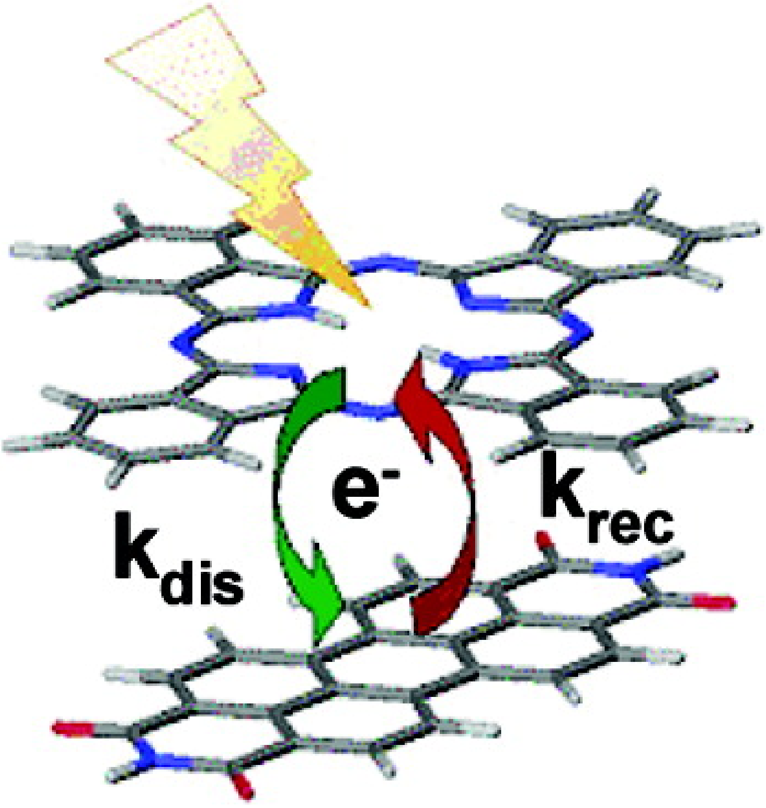
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Photoinduced Charge Generation and Recombination Dynamics in Model Donor/Acceptor Pairs for Organic Solar Cell Applications: A Full Quantum-Chemical Treatment

Vincent Lemaur, Michelle Steel, David Beljonne, Jean-Luc Brdas, and Jrme Cornil

J. Am. Chem. Soc., **2005**, 127 (16), 6077-6086• DOI: 10.1021/ja042390l • Publication Date (Web): 05 April 2005



ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES
Published on Web 04/05/2005

Photoinduced Charge Generation and Recombination Dynamics in Model Donor/Acceptor Pairs for Organic Solar Cell Applications: A Full Quantum-Chemical Treatment

Vincent Lemaur,[†] Michelle Steel,[†] David Beljonne,[†,‡] Jean-Luc Brédas,[†,‡] and Jérôme Cornil*,[†,‡]

Contribution from the Laboratory for Chemistry of Novel Materials, Center for Research in Molecular Electronics and Photonics, University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium, and School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received December 17, 2004; E-mail: Jerome@averell.umh.ac.be

Abstract: This work focuses on two fundamental processes in organic solar cells—exciton dissociation and charge recombination—and describes how quantum-chemical calculations can be exploited to estimate the molecular parameters that determine the rates of these processes. The general concepts behind our approach are illustrated by considering a donor–acceptor complex made of a phthalocyanine (electron donor) molecule and a perylene (acceptor) molecule. The results highlight how the relative rates of the two processes depend on the dimensionality of the molecules, their relative positions, the symmetry of the relevant electronic levels, and the polarity of the medium. It is shown, for instance, that highly symmetric configurations of the complex can strongly limit charge recombination; this emphasizes the need for a fine control of the supramolecular organization at organic–organic interfaces in donor–acceptor blends.

I. Introduction

The emerging field of plastic electronics is attracting considerable interest. The use of organic conjugated materials as active elements in light-emitting displays, envisioned nearly two decades ago, has now reached the stage of commercialization.[1,2] In addition, many efforts are geared toward the fabrication of organic-based solar cells, transistors (and integrated circuits), lasers, or (bio)sensors.[3-6]

Organic solar cells are the focus of the present work. They are fabricated by sandwiching an organic layer between two electrodes of a different nature, typically ITO (indium tin oxide, a transparent metallic material) and aluminum. Their working principle relies on the conversion of solar emission into electrical charges that are collected in an external circuit.[7] The main steps of operation are (i) light absorption: light is absorbed in the organic layer and generates electron–hole pairs (excitons); the absorption characteristics of the organic layer should match the solar spectrum as closely as possible, (ii) exciton dissociation: excitons then have to dissociate, that is, charge separate; for the charge-separation process to be efficient the reverse process, that is, charge recombination, must be limited, (iii) charge transport: the charges that remain separated (and hence do not recombine after exciton dissociation) have to drift in the organic layer under the influence of the electric field generated by the equalization of the Fermi energies of the two electrodes, and (iv) charge collection: the charges ultimately have to be collected at the electrodes.

The key aspect we investigate here is the dissociation of the photogenerated excitons into separate charges. Generally, the efficiency of the charge-generation process is extremely low when a single compound forms the organic layer. This is because in conjugated materials the binding energy of the lowest singlet exciton (i.e., the strength of the Coulombic attraction between the electron and hole) is significant (it is considered to be around 0.3–0.4 eV in conjugated polymers and even larger in small molecules[8]); this makes excitons rather stable species. As a result, current organic solar cells rely on either multilayered structures or blends made from an electron-donor component and an electron-acceptor component. The components can be two polymers (for instance, polyphenylenevinylene chains with different substituents[9,10]), two different molecules,[11,12] or a combination of a polymer and a molecule (for instance, a conjugated polymer as the donor and C_{60} as the acceptor[3,13]).

[‡] Georgia Institute of Technology.

[†] University of Mons-Hainaut.

(1) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; dos Santos, D. A.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.
(2) Borchardt, J. K. *Mater. Today*, September **2004**, 42.
(3) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *58*, 1474.
(4) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365.
(5) Tessler, N. *Adv. Mater.* **1999**, *11*, 363.
(6) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
(7) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15.
(8) Hill, I. G.; Kahn, A.; Soos, Z. G.; Pascal, R. A. *Chem. Phys. Lett.* **2000**, *327*, 181.
(9) Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498.
(10) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.
(11) Tang, C. W. *Appl. Phys. Lett.* **1986**, *48*, 183.
(12) Wöhrle, D.; Meissner, D. *Adv. Mater.* **1991**, *3*, 129.

10.1021/ja042390l CCC: $30.25

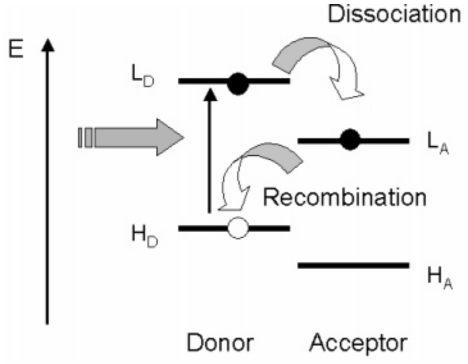


Figure 1. Exciton dissociation and charge recombination processes in a donor/acceptor pair (H = HOMO; L = LUMO; D = Donor; A = Acceptor).

In such organic blends, the photons are absorbed by the donor and/or the acceptor. When the donor absorbs most of the incident light, bound electron−hole pairs are generated on the donor sites following (if we take a simple one-electron picture) the promotion of a π-electron from their HOMO level to their LUMO level. To dissociate into charge carriers, the excitons then have to migrate toward a donor/acceptor interface via energy-transfer processes. This underlines the major role played by the blend morphology in determining the efficiency of the exciton dissociation process. Once an exciton reaches the donor/acceptor interface, the electron promoted in the LUMO level of the excited donor (L_D) can be transferred to the lower-lying LUMO level of the acceptor (L_A) (see Figure 1), with the hole remaining on the HOMO level of the donor, thereby forming a polaron pair.

Thus, this photoinduced *electron-transfer* process has converted light into charges. Note that the same final charge-separated state can be reached when the acceptor is initially photoexcited, following a photoinduced *hole-transfer* from the HOMO level of the acceptor (H_A) to the HOMO level of the donor (H_D). To produce a current, the charges have to escape from their mutual Coulombic attraction and migrate toward the electrodes, usually via a polaron-hopping mechanism, under the influence of the built-in electric potential created by connecting the two electrodes.

The previous discussion and the energy scheme presented in Figure 1 might suggest that an offset of the frontier electronic levels of the donor and acceptor units is just what it takes to induce exciton dissociation. However, the situation is far from being that simple (and requires going beyond the one-electron approximation): exciton dissociation into a polaron pair can take place only if the energy stabilization of the electron [hole] when it transfers from the LUMO of the donor L_D to the LUMO of the acceptor L_A [from the HOMO of the acceptor H_A to the HOMO of the donor H_D] more than compensates for the binding energy of the intrachain exciton; in other words, the charge-separated state has to be lower in energy than any intramolecular excited state.[14] This can be assessed by estimating to first approximation the ordering of three key excited states: (i) the lowest intramolecular excited state of the donor with an energy $E_D = L_D - H_D - \Delta_D$ (with Δ_D being the binding energy of the donor intrachain exciton), (ii) the lowest intramolecular excited state of the acceptor with an energy $E_A = L_A - H_A - \Delta_A$, and (iii) the lowest charge-transfer (CT) excited state with an energy $E_{CT} = H_D - L_A - \Delta_{CT}$ (with Δ_{CT} being the binding energy of the photoinduced polaron pair). Though being instructive, such a model suffers from strong limitations since the excitations are based on a one-electron picture and the exciton binding energies are introduced rather arbitrarily. As a result, it cannot be readily applied to predict the energy ordering of the lowest excited states in any donor/acceptor pair.

In addition, it is critical to go beyond the static view that such a model provides on the basis of the ordering of various excited states and to address the dynamics of the photoinduced processes. Indeed, the exciton dissociation process competes with charge recombination, the mechanism by which the charge-separated state decays back to the ground state of the blend (i.e., the electron in the LUMO level of the acceptor transfers to the HOMO level of the donor; see Figure 1). Charge recombination must be prevented to the highest possible extent to ensure efficient generation of charge carriers in the device.

The major goal of the present work is to show how reliable estimates for the molecular parameters governing the rates of exciton dissociation and charge recombination in donor/acceptor pairs of relevance for organic solar cells can be obtained from quantum-chemical calculations. Our approach, similar to that used recently to describe electron-transfer reactions in donor−bridge−acceptor architectures,[15] contrasts with many previous studies in which only part of the parameters was calculated and the others were extracted from or fitted to experimental data.[16−19] The fully theoretical approach we follow here is geared toward establishing guidelines and helping in the design of optimal molecular partners and of the most appropriate supramolecular architectures to fabricate highly efficient solar cells; up to now, this design has been performed mainly on an empirical basis.

We illustrate our approach by considering the electronic structure and lowest excited states of a donor−acceptor complex built from a free-base phthalocyanine (Pc) as the donor and perylene bisimide (PTCDI) as the acceptor (see the chemical structures in Figure 2). The choice of these conjugated molecules is motivated by the fact that the electronic and optical properties of blends made of Pc and PTCDI derivatives have been the focus of many experimental studies.[20−25] Moreover, Pc molecules are low-energy absorbers, with the lowest absorption band peaking around 1.8 eV;[26] this closely matches the spectral region where solar emission is most intense.

This article is structured as follows. The next section introduces the general formalism adopted to evaluate the rates

---

(13) Svensson, M.; Zhang, F. L.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganas, O.; Andersson, M. R. *Adv. Mater.* **2003**, *15*, 988.
(14) Halls, J. J. M.; Cornil, J.; dos Santos, D. A.; Silbey, R.; Hwang, D. H.; Holmes, A. B.; Brédas, J. L.; Friend, R. H. *Phys. Rev. B* **1998**, *60*, 5721.
(15) Pourtois, P.; Beljonne, D.; Cornil, J.; Ratner, M. A.; Brédas, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 4436.
(16) Clayton, A. H. A.; Ghiggino, K. P.; Wilson, G. J.; Paddon-Row, M. N. *J. Phys. Chem.* **1993**, *97*, 7962.
(17) Filatov, I.; Larsson, S. *Chem. Phys.* **2002**, *284*, 575.
(18) Redmore, N. P.; Rubtsov, I. V.; Therien, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 8769.
(19) Weiss, E. A.; Ahrens, M. J.; Sinks, L. E.; Gusev, A. V.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2004**, *126*, 5577.
(20) Tang, C. W. *Appl. Phys. Lett.* **1986**, *48*, 183.
(21) Wöhrle, D.; Meissner, D. *Adv. Mater.* **1991**, *3*, 129.
(22) Adams, D. M.; Kerimo, J.; Olson, E. J. C.; Zaban, A.; Gregg, B. A.; Barbara, P. F. *J. Am. Chem. Soc.* **1987**, *119*, 10608.
(23) Lane, P. A.; Rostalski, J.; Giebeler, C.; Martin, S. J.; Bradley, D. D. C.; Meissner, D. *Sol. Energy Mater. Sol. Cells* **2000**, *63*, 3.
(24) Hiromitsu, I.; Murakami, Y.; Ito, T. *J. Appl. Phys.* **2003**, *94*, 2434.
(25) Aroca, R.; Del Cano, T.; de Saja, J. A. *Chem. Mater.* **2003**, *15*, 38.
(26) Edwards, L.; Gouterman, M. *J. Mol. Spectrosc.* **1979**, *33*, 292.

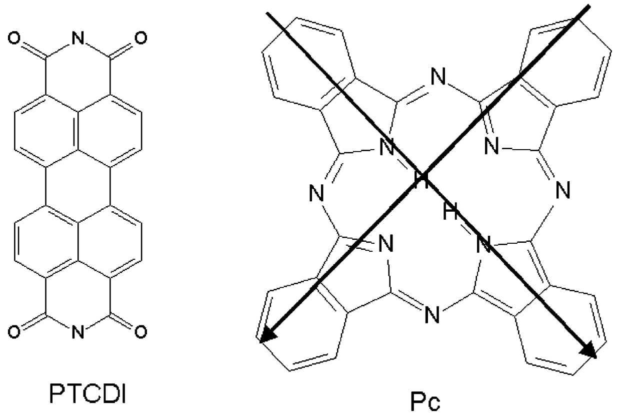


Figure 2. Chemical structures of perylenebismide (PTCDI, left) and phthalocyanine (Pc, right). The arrows represent the polarization directions of the lowest two excited states of Pc.

of exciton dissociation and charge recombination and the various parameters these processes involve. We then describe the way in which each of these parameters has been computed and provide its order of magnitude. The various pieces of information are finally collected together, which allows us to estimate the rates of charge separation and charge recombination and to draw conclusions of general applicability.

II. Methodological Framework

Since exciton dissociation and charge recombination both correspond to an electron-transfer reaction, their rates can be estimated in the framework of Marcus theory and extensions thereof.[27] This formalism has been developed in the weak coupling limit; in the case of exciton dissociation, this implies that the excitation is initially localized and relaxes on the donor (or on the acceptor) and eventually produces a positive polaron localized on the donor and a negative polaron localized on the acceptor. Given the intrinsic disorder of the heterostructures, we have not considered situations where the excitations and/or charges are delocalized over several molecules, as could occur in highly crystalline phases. In the semiclassical limit of Marcus theory, the charge-transfer rate is expressed as:[28]

$$k = A\exp(-\Delta G^{\#}/kT) = \left(\frac{4\pi^2}{h}\right)V_{\mathrm{RP}}^2\left(\frac{1}{\sqrt{4\pi\lambda kT}}\right)\exp\left[\frac{-(\Delta G^\circ+\lambda)^2}{4\lambda kT}\right] \qquad (1)$$

where ΔG° represents the Gibbs free energy of the reaction, V_{RP} is the electronic coupling between the initial and final states, and λ is the reorganization energy. The latter parameter includes two contributions: (i) the internal part λ_i, which describes the changes in the geometry of the donor and acceptor moieties upon charge transfer[29,30] and (ii) the external part λ_s related to the change in electronic and nuclear polarizations of the surrounding medium. When taking ΔG° as negative, the square dependence in $(\Delta G^\circ + \lambda)$ of the exponential term implies that the transfer rate displays a peak profile as a function of λ (which has a positive value) and reaches a maximum when $|\Delta G^\circ|$ is equal to λ. The rate is smaller when $|\Delta G^\circ| < \lambda$ (this is referrred to as the normal region) and when $|\Delta G^\circ| > \lambda$ (the so-called inverted region).

The semiclassical formalism is based on the assumption that the system has to reach the transition state for the transfer to occur; it neglects tunneling effects that can assist the transfer, especially at low temperatures. These can be treated quantum mechanically by introducing into the rate expression the density of vibrational modes in the initial and final states and their overlap. This is accounted for in Marcus−Levich−Jortner's formalism where the electron-transfer rate is written as:[31]

$$k = \left(\frac{4\pi^2}{h}\right)V_{\mathrm{RP}}^2\left(\frac{1}{\sqrt{4\pi\lambda_s kT}}\right)\times \sum_{v'}\exp(-S)\frac{S^{v'}}{v'!}\exp\left[\frac{-(\Delta G^\circ+\lambda_s+v'\hbar\langle\omega\rangle)^2}{4\lambda_s kT}\right] \qquad (2)$$

In this equation, a single effective high-frequency mode of energy $\hbar\omega$ (that we have set equal to 0.20 eV, which is the typical energy of a carbon−carbon bond stretch in a conjugated system) is treated quantum mechanically; the low-frequency vibrations (i.e., librations) are treated classically and incorporated into λ_s. We note that the transfer rate can vary by up to a factor of 5 when tuning the frequency of the effective mode in the range 0.15−0.20 eV typical of carbon-based conjugated skeletons;[32] this does not change the general picture provided below. The Huang−Rhys factor S is directly related to the internal reorganization energy ($S = \lambda_i/\hbar\omega$), and the summation runs over the vibrational levels in the final state. In the next section, we evaluate successively the three main parameters affecting eq 2: the free energy of reaction, the reorganization energy, and the electronic coupling.

III. Results and Discussion

a. Gibbs Free Energy of Reaction. ΔG° has been estimated as the energy difference of the constituents in their final and initial states, accounting for the Coulombic attraction between the two charges in the charge-separated state. Thus, for exciton dissociation, $\Delta G_{\mathrm{dis}}{}^\circ$ is written as:

$$\Delta G_{\mathrm{dis}}{}^\circ = E^{\mathrm{D}^+} + E^{\mathrm{A}^-} - E^{\mathrm{D}+} - E^{\mathrm{A}} + \Delta E_{\mathrm{coul}} \qquad (3)$$

with

$$\Delta E_{\mathrm{coul}} = \sum_{D^+}\sum_{A^-}\frac{q_{\mathrm{D}^+}q_{\mathrm{A}^-}}{4\pi\epsilon_0\epsilon_s r_{\mathrm{D}^+\mathrm{A}^-}} - \sum_{D^*}\sum_{A}\frac{q_{\mathrm{D}^*}q_{\mathrm{A}}}{4\pi\epsilon_0\epsilon_s r_{\mathrm{D}^*\mathrm{A}}} \qquad (4)$$

where $E^{\mathrm{D}*}$, $E^{\mathrm{D}+}$, E^{A}, and $E^{\mathrm{A}-}$ represent the total energies of the isolated donor in the equilibrium geometries of the lowest excited state and of the cationic state and the total energies of the isolated acceptor in the equilibrium geometries of the ground state and of the anionic state, respectively; q_{D} and q_{A} correspond to the atomic charges on the donor and the acceptor in their relevant state, respectively, with a separation r_{DA}; and ϵ_s is the static dielectric constant of the medium. The sums run over all the atoms of the two individual molecules. Note that the entropy contributions are neglected; they are expected to be vanishingly small in particular since in the solid state motions of molecules are strongly hindered. The Gibbs free energy for charge recombination has been estimated from expressions similar to

---

(27) Marcus, R. A. *Rev. Mod. Phys.* **1993**, *65*, 599.

(28) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148.

(29) Sakanoue, K.; Motoda, M.; Sugimoto, M.; Sakaki, S. *J. Phys. Chem. A* **1999**, *103*, 5551.

(30) Coropceanu, V.; Malagoli, M.; da Silva Filho, D. A.; Gruhn, N. E.; Bill, T. G.; Brédas, J. L. *Phys. Rev. Lett.* **2002**, *89*, 275503.

(31) *Electron Transfer: From Isolated Molecules to Biomolecules*; Bixon, M., Jortner, J., Eds.; Advances in Chemical Physics, Vol. 106−107; Wiley: New York, 1999.

(32) Cornil, J.; Beljonne, D.; Shuai, Z.; Hagler, T.; Campbell, I.; Bradley, D. D. C.; Brédas, J. L.; Spangler, C. W.; Müllen, K. *Chem. Phys. Lett.* **1995**, *247*, 425.

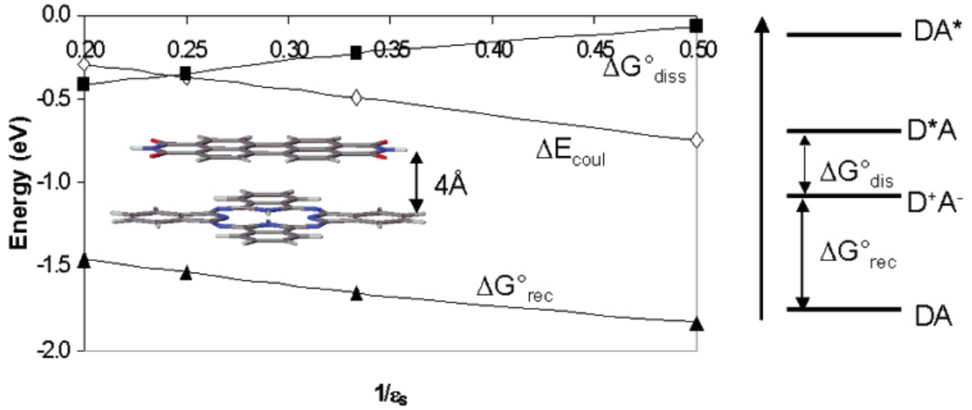


Figure 3. AM1-CI/COSMO evolutions of $\Delta G°$ for exciton dissociation ($\Delta G_{\mathrm{dis}}°$) and charge recombination ($\Delta G_{\mathrm{rec}}°$) and of the Coulombic attraction term (ΔE_{coul}), as a function of the inverse static dielectric constant ϵ_s in a Pc/PTCDI complex (with the two molecules superimposed and separated by 4 Å).

eqs 3 and 4, but involving this time the charge-separated state and the ground state.

To compute the first four terms, we have first optimized the geometry of the individual molecules in their various redox states with the help of the Austin Model 1 (AM1) method[33] coupled to a full configuration interaction (FCI) scheme within an active space built from a few frontier electronic levels, as implemented in the AMPAC package.[34] The size of the active space has been chosen in all instances so as to ensure the convergence of the results. The influence of the dielectric properties of the medium has also been taken into account by means of the COSMO model,[35] without further geometry optimization. The atomic charges on the donor and the acceptor have been obtained from a Mulliken population analysis performed on the AM1-CI/COSMO results. The static dielectric constant ϵ_s has been varied in the range between 2 and 5, which is typical of organic thin films.[36,37]

The free-base Pc molecule exhibits two close, low-lying excited states separated by just 0.09 eV (in agreement with the absorption spectrum in dilute solution[38]) and polarized perpendicularly to one another along the two main branches of the conjugated core; see Figure 2. These two states mainly originate from an electronic transition between the HOMO level and the LUMO and LUMO + 1 levels, respectively; the latter two are quasi-degenerate and localize each over a given branch of the molecule with a very similar shape. Thus, in the case of exciton dissociation, two different pathways based on these two states have to be considered. In the following, we assume that the energetics of the two states are the same (i.e., they are characterized by the same $\Delta G°$ and λ).

We report in Figure 3 the evolution of $\Delta G°$ for exciton dissociation upon donor photoexcitation ($\Delta G_{\mathrm{dis}}°$) and charge recombination ($\Delta G_{\mathrm{rec}}°$) as a function of the inverse dielectric constant of the medium (in the range $\epsilon_s = 2-5$); we consider a cofacial complex made of one Pc and one PTCDI molecule with the molecular planes separated by a distance of 4 Å, which is typical of those found in such aggregates (note that in this approach varying the intermolecular distance only affects the Coulombic term; changing the intermolecular distance for instance from 4 to 3.5 Å increases the absolute value of $\Delta G_{\mathrm{dis}}°$ by just ~15%).

$\Delta G_{\mathrm{dis}}°$ is consistently calculated to be negative, which indicates that exciton dissociation is favorable whatever the polarity of the medium. $\Delta G_{\mathrm{dis}}°$ becomes increasingly negative when the dielectric constant is increased (going from −0.23 eV at $\epsilon_s = 3$ to −0.41 eV at $\epsilon_s = 5$) even though the Coulombic term ΔE_{coul} is reduced by screening effects (from −0.49 eV at $\epsilon_s = 3$ to −0.29 eV at $\epsilon_s = 5$; see Figure 3). Such an evolution in the energy of the charge-transfer state upon variation of the medium polarity has been observed experimentally for electron-transfer reactions in different solvents.[39] In contrast, $\Delta G_{\mathrm{rec}}°$ becomes less negative when the polarity of the medium increases, as a result of the increasing stabilization of the charge-separated state. The sum of $\Delta G_{\mathrm{rec}}°$ and $\Delta G_{\mathrm{dis}}°$ has an almost constant value (on the order of 1.9 eV, which is consistent with the energy of the lowest excited state of Pc) because the separation between the ground state and the intramolecular excited state is only slightly affected by the medium polarity.

A detailed analysis of the results reveals that exciton dissociation would not occur or would be only weakly thermodynamically favored if the Coulombic attraction between the two polarons of opposite sign was neglected. Thus, it has to be realized that the two photogenerated charges cannot easily escape from their mutual attraction and yield free polarons (for instance, to have enough thermal energy to compensate for the Coulombic attraction, the two charges have to be separated by about 12 nm at room temperature when $\epsilon_s = 5$). It is clear that the Coulombic attraction between the polarons is detrimental to the operation of the solar cells. This raises the important question of the nature of the mechanism allowing for the separation of the bound polaron pairs into free polarons. Several models have been proposed, attributing the mechanism of separation to, for instance, (i) the role of interfacial dipoles between the donor and acceptor units in their ground state, which would facilitate the dissociation of the polaron pairs[40] or (ii) the role of disorder intrinsic to organic thin films; in this model, the energy that the hole or the electron would gain by being transferred to a segment of lower energy would help to

---

(33) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(34) Ampac 6.55; created by Semichem Inc.: Shawnee, KS, 1997.

(35) Klamt, A.; Schürmann, G. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 799.

(36) Zang, D. Y.; So, F. F.; Forrest, S. R. *Appl. Phys. Lett.* **1991**, *59*, 823.

(37) Brocks, G.; van den Brink, J.; Morpurgo, A. F. *Phys. Rev. Lett.* **2004**, *93*, 146405.

(38) Tant, J.; Lehmann, M.; De Cupere, V.; Zucchi, G.; Lemaur, V.; Marcq, V.; Burquel, A.; Hennebicq, E.; Gardebien, F.; Lazzaroni, R.; Cornil, J.; Laursen, B. W.; Bjornholm, T.; Geerts, Y., submitted for publication.

(39) van Hal, P. A.; Janssen, R. A. J.; Lanzani, G.; Cerullo, G.; Zavelani-Rossi, M.; De Silvestri, S. *Phys. Rev. B* **2001**, *64*, 075206.

(40) Arkhipov, V. I.; Heremans, P.; Bässler, H. *Appl. Phys. Lett.* **2003**, *82*, 4605.

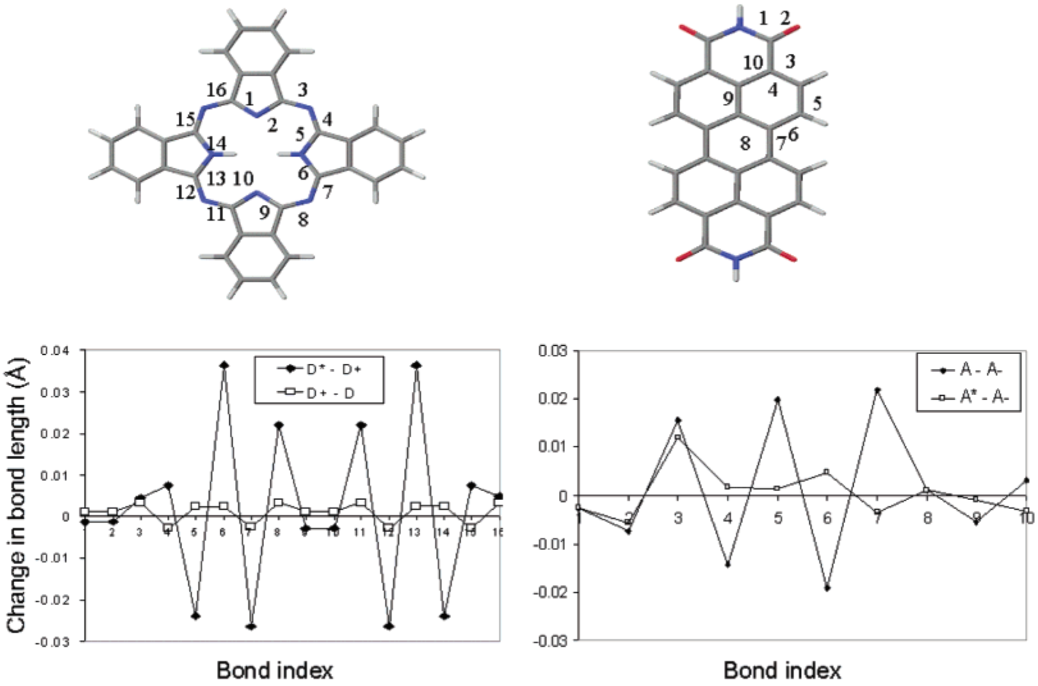


Figure 4. AM1-CI-calculated changes in the bond lengths of Pc associated to the D* → D^+ and D^+ → D transitions and of PTCDI for the A → A^- and A* → A^- transitions. The bond labeling is defined in the chemical structures above the graphs.

compensate for the Coulombic attraction.[41] The separation can also be facilitated if it occurs before the full relaxation of the polaron pairs, as suggested by recent experimental studies on polymer heterojunctions,[42] or if the polarization energy of the surrounding medium is increased when the charges get separated, a feature that cannot be simply accounted for in the present approach.

b. Reorganization Energy. The internal part of the reorganization energy λ_i can be estimated in either of two ways: in the first case, λ_{i1} corresponds to the difference between the energy of the reactants in the geometry characteristic of the products and that in their equilibrium geometry; in the second case, λ_{i2} corresponds to the difference between the energy of the products in the geometry characteristic of the reactants and that in their equilibrium geometry. These two ways of estimating λ_i are equal only when the two potential energy surfaces representing the reactants and the products have the same curvature. Since this is often not the case, λ_i is actually estimated as the average of λ_{i1} and λ_{i2}; in the case of exciton dissociation: [43]

$$\lambda_{i1} = [E^{D^*}(Q_P) + E^{A}(Q_P)] - [E^{D^*}(Q_R) + E^{A}(Q_R)] \quad (5)$$

$$\lambda_{i2} = [E^{D^+}(Q_R) + E^{A^-}(Q_R)] - [E^{D^+}(Q_P) + E^{A^-}(Q_P)] \quad (6)$$

where Q_R and Q_P refer to the equilibrium geometries of the reactants and products, respectively. We have evaluated all these terms at the AM1/CI level.

For exciton dissociation with Pc initially excited, the relaxation energy required to promote the discotic molecule from its equilibrium geometry in the excited state to that optimal in the radical cation state amounts to 0.077 eV; it amounts to 0.098 eV when going from the charged state to the excited state. The corresponding values for perylene are much larger: 0.263 eV from the ground-state geometry to that characteristic of the radical anion and 0.120 eV from A^- to A. These larger relaxation energies result from pronounced geometric distortions over the whole conjugated backbone between the two redox states; see Figure 4. The reorganization energies λ_{i1} and λ_{i2} obtained on the basis of these relaxation energies are thus equal to 0.340 and 0.218 eV, respectively, yielding an average value of 0.279 eV. In the case of charge recombination, the energy required to promote Pc from the geometry characteristic of the radical cation state to the ground-state geometry amounts to 0.028 eV (and 0.022 eV from D to D^+); this small value is rationalized by the fact that the geometry of Pc is very similar in the two states, as illustrated in Figure 4. The value associated with perylene going from the radical anion state to the ground state is the same as to that estimated for exciton dissociation. The reorganization energies λ_{i1} and λ_{i2} are equal to 0.147 and 0.285 eV, respectively, yielding an average value of 0.216 eV.

The external part of the reorganization energy λ_s has been estimated by the classical dielectric continuum model initially developed by Marcus for electron-transfer reactions between spherical ions in solution.[44] Here, we thus make the assumption, which should be reasonable for amorphous blends, that the electron transfer occurs in an isotropic dielectric environment (to the best of our knowledge, no simple expressions have been developed to account for the anisotropy of the medium). The reorganization term is given by:

$$\lambda_s = \frac{1}{8\pi\epsilon_0}\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right)\left(\frac{1}{R_D} + \frac{1}{R_A} - 2\sum_D \sum_A \frac{q_D q_A}{r_{DA}}\right) \quad (7)$$

where ϵ_s is the static dielectric constant of the medium and ϵ_{op}

---

(41) Offermans, T.; Meskers, S. C. J.; Janssen, R. A. J. *J. Chem. Phys.* **2003**, *119*, 10924.

(42) Morteani, A. C.; Sreearunothai, P.; Herz, L. M.; Friend, R. H.; Silva, C. *Phys. Rev. Lett.* **2004**, *92*, 247402.

(43) Brédas, J. L.; Beljonne, D.; Coropceanu, V.; Cornil, J. *Chem. Rev.* **2004**, *104*, 4971.

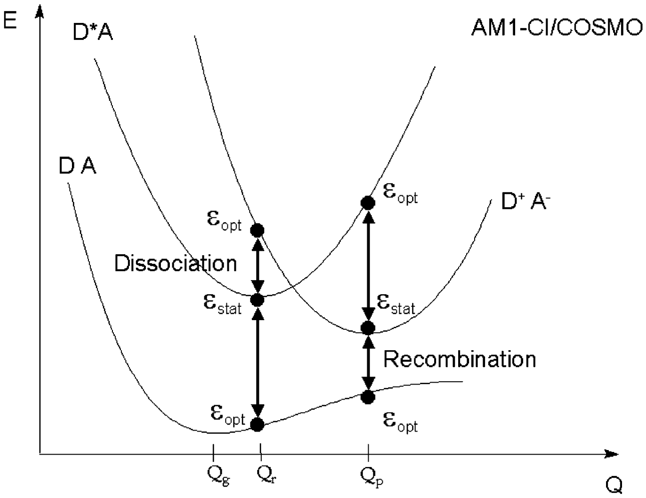


Figure 5. Potential energy curves of the donor/acceptor pair in the ground state (DA), the lowest intramolecular excited state (D*A), and the lowest charge-transfer state (D^+A^-). We illustrate the nature of the transitions calculated at the AM1-CI/COSMO level and the dielectric constants chosen to do so in order to calibrate the location of the CT state in the INDO/SCI calculations for the two processes.

is the optical dielectric constant; since the refractive index does not change significantly going from one solvent to another, we have set ϵ_{op} equal to a typical value of 2.25;[45,46] R_D (= 4.06 Å) and R_A (= 3.45 Å) are the effective radii of the Pc and PTCDI molecules estimated as the radius of the sphere having the same surface as the surface accessible area of the molecule provided by COSMO. The q_D and q_A terms denote the atomic charges on the ions, as estimated at the AM1/CI-COSMO level (the sum runs over all atoms of the donor and acceptor, respectively); these terms have been introduced in the Marcus expression, whose original form merely considers the separation between the centers of the two spherical ions,[44] to better account for the molecular topologies of the donor and acceptor units. The λ_s reorganization energy evolves from 0.237 to 0.524 eV in going from a static dielectric constant of 3 to 5; as expected, it increases with medium polarity.

c. Electronic Coupling. The electronic coupling V_{RP} appearing in eq 2 is in principle to be evaluated in a diabatic description (where the initial and final states do not interact) as half the splitting at the transition geometry. Since the excited states of the systems are described by means of a configuration interaction (CI) scheme in a supramolecular approach, we do take into account the interaction between the two states and hence actually obtain an adiabatic description of the system. In that case, V_{RP} can be estimated from quantities given directly by the CI calculations in the framework of the generalized Mulliken−Hush (GMH) formalism, which refers to a vertical transition from the initial to the final state,[47,48] as illustrated in Figure 5. In a two-state model, V_{RP} is written as:

$$V_{RP} = \frac{\mu_{RP}\Delta E_{RP}}{\sqrt{(\Delta\mu_{RP})^2 + 4(\mu_{RP})^2}} \tag{8}$$

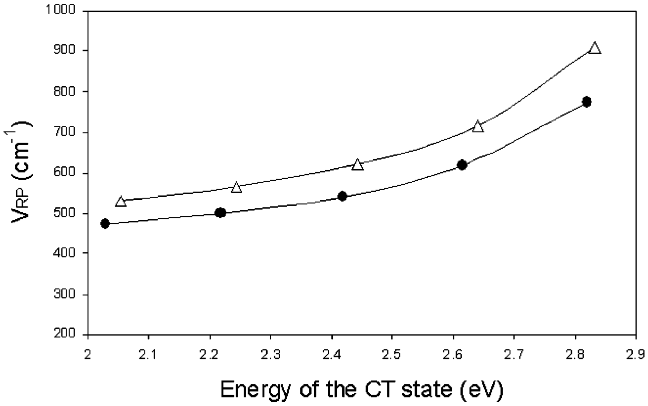


Figure 6. Evolution of the electronic coupling associated with the most efficient pathway for exciton dissociaton in a cofacial complex with the two molecules separated by 4 Å as a function of the energy of the charge-transfer excited state. We report the values obtained when involving all the main configurations that describe the two states (●) and when mixing only the $H_D \rightarrow L_D$ and $H_D \rightarrow L_A$ configurations (▲).

where ΔE_{RP} corresponds to the energy difference, $\Delta\mu_{RP}$ to the dipole moment difference (on the order of 20 D for an intermolecular distance of 4 Å), and μ_{RP} to the transition dipole moment between the initial and final states (projected in all cases along the $\Delta\mu_{RP}$ direction, which is mainly oriented along the stacking axis[49]). Here, these parameters have been evaluated using the semiempirical Hartree−Fock intermediate neglect of differential overlap (INDO) method[50] coupled to a single configuration interaction (SCI) scheme.

For each of the two pathways of exciton dissociation, the electronic coupling between its intramolecular excited state and the charge-transfer CT excited state (which is mainly described by a transition between the HOMO level of Pc and the LUMO level of PTCDI) has been computed with a CI expansion, including all the relevant electronic configurations (note that the configurations describing the lowest intramolecular state of the acceptor are excluded to prevent any exciton delocalization across the donor/acceptor interface, which is pronounced when the two molecules have similar optical gaps; this is motivated by the fact that excitons are expected to be localized over a single molecule as a result of lattice vibrations, as in the case of charge carriers[43]).

Since the INDO/SCI calculations do not take the medium effects into account and hence do not necessarily provide reliable energies for the charge-transfer excited states, we have first checked whether the electronic coupling is sensitive to the actual energetic location of the CT state. To do so, we have applied a static electric field along the charge-transfer direction (i.e., along the "stacking" axis) to tune the energy of the CT state while keeping the energies of the intramolecular states almost unaffected. We plot in Figure 6 the evolution of the largest electronic coupling for exciton dissociation in a complex made of the two molecules in a cofacial configuration, with an intermolecular distance fixed at 4 Å, when varying the position of the charge-transfer excited state between 2.0 and 2.8 eV (note that a single dissociation pathway is efficient in this geometry). We observe that the electronic coupling increases from ~500 to ~800 cm^{-1} when the energy of the CT state is raised. This evolution, leading to an increase in the transfer rate by a factor of 2.5, cannot be

---

(44) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.
(45) *Handbook of Chemistry and Physics*, 76th ed.; Lide, R. D., Frederikse, H. P. R., Eds.; CRC Press: Boca Raton, FL, 1995.
(46) Madigan, C. F.; Bulovic, V. *Phys. Rev. Lett.* **2003**, *91*, 247403.
(47) Cave, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1996**, *249*, 15.
(48) Cave, R. J.; Newton, M. D. *J. Chem. Phys.* **1997**, *106*, 9213.
(49) Nelsen, S. F.; Newton, M. D. *J. Phys. Chem. A* **2000**, *104*, 10023.
(50) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111.

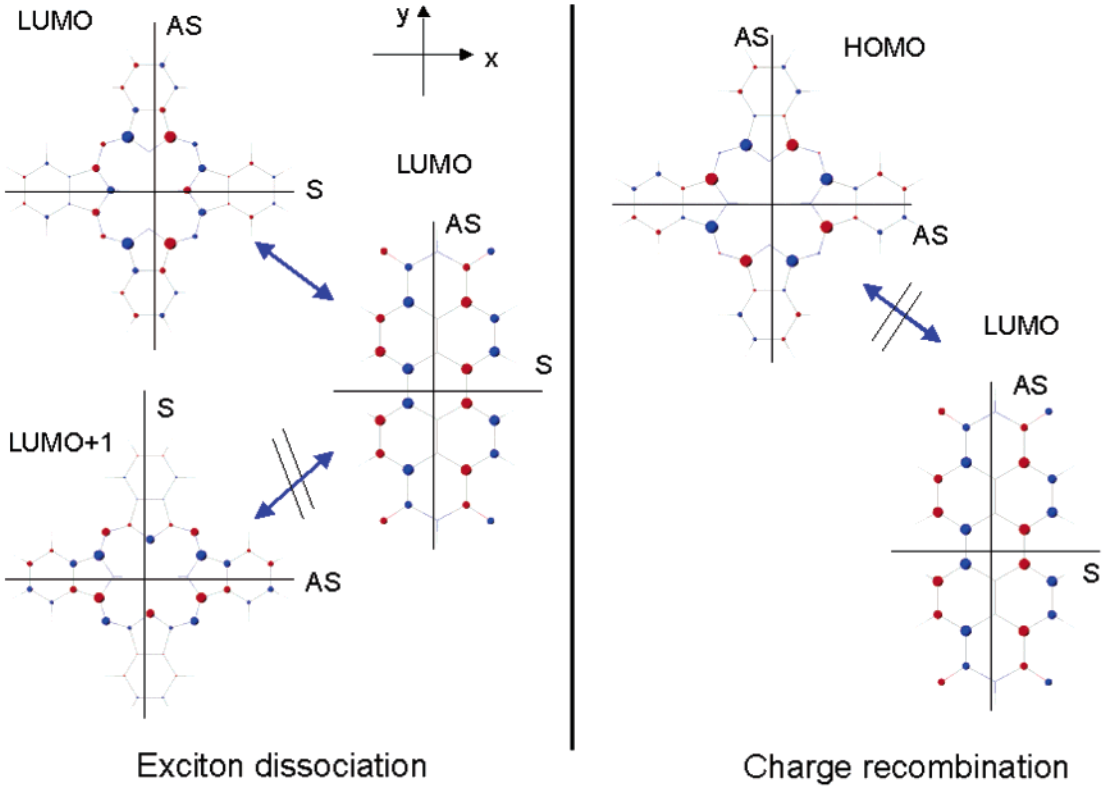


Figure 7. Symmetry of the relevant electronic levels to describe the exciton dissociation and charge recombination processes in the Pc/PTCDI pair.

associated with a change in the mixing of the different electronic configurations when the amplitude of the electric field is tuned; indeed, the same behavior is obtained from CI calculations mixing only the $H_D \rightarrow L_D$ and $H_D \rightarrow L_A$ configurations (Figure 6); rather, we attribute this evolution to the polarization of the π-electronic cloud upon application of the electric field. These results contrast with a previous theoretical study by Rust et al. showing that an electric field created by external charges preserves the amplitude of the electronic coupling;[51] this discrepancy might be attributed to the strength of the coupling in that work being much weaker (around 16 cm^{-1}).

Since the actual position of the CT state influences the calculated couplings, we have developed a strategy to locate the CT state at an energy consistent with the AM1/CI-COSMO results and to depict reliably the relative energies of the potential energy curves associated to the DA, D*A, and D$^+$A$^-$ states. To do so for exciton dissociation, the idea is to calculate at the AM1/CI-COSMO level: (i) the energy of the D*A state for a given static dielectric constant (since the dissociation process starts from the fully relaxed D*A geometry) and (ii) those of the DA and D$^+$A$^-$ states with the optical dielectric constant (since in the spirit of the GMH formalism these two states are reached optically from D*A, thus preventing any nuclear relaxation of the surrounding molecules due to the fast time scale of optical excitations). The value of the electric field is then tuned in the INDO/SCI calculations to reproduce the same ratio for the energies of the DA → D*A and D*A → D$^+$A$^-$ transitions; see Figure 5. In doing so, we obtain electronic couplings of 472 and 775 cm^{-1} for static dielectric constants of 3 and 5, respectively.

In the case of charge recombination, we have first verified the absence of significant three-state effects (i.e., linked in particular to a borrowing intensity of CT from the closely lying intramolecular state), thus validating the use of the two-state GMH formalism; this was not explicitly done in the approach described in ref 43 and led to overestimated couplings. The strength of the electronic coupling is found to be much smaller for charge recombination (0.04 and 0.05 cm^{-1} for static dielectric constants of 3 and 5, respectively); this coupling is nearly unaffected by the actual location of the CT state due to its vanishingly small amplitude.

The significant variation in the magnitude of the electronic coupling between the two processes is actually driven by the symmetry of the relevant molecular orbitals (Figure 7).[52,53] In the case of exciton dissociation, the electronic coupling reflects the degree of overlap between the LUMO/LUMO + 1 level of the donor and the LUMO level of the acceptor. Figure 7 depicts the shape and symmetry (with respect to the two symmetry planes perpendicular to the conjugated core) of these orbitals. We clearly see from the linear combination of atomic orbitals (LCAO) patterns that the pathway involving the Pc LUMO + 1 leads to a global cancellation of the overlap in the cofacial configuration and hence yields a very small electronic coupling; however, the situation is different for the LUMO level of the molecule, which thus becomes responsible for the dominant dissociation pathway. In the case of charge recombination, it is the overlap between the LUMO of the acceptor and the HOMO of the donor that dictates the amplitude of the electronic coupling; this overlap vanishes for a cofacial configuration, thus

---

(51) Rust, M.; Lappe, J.; Cave, R. J. *J. Phys. Chem. A* **2002**, *106*, 3930.

(52) Verhoeven, J. W. *Adv. Chem. Phys.* **1999**, *106*, 603.

(53) Cave, R. J.; Newton, M. D.; Kumar, K.; Zimmt, M. B. *J. Phys. Chem.* **1995**, 99, 17501.

rationalizing the small calculated values. We stress that this picture is valid only for a cofacial geometry; significant couplings are expected for both processes when moving away from such highly symmetric structures (vide infra).

d. Charge Generation and Recombination Rates. We are now in a position to estimate the rates of exciton dissociation and charge recombination by plugging all the parameters estimated in the previous sections into eq 2. When Pc is photoexcited in a cofacial complex with the intermolecular distance fixed at 4 Å, we obtain values of 3.6×10^{13} s^{-1} and 5.4×10^{13} s^{-1} for the exciton dissociation rate for $\epsilon_s = 3$ and 5, respectively. This process occurs in the normal region of Marcus since $|\Delta G°| < \lambda$ (0.23 versus 0.52 eV). The transfer rate would increase significantly if $|\Delta G°|$ and λ were to converge toward a similar value; this does not occur here since the absolute values of $\Delta G_{dis}°$ and λ both increase with medium polarity. For the same geometry, recombination rates of 1.7×10^2 s^{-1} and 2.7×10^4 s^{-1} are estimated for $\epsilon_s = 3$ and 5. The extreme slowness of the recombination process originates in the vanishingly small electronic couplings and from the fact that recombination occurs deep into the inverted region of Marcus ($|\Delta G°| = 1.65$ eV $\gg \lambda = 0.45$ eV for $\epsilon_s = 3$). Charge recombination gets faster when the dielectric constant is increased due to the opposite evolutions of $\Delta G_{rec}°$ and λ_s, which tends to reduce the gap between their absolute values. We stress that the transfer rates are only slighly affected (by less than 1 order of magnitude) when the free Gibbs energy or the external reorganization energy is made to vary by a few tenths of an electronvolt (except when the process occurs deep into the inverted region).

If we assume that the acceptor is initially excited, we calculate the following parameters for exciton dissociation at $\epsilon_s = 3$ [$\epsilon_s = 5$]:

$\lambda_i = 0.055$ [0.055] eV; this small value is rationalized by the fact that Pc and PTCDI exhibit almost the same geometry in going from D to D$^+$ and from A* to A$^-$, respectively (see Figure 4);

$\Delta G° = -1.16$ [-1.34] eV; this locates the lowest excited state of PTCDI at about 0.9 eV above that of Pc, in agreement with experimental values (~1.8 eV for Pc[26] versus ~2.5 eV for PTCDI[41]);

$V_{RP} = 373$ [544] cm^{-1}; and

$k = 1.1 \times 10^{10}$ [2.7×10^{11}] s^{-1}.

This translates into a ratio k_D/k_A (where k_D [k_A] corresponds to the rate when the donor [acceptor] is initially excited) of about 3.3×10^3 and 2×10^2 for $\epsilon_s = 3$ and 5, respectively. The reduction in the exciton dissociation rate when exciting the acceptor is associated with the increase in energy gap between $|\Delta G°|$ and λ, the dissociation actually taking place in the inverted region. Thus, the nature of the excited species also plays a significant role in the dynamics of charge generation in solar cells.

e. Influence of Structural Disorder. Since highly symmetric arrangements are not expected to be frequently met at the organic−organic heterojunction, we briefly discuss here the way the transfer rates for exciton dissociation and charge recombination vary when changing the relative positions of the two interacting units away from a cofacial geometry while keeping an intermolecular distance of 4 Å. We focus here exclusively on the electronic coupling V_{RP}, which is the parameter mostly affected by structural “disorder”.

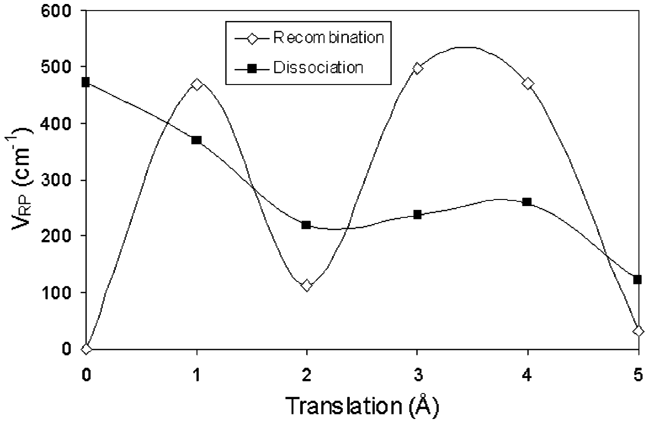


Figure 8. Evolution of the INDO/SCI-calculated electronic couplings for the efficient pathway of exciton dissociation and for charge recombination in the Pc/PTCDI complex (with the two molecules separated by 4 Å) when translating the PTCDI molecule along the *y* axis defined in Figure 7.

An increase in intermolecular distance *d* between the donor and the acceptor leads in both cases to an exponential decay of the electronic coupling. V_{RP} is proportional to $\exp\{-\beta d\}$, with the decay factor β estimated to be 2.5 for exciton dissociation and 3.2 for charge recombination at $\epsilon_s = 3$ (note that the corresponding decay factors β' that can be associated to the transfer rates amount to 5.2 and 6.5, respectively). In the case of exciton dissociation, the lateral translation of the PTCDI molecule along either the *x* or *y* axis (as defined in Figure 7) typically decreases the strength of the interactions initially favored by symmetry rules by reducing the spatial overlap between the wave functions of the two molecules (see Figure 8); the efficiency of the second pathway is kept low for symmetry reasons.

In the case of charge recombination, the translation of the PTCDI molecule along the *x* axis does not yield a large electronic coupling since this symmetry operation keeps the global cancellation of the wave function overlap; in contrast, shifting the molecule along the *y* axis breaks the symmetry constraints and can generate electronic couplings as high as ~500 cm^{-1} for charge recombination; see Figure 8. For a translation of 3 Å along the *y* axis, the transfer rates for exciton dissociation and charge recombination amount to 9.1×10^{12} s^{-1} and 3.3×10^{10} s^{-1}; this translates into a ratio of about 2.8×10^2 between the rates of the two processes. Thus, it appears that staggered complexes, which are expected to be often encountered in the solid state, favor the charge recombination process. This is further supported by the results plotted in Figure 9, where we report the transfer rates for exciton dissociation and charge recombination as well as their ratio when translating the PTCDI molecule by up to 5 Å. The results indicate that the charge recombination process becomes highly efficient (with rates approaching 10^{10} s^{-1}) as soon as the PTCDI molecule is slightly translated along the *y* axis.

We have also analyzed the evolution of the electronic coupling associated to the two dissociation pathways for exciton dissociation and to charge recombination when rotating one molecule around the “stacking” axis for a static dielectric constant of 3. Interestingly, we find that there always exists an efficient pathway for exciton dissociation whatever the rotational

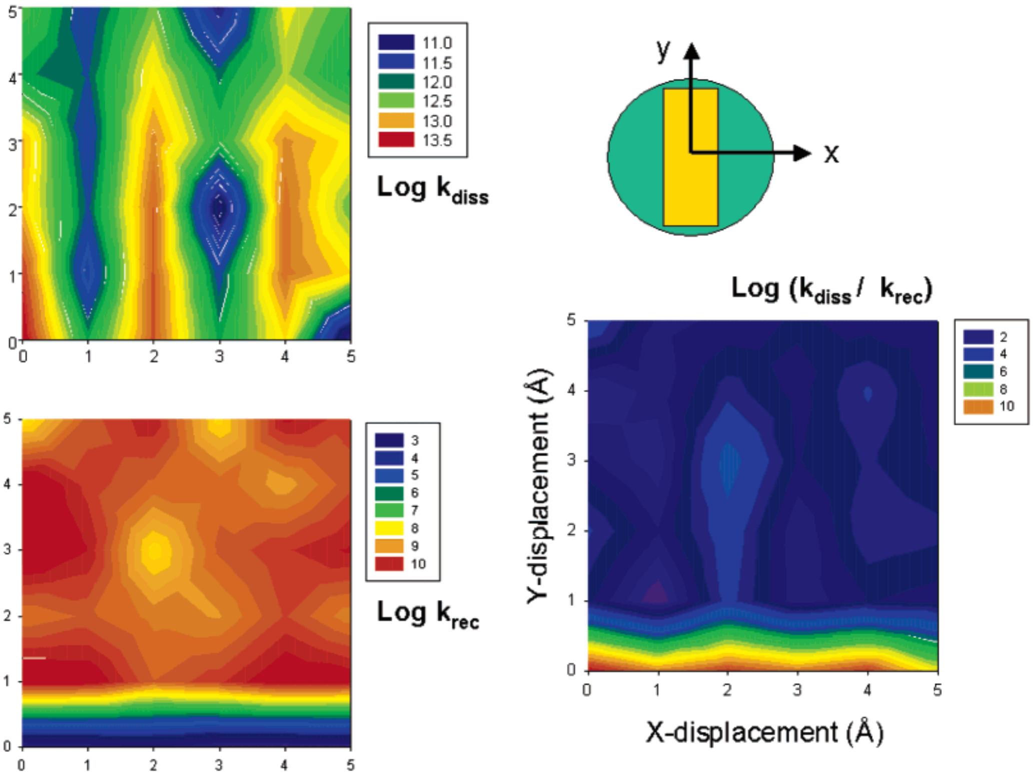


Figure 9. Evolution of the INDO/SCI-calculated electronic couplings for exciton dissociation and charge recombination and their ratio in the Pc/PTCDI complex (with the two molecules separated by 4 Å) when translating the PTCDI molecule as shown in the upper right quadrant by up to 5 Å. For exciton dissociation, V_{RP} is set equal to $\sqrt{V_{\mathrm{RP1}}^2+V_{\mathrm{RP2}}^2}$, with V_{RP1} and V_{RP2} the transfer rates associated with the two different dissociation pathways.

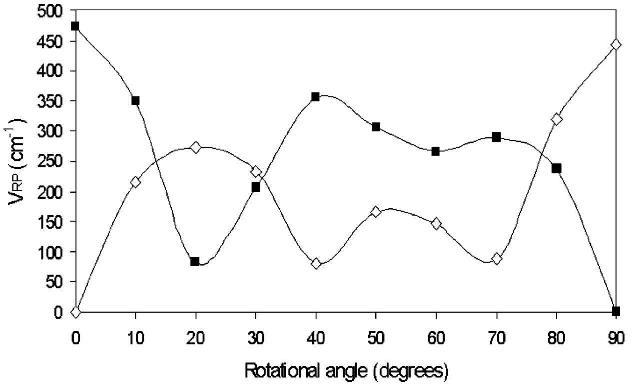


Figure 10. Evolution of the INDO/SCI-calculated electronic couplings of the two different pathways for exciton dissociation in the Pc/PTCDI complex (with the two molecules separated by 4 Å) when rotating the PTCDI molecule around the stacking axis; the zero value corresponds to the cofacial geometry initially chosen.

angle and that the nature of the dominant pathway reverses in going from 0° to 90° (Figure 10); this is explained by the fact that the lowest two unoccupied orbitals of Pc are polarized in perpendicular directions. The calculated amplitudes result from a fine balance between the relative positions of the two molecules and the shape of the relevant wave functions.[54]

The dimensionality of the Pc molecule thus appears to be a key parameter that contributes to high efficiencies in organic solar cells by creating a quasi-degeneracy of electronic levels and in turn a strong insensitivity to rotational disorder; such behavior is not expected when mixing two rodlike molecules. The charge recombination rate is also weakly affected by the rotational angle because the HOMO level of Pc is fully delocalized over the conjugated core; thus, rotational disorder does not influence the exciton dissociation process.

IV. Summary

Focusing on the rates of exciton dissociation and charge recombination in model donor/acceptor pairs that can be used in solar cell applications, we have introduced a theoretical approach aimed at estimating all the molecular parameters entering the Marcus−Levich−Jortner expression. This approach has been applied to a complex made of a phthalocyanine molecule as the donor and a perylene molecule as the acceptor.

The results point to the role of several factors in defining the rates of the two processes:

(i) the relative positions of the interacting molecules, which drive the extent of spatial overlap between the electronic wave functions;

(ii) the symmetry of the relevant electronic levels, which can be exploited to strongly limit the detrimental charge recombination process; and

(iii) the two-dimensional character of the phthalocyanine molecule, which introduces a quasi-degeneracy in the electronic levels and by extension a high insensitivity to rotational disorder; this might rationalize the reason for which the most efficient solar cells to date incorporate derivatives of the three-dimensional C_{60} molecule, which is characterized by the presence of several quasi-degenerate frontier electronic levels.

We believe that, in conjunction with synthetic works and device characterizations, our approach paves the way toward

---

(54) Lemaur, V.; da Silva Filho, D. A.; Coropceanu, V.; Lehmann, M.; Geerts, Y.; Piris, J.; Debije, M. G.; van de Craats, A. M.; Senthilkumar, K.; Siebbeles, L. D. A.; Warman, J. M.; Brédas, J. L.; Cornil, J. *J. Am. Chem. Soc.* **2004,** *126*, 3271.

the establishment of general guidelines to determine the optimal matching partners and supramolecular architectures for the development of highly efficient organic solar cells.

Acknowledgment. We acknowledge very stimulating discussions with Profs. M. J. Newton and R. J. Cave. The work in Mons is partly supported by the Belgian Federal Governement “Interuniversity Attraction Pole in Supramolecular Chemistry and Catalysis, PAI 5/3” and “Technological Attraction Pole SOLTEX”, the Région Wallonne (Program PIMENT−SOLPLAST), the European Integrated Project project NAIMO (NMP4-CT-2004-500355), and the Belgian National Fund for Scientific Research (FNRS/FRFC). The work at Georgia Tech is partly supported by the National Science Foundation through Grant CHE-0342321, the Office of Naval Research, NREL, and the IBM Shared University Research Program. J.C. and D.B. are FNRS Research Associates, and V.L. acknowledges a grant from “Fonds pour la Formation à la Recherche dans l’Industrie et dans l’Agriculture (FRIA)”.

JA042390L