C₆₀) energies, respectively (see Figure 3S and the detailed discussion in Supporting Information). Interestingly, the equality between the vertical ionization potentials and the absolute values of the HOMO energies has been proposed by Stein et al. as the figure of

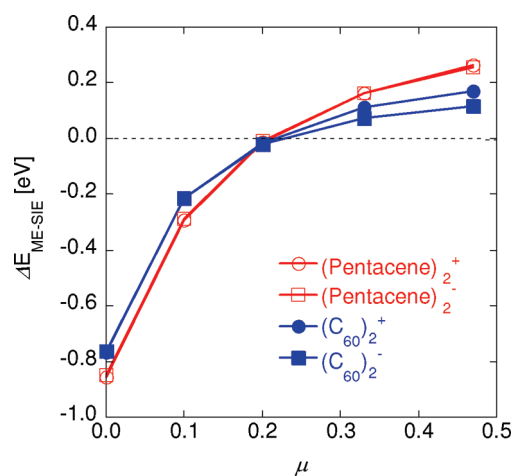


Figure 2. ME-SIE for the pentacene dimer and C₆₀ dimer. The ME-SIE is evaluated by the energy difference between the delocalized and localized charge states in the dissociation limit [$\Delta E_{\text{ME-SIE}} = E(R^{0.5\pm} - R^{0.5\pm}) - E(R^{\pm} - R)$], where R indicates the monomer.

merit to optimize μ in alternative tuning methods.^{30,31} The consistency between these various tuning schemes is discussed in the Supporting Information. As is already shown in Table 1, the LC-BLYP ($\mu = 0.20$) tuned under the ME-SIF condition succeeds in the semiquantitative description of LXP and CTX and in the qualitative description of the CTX-LXP energy difference in the pentacene/C₆₀ complex model.

The relationship between the ME-SIF condition and excitation energy is discussed in terms of interelectron interaction and delocalization/localization errors. For one (or less) electron systems, most of conventional xc-functionals give the nonzero SIE ($= J[\rho] + E_{\text{XC}}[\rho]$) (<0), where $J[\rho]$ (>0) and $E_{\text{XC}}[\rho]$ (<0) represent the classical Coulomb repulsion and the xc-interaction between (fractional) electrons, respectively, while the SIE becomes zero at the HF level of approximation, which is exact in this case. This SIE induces incorrect delocalization of electrons (delocalization error) due to the excess suppression of interelectron repulsion by xc-interaction.³² Similarly, the delocalization error is also known to be observed for $N (>1)$ -electron systems calculated by using most of conventional xc-functionals.³³ This delocalization error of electrons also emerges as a decrease of the HOMO–LUMO (or band) gap,^{34,35} which causes the underestimation of excitation energy in the region of negative SIE. It is indeed found that the BLYP method (LC-BLYP with $\mu = 0$), which causes the largest delocalization error ($\Delta E_{\text{ME-SIE}} < 0$) (see Figure 2), undershoots the excitation energies compared to the estimated value (see Table 1). By increasing the μ value, $\Delta E_{\text{ME-SIE}}$ positively increases due to the growing of the HF exchange fraction in a range-separating manner (see Figure 2). However, in contrast to one-electron systems where the HF solution is exact, the excess inclusion of the HF exchange (such as $\mu = 0.33$ and 0.47) inversely leads to the localization error (originating in the excess localization of electrons at the HF level of approximation) ($\Delta E_{\text{ME-SIE}} > 0$) due to the insufficient xc-interaction. Since this localization error leads to an increase of the HOMO–LUMO gap as observed in the HF solution,³⁴ the LC-BLYP ($\mu = 0.33$ and 0.47) methods are found to overshoot the excitation energies of the pentacene/C₆₀ complex (see Table 1). These results indicate that too high/low HF exchange fractions fail to predict the excitation energies due to the localization/

delocalization errors originating from the inadequate xc-functionals of conventional DFT methods.

However, in general, even when an xc-functional has no delocalization/localization error, there still exists the possibility to fail to predict the HOMO–LUMO gap due to the nonzero derivative discontinuity, which is defined as the difference of the $(N+1)$ th orbital energies in (N) - and $(N+1)$ -electron systems [$\Delta_{\text{xc}} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N)$],¹⁷ where the $(N+1)$ th orbital corresponds to the LUMO for the N -electron system and to the HOMO for the $(N+1)$ -electron system. In this regard, we have found that these values are negligible for isolated pentacene (0.03 eV) and C₆₀ (0.07 eV) in the case of $\mu = 0.20$ (see Figure 4S and detailed discussion in the Supporting Information). Therefore, we have concluded that the success of the LC-BLYP method optimized under the ME-SIF condition in the semiquantitative description of the excitation energy for pentacene/C₆₀ model complex originates from (1) the negligible delocalization/localization error and (2) the small derivative discontinuity.

In summary, we have clarified that the LC-BLYP method with a range separating parameter μ equal to 0.20 semiquantitatively reproduces the excitation energies both for the lowest local excitation of pentacene and the CT excitation of the pentacene/C₆₀ complex. The suitability of this parameter is exemplified by imposing the ME-SIF condition and by the negligible derivative discontinuity for pentacene and C₆₀. The present tuning scheme of μ in the LC-BLYP method based on the ME-SIF condition is also expected to be applicable to the well-balanced description of excitation energy for arbitrary systems even when experimental data are unavailable. It is noted that the other calculation methods [CIS, B3LYP, and LC-BLYP ($\mu = 0.10, 0.33, 0.47$)] fail to reproduce the experimentally estimated CT and local excitation energies, and that in particular, the B3LYP method gives an incorrect order of energy among these states.

Finally, we stress that in the case of the isolated pentacene/C₆₀ complex investigated here, the CT excited state lies above the local excitation state, while the reverse order is found when considering the effects of the environment.¹³ Indeed, in the solid state, intermolecular polarization effects substantially modify the electron–hole interaction as well as the ionization energy and electron affinity of the donor and acceptor molecules from their gas phase values (IP_{pentacene} = 5.1 eV,³⁶ EA_{C60} = 3.5 eV³⁷), which tends to significantly reduce the CT state energy. This illustrates the need for an explicit account of polarization contributions to obtain a reliable description of the exciton dissociation and charge separation processes at the pentacene/C₆₀ interface.^{38,39} Investigations toward this direction are in progress in our laboratories, and should contribute to the reliable prediction of the energetics and the fundamental and precise understanding of these processes in organic solar cells.

■ ASSOCIATED CONTENT

S Supporting Information. The frontier molecular orbitals of the pentacene/C₆₀ dimer model. The CI configurations of the lowest CT excited state in the pentacene/C₆₀ model. The ground state energies of delocalized ($R^{0.5\pm} - R^{0.5\pm}$) and localized ($R^{\pm} - R$) charge states for pentacene dimer and C₆₀ dimer in the dissociation limit. Comparison of the present results with those obtained by the other optimization schemes proposed by Stein et al. The detailed discussion of the relationship between

orbital energies and vertical electron (de-) attachment energies in the ME-SIF condition. The material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) Hains, A. W.; Liang, Z.; Woodhouse, M. A.; Gregg, B. A. Molecular Semiconductors in Organic Photovoltaic Cells. *Chem. Rev.* **2010**, *110*, 6689–6735.
- (2) Cai, W.; Gong, X.; Cao, Y. Polymer Solar Cells: Recent Development and Possible Routes for Improvement in the Performance. *Sol. Energy Mater. Sol. Cells.* **2010**, *94*, 114–127.
- (3) Ameri, T.; Dennler, G.; Lungenschmied, C.; Brabec, C. J. Organic Tandem Solar Cells: A Review. *Energy Environ. Sci.* **2009**, *2*, 347–363.
- (4) Brabec, C.; Scherf, U.; Dyakonov, V. *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies*; Wiley-VCH: Weinheim, Germany, 2008.
- (5) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. Bulk Heterojunction Solar Cells with Internal Quantum Efficiency Approaching 100%. *Nat. Photonics* **2009**, *3*, 297–303.
- (6) Liang, Y.; Xu, Z.; Xia, J.; Tsai, T.-S.; Wu, Y.; Li, G.; Ray, C.; Yu, L. For the Bright Future—Bulk Heterojunction Polymer Solar Cells with Power Conversion Efficiency of 7.4%. *Adv. Mater.* **2010**, *22*, E135–E138.
- (7) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W. Solar Cell Efficiency Tables (Version 37). *Prog. Photovoltaics: Res. Appl.* **2011**, *19*, 84–92.
- (8) Clarke, T. M.; Durrant, J. R. Charge Photogeneration in Organic Solar Cells. *Chem. Rev.* **2010**, *110*, 6736–6767.
- (9) Brédas, J. L.; Norton, J. E.; Cornil, J.; Coropceanu, V. Molecular Understanding of Organic Solar Cells: The Challenges. *Acc. Chem. Res.* **2009**, *42*, 1691–1699.
- (10) Beljonne, D.; Cornil, J.; Muccioli, L.; Zannoni, C.; Brédas, J.-L.; Castet, F. Electronic Processes at Organic–Organic Interfaces: Insight from Modeling and Implications for Opto-electronic Devices. *Chem. Mater.* **2011**, *23*, 591–609.
- (11) Yoo, S.; Domercq, B.; Kippelen, B. Efficient Thin-Film Organic Solar Cells Based on Pentacene/C₆₀ Heterojunctions. *Appl. Phys. Lett.* **2004**, *85*, 5427–5429.
- (12) Salzmann, I.; Duhm, S.; Opitz, R.; Johnson, R. L.; Rabe, J. P.; Koch, N. Structural and Electronic Properties of Pentacene–Fullerene Heterojunctions. *J. Appl. Phys.* **2008**, *104*, 114518–1–11.
- (13) Yi, Y.; Coropceanu, V.; Brédas, J. L. Exciton-Dissociation and Charge-Recombination Processes in Pentacene/C₆₀ Solar Cells: Theoretical Insight into the Impact of Interface Geometry. *J. Am. Chem. Soc.* **2009**, *131*, 15777–15783.
- (14) Dreuw, A.; Weisman, J. L.; Head-Gordon, M. Long-Range Charge-Transfer Excited States in Time-Dependent Density Functional Theory Require Non-local Exchange. *J. Chem. Phys.* **2003**, *119*, 2943–2946.
- (15) Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. A Long-Range-Corrected Time-Dependent Density Functional Theory. *J. Chem. Phys.* **2004**, *120*, 8425–8433.
- (16) Wong, B. M.; Hsieh, T. H. Optoelectronic and Excitonic Properties of Oligoacenes: Substantial Improvements from Range-Separated Time-Dependent Density Functional Theory. *J. Chem. Theory Comput.* **2010**, *6*, 3704–3712.
- (17) Baer, R.; Livshits, E.; Salzner, U. Tuned Range-Separated Hybrids in Density Functional Theory. *Annu. Rev. Phys. Chem.* **2010**, *61*, 85–109.
- (18) Dougherty, D. B.; Jin, J.; Cullen, W. G.; Reutt-Robey, J. E.; Robey, S. W. Striped Domains at the Pentacene/C₆₀ Interface. *Appl. Phys. Lett.* **2009**, *94*, 023103–1–3.
- (19) Heinecke, E.; Hartmann, D.; Müller, R.; Hese, A. Laser Spectroscopy of Free Pentacene Molecules (I): The Rotational Structure of the Vibrationless S₁ ← S₀ Transition. *J. Chem. Phys.* **1998**, *109*, 906–911.
- (20) Mulliken, R. S. Molecular Compounds and Their Spectra. III. The Interaction of Electron Donors and Acceptors. *J. Phys. Chem.* **1952**, *56*, 801–822.
- (21) Gruhn, N. E.; da Silva Filho, D. A.; Bill, T. G.; Malagoli, M.; Coropceanu, V.; Kahn, A.; Brédas, J.-L. The Vibrational Reorganization Energy in Pentacene: Molecular Influences on Charge Transport. *J. Am. Chem. Soc.* **2002**, *124*, 7918–7919.
- (22) Wang, X.-B.; Woo, H.-K.; Wang, L.-S. Vibrational Cooling in a Cold Ion Trap: Vibrationally Resolved Photoelectron Spectroscopy of Cold C₆₀[−] Anions. *J. Chem. Phys.* **2005**, *123*, 051106–1–4.
- (23) Foster, J. P.; Weinhold, F. Natural Hybrid Orbitals. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.
- (24) Castet, F.; Aurel, P.; Fritsch, A.; Ducasse, L.; Liotard, D.; Linares, M.; Cornil, J.; Beljonne, D. Electronic Polarization Effects on Charge Carriers in Anthracene: A Valence Bond Study. *Phys. Rev. B* **2008**, *77*, 115210–1–14.
- (25) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, M. A. General Atomic and Molecular Electronic Structure System. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- (26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalapini, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.
- (27) Livshits, E.; Baer, R. A Density Functional Theory for Symmetric Radical Cations from Bonding to Dissociation. *J. Phys. Chem. A* **2008**, *112*, 12789–12791.
- (28) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. Insights into Current Limitations of Density Functional Theory. *Science* **2008**, *321*, 792–794.
- (29) Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L. Density Functional Theory for Fractional Particle Number: Derivative Discontinuities of the Energy. *Phys. Rev. Lett.* **1982**, *49*, 1691–1694.
- (30) Stein, T.; Kronik, L.; Baer, R. Reliable Prediction of Charge Transfer Excitations in Molecular Complexes Using Time-Dependent Density Functional Theory. *J. Am. Chem. Soc.* **2009**, *131*, 2818–2820.
- (31) Stein, T.; Kronik, L.; Baer, R. Prediction of Charge-Transfer Excitations in Coumarin-Based Dyes Using Range-Separated Functional Tuned from First Principles. *J. Chem. Phys.* **2009**, *131*, 244119–1–5.
- (32) Zhang, Y.; Yang, W. A Challenge for Density Functionals: Self-Interaction Error Increases for Systems with a Noninteger Number of Electrons. *J. Chem. Phys.* **1998**, *109*, 2604–2608.
- (33) Song, J.-W.; Watson, M. A.; Nakata, A.; Hirao, K. Core-Excitation Energy Calculations with a Long-Range Corrected Hybrid Exchange-Correlation Functional Including a Short-Range Gaussian Attenuation (LCgau-BOP). *J. Chem. Phys.* **2008**, *129*, 184113–1–9.
- (34) Garza, J.; Nichols, J. A.; Dixon, D. A. The Optimized Effective Potential and the Self-Interaction Correction in Density Functional Theory: Application to Molecules. *J. Chem. Phys.* **2000**, *112*, 7880–7890.
- (35) Mori-Sánchez, P.; Cohen, A. J.; Yang, W. Localization and Delocalization Errors in Density Functional Theory and Implications for Band-Gap Prediction. *Phys. Rev. Lett.* **2008**, *100*, 146401–1–4.
- (36) Hwang, J.; Wan, A.; Kahn, A. Energetics of Metal–Organic Interfaces: New Experiments and Assessments of the Field. *Mater. Sci. Eng. Rep.* **2009**, *64*, 1–31.

(37) Schwedhelm, R.; Kipp, L.; Dallmeyer, A.; Skibowski, M. Experimental Band Gap and Core–Hole Electron Interaction in Epitaxial C₆₀ Films. *Phys. Rev. B* **1998**, *58*, 13176–13780.

(38) Verlaak, S.; Beljonne, D.; Cheyns, D.; Rolin, C.; Linares, M.; Castet, F.; Cornil, J.; Heremans, P. Electronic Structure and Geminate Pair Energetics at Organic–Organic Interfaces: The Case of Pentacene/C₆₀ Heterojunctions. *Adv. Funct. Mater.* **2009**, *19*, 3809–3814.

(39) Linares, M.; Beljonne, D.; Cornil, J.; Lancaster, K.; Brédas, J-L; Verlaak, S.; Mityashin, A.; Heremans, P.; Fuchs, A.; Lennartz, C.; Idé, J.; Méreau, R.; Aurel, A.; Ducasse, L.; Castet, F. On the Interface Dipole at the Pentacene–Fullerene Heterojunction: A Theoretical Study. *J. Phys. Chem. C* **2010**, *114*, 3215–3224.