

DSM Science & Technology Awards 2005

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Research Report

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The 1976 discovery by Heeger, MacDiarmid, and Shirakawa that organic conjugated polymers become good electrical conductors upon a redox treatment (doping) has opened the field of plastic electronics [1]. Organic materials are now exploited as the active semiconductor element in (opto-)electronic devices, that in some cases have reached the stage of commercialization already. Companies such as Pioneer, Kodak, or Philips incorporate organic light-emitting diodes (LEDs) in low-resolution displays for car stereo systems, digital cameras, and electric shavers and are developing high-resolution full-color flexible displays. Organic materials are also envisioned for use in photovoltaic / solar cells and in field-effect transistors (FETs), and by extension in electronic circuits or matrix boards. It is critical for the success of plastic electronics to gain a fundamental understanding of the key physical and chemical processes that determine the operation of organic-based devices and to assess the nature of the best materials to be used. During our Ph.D. thesis, we have brought major contributions to this understanding. With the help of quantum-chemical calculations, we have uncovered the molecular parameters governing two important processes, namely charge transport and photo-induced charge separation. Hereafter, we first briefly recall the operation of three main organic-based devices (LEDs, FETs, and solar cells), which will help to highlight the relevance of our work; we then describe our major findings.

Mode of operation of organic electronic devices

An organic light-emitting diode is fabricated by sandwiching an organic layer between a low-workfunction metal (for instance, Al, Ca, or Mg) and a high-workfunction transparent electrode (typically indium tin oxide, ITO). The goal is to generate light upon electrical excitation. The working principle of a LED relies on four successive steps [2]: (i) electrons and holes are injected from the cathode and anode into the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the organic molecules, respectively; (ii) the electrons and holes migrate through the organic layer(s) in opposite directions under the influence of the applied voltage; (iii) electrons and holes meet and recombine into bound electron-hole pairs (also referred to as excitons); and finally (iv) the excitations decay radiatively to produce the luminescence signal. High carrier mobilities (charge transport) for both electrons and holes are required; this is to ensure that there occurs no charge accumulation at the electrode/organic interfaces (which would impede further charge injection) and that charge recombination occurs in the bulk of the organic layer (and not close to the electrodes where excitons would dissociate, resulting in strong luminescence quenching).

The architecture of an organic field-effect transistor consists of an organic semiconductor layer deposited on top of an insulating layer (Al_2O_3 , SiO_2) [3]. Three metallic electrodes are present: the source and drain electrodes, that are in direct contact with the semiconductor, and the gate electrode present beneath the insulating layer. The gate voltage allows one to modulate the current flowing from source to drain across the semiconducting layer. Field-effect transistors have to display fast response times and high

on/off ratios; fast switching speed requires high charge mobilities in the semiconductor, which points once again to the key role played by charge-transport processes.

Another type of devices that holds great promise for the future is organic solar cells. Organic photovoltaics represents a major target in the search for safe, low-cost, and renewable energies that could eventually compensate for the foreseen reduction in oil production in the future. An organic solar cell is made by sandwiching an organic layer between two metallic electrodes of a different nature. The organic layer itself has to include two different components: a material characterized by a low ionization potential, that acts as an electron donor, and a material with a high electron affinity, acting as an electron acceptor. In contrast to light-emitting diodes that convert an electrical current into light, a photovoltaic cell converts light into electrical charges. Its operation relies on four successive steps [4]: (i) a photon is first absorbed by the donor (or acceptor), leading to the formation of an electron-hole pair (exciton); (ii) the excitation then migrates towards the interface between the two organic materials; (iii) at the heterojunction, the bound electron-hole pair has to dissociate into separated charges; and (iv) the charges drift across the organic layer towards the electrodes, under the influence of the built-in electric field generated by connecting the two different electrodes. In addition to charge transport, a key process to understand and optimize in such a device is the dissociation of excitons into charges. In a simple molecular-orbital picture (see Figure 1), the photoinduced charge-transfer process is initiated by the promotion of one electron from the HOMO level of the donor to its LUMO level (assuming that only the donor is excited). When this excitation reaches the organic heterojunction, the electron promoted to the LUMO level of the donor is transferred to the lower-lying LUMO level of the acceptor. The separation of the charges and their migration towards the electrodes is then in competition with a charge recombination mechanism in which the electron in the LUMO level of the acceptor is transferred back to the HOMO of the donor. Thus, for organic solar cells, it is most desirable to find strategies to favor exciton dissociation and charge transport and to limit as much as possible the efficiency of the charge recombination process.

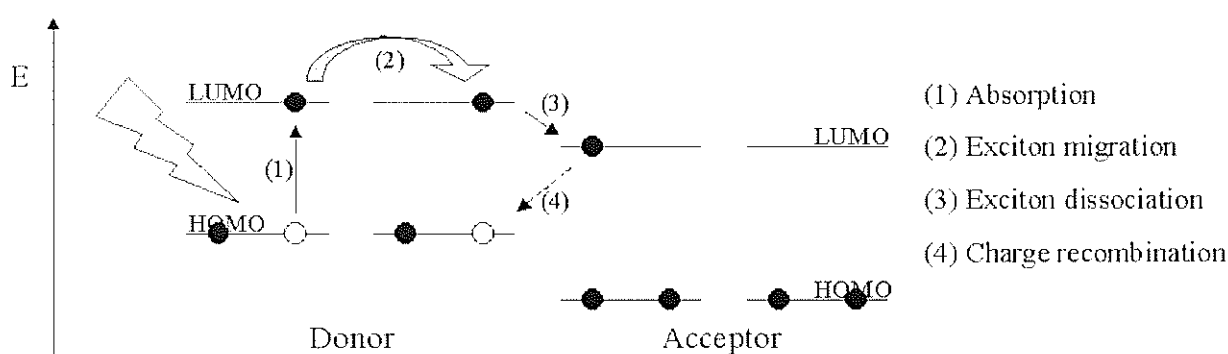


Figure 1: Schematic representation of the relevant electronic levels in an organic solar cell.

Organic solar cells generally incorporate either small organic conjugated molecules or polymers. Both types of materials have disadvantages. High charge mobilities require a high degree of order. This can be obtained with molecules by using expensive techniques such as vacuum deposition. Inkjet-printing techniques allow for cheap processing of polymers and large-scale production but give rise to low charge mobilities due to the inherent disorder in the deposited films. In this context, discotic liquid crystals

represent an interesting alternative to small organic conjugated molecules and polymers; their self-assembly, self-healing properties, and ease of processing make them promising candidates to transport charges and excitations efficiently. Discotic liquid crystals self-assemble into columns, due to the microsegregation of their rigid conjugated cores and flexible alkyl-type side chains, and provide efficient one-dimensional pathways for transport. Moreover, even cheap processing techniques can lead to the formation of micrometer-long channels without the grain boundary defects usually obtained in crystalline materials, due to the self-healing properties.

Our contributions

In the first part of our Ph.D. work, we have characterized the parameters that control charge transport at the molecular scale in discotic columns [5-7]. Our approach, by incorporating the exact chemical nature of the molecules, is very original; it contrasts with the phenomenological models that have been mostly used to date and that rely on a large number of ill-defined constants. Our “bottom-up” approach is of general applicability; it gives us the opportunity to assess the performance of various molecular structures and to connect the molecular and macroscopic worlds. The second part of our Ph.D. thesis focuses on the description of the charge generation and recombination dynamics in donor/acceptor complexes [8]. This basically constitutes an unexplored field at the theoretical level. We have started to develop an understanding of these dynamics by estimating the key molecular parameters that control the charge separation and recombination processes. Our theoretical efforts have been performed in close collaboration with several experimental groups, namely in the framework of the European project DISCEL whose aim was the incorporation of discotic materials in organic devices. Our work has contributed to the design, prior to any chemical synthesis, of new molecular structures with enhanced transport properties [9-11] and to the rationalization of experimental mobility measurements [6].

Typically, charge carriers in discotic columns are localized on a single molecule and jump from disc to disc along the stack to yield a current. The rate k_{ET} for a vibration-assisted hopping process between two adjacent molecules can be expressed to first approximation with the semi-classical Marcus theory as [12]:

$$k_{ET} = \frac{4\pi^2}{h} t^2 \sqrt{\frac{1}{4\pi\lambda kT}} \exp\left(\frac{-\lambda}{4kT}\right) \quad (1)$$

The rate depends on two fundamental parameters: the reorganization energy, λ , and the intermolecular transfer integral, t . The reorganization energy consists of two contributions: the inner part, λ_i , measures the amplitude of the geometric modifications of the two molecules when going from the initial state to the final state; the outer part, λ_s , reflects the change in the polarization of the surrounding medium. The intermolecular transfer integral describes the strength of the interactions (electronic coupling) between the HOMO (for holes) and LUMO (for electrons) levels of the two molecules. We stress that λ has to be minimized and t maximized to ensure high electron-transfer rates, and hence high

charge mobilities. While λ only slightly depends on the degree of structural order, t is expected to vary strongly as a function of the relative positions of the two interacting molecules.

We have estimated the inner reorganization energies at the density functional theory (DFT) level for a large number of unsubstituted discotic molecules (triphenylene, hexaazatriphenylene, trinaphthylene, hexaazatrinaphthylene, coronene, and hexabenzocoronene, see chemical structures in Figure 2) as well as for some of these molecules substituted by alkylthiol and alkyloxy groups. We found that λ_i fluctuates in the range 0.05-0.50 eV depending on the chemical structure. Our results indicate that:

- (i) the larger the conjugated core, the smaller the reorganization energy;
- (ii) the reorganization energy associated to positively charged carriers (holes) is smaller than that of negatively charged carriers (electrons);
- (iii) substituents, while needed to ensure a liquid crystalline character, can in some instances result in large values of λ_i .

This demonstrates that the choice of the conjugated core and of the substituents is critical to ensure good transport properties; these cannot be predicted at the simple view of a chemical structure, which points to the relevance of our quantum-chemical calculations.

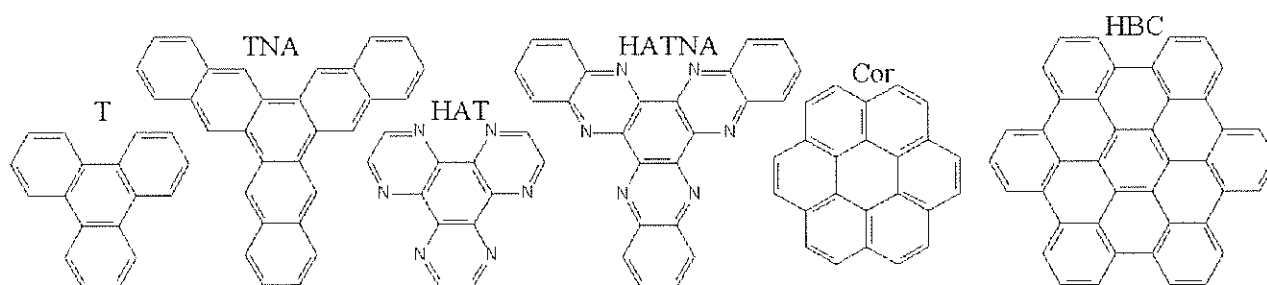


Figure 2: Chemical structures of triphenylene (T), hexaazatriphenylene (HAT), trinaphthylene (TNA), hexaazatrinaphthylene (HATNA), coronene (Cor), and hexabenzocoronene (HBC).

The intermolecular transfer integrals t for both holes and electrons have been estimated (at the Hartree-Fock semi-empirical intermediate neglect of differential overlap (INDO) level) by examining the splittings of the HOMO and LUMO levels, respectively, upon interaction between adjacent molecules. Since the discotic molecules have freedom to move within the columns, we have investigated the impact of three main motions (*i.e.*, changes in intermolecular separation, rotations, and translations out of the columns) on the electronic splittings. We have found that the electronic splittings decay exponentially with an increase in intermolecular distance. This motivates the synthesis of molecules that promote short intermolecular distances, for instance through hydrogen bondings [13]. The translation of a molecule out of the column has also a significant impact on the electronic splittings; the latter are generally reduced with an increasing degree of translation, except for few specific geometries that yield an efficient overlap between the frontier electronic levels. The degree of freedom affecting the most the electronic splittings is the rotational angle between two molecules in the stacks. For triphenylene, going from a cofacial dimer to a 60°-rotated dimer, the electronic splittings decay by up to two orders of magnitude, which results in a situation where the charge carriers are nearly trapped on a given molecule. At first sight, a simple explanation of this result would be related to the presence of voids between the three branches of the

triphenylene core, which do not favor a strong overlap between the molecules at 60 degrees. However, this is contradicted by the fact that a fully circular molecule such as HBC also exhibits strong oscillations as a function of the rotational angle. Thus, our results demonstrate that the shape of the frontier electronic wavefunctions (that are hardly predictable without quantum-chemical calculations), rather than the shape of the molecule, is responsible for the observed evolutions.

It has been possible at this stage to perform some molecular engineering and to design molecules with charge transport properties largely insensitive to the rotational disorder. In particular, we have found that the HAT molecule (see Figure 2), which differs from triphenylene by the introduction of 6 nitrogen atoms in the conjugated core, has a HOMO splitting that decreases only by a factor of 2 going from a cofacial configuration to the 60°-rotated geometry [5].

Since the actual rotational angle between adjacent molecules is a key parameter to understand charge transport, we went a step further and estimated this parameter for various discotic molecules with the help of molecular mechanics simulations; the relative energies of the different conformers are then used as input to calculate the Boltzmann distribution of rotational angles and, by extension, the average intermolecular transfer integrals [6]. The calculated molecular parameters can then be plugged into Eq. 1 to estimate the ratio of the transfer rates for different discotic molecules (this allows us not to have to take account of the λ_s parameter) and to compare them with experimental mobility values. In doing so, we predicted that the HATNA molecule is a promising molecule for hole transport due to the strong insensitivity of its HOMO splitting to rotational disorder and its low reorganization energy for positive charge carriers; this conclusion has been fully supported by experimental mobility measurements.

Thus, we have in hand a series of theoretical tools that allow us to define the best materials and the most appropriate supramolecular organizations for optimized charge transport in organic-based devices. In the remainder of our thesis work, we plan to exploit the transfer rates calculated at the molecular level in the context of Monte-Carlo simulations. In these simulations, the charges will be propagated over large distances. We will thereby assess explicitly the influence of several parameters (electric field, temperature, disorder, traps, and charge carrier density) on charge mobility.

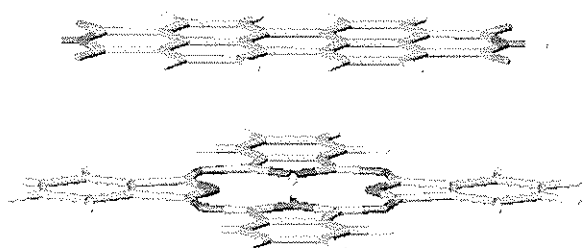
The second part of our Ph.D. thesis deals with the quantum-chemical characterization of the molecular parameters controlling the rate of charge generation and recombination in donor/acceptor heterojunctions. Our theoretical approach is illustrated below by considering complexes made of a phthalocyanine molecule (Pc, as donor) and a perylenebisimide molecule (PTCDI, as acceptor). The choice of phthalocyanines is motivated by several reasons: (i) phthalocyanines are characterized by a low reorganization energy for positive charge carriers and by significant transfer integrals for rotational angles close to the 45 degrees expected in stacks in order to reduce the steric hindrance between the saturated side-chains; these are two ingredients that favor efficient hole transport, as discussed earlier; (ii) their two-dimensional character and symmetry promotes a quasi-degeneracy of the lowest two excited states, which are polarized perpendicularly; there thus exist four different pathways to transfer excitations between adjacent molecules in the columns, with at least one of them being efficient whatever the

geometric configuration [7]. This contrasts with the situation for rod-like molecules for which an increase in the angle between the long molecular axes is highly detrimental; and (iii) they are low-energy absorbers (with a lowest absorption band peaking around 1.8 eV) and match fairly well the solar emission spectrum.

In a paper now in press in the Journal of the American Chemical Society, we have computed the charge generation and recombination rates by using the Marcus-Levich-Jortner formalism; this formalism improves on the semi-classical Marcus description by taking an explicit account of tunneling effects across the potential energy surfaces of the reactants and products and allows for quantitative estimates of the rates. In this framework, the rate of charge transfer writes:

$$k_{\text{ET}} = \frac{4\pi^2}{h} V_{\text{RP}}^2 \sqrt{\frac{1}{4\pi\lambda kT}} \sum_{\nu'} \exp(-S) \frac{S^{\nu'}}{\nu'!} \exp\left[\frac{-(\lambda + \nu'h\omega/2\pi + \Delta G^\circ)^2}{4\lambda kT}\right] \quad (2)$$

where ΔG° is the Gibbs free energy of the reaction (estimated as the energy difference between the initial and final states, including the Coulomb attraction between the two charges in the charge-separated state); λ_s is the reorganization energy of the surrounding medium (evaluated from simple expressions); S is the Huang-Rhys factor, directly related to the easily accessible λ_i term (the internal reorganization energy that describes the changes in the geometry of the donor and acceptor during the charge transfer); and V_{RP} is the electronic coupling between the initial and final states (calculated by means of the Generalized Mulliken-Hush formalism). Note that Eq. 2 assumes that a single vibrational mode is treated at the quantum level [8].



For a cofacial dimer made of PTCDI on top of Pc (with an interchain distance of 4 Å), see sketch on the left, we found ΔG° values of -0.2 eV and -1.65 eV for exciton dissociation and charge recombination, respectively, when the surrounding medium is characterized by a static dielectric constant ϵ_s of 3 (*i.e.*, a

value typical of organic thin films). If ϵ_s is increased, ΔG° becomes more negative for the dissociation process and less negative for the recombination process as a result of the stabilization of the charge-separated state with an increase in the polarity of the medium. The λ_s term is obviously very sensitive to the polarity of the surrounding medium since it represents a measure of its response to the charge transfer; it evolves in our case from 0.24 eV to 0.52 eV when ϵ_s goes from 3 to 5. The internal reorganization energies amount to 0.28 eV and 0.22 eV for the dissociation and recombination processes, respectively. The electronic couplings are estimated to be 472 cm^{-1} for dissociation (when considering two pathways associated to the quasi-degenerate lowest two unoccupied orbitals of the phthalocyanine molecule that are polarized perpendicularly) and 0.04 cm^{-1} for recombination. All together, these data lead to a dissociation rate of $3.6 \times 10^{13} \text{ s}^{-1}$ and a recombination rate of $1.7 \times 10^2 \text{ s}^{-1}$. The huge difference between these two

numbers is mostly driven by the electronic coupling term (the medium polarity that mainly affects ΔG° and λ_s has a much weaker influence on the transfer rates). This cofacial geometry is thus ideal for a solar cell since it favors the dissociation process and strongly limits the recombination mechanism. It is, however, of interest to analyze the way the electronic coupling changes as a function of the relative position of the two molecules.

We find that V_{RP} decays exponentially with an increase in the intermolecular distance since the overlap between the molecular orbitals is reduced. Interestingly, a lateral displacement of one molecule can increase the recombination rate by almost 8 orders of magnitude while keeping the dissociation rate nearly constant. This drastic evolution is understood simply by looking at the symmetry of the molecular orbitals involved in each process. For recombination, small V_{RP} values are obtained in the cofacial geometry as a result of the global cancellation of the overlap between the LUMO orbital of the acceptor and the HOMO orbital of the donor; the translation of a molecule can break these symmetry constraints and promote transfer rates as high as for exciton dissociation (which is not affected by such symmetry considerations). The two-dimensional character of the phthalocyanine molecule also results in a strong insensitivity of the dissociation rate with respect to the rotation of PTCDI on top of Pc. Since such a behavior cannot occur with rod-like molecules, the dimensionality of the donor and/or acceptor appears to be a key parameter to favor high charge generation yield in solar cells.

Thus, we have developed an original approach of general applicability to estimate quantitatively charge generation and recombination rates in organic solar cells; this approach will be largely exploited in the next few months to design the best matching partners and to define the most appropriate blend morphologies for organic solar cells. The establishment of such guidelines through theoretical design truly represents a significant advance in the field.

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