Maximizing Singlet Fission by Intermolecular Packing

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Supporting Information

ABSTRACT: A novel nonadiabatic molecular dynamics scheme is applied to study the singlet fission (SF) process in pentacene dimers as a function of longitudinal and lateral displacements of the molecular backbones. Detailed two-dimensional mappings of both instantaneous and long-term triplet yields are obtained, characterizing the advantageous and unfavorable stacking arrangements, which can be achieved by chemical substitutions to the bare pentacene molecule. We show that the SF rate can be increased by more than an order of magnitude through tuning the intermolecular packing, most notably when going from cofacial to the slipped stacked arrangements encountered in some pentacene derivatives. The simulations indicate that the SF process is driven by thermal electron–phonon fluctuations at ambient and high temperatures, expected in solar cell applications. Although charge-transfer states are key to construct continuous channels for SF, a large charge-transfer character of the photoexcited state is found to be not essential for efficient SF. The reported time domain study mimics directly numerous laser experiments and provides novel guidelines for designing efficient photovoltaic systems exploiting the SF process with optimum intermolecular packing.

SECTION: Energy Conversion and Storage; Energy and Charge Transport

Semiconductor materials usually generate one exciton per absorbed photon. This rule, however, breaks down in some quantum dots,1−7 where a process known as multiple exciton generation has been demonstrated. A similar phenomenon is also observed in molecular materials, for example, tetracene,8−11 pentacene,10−15 polydiacetylene,16 carotenoids,17 and their derivatives.18,19 There, one photogenerated singlet exciton can undergo a spin-conserving fission process,20 whereby two triplet excitons are generated when harvesting only one phonon, thereby potentially doubling the yield of photogenerated electron–hole pairs in solar cells.21 In addition, the isolated triplets obtained as the outcome of singlet fission (SF) have long lifetimes as their recombination to the singlet ground state is spin-forbidden, which should improve their diffusion to donor−acceptor interfaces when they can dissociate to produce free charges, hence further enhancing the quantum efficiency of photovoltaic devices.13 By efficiently utilizing higher-energy photons, solar cell device architectures taking advantage of SF have the potential to break the Shockley−Queisser limit,22 which is the maximum detailed balance efficiency of single p−n junction bulk solar cells. Not surprisingly, SF has attracted significant attention in recent years.19,20

On the basis of the nature and alignment of excited states, chromophores exhibiting SF phenomena have been grouped by Smith and Michl into three classes.19 Pentacene is a typical example of the first class, where the first singlet excitation is dominated by the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and is separated significantly in energy from the second singlet excited state. Here, SF can be realized through two basic mechanisms, direct and mediated.9,19 In the former case, direct coupling between the singlet and triplet pair states involves two-electron integrals.7 Multistate density functional theory calculations, however, have shown that these direct couplings are too weak (several meV) to explain the fast SF seen in the experiment.23 In contrast, indirect couplings via charge-transfer (CT) intermediate states are generally 2 orders of magnitude stronger (around 100 meV), and thus, the mediated mechanism is expected to dominate SF in pentacene.23,24

In the mediated mechanism for SF, CT states are key to construct continuous channels for SF. A natural question arises, how much CT character in the photoexcited state can maximize the SF efficiency. For high-energy CT states, a very limited wave function admixture occurs in the lowest adiabatic state, and SF proceeds via a superexchange mechanism (through “virtual” CT states) that scales inversely with the energy mismatch between Frenkel and CT states.25 On the other hand, if the CT character is too strong, excimer states will form.13 Excimers can be even more stable than the triplet pair state, which is also detrimental for the triplet generation.

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A great variety of chemical functionalization strategies produce pentacene derivatives with similar single-molecule electronic properties but distinct orientation and separation between pentacene backbones in a crystal. Recent experiments show that the SF process in perfluoropentacene strongly depends on the intermolecular packing; slip stacking allows efficient SF, while face-to-edge molecular orientations even suppress it. Crystal packing determines intermolecular couplings and CT state energies and, therefore, the CT character of the photoexcited state. As a result, pentacene and its derivatives constitute ideal systems for systematic computational studies to reveal the optimum intermolecular packing and CT character, maximizing the SF performance. While available theoretical investigations along this direction are largely based on static models, comprehensive real time simulations on SF are strongly needed for the design of optimum molecular packing aimed at SF applications.

In this Letter, we apply the recently developed self-consistent fewest switches surface hopping (SC-FSSH) technique, in combination with ab initio and semiempirical electronic structure calculations, to investigate the time domain dynamics of SF in pentacene dimers over a broad range of mutual conformations. Detailed mappings of both instantaneous and long-term triplet yields are obtained as functions of crystal packing parameters. Thermal fluctuations arising due to electron–phonon coupling drive SF at temperatures relevant for solar light harvesting. Quite unexpectedly, the study shows that efficient SF does not have to rely on a significant CT character of the photogenerated state. We find that by a judicious choice of the longitudinal and lateral displacements of the molecular backbone, one can drastically improve the rate of the SF process. Slipped stacked configurations are much more prone to fast SF than cofacial arrangements. Using chemical modifications to the bare pentacene molecule, one should strive to create slipped stacked arrangements, moving away from the cofacial packing, which is seen as the ideal organization to achieve good charge transport properties. The detailed analysis of the photoinduced SF process reported below provides key guidelines for the development and optimization of SF solar cell materials.

As shown in Figure 1A, we consider a series of pentacene dimers in which the two molecules are stacked parallel to each other with a 3.4 Å separation and the center of mass shifted by \( T \) and \( L \) along the transverse and longitudinal axes, respectively. Note that many pentacene derivatives, for example, the well-known 6,13-bis(trisopropylsilyl)pentacene (TIPS pentacene), have the backbone orientation very similar to our model dimers (see Figure 1B). We use different \( T \) and \( L \) values to represent the packing of various possible pentacene derivatives, and investigate two-dimensional (2D) mappings of both early stage and long-term SF properties. Calculations on the TIPS pentacene and the standard herringbone pentacene dimers (see Figure 1C) are carried out as well.

To describe SF in pentacene dimers, we include five electronic basis states, that is, singlet excitation on one of the molecules (\( S_1S_0 \) and \( S_0S_1 \)), electron transfer from one molecule to the other (\( CA \) and \( AC \)), and the correlated triplet pair (\( TT \)). The Holstein Hamiltonian, which has been widely used to characterize electron–phonon interactions in molecular materials, is adopted. In conjugated molecules like pentacene, the carbon–carbon stretching mode is most strongly coupled to the electronic states. Thereby, in the present study, we consider that each electronic state is linearly coupled to only one vibrational mode in contact with a heat bath. The Hamiltonian is a summation of the electronic part, \( H_e \), and the nuclear part, \( H_n \):

\[
H = H_e + H_n
\]

\[
H_e = \sum_i E_i |i\rangle\langle i| + \sum_{i\neq j} V_{ij} |i\rangle\langle j| + \sum_i \alpha x_i |i\rangle\langle i|
\]

\[
H_n = \frac{1}{2} \sum_i (K x_i^2 + m v_i^2)
\]

Here, each electronic state \( i \) has energy \( E_i \) and the electronic coupling between states \( i \) and \( j \) is \( V_{ij} \). The nuclear coordinate, velocity, effective mass, and force constant associated with state \( i \) are \( x_i, v_i, m_i, \) and \( K_i \) respectively. \( \alpha \) is the local electron–phonon coupling constant. The frequency of the harmonic vibration is \( \omega = (K/m)^{1/2} \). From previous studies, we know that this kind of Hamiltonian gives an electronic reorganization energy of \( \lambda = \alpha^2 / K \). Note that \( H_n \) in eq 2 can be split into two parts: \( H_{\text{static}}^e = \sum_i E_i |i\rangle\langle i| + \sum_{i\neq j} V_{ij} |i\rangle\langle j| \) is the static part of the electronic Hamiltonian, and \( H_{\text{disorder}}^e = \sum_i \alpha x_i |i\rangle\langle i| \) expresses thermal disorder of the electronic Hamiltonian due to electron–phonon coupling. Note that the Hamiltonian given in eqs 1–3 can be generalized to multiple vibrational modes per exciton state, and the SF dynamics can be well-solved within the Redfield framework coupled with specific spectral density description of electron–phonon couplings.

For simplicity, we only consider two molecular orbitals, that is, HOMO and LUMO, for each molecule in the dimer. Then, \( H_{\text{static}}^e \) can be expressed as:

\[
H_{\text{static}}^e = \sum_{\text{orbitals}} |\text{orbital}_i\rangle\langle \text{orbital}_i| E_i
\]
Here, $J_{ex}$ is the exciton coupling between singlet states $S_1S_0$ and $S_0S_1$. Note that it is essential to go beyond the point-dipole approximation for an accurate description of resonance energy transfer. It is the transfer integral between molecular orbital $A$ of the first molecule and molecular orbital $B$ of the second molecule, and $H (L)$ is used as the abbreviation of HOMO (LUMO).

Similar to charge transport and other types of exciton dynamics (e.g., exciton relaxation, dissociation, and recombination), SF can be well-described by the surface hopping method. Internal consistency is a key feature of the FSSH method. It ensures that the fraction of trajectories on each surface is equivalent to the corresponding average quantum probability. However, together with several other reasons, this consistency is not fulfilled when experiencing trivial, or unavoidable, crossings, where a negligible energy gap between two potential energy surfaces induces enormous computational error. To solve this problem, we developed the SC-FSSH algorithm.

Previous studies have shown that SC-FSSH allows us to achieve great accuracy and reduce the simulation time by several orders of magnitude relative to the original FSSH. In this study, SC-FSSH is implemented to study the SF dynamics, where the indirectly coupled singlet and triplet pair states induce trivial crossings.

The computational details are given in the Supporting Information (SI). Figure S1 in the SI shows the transition energy to the lowest and second excited states of pentacene dimers as a function of the longitudinal and transverse displacements. The supramolecular calculations have been performed at the INDO/SCI level. We also employ a simple four-state model ($S_1S_0$, $S_0S_1$, CA, and AC) similar to eq 4 using INDO transfer integrals and a CT state energy calculated in vacuum for Mulliken cation and anion charge distributions. The very good agreement between these two sets of data shows the reliability of the minimal model adopted in the present study.

Figure 2 shows the calculated 2D mappings of the transfer integrals. The magnitude of the transfer integral between the two molecules relies strongly on the overlap between the wave function of the frontier orbitals as well as the orientation of the dimer. As shown in Figure 1D, the HOMO wave function changes its sign along both transverse and longitudinal axes. The distance between the nearest local regimes with opposite signs for the wave function is about 2 Å. Thus, we expect $t_{HH}$ to vary with a similar period (see Figure 2A). The sign of the LUMO wave function varies along the longitudinal axis but is unchanged in the transverse direction. This phenomenon is
preserved in the 2D mapping of $t_{LL}$ (see Figure 2B). For $t_{HL}$ and $t_{LH}$, the 2D mapping is more complex, showing mixed character of $t_{HH}$ and $t_{LL}$. Especially, for $T \approx 0 \, \text{Å}$, both $t_{HL}$ and $t_{LH}$ are negligible because the HOMO and LUMO wave functions have opposite parity along the $T$ direction.

We now move to the SC-FSSH results. Initially, all nuclear positions and momenta are randomly chosen from Boltzmann distributions taking quantum effects into account. The average singlet, CT, and triplet character of each adiabatic state is shown in Figure S2 in the SI. The initial electronic wave function is assigned as the adiabatic state with the largest transition dipole moment, that is, the one with ultimate symmetric singlet components. Due to the direct coupling between the singlet and CT states through $t_{HH}$ and $t_{LL}$ as shown in eq 4, the initial optical excitation is associated with a certain amount of CT character (see Figure 3A). Because the maximum absolute value of $t_{HH}$ and $t_{LL}$ is about 400 meV (see Figure 2A and B), significant CT character is only possible when the CT energy falls below 400 meV (with respect to the local, Frenkel excitations). From Figure S3 in the SI, we know that this corresponds to the dimer conformations with intermolecular distance less than about 6 Å. In addition, both $t_{HH}$ and $t_{LL}$ change periodically along the $L$ direction with minimum values around every 2 Å, inducing the strip structures in the 2D mapping of the initial CT character.

Figure 3. 2D mappings of the (A) CT character of the photoexcited state at time zero, (B) yield of the TT state at 50 ps, and (C) SF time constant in ps. Characteristic packings are indicated with Roman numbers. (D) SF time constant as a function of the initial CT character. (E) Intermolecular packings for the specified configurations.
We display in Figure 3B the 2D mapping for the long-term yield of correlated triplet pairs. For all conformations, the SF dynamics reaches equilibrium within 50 ps, and thus, the population of the TT state at 50 ps is used. The mapping is highly consistent with the average triplet character of the lowest adiabatic state indicated in Figure S2 (SI). This is because the system generally relaxes into the lowest adiabatic state after a long time of dynamics. To achieve a high net triplet yield for SF, high $E_{\text{CT}}$ configurations seem to be preferred in order to avoid creating excimer (strongly mixed FE$-$CT) states with lower energy than the TT state; these correspond to a relatively large distance between the two pentacene molecules in the dimer (see Figure S3, SI). This requirement means that large CT character is generally not necessary for significant long-term triplet yield (cf. Figure 3A and B). Note that coupling our model Hamiltonian to hierarchy equation of motion (HEOM) calculations leads to similar conclusions, showing that the observations obtained in this study using surface hopping are reliable.

The time scale for SF can be fitted from the time-dependent population of the TT state with a three-parameter function $f(t) = a - b \exp(-t/\tau)$, where $a$ corresponds to the triplet yield at infinite time, and $\tau$ is the SF time constant. We fit $\tau$ within the first 1 ps of the SF simulation. The 2D mapping of $\tau$ in Figure 3C demonstrates that fast SF occurs in several localized regions indicated by I, II, III, and IV. All of them correspond to configurations slipped along the transverse direction for approximately one ring (see Figure 3E). This finding agrees very well with recent experiments validating our adopted method for SF. The 2D mapping of $\tau$ agrees with the distribution of $t_{\text{HL}}$ and $t_{\text{LH}}$ shown in Figure 2C and D. We know that SF is dominated by two interactions: the first one is between the singlet and CT states, and the second is between the CT states and the TT state. If thermal fluctuations of the state energies due to electron–phonon coupling are larger or comparable to the interstate couplings (we will justify this later), the first interaction is governed by $t_{\text{HH}}$ and $t_{\text{LL}}$, while the second one is governed by $t_{\text{HL}}$ and $t_{\text{LH}}$. As shown in Figure 2A and B, the distributions of $t_{\text{HH}}$ and $t_{\text{LL}}$ complement each other, resulting in a uniformly large interaction between the singlet and CT states. In contrast, $t_{\text{HL}}$ and $t_{\text{LH}}$ have similar phases in the 2D mapping, and thus, the interaction between CT and TT is also packing-dependent. As a result, the mapping of the SF time constant follows the distribution of $t_{\text{HL}}$ and $t_{\text{LH}}$ perfectly.

Figure 3D displays the relation between the SF time constant and CT character. On the basis of the average behavior, a large CT character tends to have a smaller SF time constant. However, the data points spread significantly out of the average behavior, and thus, there is no overall rigorous relation between the SF time constant and the CT character. For example, conformations V and VI have large CT character but slow SF. Besides, on the basis of $L$ and $T$ values,
region I roughly corresponds to herringbone pentacene, giving rise to both high CT character and fast SF.

In a previous study, a symmetry argument was proposed to analyze the SF mechanism. There, one switches from the diabatic representation used in eq 4 to a new representation using symmetry-adapted basis states, FE+, FE−, CT+, CT−, and TT, which are defined as

\[
FE^+ = \sqrt{2/2} \cdot (S_1 S_0 + S_0 S_1),
FE^- = \sqrt{2/2} \cdot (S_1 S_0 - S_0 S_1),
CT^+ = \sqrt{2/2} \cdot (CA + AC),
CT^- = \sqrt{2/2} \cdot (CA - AC).
\]

Then, the static electronic Hamiltonian matrix reads

\[
H_{\text{static}}^{\text{const}} = \begin{pmatrix}
E_{FE^+} & -(t_{HH} - t_{LL}) \\
-(t_{HH} - t_{LL}) & E_{CT^+} \\
0 & 0 \\
0 & 0 \\
0 & \sqrt{3/2} (t_{HL} + t_{LH}) \\
\end{pmatrix}
\]

Here, \(E_{CT^+} = E_{CT^-} = E_{CA} = E_{AC}\), and \(E_{FE^+} = E_{FE^-} = 2J_{ex}\). There are two ways to generate triplets from the initial photo-excitation, (1) \(FE^+ \rightarrow CT^+ \rightarrow TT\) (the symmetric channel) and (2) \(FE^- \rightarrow CT^- \rightarrow TT\) (the asymmetric channel). The efficiency of the former relies on the magnitude of \(|t_{HH} - t_{LL}|\) and \(|t_{HL} + t_{LH}|\), while the latter depends on \(|t_{HH} + t_{LL}|\) and \(|t_{HL} - t_{LH}|\). The 2D mapping of these quantities are given in Figure S4 (SI), from which we can find that \(|t_{HL} + t_{LH}|\) is always very small due to symmetry while the other couplings are generally 1 order of magnitude larger.

At 0 K, \(H_{\text{static}}^{\text{const}}\) vanishes completely, and \(H_e\) is solely determined by \(H_{\text{static}}^{\text{const}}\). \(t_{HL} + t_{LH}\) becomes the bottleneck of the symmetric channel. As a result, the instantaneous triplet yield starting from the adiabatic state with the \(FE^+\) main contribution is generally negligible (see Figure 4A). Only several rare conformations, where the interaction with \(CT^+\) pushes \(FE^+\) very close to \(TT\), have a considerable instantaneous \(TT\) yield. In contrast, the instantaneous triplet yield along the asymmetric channel is much more significant (see Figure 4B). From Figure S4 (SI), we can find that \(|t_{HH} + t_{LL}|\) and \(|t_{HL} - t_{LH}|\) have similar

Figure 5. 2D mappings of the effective coupling (A) W+ and (B) W− in meV, characterizing the singlet–triplet state mixing. The SF time as a function of (C) the instantaneous triplet pair yield and (D) W+. The blue dashed lines are shown to guide the eye.

\[
H_e^{\text{order}} = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & \sqrt{3/2} (t_{HL} + t_{LH}) \\
0 & \sqrt{3/2} (t_{HH} + t_{LL}) & E_{CT^-} \\
\end{pmatrix}
\]

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periodicity along the longitudinal direction but distinct variation along the transverse direction. Thereby, the instantaneous triplet yield follows the 2D mapping of \( |t_{HH}^i - t_{IL}^j|^2 \), which is also very similar to that of \( t_{IH} \) and \( t_{IL} \).

The 2D mapping for instantaneous triplet yield in the symmetric channel at 300 K is strongly different from that at 0 K (see Figure 4C). Clear patterns appear, resembling closely the instantaneous triplet yield in the asymmetric channel (see Figure 4D), which only changes slightly with temperature increase. Thus, we justify that thermal fluctuations wipe off the symmetry argument with increasing temperature, and the key quantities change from \( t_{HH}^i + t_{IL} \), \( t_{HH}^i - t_{IL} \), \( t_{IL} + t_{IL} \), and \( t_{IL} - t_{IL} \) to simply \( |t_{HH}^i|, |t_{IL}|, |t_{IL}|, |t_{IL}|, \) as previously used to understand the long-term SF properties in Figure 3.

We next diagonalize the static electronic Hamiltonian in eq 5 and take the new eigenstates as a basis for \( H^{\text{disorder}} \), mostly FE’ state (FE’), mostly FE’ state (FE’), mostly CT’ state (CT’), mostly CT’ state (CT’), and mostly TT state (TT’). The effective couplings, \( W^+ = (\text{FE’HTT}) \) and \( W^- = (\text{FE’HTT}) \), are nonzero at 300 K in the new Hamiltonian matrix, characterizing the mixing strength between the singlet and triplet states. The 2D mappings of \( W^+ \) and \( W^- \) are shown in Figure 5A and B, respectively. The maxima obtained here are very close to the prediction in the previous studies.\(^{4,24} \) One can immediately notice that these mappings agree very well with the instantaneous triplet yield shown in Figure 4C and D. Both \( W^+ \) and \( W^- \) strongly rely on the electron–phonon couplings and temperature, as does the instantaneous triplet yield. Particularly interestingly, we find a direct relation between the SF time constant and the instantaneously generated triplet. This finding is quite helpful for material design to achieve better SF performance by both large instantaneous triplet yield and fast SF simultaneously. Finally, we show the relation between the SF time constant and effective coupling in Figure 5D. Our results comply with the change from a nonadiabatic regime (rate insensitive to coupling) to an adiabatic regime (rate influenced).\(^{5}\) As shown in Figure 1B, the parallel packed TIPS pentacene belongs to the class of model dimers studied above, with \( T = 1.46 \) Å and \( L = 6.68 \) Å (similar to the pentacene in Figure 3). We have investigated the TIPS pentacene in detail, using the standard herringbone pentacene dimer as a reference. The dimer geometries are obtained from experiment. The calculated CT’ energy, exciton coupling, and transfer integrals are given in Table S1 in the SI. For both systems, \( t_{HH} \) and \( t_{IL} \) are of opposite signs. This is true for \( t_{HH} \) and \( t_{IL} \) as well. The other parameters are the same as those in the 2D mapping studies. A global fit to the time-dependent TT yield gives a SF time constant of 0.83 ps for the TIPS pentacene. Because the angle between the two pentacene plains in the herringbone dimer is about 45°, we perform two sets of surface hopping dynamics; one starts from adiabatic states with the largest symmetric singlet contribution, and the other adopts the most significant asymmetric states. The obtained SF time constants are 0.62 and 0.70 ps, respectively. Both values are smaller than those for the TIPS pentacene, agreeing with the experimental observations, where \( r = 0.11 \) ps for TIPS pentacene and 0.08 ps for pentacene.\(^{11} \)

The SF time constant is overestimated in the simulation for several reasons. First, each molecule has many neighbors in real materials, allowing multiple channels that speed up the SF dynamics. When the closest molecular shell is taken into account, the \( W^+ \) and \( W^- \) couplings will be 4 times stronger, resulting in larger instantaneous triplet yield and faster SF. Calculations based on larger pentacene aggregates are under way. Second, in the present model, we use classical mechanics to deal with high-frequency vibrations. Although we have considered quantum effects in the initial nuclear distributions, the lack of exact quantum treatment is still expected to slow down the SF dynamics. Third, decoherence has not been included in the present surface hopping dynamics, and the role of decoherence needs to be further investigated.\(^{51} \) Finally, recent studies of Krylov and coauthors show that molecular packing can affect the free energy of each electronic state via entropy, and SF dynamics can also be influenced.\(^{52} \) They found that the entropic contribution is always beneficial for SF, and increase of exciton delocalization will further enhance the relative importance of the entropic contribution. Nevertheless, our studies ignoring entropy effects reproduce qualitatively well the experimental trends for TIPS and herringbone pentacene.

As shown in Figures 3–5, many dimer conformations in our 2D mapping have large instantaneous triplet yield and small SF time constant comparable with those of the TIPS and herringbone pentacenes. The packings labeled as II and III in Figure 3E are particularly advantageous. They are both shifted along the transverse direction by about one ring. The offset along the longitudinal direction is about one ring for packing II and two rings for packing III. Using these packings, SF can be sped up by more than 1 order of magnitude. Considering the fact that SF in a system like pentacene is already very fast, these packings at least provide additional candidate conformations with SF efficiencies similar to that of pentacene.

In summary, we have applied a recently developed nonadiabatic molecular dynamics method to study SF dynamics in pentacene. By studying systematically a broad range of pentacene dimer conformations, we have obtained 2D mappings for both instantaneous and long-term triplet yields, as well as the SF time scales. We have found that thermal fluctuations repudiate the symmetry arguments often used in SF analysis. Moreover, large CT character of the photoexcited state is not necessary for efficient SF. A direct relation has been observed between the SF time constant and the instantaneous triplet yield, allowing one to maximize SF efficiency through both instantaneous triplet yield and SF rate simultaneously. The relative values of the calculated time constant for SF in the TIPS and herringbone pentacene show good agreement with experiment. The experimental values are faster than those for the TIPS pentacene, agreeing with the experimental observations, where \( r = 0.11 \) ps for TIPS pentacene and 0.08 ps for pentacene.\(^{11} \)
findings provide clear guidelines for further development of pentacene derivatives toward highly efficient SF solar cells.

**ASSOCIATED CONTENT**

- Supporting Information
  - fewest switches surface hopping (FSSH) and self-consistent FSSH (SC-FSSH) theories; computational details for parameters; comparison of excited-state energies calculated at the INDO/SCI level and a four-state model; average singlet, CT, and triplet characters of all adiabatic states in pentacene dimers; CT state energy and exciton coupling; symmetric and asymmetric transfer integrals; and details for TIPS pentacene and herringbone pentacene. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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