Charge Recombination Suppressed by Destructive Quantum Interference in Heterojunction Materials

Roel Tempelaar,[†] L. Jan Anton Koster,[†] Remco W. A. Havenith,^{†,‡,¶}

Jasper Knoester,[†] and Thomas L. C. Jansen^{*,†}

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands, and Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), B-9000 Gent, Belgium

E-mail: t.l.c.jansen@rug.nl

^{*}To whom correspondence should be addressed

[†]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

[‡]Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

[¶]Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), B-9000 Gent, Belgium

Abstract

We show that charge recombination in ordered heterojunctions depends sensitively on the degree of coherent delocalization of charges at the donor-acceptor interface. Depending on the relative sign of the electron and hole transfer integrals, such delocalization can dramatically suppress recombination through destructive quantum interference. This could explain why measured recombination rates are significantly lower than predictions based on Langevin theory for a variety of organic bulk heterojunctions. Moreover, it opens up a design strategy for photovoltaic devices with enhanced efficiencies through coherently suppressed charge recombination.

TOC graphic:

Keywords: bimolecular recombination, Langevin theory, quantum coherence, organic photovoltaics

The recombination of mobile electrons and holes forms a serious factor hindering the photoconversion in organic solar cells. It is currently regarded as the primary obstacle to overcome in order to realize commercially feasible cells based on bulk heterojunctions of polymers and fullerene derivatives.¹ Originally, charge recombination was considered in the framework of Langevin theory;² a macroscopic description based on electron and hole diffusion constants which was known to provide reliable recombination rates for single organic materials.³⁻⁵ However, for a variety of polymer:fullerene heterojunctions, experimentally determined recombination rates were found to be significantly lower than estimates based on Langevin theory.⁶⁻⁹ Particularly for annealed blends of poly-3-hexylthiophene (P3HT) and the fullerene derivative PCBM, recombination turns out to be suppressed by up to 4 orders of magnitude.^{6,8} An understanding of the mechanism responsible for this suppression opens an avenue to deliberately engineer photovoltaics with low recombination, and hence optimized photoconversion efficiency. To this end, several modifications to Langevin theory were proposed, yet no candidate was found to explain recombination fully satisfactory.¹⁰⁻¹⁶ It has since become clear that such theories based on a macroscopic description are inherently insufficient, and that instead a molecular representation is necessary.^{17,18} In this Letter, we present a principle based on molecular charge excitations that possibly accounts for the observed low recombination rates. Through calculations, we show that a coherent delocalization of the electron and hole can result in a dramatic suppression of their recombination, as the occurrence of recombination is sensitively dependent on the phase of the electron-hole wavefunction along the heterojunction interface.

The process of recombination of mobile charges (also referred to as bimolecular recombination) is illustrated schematically in Figure 1, which shows an energy level diagram for the manifolds of free charges (FC), charge transfer (CT) states, and recombined (R) states. FC consist of holes and electrons that migrate through donor and acceptor materials, respectively, and which are extracted at electrodes in order to generate the desired current. These carriers are likely to have encounters at heterojunctions along the way, mediated by

Figure 1: Energy level diagram of the manifolds of recombined (R) states, charge transfer (CT) states, and free carriers (FC). CT states can either dissociate (green arrow), or recombine followed by fast thermal relaxation (yellow wiggling arrow). The lowest-energy CT state (indicated as yellow) experiences an enhancement (red arrow) or suppression (blue arrow) of the associated recombination rate, depending on its spatial phase relation. Two examples of CT states are illustrated by means of a 2D plot of their wavefunction coefficients at the interface (see Figure 3 and text for details).

their mutual Coulomb attraction.¹⁴ Ultimately, this could result in R states through an electron-hole annihilation event, upon which the energy is inevitably lost. CT states, where an electron and hole are Coulombically bound at a heterojunction interface, naturally form the intermediate between FC and R states. Hence, for CT states there is a competition between recombination and a dissociation back to FC. A recent experimental study by Rao *et al.* showed that the barrier for dissociation is effectively lowered by a delocalization of the charge wavefunctions.¹⁸ In this Letter, instead of dissociation, we investigate how recombination is directly affected by delocalization.

Note that spin is not included in the diagram shown in Figure 1. Encounters between mobile electrons and holes result in ^1CT and ^3CT states, with the difference that recombination of ^1CT is spin-allowed only towards the ground state,¹⁹ whereas ^3CT recombines to form a triplet exciton.¹⁸ For simplicity, in this Letter we restrict ourselves to the case of ^3CT (hereafter referred to as “CT”), which according to spin statistics is the dominant channel for charge recombination. A generalization of our results to the case of ^1CT is given in the Supporting Information. Assuming the coupling between CT and R states to be small compared to the phonon-assisted relaxation rate in the R manifold, the rate of recombination is

Figure 2: Hole and electron transfer integrals, depicted for an idealized heterojunction where the molecular sites (black dots) are assumed to form a cubic lattice. Holes (electrons) in the donor (acceptor) material experience couplings in the x , y , and z -direction (indicated as $t_{h(e)}^{x,y,z}$). Charge recombination follows from a hopping of the electron (or hole) across the interface, mediated by the coupling t_i .

governed by Fermi's Golden Rule,

$$\Gamma_{CT} = \frac{2\pi}{\hbar} |\langle R | H_r | CT \rangle|^2 \rho_R, \quad (1)$$

where H_r is the recombination Hamiltonian and ρ_R is the density of R states.

To demonstrate the effect of charge delocalization on the recombination rate Γ_{CT} we consider an idealized heterojunction as shown schematically in Figure 2. Accordingly, the heterojunction consists of a $2N \times M \times M$ cubic lattice of molecular units, while the donor-acceptor interface extends in the y, z -plane, and separates the lattice halfway along the x -axis (between N and $N + 1$). Such a structure could for example serve to represent an ordered domain in an organic blend. In case of P3HT, the units then correspond to thiophene rings, being assembled in molecular chains extending in the x , y , or z -direction.²⁰ Nevertheless, as argued below, it is reasonable to assume that the physics found for this lattice is essentially retained for materials with a lesser degree of order and/or lower symmetry.

Electrons and holes are described in a coarse-grained approximation which retains a single HOMO and LUMO in each unit cell,²⁰ and CT states are accounted for in the subspace containing a single electron in the LUMOs of the acceptor units and a single hole in the

HOMOs of the donor units. Both hole and electron experience couplings between neighboring sites in all three directions due to the overlap of adjacent HOMOs and LUMOs, respectively. The relative signs of these transfer integrals are based on translational symmetry in the x , y , and z -direction. The Hamiltonian in the subspace of CT states is given by

$$\begin{aligned}
H_0 = & \sum_{\vec{m}, \vec{n} \in \text{D}} b_{\vec{m}}^{\dagger} b_{\vec{n}} \left(t_{\text{h}}^x \delta(\vec{m}, \vec{n} \pm \hat{x}) + t_{\text{h}}^y \delta(\vec{m}, \vec{n} \pm \hat{y}) + t_{\text{h}}^z \delta(\vec{m}, \vec{n} \pm \hat{z}) \right) \\
& + \sum_{\vec{m}, \vec{n} \in \text{A}} c_{\vec{m}}^{\dagger} c_{\vec{n}} \left(t_{\text{e}}^x \delta(\vec{m}, \vec{n} \pm \hat{x}) + t_{\text{e}}^y \delta(\vec{m}, \vec{n} \pm \hat{y}) + t_{\text{e}}^z \delta(\vec{m}, \vec{n} \pm \hat{z}) \right) \\
& - \sum_{\vec{m} \in \text{D}, \vec{n} \in \text{A}} b_{\vec{m}}^{\dagger} b_{\vec{m}} c_{\vec{n}}^{\dagger} c_{\vec{n}} \frac{U}{|\vec{m} - \vec{n}|}. \tag{2}
\end{aligned}$$

Here, summations are taken over molecular sites in the donor (D) and acceptor (A) regions of the heterojunction, labeled with $\vec{m} = (m_x, m_y, m_z)$ in units of the lattice constant (similarly for $\vec{n}$). The operator $b_{\vec{m}}^{(\dagger)}$ annihilates (creates) a hole in the HOMO of site $\vec{m}$, whereas $c_{\vec{m}}^{(\dagger)}$ represents the equivalent for the electron in the $\vec{m}$ th LUMO.

The first and second row of eq 2 describe the hole and electron transfer integrals in the x , y , and z -direction, denoted $t_{\text{h/e}}^{x,y,z}$, employing the unit vectors $\vec{x} = (1, 0, 0)$, $\vec{y} = (0, 1, 0)$, and $\vec{z} = (0, 0, 1)$, and the Kronecker delta δ . The bottom row accounts for the Coulomb interaction between electron and hole, where U is the energy needed to fully separate a neighboring electron-hole pair. Solving the Schrödinger equation, $H_0|\alpha\rangle = E_{\alpha}|\alpha\rangle$, yields the CT energies and states. The latter can be expanded in the local basis as $|\alpha\rangle = \sum_{\vec{m} \in \text{D}, \vec{n} \in \text{A}} c_{\vec{m}, \vec{n}}^{\alpha} |\vec{m}, \vec{n}\rangle$, where $|\vec{m}, \vec{n}\rangle$ represents a hole at donor site $\vec{m}$ accompanied by an electron at acceptor site $\vec{n}$.

Recombination results from hopping of an electron (or, alternatively, a hole) across the interface, mediated by the molecular orbital overlap of neighboring acceptor and donor units. Denoting the associated trans-interface coupling parameter as t_i , the recombination Hamil-

tonian is given by

$$H_r = \sum_{\vec{m} \in D, \vec{n} \in A} d_{\vec{m}}^\dagger b_{\vec{m}} c_{\vec{n}} t_i \delta(\vec{m}, \vec{n} - \hat{x}), \quad (3)$$

where $d_{\vec{m}}^\dagger$ creates an R state in the form of spin-triplet electron-hole pair located at donor site $\vec{m}$. (For materials where instead the hole hops, a spin-triplet is created at an acceptor site. This gives the same outcome in what follows.) Substitution of this Hamiltonian in eq 1 yields the recombination rate of the CT state $|\alpha\rangle$,

$$\begin{aligned} \Gamma_\alpha &= \frac{2\pi}{\hbar} \left| \sum_{\vec{m} \in D, \vec{n} \in A} \langle R_{\vec{m}} | d_{\vec{m}}^\dagger b_{\vec{m}} c_{\vec{n}} t_i \delta(\vec{m}, \vec{n} + \hat{x}) | \alpha \rangle \right|^2 \rho_R \\ &\propto \left| \sum_{y,z} c_{(N,y,z),(N+1,y,z)}^\alpha \right|^2, \end{aligned} \quad (4)$$

where the density of states is assumed to be equal for all molecular triplet excitations.

Eq 4 shows that the rate of recombination of a delocalized CT state is proportional to a coherent sum of the associated wavefunction coefficients at the donor-acceptor interface, that is, the coefficients for which a neighboring hole and electron are located at x -positions N and $N + 1$, respectively. We will proceed to demonstrate that this coherent sum translates to a sensitive dependence of the recombination rate to the *relative signs* of the hole and electron couplings $t_h^{x,y,z}$ and $t_e^{x,y,z}$. In doing so, we assume that the excitations in the heterojunction material are in thermal equilibrium at the advent of the recombination event. For the bandwidths typical to organic photovoltaics, this implies that the CT state resides predominantly at the bottom of the band.

Figure 3 presents a characterization of the band-bottom CT states calculated for a $4 \times 5 \times 5$ heterojunction (using open boundary conditions) where both the electron and hole couplings are taken to be positive (Figure 3b), and for the case where the hole couplings have changed sign so as to become negative (Figure 3c). As typical values for organic blends and molecular crystals, the magnitude of all electron and hole couplings is set to 0.15 eV,^{21–23} while the

Figure 3: Band-bottom CT state calculated for an idealized heterojunction, shown in (a). The hole (yellow) and electron (green) occupation per lattice site is represented by spheres. Also shown is a 2D representation of the wavefunction coefficients for pairs of electrons and holes located on both sides of the interface (see text for details). Depending on the electron and hole couplings, these coefficients are in-phase (b) or sign-alternating (c) resulting in enhanced and suppressed recombination, respectively.

interface coupling and electron-hole binding energy are taken to be $t_i = 0.075$ eV and $U = 0.3$ eV, respectively.^{19,24} Shown as yellow spheres are the hole site occupancies, such that the sphere radius is taken to be proportional to $p_h^\alpha(\vec{m}) = \sum_{\vec{n} \in A} |c_{\vec{m}, \vec{n}}^\alpha|^2$. The green spheres indicate the electron occupancies in an analogous fashion. From this, the delocalization of the charge wavefunction is obvious, while at the same time a Coulomb attraction of charges towards the interface is observable.

As is apparent in Figure 3, the band-bottom CT state occupation is independent of the relative signs of the electron and hole couplings. However, this is quite the opposite for the interface coefficients, which are mapped onto the donor-acceptor interface in Figure 3. When all couplings are positive (Figure 3b), the coefficients are in-phase over the entire junction, whereas changing the sign of the hole couplings (Figure 3c) causes the coefficients to take up a sign-alternating profile. This behavior is similar to a simple one-dimensional Bloch model where the band-edge states are the $k = 0$ and $k = \pi$ wavefunctions. The former

is in-phase, whereas the latter changes sign between neighboring sites. In what follows, we distinguish between two types of donor-acceptor materials based on this analogy: for ($k =$) 0-heterojunctions the band-bottom CT state has monosignate interface coefficients, whereas for π -heterojunctions these coefficients are sign-alternating. The contrast in phase-behavior along the interface translates to a dramatic difference between the rate of charge recombination of 0-heterojunctions and that of π -heterojunctions. According to eq 4, this rate scales as a coherent sum over the interface coefficients $c_{(N,y,z),(N+1,y,z)}^\alpha$. Hence, in-phase coefficients constructively contribute to Γ_α , whereas the sign-alternating coefficients tend to cancel one another. In fact, the rate associated with the wavefunction shown in Figure 3c is rigorously zero due to this destructive interference, in spite of the electron and hole being in very close proximity.

The marked contrast in charge recombination between 0 and π -heterojunctions is further substantiated by Figure 4a. Here, a histogram is shown containing the recombination rates for all CT states $|\alpha\rangle$ as a function of the associated energies E_α . For the case of a 0-heterojunction (red sticks) a pronounced peak is apparent at zero energy, corresponding to the band-bottom state represented in Figure 3b. The remainder of the histogram shows a rich pattern of recombination intensities distributed over the entire band. This is quite different for π -heterojunctions (blue sticks), where nonzero recombination rates are concentrated in only a few peaks located at least ~ 0.9 eV above the band minimum. Hence, not only does the lowest-energy CT state destructively contribute to Γ_α , a similar cancellation is in effect for all states that are within thermal reach.

The coherent suppression of charge recombination can be further appreciated when considering the simplified case of a $2 \times 1 \times 2$ (hence, two-dimensional) heterojunction while disregarding the Coulomb interaction. For this case, quantum interference of recombination can be shown analytically, as demonstrated in the Supporting Information. There, it is also shown that t_e^y and t_h^y should have opposite sign for destructive interference to occur. Generalized to three dimensions, the requisite for coherently-suppressed recombination is

Figure 4: (a) Histogram (bin size 0.05 eV) showing the density of recombination rates as a function of the energy relative to the band-bottom CT state. Shown are the results for a disorder-free 0-heterojunction (red) and π -heterojunction (blue), as well as a 0-heterojunction with disordered couplings (grey). (b) Total recombination rate for a heterojunction thermalized at room temperature, as a function of disorder (σ) in the electron and hole transfer integrals. (Shown as insets are histograms of $\cos(\pi x)$ for $\sigma = 0.2$ and 0.5 .)

that $\text{sign}(t_e^y) = -\text{sign}(t_h^y)$ and/or $\text{sign}(t_e^z) = -\text{sign}(t_h^z)$. Hence, sign-alternations of the wavefunction should occur at least in one direction along the interface. Note that the sign of the couplings in the x -direction has no impact on the wavefunction along the interface, and therefore does not impact on charge recombination.

The sensitivity of the recombination rate to the interplay between wavefunction delocalization and the sign of the couplings between molecular sites is reminiscent of the enhanced and suppressed photoluminescence of Frenkel excitons in J- and H-aggregates, respectively.²⁵ Furthermore, recent studies have demonstrated that the coexistence of excitonic interactions and charge transfer integrals accounts for the complex absorption spectrum displayed by molecular crystals,²⁶ and that it could result in accelerated or halted exciton transport, de-

pending on the sign-relation between these couplings.²⁷ Such coherent phenomena have been shown to be reasonably robust against disorder common to organic materials.^{25,27,28} We will proceed to show that a comparable robustness applies to the coherent suppression of charge recombination. More so than typical disorder in the electron and hole site energies, which results in some degree of localization of the charge wavefunctions, Γ_α was found to be dependent on “off-diagonal” disorder due to inhomogeneities in the electron and hole couplings, which can result in phase disruptions in the interface wavefunction. This is particularly so for transverse slip defects between molecular constituents, which could even impose a sign change of electron and hole couplings through their dependence on molecular orbital overlaps.²⁷ Rather than rigorously accounting for this effect, we employ the simplest model that qualitatively describes this disorder behavior. Accordingly, the couplings between any pair of neighboring sites (including trans-interface neighbors) have been individually modulated with $\cos(\pi x)$, where x is randomly drawn from a normal distribution using a standard deviation σ , centered around 0.

Shown in Figure 4b is the recombination rate as a function of σ . All parameters are identical to those from Figure 3, including the couplings (before application of the $\cos(\pi x)$ modulation). In order to assure convergence, the results for $\sigma = 0.1, 0.2, 0.3, 0.4$, and 0.5 have been averaged over 100, 200, 300, 400, and 500 disorder realizations, respectively. Furthermore, the total recombination rate is obtained through a Boltzmann average of the CT state contributions, $\Gamma = \sum_\alpha e^{-E_\alpha/k_B T} \Gamma_\alpha$, using $T = 300$ K. Figure 4b demonstrates a clear trend: with increasing off-diagonal disorder, the recombination rates of 0 (red curve) and π -heterojunctions (blue curve) converge towards the same value. However, the point of convergence is reached only at $\sigma = 0.5$. For such a disorder strength, the couplings have become significantly modulated between positive and negative values, as illustrated by the histograms of $\cos(\pi x)$ (see insets). Consequentially, the difference between 0 and π -heterojunctions is lifted, which is also reflected in a convergence of the associated Γ_α histograms, of which the 0-heterojunction variant is demonstrated in Figure 4a. Importantly, a slight increase in the

ordering has a dramatic effect on the recombination rate. Already for $\sigma = 0.4$, Γ is found to differ by almost an order of magnitude between 0 and π -heterojunctions.

The discussion so far was limited to heterojunctions that consist of a cubic lattice. It is not unreasonable to assume that the coherent suppression of charge recombination is retained in more amorphous materials such as blends of P3HT and PCBM. What is important is that the material supports delocalization of both the hole and electron such that the associated phase experiences a sign change over the donor-acceptor interface. The importance of this requisite is reinforced by measurements on successful organic photovoltaic blends showing that enhancing the order (e.g., by thermal annealing) results in a dramatic decrease of recombination rates.^{8,18,29} The results presented here seem to also be in line with a recent theoretical study by Bittner et al., where the effects of energetic disorder, electron and hole couplings, and dimensionality on the recombination of ^3CT was examined.³⁰ There, an increase in Γ was observed upon enhanced charge delocalization in cofacial donor and acceptor chains, which seemingly was at odds with experimental results.¹⁸ However, the theoretical examination was restricted to positive couplings only, which causes 0-heterojunction behavior. Our findings predict that the expected suppression in Γ is obtained upon a sign change in either the hole or electron transfer integrals.

A substantiation of the idea that recombination in organic heterojunctions is suppressed by destructive quantum interference demands for *ab initio* calculations including multiple donor and acceptor units. A very important remark should be made at this point. This study underscores the importance of using translational symmetry to assign the relative signs of transfer integrals between equivalent molecular units. Similarly to our findings, these relative signs have been shown in recent studies to give rise to quantum interference impacting on a variety of processes. For example, interference between charge transfer integrals and excitonic coupling is found to modulate excitation mobility in molecular crystals^{26,27} as well as the optoelectronic properties of singlet fission materials.³¹ In this context, it is also interesting to note that Maggio *et al.* suggested to suppress charge recombination in dye

sensitized solar cells through engineering of the dye molecular orbitals³² (which does not require charge delocalization), or alternatively by using an appropriate cross-conjugated bridge where interference of molecular orbitals prohibits recombination.³³

To conclude, we proposed a molecular mechanism that impacts on charge recombination in donor-acceptor materials. At ordered heterojunction regions, the recombination rate is found to depend on a coherent sum of the charge wavefunction coefficients along the donor-acceptor interface. Upon wavefunction delocalization, this sum can experience a destructive interference, depending on the relative signs of the electron and hole transfer integrals. Besides forming a possible explanation of why recombination rates are found to be significantly lower than predictions based on Langevin theory, this finding suggests the possibility to deliberately engineer optimized heterojunction devices through molecular crystal engineering. For example, the electron and hole couplings in a crystal can be modulated by inducing small slips between neighboring molecules, which can potentially be achieved through chemical modifications³⁴ or lattice strain.³⁵ We anticipate that by means of this principle, microscopic heterojunction structures with negligible recombination can be realized.

Supporting Information Available

Generalization of our findings to ¹CT states, and an analytical demonstration of the coherent suppression of charge recombination in a $2 \times 1 \times 2$ heterojunction without Coulomb interaction. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

References

- (1) Lakhwani, G.; Rao, A.; Friend, R. H. Bimolecular Recombination in Organic Photovoltaics. *Annu. Rev. Phys. Chem.* **2014**, *65*, 557–581.

- (2) Langevin, P. Recombinaison et Mobilites Des Ions Dans Les Gaz. *Ann. Chim. Phys* **1903**, *28*, 122.
- (3) Albrecht, U.; Bäessler, H. Langevin-Type Charge Carrier Recombination in a Disordered Hopping System. *Phys. Status Solidi B* **1995**, *191*, 455–459.
- (4) Pivrikas, A.; Juška, G.; Österbacka, R.; Westerling, M.; Viliūnas, M.; Arlauskas, K.; Stubb, H. Langevin Recombination and Space-Charge-Perturbed Current Transients in Regiorandom Poly(3-Hexylthiophene). *Phys. Rev. B* **2005**, *71*, 125205.
- (5) van der Holst, J. J. M.; van Oost, F. W. A.; Coehoorn, R.; Bobbert, P. A. Electron-Hole Recombination in Disordered Organic Semiconductors: Validity of the Langevin Formula. *Phys. Rev. B* **2009**, *80*, 235202.
- (6) Pivrikas, A.; Sariciftci, N. S.; Juška, G.; Österbacka, R. A Review of Charge Transport and Recombination in Polymer/fullerene Organic Solar Cells. *Prog. Photovoltaics Res. Appl.* **2007**, *15*, 677–696.
- (7) Clarke, T. M.; Rodovsky, D. B.; Herzing, A. A.; Peet, J.; Dennler, G.; DeLongchamp, D.; Lungenschmied, C.; Mozer, A. J. Significantly Reduced Bimolecular Recombination in a Novel Silole-Based Polymer: Fullerene Blend. *Adv. Energy Mater.* **2011**, *1*, 1062–1067.
- (8) Koster, L. J. A.; Kemerink, M.; Wienk, M. M.; Maturová, K.; Janssen, R. A. J. Quantifying Bimolecular Recombination Losses in Organic Bulk Heterojunction Solar Cells. *Adv. Mater.* **2011**, *23*, 1670–1674.
- (9) Albrecht, S.; Janietz, S.; Schindler, W.; Frisch, J.; Kurpiers, J.; Kniepert, J.; Inal, S.; Pingel, P.; Fostiropoulos, K.; Koch, N. et al. Fluorinated Copolymer PCPDTBT with Enhanced Open-Circuit Voltage and Reduced Recombination for Highly Efficient Polymer Solar Cells. *J. Am. Chem. Soc.* **2012**, *134*, 14932–14944.

- (10) Koster, L. J. A.; Mihailetschi, V. D.; Blom, P. W. M. Bimolecular Recombination in Polymer/fullerene Bulk Heterojunction Solar Cells. *Appl. Phys. Lett.* **2006**, *88*, 052104.
- (11) Groves, C.; Greenham, N. C. Bimolecular Recombination in Polymer Electronic Devices. *Phys. Rev. B* **2008**, *78*, 155205.
- (12) Juška, G.; Genevičius, K.; Nekrašas, N.; Sliaužys, G.; Österbacka, R. Two Dimensional Langevin Recombination in Regioregular Poly(3-Hexylthiophene). *Appl. Phys. Lett.* **2009**, *95*, 013303.
- (13) Szmytkowski, J. Analysis of the Image Force Effects on the Recombination at the Donor–Acceptor Interface in Organic Bulk Heterojunction Solar Cells. *Chem. Phys. Lett.* **2009**, *470*, 123–125.
- (14) Hilczer, M.; Tachiya, M. Unified Theory of Geminate and Bulk Electron-Hole Recombination in Organic Solar Cells. *J. Phys. Chem. C* **2010**, *114*, 6808–6813.
- (15) Ferguson, A. J.; Kopidakis, N.; Shaheen, S. E.; Rumbles, G. Dark Carriers, Trapping, and Activation Control of Carrier Recombination in Neat P3HT and P3HT:PCBM Blends. *J. Phys. Chem. C* **2011**, *115*, 23134–23148.
- (16) Rauh, D.; Deibel, C.; Dyakonov, V. Charge Density Dependent Nongeminate Recombination in Organic Bulk Heterojunction Solar Cells. *Adv. Funct. Mater.* **2012**, *22*, 3371–3377.
- (17) Cheung, D. L.; Troisi, A. Theoretical Study of the Organic Photovoltaic Electron Acceptor PCBM: Morphology, Electronic Structure, and Charge Localization. *J. Phys. Chem. C* **2010**, *114*, 20479–20488.
- (18) Rao, A.; Chow, P. C. Y.; Gelinas, S.; Schlenker, C. W.; Li, C.-Z.; Yip, H.-L.; Jen, A. K. Y.; Ginger, D. S.; Friend, R. H. The Role of Spin in the Kinetic Control of Recombination in Organic Photovoltaics. *Nature* **2013**, *500*, 435–439.

- (19) Morteani, A. C.; Sreearunothai, P.; Herz, L. M.; Friend, R. H.; Silva, C. Exciton Regeneration at Polymeric Semiconductor Heterojunctions. *Phys. Rev. Lett.* **2004**, *92*, 247402.
- (20) Yamagata, H.; Spano, F. C. Interplay Between Intrachain and Interchain Interactions in Semiconducting Polymer Assemblies: The HJ-Aggregate Model. *J. Chem. Phys.* **2012**, *136*, 184901.
- (21) Wu, M. W.; Conwell, E. M. Effect of Interchain Coupling on Conducting Polymer Luminescence: Excimers in Derivatives of Poly(phenylene Vinylene). *Phys. Rev. B* **1997**, *56*, R10060–R10062.
- (22) Rivnay, J.; Noriega, R.; Northrup, J. E.; Kline, R. J.; Toney, M. F.; Salleo, A. Structural Origin of Gap States in Semicrystalline Polymers and the Implications for Charge Transport. *Phys. Rev. B* **2011**, *83*, 121306.
- (23) Tamura, H.; Tsukada, M. Role of Intermolecular Charge Delocalization on Electron Transport in Fullerene Aggregates. *Phys. Rev. B* **2012**, *85*, 054301.
- (24) Gélinas, S.; Paré-Labrosse, O.; Brosseau, C.-N.; Albert-Seifried, S.; McNeill, C. R.; Kirov, K. R.; Howard, I. A.; Leonelli, R.; Friend, R. H.; Silva, C. The Binding Energy of Charge-Transfer Excitons Localized at Polymeric Semiconductor Heterojunctions. *J. Phys. Chem. C* **2011**, *115*, 7114–7119.
- (25) Spano, F. C. The Spectral Signatures of Frenkel Polarons in H- and J-Aggregates. *Acc. Chem. Res.* **2010**, *43*, 429–439.
- (26) Yamagata, H.; Maxwell, D. S.; Fan, J.; Kittilstved, K. R.; Briseno, A. L.; Barnes, M. D.; Spano, F. C. HJ-Aggregate Behavior of Crystalline 7,8,15,16-Tetraazaterrylene: Introducing a New Design Paradigm for Organic Materials. *J. Phys. Chem. C* **2014**, *118*, 28842–28854.

- (27) Hestand, N. J.; Tempelaar, R.; Knoester, J.; Jansen, T. L. C.; Spano, F. C. Exciton Mobility Control Through Sub-Å Packing Modifications in Molecular Crystals. *Phys. Rev. B* **2015**, *91*, 195315.
- (28) Fidler, H.; Knoester, J.; Wiersma, D. A. Optical Properties of Disordered Molecular Aggregates: A Numerical Study. *J. Chem. Phys.* **1991**, *95*, 7880–7890.
- (29) Deibel, C.; Baumann, A.; Wagenpfahl, A.; Dyakonov, V. Polaron Recombination in Pristine and Annealed Bulk Heterojunction Solar Cells. *Synt. Met.* **2009**, *159*, 2345–2347.
- (30) Bittner, E. R.; Lankevich, V.; Gelinas, S.; Rao, A.; Ginger, D. A.; Friend, R. H. How Disorder Controls the Kinetics of Triplet Charge Recombination in Semiconducting Organic Polymer Photovoltaics. *Phys. Chem. Chem. Phys.* **2014**, *16*, 20321–20328.
- (31) Hestand, N. J.; Yamagata, H.; Xu, B.; Sun, D.; Zhong, Y.; Harutyunyan, A. R.; Chen, G.; Dai, H.-L.; Rao, Y.; Spano, F. C. Polarized Absorption in Crystalline Pentacene: Theory Vs Experiment. *J. Phys. Chem. C* **2015**, *119*, 22137–22147.
- (32) Maggio, E.; Martsinovich, N.; Troisi, A. Using Orbital Symmetry to Minimize Charge Recombination in Dye-Sensitized Solar Cells. *Angew. Chem. Int. Ed.* **2013**, *52*, 973–975.
- (33) Maggio, E.; Solomon, G. C.; Troisi, A. Exploiting Quantum Interference in Dye Sensitized Solar Cells. *ACS Nano* **2014**, *8*, 409–418.
- (34) Hartnett, P. E.; Timalina, A.; Matte, H. S. S. R.; Zhou, N.; Guo, X.; Zhao, W.; Facchetti, A.; Chang, R. P. H.; Hersam, M. C.; Wasielewski, M. R. et al. Slip-Stacked Perylenediimides As an Alternative Strategy for High Efficiency Nonfullerene Acceptors in Organic Photovoltaics. *J. Am. Chem. Soc.* **2014**, *136*, 16345–16356.

- (35) Giri, G.; Verploegen, E.; Mannsfeld, S. C. B.; Atahan-Evrenk, S.; Kim, D. H.; Lee, S. Y.; Becerril, H. A.; Aspuru-Guzik, A.; Toney, M. F.; Bao, Z. Tuning Charge Transport in Solution-Sheared Organic Semiconductors Using Lattice Strain. *Nature* **2011**, *480*, 504–508.