Effect of Molecular Packing and Charge Delocalization on the Nonradiative Recombination of Charge-Transfer States in Organic Solar Cells

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Organic photovoltaic (OPV) devices have a great potential to become a low-cost technology for producing large-area, flexible solar modules that can be exploited, for instance, in portable and building-integrated applications. The organic electron donor (D) and acceptor (A) materials, used as active layer in an OPV device, are assembled into either a bilayer or bulk heterojunction structure. In high-performance organic solar cells, external quantum efficiencies can reach 70%–80% with internal quantum efficiencies approaching 100%. In these cases, nearly all photons absorbed by the donors or acceptors can be converted into collected electrons at short circuit and, hence, the achieved short-circuit currents (JSC) are close to their predicted maximum. However, in contrast, the open-circuit voltages (VOC) of these devices remain low, which limits the power conversion efficiencies (PCEs); to date, the highest PCEs reach 11.7% in a single-junction device, to be compared to ≈25% in silicon solar cells. Thus, it is crucial to better understand the factors limiting the open-circuit voltage in OPV devices in order to ultimately improve efficiency.

In an organic solar cell, the photogenerated excitons dissociate across a donor–acceptor interface, resulting in immediate long-range charge separation or formation of interfacial charge-transfer states with singlet character, which vibrationally relax to the lowest 1CT1 state. The 1CT1 states can separate into free charge carriers or decay to the ground state via either radiative emission or a nonradiative (NR) process. Numerous experimental investigations have demonstrated that the VOC values correlate linearly with the energies of the 1CT1 states. An empirical relation has been deduced: qVOC = El(1CT1) – (0.6 ± 0.1 eV), with the 0.6 eV energy difference (loss) between El(1CT1) and VOC attributed to radiative and nonradiative recombinations. Electroluminescence measurements on polymer-fullerene complexes show that the electroluminescent external quantum efficiency (EQEEL) is very low, on the order of <10−6, which means that the 1CT1 nonradiative recombination rates are expected to dominate the decay to the ground state and represent the major voltage loss between El(1CT1)/q and VOC. Therefore, a better understanding of the nonradiative energy loss mechanisms is highly desirable. We note that nonradiative recombination processes can also occur, for instance, because of poor contacts at the electrodes and, in the case of nongeminate recombination, not only via singlet 1CT states but also via triplet 3CT states (a topic of future studies in our group).

Up to now, the theoretical investigations of the NR recombination process in organic solar cells have been conducted under the Born-Oppenheimer (BO) approximation. Thus, the possible impact of nonadiabatic vibronic coupling due to the breakdown of the BO approximation (for instance, in particular, when the energy difference between the initial and final states is small) has been neglected. We note that the nonradiative recombination via nonadiabatic coupling (NAC) was initially investigated in inorganic semiconductors in the early 1950s; there, it was found to play an important role in reducing the number of photogenerated carriers, suppressing luminescence, and decreasing the carrier lifetimes.

In molecular systems, the NR transition between two excited states or between an excited state and the ground state (with the same spin multiplicity) due to nonadiabatic coupling, is referred to as internal conversion. In the case of organic emitters, the theoretical studies of Shuai and co-workers have demonstrated that internal conversion significantly limits the fluorescence quantum yields. Compared to the energies (usually in the range 2.0–4.0 eV) of the first excited states in organic emitters, the 1CT1-state energies are generally much lower in organic solar cells, on the order of 0.5–1.7 eV. Thus, the nonadiabatic coupling between the 1CT1 state and the ground state can be expected to be large and it becomes important to evaluate the role that nonadiabatic coupling can play in the NR recombination of 1CT1 states at donor–acceptor interfaces. We emphasize that the NR recombination rates of interfacial 1CT1 states are difficult to measure experimentally since the distribution of the 1CT1 states in transient experiments is far from equilibrium.

Here, we have chosen the pentacene–C60 interface as a representative system to study the factors determining the NR recombination rates in the context of OPV applications, since a large number of data are available from earlier experimental and theoretical studies. As the recombination process is expected to depend on the local D–A interface geometry, we have considered both edge-on and face-on interfacial orientations of the pentacene molecules relative to C60. Also, we consider two different packing modes of the pentacene molecules: (i) a herringbone-type packing (referred to as P:herringbone) hereafter) directly taken from the pentacene crystal structure; and (ii) a co-facial-type packing (referred to as P:co-facial)
hereafter) describing a general model system, see Figure 1. In the [P:herringbone] packing, the edge-on configuration corresponds to the pentacene (001) crystal facet and the face-on configuration corresponds to the (011) facet. We note that the [P:co-facial] packing is considered here to provide a more general understanding of the impact of donor packing (“local morphology”) on the recombination process at D–A interfaces; it can serve to represent the reported co-facial packing of donors in some high-performance small-molecule organic solar cells, such as $p$-DTS(FBTTh$_2$)$_2$-PC$_{71}$BM and benzodithiophene-terthiophene-rhodanine-PC$_{71}$BM, which both lead to high PCE values (8.0% and 9.3%, respectively);[50–53] in polymer-fullerene solar cells, co-facial $\pi$–$\pi$ stacks between polymer fragments can also form in locally ordered domains.[54–58] These model systems help us provide a comprehensive understanding, from a theoretical standpoint, of how molecular packing and charge delocalization can impact the NR recombination of donor–acceptor interfacial CT states in organic solar cells.

A complete description of our computational methodology is given in the Experimental Section.

For both edge-on and face-on configurations with either [P:co-facial] or [P:herringbone] packing, the calculated energy of the lowest charge-transfer excited state, $E^{(1\text{CT})}$, decreases consistently with the increase in the number of pentacene molecules (see Figure 2; for the face-on cluster with one pentacene and one C$_{60}$, the results can be found in Part A of the Supporting Information). For the [P:co-facial] packing, $E^{(1\text{CT})}$ converges down to ~0.70 eV in the edge-on configuration and 0.94 eV in the face-on configuration. For the [P:herringbone] packing, the calculated $E^{(1\text{CT})}$ in both edge-on and face-on configurations are ~0.1 eV higher than the corresponding values for the [P:co-facial] packing (with $E^{(1\text{CT})}$ for the 5P cluster reaching 0.81 and 1.04 eV in edge-on and face-on configuration, respectively).

Clear trends are also obtained for the natural transition orbitals (NTOs) and the hole–electron overlaps ($O_{h-e}$) and spatial distances ($D_{h-e}$), see Figure 2 and Figure 3, respectively. As could be expected, in the edge-on configuration, the hole–electron overlaps ($O_{h-e}$) and spatial distances ($D_{h-e}$) show very little change with the increase in cluster size (see Figure 3). In contrast, in the face-on configuration, there occurs a significant increase in the hole–electron distance $D_{h-e}$ and a corresponding large decrease in the overlap $O_{h-e}$ (see Figure 3); this evolution is related to a more pronounced hole delocalization, leading to a migration of the hole centroid away from the pentacene–C$_{60}$ interface. (Results for larger clusters with the face-on [P:herringbone] packing are given in Part B of the Supporting Information).

From detailed analyses of the evolution of the calculated excitation energies and characteristics of the NTO orbitals, we can underline the following points:
A comparison of the $E(1\text{CT}_1)$s for the edge-on and face-on configurations underlines that the $E(1\text{CT}_1)$s for the edge-on configuration are always lower than those for the face-on configuration by some 0.10–0.25 eV, regardless of the packing of pentacene molecules. This can be understood by considering the zeroth-order approximation to $E(1\text{CT}_1)$ as

![Diagram of calculated excitation energies and natural transition orbitals](image)

**Figure 2.** Calculated excitation energies $E(1\text{CT}_1)$ and illustration of the natural transition orbitals (h: hole; e: electron) for the $1\text{CT}_1$ states by using the TD-ωB97XD/6-31G(d,p) method coupled with the PCM model for clusters in the: a) edge-on [P:co-facial], b) face-on [P:co-facial], c) edge-on [P:herringbone], and d) face-on [P:herringbone] configurations.

![Diagram of overlap and spatial distance](image)

**Figure 3.** a) Overlap ($O_{h-e}$) between the hole and electron density distributions. b) Spatial distance ($D_{h-e}$) between the centroids of the hole and electron density distributions for the $1\text{CT}_1$ states in the clusters shown in Figure 2.
$E \left( ^1CT_1 \right) = IP_P - EA_{C_{60}} + E_{\text{Coul}} \left( P : C_{60} \right)$  \hspace{1cm} (1)

where $IP_P$ denotes the ionization potential of pentacene ($P$), $EA_{C_{60}}$ denotes the electron affinity of $C_{60}$, and $E_{\text{Coul}}(P:C_{60})$ represents the Coulomb attraction energy between the hole on pentacene and electron on $C_{60}$ (we recall that the first two items have positive values while the third one has a negative value). The $IP_P$, $EA_{C_{60}}$, and energy gap $[IP_P - EA_{C_{60}}]$ values for all clusters are illustrated in Figure 4. We find that the edge-on configurations have slightly smaller $IP_P$ values by 0.01–0.04 eV, larger $EA_{C_{60}}$ values by 0.18–0.23 eV, and thus lower energy gap $[IP_P - EA_{C_{60}}]$ values by 0.19–0.25 eV, compared to the face-on configurations. These results underline that the variation in $EA_{C_{60}}$ (and hence in the energy gap $[IP_P - EA_{C_{60}}]$) has a dominant contribution to the difference in the $E \left( ^1CT_1 \right)$s between the edge-on and face-on configurations. The large variation in the $EA_{C_{60}}$ values can be attributed mainly to the difference in electrostatic interactions between $C_{60}$ and the multipole moments of face-on versus edge-on configurations of pentacene clusters, a feature underlined earlier, for instance, by Beljonne and co-workers.[59,60] In a face-on configuration, $C_{60}$ interacts primarily with the negative poles ($\pi$-electron cloud) of the pentacene quadrupole moments, which leads to a destabilization of the $C_{60}$  electronic levels; in an edge-on configuration, it interacts mainly with the positive poles (slightly positively charged hydrogen atoms), which leads to a stabilization of the $C_{60}$ levels. This difference in $E \left( ^1CT_1 \right)$ values between face-on and edge-on configurations has been experimentally observed in other OPV systems.[23]

The $E \left( ^1CT_1 \right)$ values for the [P:herringbone] packing in both edge-on and face-on configurations are consistently ~0.1 eV higher than the corresponding values for equally sized clusters with [P:co-facial] packing. This comes from two main effects:

(i) A larger electronic coupling among pentacene molecules in co-facial packing due to the molecular packing dependence of the intermolecular electronic couplings,[64] results in a higher HOMO (highest occupied molecular orbital) level, smaller $IP_P$ value, and thus lower $^1CT_1$ energy.

(ii) The co-facial and herringbone packing modes lead to different intermolecular polarization interactions. In a co-facial packing, a pentacene molecule mainly interacts with the negatively charged $\pi$-electron densities on neighboring molecules; in a herringbone packing, a pentacene molecule interacts with both the positively charged peripheral hydrogens and negatively charged $\pi$-electron clouds. Thus, in co-facial packing, an excess hole on a pentacene molecule feels an attractive interaction from the $\pi$-electron clouds of the neighboring pentacene molecules and is therefore stabilized; in herringbone packing, it feels both attractive and repulsive interactions and is less stabilized, which leads to larger $IP_P$ values.[62,63]

Comparing the NTOs for clusters in face-on configuration in Figure 2b, we observe that the hole more strongly delocalizes and its centroid migrates away from the D–A interface when the cluster size increases. This leads to a significant increase in the $D_{ho-e}$ value and hence a large decrease in the hole–electron density overlap, $O_{ho-e}$, with both values approaching the results for the edge-on configuration when the cluster size is increased to five pentacenes (see Figure 3). In contrast, the $D_{ho-e}$ and $O_{ho-e}$ values remain nearly constant for the edge-on configuration. Such a difference in hole–electron density overlap for face-on versus edge-on configurations, plays a major role in the evaluations of the nonadiabatic coupling matrix elements (NACMEs), which will be discussed below.

Finally, we stress that the $^1CT_1$ excitation energies we have calculated are in very good agreement with experimental estimates. $V_{OC}$ values in pentacene–$C_{60}$ heterojunctions (including bilayer and bulk-heterojunction devices) have been reported to be in the range 0.2–0.4 V,[45–48] taking into account the empirical relationship: $qV_{OC} = E \left( ^1CT_1 \right) - (0.6 \pm 0.1$ eV), this gives a range of 0.7–1.1 eV for the $E \left( ^1CT_1 \right)$ values in these systems.

To evaluate the internal conversion rate from the $^1CT_1$ state to the ground state, taking into account the nonadiabatic (vibronic) coupling, the NACMEs were calculated using Equations (3)–(7) in the Experimental Section; the results are collected in Figure 5. We first compare the results obtained for [P:co-facial] packing with an increasing size of clusters in the edge-on and face-on configurations (Figure 5a,b). As pointed out in the Experimental Section, the NACME values will come
down upon increasing the energy gap between the $^1\text{CT}_1$ and ground states and reducing the hole–electron density overlap in the $^1\text{CT}_1$ state. Such a correlation can be observed in the calculated NACMEs for both edge-on and face-on configurations in Figure 5a,b. For the edge-on [P:co-facial] configuration, we find that the NACMEs increase with cluster size, as a result of $^1\text{CT}_1$ excitation energy decrease and nearly constant $O_{h–e}$. In contrast, in the face-on [P:co-facial] configuration, the NACMEs significantly decrease when the cluster size increases from 2P to 4P and start converging in going from 4P to 5P. This evolution can be attributed to the strong decrease in hole–electron overlap $O_{h–e}$ due to hole delocalization and migration away from the interface. The opposite evolution of the NACMEs with cluster size in the two configurations leads to the interesting observation that, when comparing the absolute NACME values for the two configurations, the NACME for the 2P cluster in the edge-on configuration is much smaller than that for the face-on configuration, while the opposite is true for the 5P clusters.

Similar trends in NACME evolution in the [P:herringbone] packing can be observed, due to hole delocalization (see Figure 5c,d). However, there exist differences between the two packing modes; for example, in the face-on configuration, the NACMEs for [P:herringbone] packing are much larger than those in equally sized clusters with [P:co-facial] packing because of the much larger $O_{h–e}$ values in the former.

Our vibrational analyses indicate that low-frequency intermolecular vibrations (<100 cm$^{-1}$), such as intermolecular rotations and slips, have minor contributions to the NACME values. It is the intramolecular vibrations in both pentacene and C$_{60}$ molecules, e.g., the carbon–carbon stretchings and the breathing motions of the carbon backbones that contribute significantly to the nonadiabatic couplings. The high-frequency C–H stretching modes (>3000 cm$^{-1}$) have also some contributions, although not large enough for deuteration, for example, to make any significant difference. The vibration normal modes for the example of the face-on [P:herringbone] cluster composed of one C$_{60}$ and five pentacene molecules are illustrated in Part C of the Supporting Information.

The internal conversion rates are calculated by using the low-temperature (LT) formula, Equation (4), in the Experimental Section. This is justified by the fact that the average phonon energies $\hbar(a)$ for the present systems are $≈$1100 cm$^{-1}$, and thus much larger than $\tilde{H}_e$ at room temperature. The energy gap between the final and initial electronic states $\Delta G_{\text{fi}}$ can be estimated as $\Delta G_{\text{fi}} = (E(^1\text{CT}) - \lambda)$. Here, we take the reorganization energy $\lambda$ as 0.3 eV, which corresponds to a typical value for

![Figure 5. Nonadiabatic coupling matrix elements between the $^1\text{CT}_1$ state and the ground state in molecular clusters with: a) edge-on [P:co-facial], b) face-on [P:co-facial], c) edge-on [P:herringbone], and d) face-on [P:herringbone] configurations. Here, $\omega$ represents the frequency of the vibration normal mode in the equilibrium geometry of the ground state.](http://www.advenergymat.de)
OPV systems where $\lambda$ is generally in the range 0.2–0.4 eV.\textsuperscript{[22,64]} (more details about $\lambda$ and $\Delta G_{\text{N}}$ are given in Part D of the Supporting Information).

The rates at 300 K for internal conversion from the $^1\text{CT}_1$ state to the ground state are illustrated in Figure 6 (the $k_{\text{EC}}$ rates estimated by the high-temperature formula are also given in Part E of the Supporting Information). Here, we focus on the discussion on the results for the [P:co-facial] packing as such a packing is commonly found in small molecules or polymers used as donor materials in OPV cells. Within the [P:co-facial] packing, the $k_{\text{LT}}^{NAC}$ values for an edge-on configuration show a monotonic increase by about two orders of magnitude with an increase in cluster size, up to $\approx 10^{12}$ s$^{-1}$ for the 5P cluster; this can be attributed to the decrease in $E(1\text{CT}_1)$ and increase in NACME values with cluster size. In contrast, the $k_{\text{LT}}^{NAC}$ values for the face-on configuration first increase, reach a maximum ($\approx 10^{11}$ s$^{-1}$) for the 3P cluster, and then slightly decrease with further increase in cluster size; this evolution results from the competition between the decrease in $E(1\text{CT}_1)$ and strong decrease in nonadiabatic coupling due to hole delocalization and migration from the interface.

When comparing the relative magnitudes of the $k_{\text{LT}}^{NAC}$ rates for edge-on versus face-on configurations in similarly sized clusters, the $k_{\text{LT}}^{NAC}$ values for clusters containing three or fewer pentacenes are smaller in the edge-on configuration than face-on; however, when the cluster size reaches four pentacenes, a reversal in the relative magnitude of the $k_{\text{LT}}^{NAC}$ values is observed (see Figure 6); $k_{\text{LT}}^{NAC}$ for the edge-on configurations then becomes an order of magnitude larger than for the face-on configuration. This is due to the enhanced difference in the $E(1\text{CT}_1)$ values between edge-on and face-on configurations with the increase in cluster size and the large decrease in NACME values in the face-on configuration.

We now turn to a discussion of the nonradiative recombination rates when the Born-Oppenheimer approximation is applied and the motions of electrons and nuclei are separated. In that instance, the rates are related to the electronic couplings modulated by the Franck–Condon overlap, see Equations (3) and (8) in the Experimental Section. The corresponding rates are illustrated in Figure 7. Figure 7a illustrates that, in most instance, the electronic couplings for the face-on configurations are larger than those for the edge-on configurations; this is consistent with the results reported in our previous investigation for single donor/acceptor complexes.\textsuperscript{[31]} However, in contrast, the rates $k_{\text{EC}}$ calculated for edge-on configurations are always larger than those for face-on configurations. This is the opposite of the trend reported in our earlier work,\textsuperscript{[31]} where the charge recombination rates for the face-on configuration were consistently calculated to be larger than in the edge-on cases. The main reason for this different trend can be found in the variation in the excitation energies $E(1\text{CT}_1)$ between the two configurations which, we recall, are mainly associated with the difference in the $[\text{IP}_p - \text{EA}_{\text{C}60}]$ values; this difference was not taken into account in our earlier work.\textsuperscript{[31]}

In line with the trends observed for the nonadiabatic internal conversion rates, the $k_{\text{EC}}$ rates for an edge-on configuration increase with cluster size, up to $\approx 10^{11}$ s$^{-1}$ for the 5P cluster; the $k_{\text{EC}}$ values for a face-on configuration first increase, reach a maximum ($\approx 10^{10}$ s$^{-1}$) for the 3P cluster, and then significantly

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**Figure 6.** Rate constants $k_{\text{LT}}^{NAC}$ at 300 K for the internal conversion process from the $^1\text{CT}_1$ state to the ground state.

**Figure 7.** a) Electronic couplings ($V_{\text{EC}}$) between the $^1\text{CT}_1$ state and the ground state in the pentacene-C$_{60}$ clusters, calculated via Equation (9). b) Rate constants ($k_{\text{EC}}$) at 300 K for the nonradiative recombination from the $^1\text{CT}_1$ state to the ground state, calculated via Equation (8).
The variations in molecular orientations at the donor–acceptor interfaces (e.g., edge-on vs face-on) can lead to very different electrostatic interactions, resulting in lower 1CT1 energies for edge-on configurations than face-on configurations (by $\approx 0.2$ eV).

(2) For edge-on configurations, due to the decrease in 1CT1 energy induced by charge delocalization, the nonadiabatic couplings between the 1CT1 state and the ground state increase with an increase in the number of pentacene molecules; on the other hand, in face-on configurations, due to the significant decrease in hole–electron density overlap ($O_{h-e}$) due to both hole delocalization and migration away from the pentacene–C60 interface, the nonadiabatic couplings are significantly reduced.

(3) For large-size aggregates, the edge-on configurations display higher nonradiative recombination rates than face-on configurations, by 1 to 2 orders of magnitude.

(4) The lower limit of 1CT1-state lifetime ($t_{\text{ct}} \approx 1 \text{ ps}$) corresponds to large-size molecular aggregates, especially in edge-on configurations while its upper limit ($t_{\text{ct}} \approx 1 \text{ ns}$) corresponds to the cluster composed of a single pentacene and a single C60. Thus, we face once more necessity of finding the right compromise between the positive impact of delocalization, which favors migration of hole and electron away from one another, and its negative role, which leads to a lower CT-state energy and faster nonradiative recombination rates.

Our findings point out again the significant role of the microscopic interfacial geometry (molecular packing and degree of molecular aggregation) at the donor–acceptor interface in controlling both the energy and lifetime of the interfacial 1CT1 states and hence in significantly impacting the open-circuit voltage in organic solar cells.

### Experimental Section

**Nonradiative Recombination Rates:** The coupling $V(1\text{CT}_1 - \text{GS})$ between the 1CT1 (initial vibronic state $|1\text{CT}_1\rangle\Theta_{\text{CT}_1}$) and the ground (final) vibronic state $|\text{GS}\rangle\Theta_{\text{GS}}$ can be written as

$$V(1\text{CT}_1 - \text{GS}) = \langle \Theta_{\text{CT}_1} | \langle 1\text{CT}_1 | \hat{H}_{\text{total}} | \text{GS} \rangle | \Theta_{\text{GS}} \rangle$$

where the total Hamiltonian of the system is $\hat{H}_{\text{total}} = \hat{H}_S + \hat{T}_N$, with $\hat{H}_S$ and $\hat{T}_N$ the electronic Hamiltonian and the nuclear kinetic energy operator, respectively ($\hat{H}_S = \hat{T}_e + U(r,Q)$, where $\hat{T}_e$ and $U(r,Q)$ denote the electron kinetic energy operator and the potential energy and $r$ and $Q$ the electronic and nuclear coordinates); $|1\text{CT}_1\rangle$ and $|\text{GS}\rangle$ denote the diabatic initial and final electronic states; $\{|\Theta_{\text{CT}_1}\rangle\}$ and $\{|\Theta_{\text{GS}}\rangle\}$ denote the vibrational states of the system corresponding to the initial and final electronic states. The coupling $V(1\text{CT}_1 - \text{GS})$ can then be written as the sum of two components

$$V(1\text{CT}_1 - \text{GS}) = \langle \Theta_{\text{CT}_1} | \langle 1\text{CT}_1 | \hat{H}_{\text{BO}} | \text{GS} \rangle | \Theta_{\text{GS}} \rangle$$

$$+ \langle \Theta_{\text{CT}_1} | \langle 1\text{CT}_1 | \hat{H}_{\text{non-BO}} | \text{GS} \rangle | \Theta_{\text{GS}} \rangle$$

Here, $\hat{H}_{\text{BO}}$ denotes the so-called BO operator appearing as the result of the breakdown of the BO approximation, which can be expressed as

decrease by about two orders of magnitude with further increase in cluster size. Importantly, our findings here underline the important role of $E(1\text{CT}_1)$ (or $\Delta G_{\text{el}}$) in controlling the nonradiative recombination process.

We also investigated the effect of electron delocalization among C60 molecules on the properties of the 1CT1 states and the nonradiative recombination rates (see Part F in the Supporting Information). Our results demonstrate that electron delocalization among C60 molecules has no remarkable effect on the $E(1\text{CT}_1)$s and the NR recombination rates. This is consistent with a recent theoretical study based on a tight-binding model Hamiltonian, which showed that electron delocalization on fullerene molecules at the P3HT–fullerene interface had negligible impact on the $k_{\text{SC}}$ rate.$^{[32]}$

Our earlier discussion on the NR recombination rate $k_{\text{NR}}$, as well as the detailed description to be found in the Experimental Section, underlines that $k_{\text{NR}}$ is composed of two components, i.e., $k_{\text{NR}} = k_{\text{NAC}} + k_{\text{SC}}$ (in the diabatic representation). In the larger molecular aggregates (e.g., those containing five pentacenes) expected to form in high-performance organic solar cells, we find that the $k_{\text{NR}}$ values for edge-on configurations are 1 to 2 orders of magnitude larger than those for face-on configurations, regardless of the pentacene packing modes (i.e., [P:cofacial] vs [P:herringbone]). The energy loss induced by nonradiative recombination can be expressed as:

$$q\Delta V_{\text{OC}}(\text{NR}) = -k_{\text{NR}} V_{\text{el}}$$

Here, $V_{\text{el}}$ is the external quantum efficiency of electroluminescence, which is inversely proportional to the nonradiative recombination rate $k_{\text{NR}}$. Thus, a larger $k_{\text{NR}}$ for the edge-on configuration in pentacene–C60 complexes should correspond to smaller $V_{\text{el}}$ values and hence a larger energy loss when comparing $E(1\text{CT}_1)$ to $qV_{\text{OC}}$. Such an observation is indeed consistent with recent experimental reports.$^{[23,65]}$

McGehee and co-workers have shown via a numerical study, that increasing the CT-state lifetime ($t_{\text{ct}} = 1/k_{\text{rec}}$; $k_{\text{rec}}$ is the total recombination rate) could be a promising way to improve $V_{\text{OC}}$. The total $k_{\text{rec}}$ term is composed of both radiative and nonradiative recombination rates ($k_{\text{rec}} = k_{\text{R}} + k_{\text{NR}}$ with $k_{\text{R}}$ the radiative rate). The radiative rates of the 1CT1 states can be evaluated by considering the simple spontaneous emission expression.$^{[32]}$ Our results indicate that $k_{\text{R}}$ is very small (generally $< 10^4$ s$^{-1}$) for the systems we are investigating and can thus be neglected in comparison with $k_{\text{NR}}$, a finding also consistent with experimental reports that the nonradiative pathway is dominant.$^{[16,22,29]}$ We note that the total recombination rate $k_{\text{rec}} = k_{\text{NR}} = k_{\text{NAC}} + k_{\text{SC}}$ is in the range $10^2-10^{12}$ s$^{-1}$, that is, the CT-state lifetime is within the range 1 ps–1 ns. The lower limit of $t_{\text{ct}}$ around 1 ps corresponds to large-size molecular aggregates (here with five pentacenes), in particular in the edge-on configuration; the upper limit around 1 ns corresponds to the cluster composed of a single pentacene and a single C60. While the parameters used to evaluate quantitatively the $k_{\text{rec}}$ or $t_{\text{ct}}$ values depend on the specifics of the molecular systems, the qualitative trends obtained here should be useful to better appreciate the nonradiative recombination processes in other OPV systems.

In summary, taking pentacene–C60 complexes as model donor–acceptor systems, we have provided a comprehensive understanding of the impact of molecular packing and charge delocalization on the nonradiative recombination process from the interfacial 1CT1 state to the ground state. The main conclusions we can draw from theoretical results are:
\[ \hat{H}_0 = \langle \text{GS} | \hat{\Theta}_C \rangle = -\hbar \sum_o \Delta_{q_{o}} \frac{\partial^2 \langle \text{GS} \rangle}{\partial \phi_o^2} \]

when neglecting the small quadratic term \[ \hat{\Theta}_C^2 \langle \text{GS} \rangle / \langle \hat{\Theta}_C \rangle^2 \].

Nonradiative recombination via the \( \hat{H}_0 \) component: This term to date has been largely neglected. Following the pioneering work by Freed and Jortner,\(^{[67]}\) under the displaced harmonic oscillator approximation, the corresponding (internal conversion) rate can be expressed in the LT limit (\( \hbar \omega/\kappa_T \gg 1 \)), which applies here, as

\[ k_{\text{NAC}}^L = \sum_i \left( \langle \alpha_i | R_i(f_i) \rangle^2 \right) \left( \frac{2\pi}{\hbar} \right) \exp \left[ -\frac{\Delta_{G_\alpha} + \lambda_j^2}{2\hbar \hbar \omega} \right] \]  

(4)

Here, \( \omega_i \) is the frequency of the \( l \)th normal mode; \( \langle \alpha \rangle \) the mean frequency: \( \langle \alpha \rangle = \sum_{\omega_i} \omega_i / N \); \( \lambda \), the reorganization energy; \( \Delta_{G_\alpha} \), the Gibbs free energy difference between the initial and final electronic states; \( k_T \), the Boltzmann constant; \( T \), the temperature; and \( R_i(f_i) \), the nonadiabatic coupling matrix element for the \( l \)th normal mode (here, we note that we had to switch to an adiabatic representation; in the case of CT states where the hole is localized on the donor and the electron on the acceptor, \( \text{CT} \rightarrow \text{CT} \) is a reasonable approximation to the \( |D^\alpha> A^\alpha \rangle \) diabatic states).

Based on first-order perturbation theory, the nonadiabatic coupling matrix element \( R_i(f_i) \) is given by\(^{[40,68]}\)

\[ R_i(f_i) = i\hbar \left( \frac{2}{\hbar} \right) \left( \frac{\partial}{\partial \phi_i} \right) \left( \frac{\partial}{\partial \phi_i} \right) = i\hbar \left( \frac{2}{\hbar} \right) \left( \frac{\partial}{\partial \phi_i} \right) \left( \frac{\partial}{\partial \phi_i} \right) \]  

(5)

where \( V_{\text{Coul}} \) denotes the Coulomb interaction potential between electrons and nuclei; \( | \phi_i^\alpha \rangle \) and \( | \phi_i^\beta \rangle \) are the electronic Eigen-states at the equilibrium geometry of the ground state; and

\[ \langle \phi_i^\alpha | \frac{\partial^2 \langle \phi_i^\beta \rangle}{\partial \phi_i^\alpha} | \phi_i^\beta \rangle = -e \sum_{\alpha} Z_{\alpha} \left( \sum_{j} L_{\alpha j} F_{i j, \alpha} \right) \]  

(6)

where \( x, y \) or \( z \); \( Z_{\alpha} \) represents the nuclear charge; \( r_i^\alpha \) and \( R_i^\beta \) are the Cartesian coordinates of electron \( \alpha \) and nucleus \( \alpha \), respectively; \( L_{\alpha j} = \frac{\partial r_i^\alpha}{\partial \phi_j} \) is the atomic displacement of normal mode \( j \); \( F_{i j, \alpha} \) represents the transition matrix element over the one-electron electric field operator at atomic center \( \sigma \)

\[ F_{i j, \alpha} = \langle \phi_i^\alpha | \sum_{\alpha} e(r_i^\beta - R_i^\alpha) \sum_{\alpha} e(r_j^\beta - R_j^\alpha) \rangle = \int d \rho_j(r) \rho_i^\beta(r) \sum_{\alpha} e(r_j^\beta - R_j^\alpha) \]  

(7)

where \( \rho_j^\beta(r) \) is the electronic transition density at the equilibrium position. \( L_{\alpha j} \) and \( F_{i j, \alpha} \) can be obtained from ab initio electronic-structure calculations. Equations (5)–(7) have been successfully applied to evaluate the nonadiabatic coupling matrix element between the excited state and ground state in organic emitters.\(^{[41,69]}\) Important implications from Equation (5) are that the matrix elements are: (i) inversely proportional to the energy gap between excited and ground state; and (ii) directly proportional to \( \rho_j^\beta(r) \), i.e., the overlap between the hole and electron density distributions in the excited state.

Nonradiative Recombination via the \( \hat{H}_1 \) Component: The corresponding rate \( k_{\text{EC}} \) is evaluated by the Marcus electron-transfer rate equation\(^{[70]}\)

\[ k_{\text{EC}} = \frac{2\pi}{\hbar} \frac{V_{\text{EC}}^2}{6\pi \lambda k_b T} \exp \left[ -\frac{(\Delta_{G_\alpha} + \lambda_j^2)}{4\lambda k_b T} \right] \]  

(8)

where the electronic couplings \( V_{\text{EC}} = \langle \text{CT}_l | \hat{R}_i | \text{GS} \rangle \) between the \( \text{CT}_l \) and ground electronic states are calculated via the fragment charge difference (FCD) scheme\(^{[71]}\) implemented in the Q-CHEM program\(^{[72]}\).