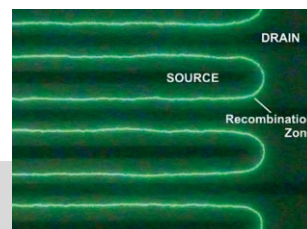


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# Ambipolar Transport in Organic Conjugated Materials\*\*

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*The relative mobility of holes versus electrons in  $\pi$ -conjugated materials is a long-standing issue in the field of organic electronics. In this Progress Report, we first argue on the basis of theoretical considerations that in general organic semiconductors are intrinsically as good electron transporters as they are hole transporters. Then, in the light of selected experimental works, we discuss the origin of the features that prevent the observation of intrinsic electron transport, and the strategies that have been developed to promote ambipolar transport in field-effect transistors.*

## 1. Introduction

The field of organic electronics has gained tremendous interest over the last ten years. A main challenge is to develop

efficient opto-electronic devices, such as light-emitting diodes (LEDs), field-effect transistors (FETs), or solar cells, in which the inorganic materials traditionally used as active elements are replaced with organic materials. Such devices can benefit from the many attractive features of organic materials, in particular the possibility to tailor their synthesis to match specific needs and the ease of processing thin films over large surfaces at low cost. The transport of charges in the organic layers plays a key role in defining the overall performance of these devices. In LEDs, electrons injected from the cathode and holes from the anode have to migrate in opposite directions throughout organic layer(s) to meet and recombine radiatively;<sup>[1]</sup> conversely, in solar cells, the charges generated by the dissociation of excitations have to reach the electrodes.<sup>[2]</sup> In FETs, a current has to flow between two electrodes (source and drain) and is modulated via a potential applied at a third electrode (gate) to perform a switching operation.<sup>[3,4]</sup>

A key quantity that characterizes transport is charge mobility, defined as the ratio between the speed of the charge carriers and the amplitude of the electric field inducing their displacement. In organic conjugated materials the charge mobility values span several orders of magnitude, from ca.  $10^{-8}$  to ca.  $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , depending on the chemical structure of the (macro)molecules and the processing conditions that determine the film morphology.<sup>[5]</sup> Good transport properties (and hence high charge mobilities) are required in all devices: in LEDs, to reduce the impact of image effects upon charge injection, to confine the light emission in the bulk of the organic layers (which helps in preventing quenching processes by the metallic electrodes), and to limit exciton-polaron quenching processes occurring at high polaron concentrations;

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in solar cells, to avoid the recombination of oppositely charged species that would occur when the charges are not sufficiently mobile<sup>[6]</sup> and in transistors, to yield short switching

times between on and off states and, by extension, to build organic-based electronic circuits with high-frequency operation.



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A long-standing issue in the field of organic electronics is to characterize the relative mobilities of holes versus electrons. The charge-transport properties of a single type of carriers can be characterized in many different ways; the most widely used approaches are: i) examining the  $I/V$  characteristics of diodes in which one electrode is specifically designed to prevent the injection of holes or electrons (i.e., electron-only and hole-only devices);<sup>[7]</sup> ii) the time-of-flight (TOF) technique, in which the charge carriers are generated by laser irradiation near one electrode and transported selectively across the organic layer depending on the polarity of the applied bias;<sup>[8]</sup> or iii) changing the sign of the potential applied to the gate in a transistor configuration in order to accumulate either holes or electrons in the conducting channel.<sup>[3,4]</sup> In the early days, the vast majority of experimental data contributed to what became the common wisdom that organic conjugated materials are intrinsically p-type conductors, that is, that the hole mobility is consistently much larger than the electron mobility. Since then, a large body of work has demonstrated that some organic materials can also be good n-type conductors. However, until recently, there were few reports showing that a given material can efficiently transport both electrons and holes.

The main goal of this Progress Report is first to demonstrate, on the basis of theoretical considerations, that generally organic conjugated (macro)molecules are intrinsically both good electron conductors and hole conductors. We then illustrate that factors that go beyond the intrinsic material properties (i.e., the nature of the electrodes, the dielectric layer in transistors, and the environment) are actually responsible for the type of transport observed. In this respect, while the use of p-type and n-type terminologies makes perfect sense for inorganic materials (the two regimes are obtained by varying the nature of the dopants), the same terminology is somewhat misleading for organic materials because a more complex structure, consisting of the organic material plus the other device components, dictates the transport properties. In a second part, we survey recent experimental works that have exploited various strategies to demonstrate ambipolar transport in a transistor configuration. The fabrication of transistors with efficient hole or electron transport within the same material as a function of the applied bias is of fundamental interest to the design of robust and efficient logic circuits.<sup>[9]</sup> Moreover, with ambipolar organic layers, electrons can be injected at the source and holes at the drain (or vice versa) in specific bias conditions, and recombine radiatively within the channel to yield light emission (vide infra).

## 2. Theoretical Considerations

The mechanisms of charge transport in organic conjugated materials are not fully characterized yet. At the molecular level, transport is mostly governed by two key parameters:

i) The transfer integral  $t$ , which describes the strength of the interaction (electronic coupling) between two adjacent molecules or polymer segments. Significant electronic couplings

tend to *delocalize* the charges over the interacting molecules. To first approximation, the transfer integral can be estimated for holes as the splitting of the HOMO (highest occupied molecular orbital) level and for electrons as the splitting of the LUMO (lowest unoccupied molecular orbital) level in a neutral dimer formed by two interacting molecules.<sup>[10,11]</sup>

ii) The polaronic relaxation energy  $E_p$ , which describes the amount of energy gained when a charge geometrically relaxes over a single molecule or polymer segment. A significant polaron relaxation thus tends to *localize* the charge carriers.

Two limiting descriptions are generally used to describe charge transport, namely the band regime and the hopping model. In the band regime, the HOMO/LUMO levels of individual molecules/segments strongly interact and generate valence/conduction bands of significant widths ( $>0.1$  eV). The charge carriers can delocalize coherently, and charge mobilities can be high (values up to  $300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  have been reported for naphthalene at 10 K).<sup>[8]</sup> The mobilities decrease with temperature owing to thermal activation of the lattice vibrational modes. The impact of such modes is to break the coherence inside the electronic bands, and hence to reduce the bandwidths by introducing fluctuations in the energies of the electronic levels and in the amplitude of the transfer integrals between adjacent molecules. A pure band model is generally applicable to highly ordered materials (molecular crystals) of high purity at low temperature.<sup>[12]</sup>

In the hopping regime, the charge carriers are localized and jump between adjacent molecules to migrate across the organic layer. Because each hop is an activated process that results from reorganization effects (vide infra), the charge mobilities are low (typically much lower than  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). Hopping is expected to be operational in organic thin films, which display a significant amount of energetic and/or positional disorder,<sup>[13]</sup> as frequently encountered in organic FETs. Thus, hereafter we focus on hopping processes and examine possible differences between electron and hole transport.

The rate of charge transfer between two molecules in a given geometric arrangement can be expressed in the limit of weak electronic coupling via semiclassical Marcus theory as:<sup>[14,15]</sup>

$$k_{\text{CT}} = \frac{4\pi^2}{h} t^2 \frac{1}{\sqrt{4\pi\lambda kT}} \exp\left[-\frac{(\lambda + \Delta E)^2}{4\lambda kT}\right] \quad (1)$$

where  $t$  denotes the transfer integral,  $\Delta E$  the free energy gained or lost by the system upon charge transfer, and  $\lambda$  the total reorganization energy, which has internal ( $\lambda_i$ ) and external ( $\lambda_s$ ) components. A high charge-transfer rate, and hence a high mobility value, requires the transfer integrals to be large and the  $\Delta E$  and  $\lambda$  terms to compensate one another (because a charge transfer between two molecules of the same nature corresponds to a self-exchange reaction,  $\Delta E$  is generally small, which means that the reorganization energies need to be minimized).

$\Delta E$  is different from zero upon application of an electric field<sup>[16]</sup> and when disorder is present, that is, when the geome-

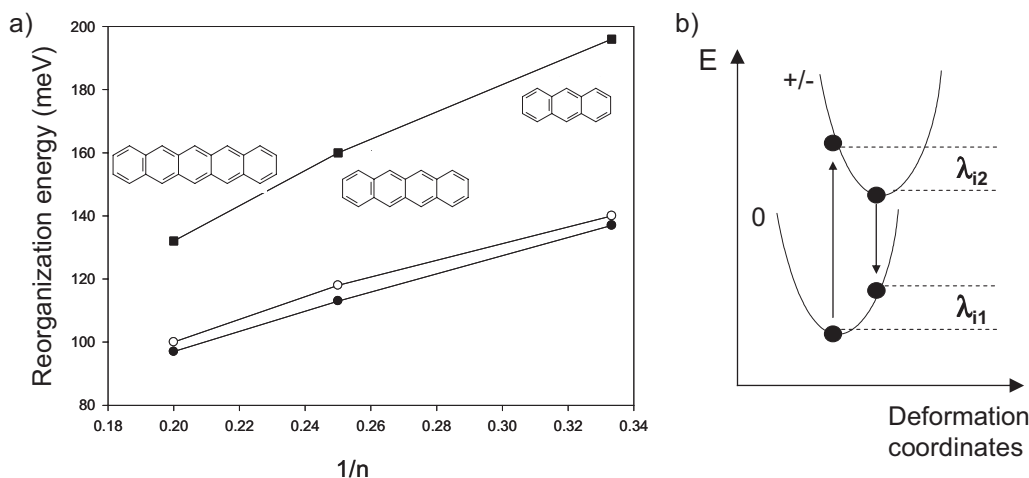
try or environment (i.e., the relative positions of the neighboring neutral molecules) of the molecules are different in the initial and final states. These two contributions are expected to be generally similar for hole and electron transport;<sup>[17]</sup> this might not hold true in cases where the negative and positive charge carriers have a very different spatial extent (e.g., in conjugated block copolymers when one type of carrier is confined into a co-monomeric unit while the other is fully delocalized over the conjugated backbone).

The external reorganization ( $\lambda_s$ ) accounts for the changes in the relative positions of the surrounding molecules upon charge transfer. In contrast to electron-transfer processes in solution, this nuclear polarization term is expected to be rather small in the bulk of organic thin films, up to ca. 0.1 eV;<sup>[18]</sup> again, it appears to be similar for holes and electrons. Note that a recent study has suggested that the nuclear dynamics of highly polarizable dielectric layers actually govern the rate of charge transfer in the organic layer of FETs (whereas the rate is limited by the strength of the electronic interactions in the framework of Marcus theory).<sup>[19]</sup>

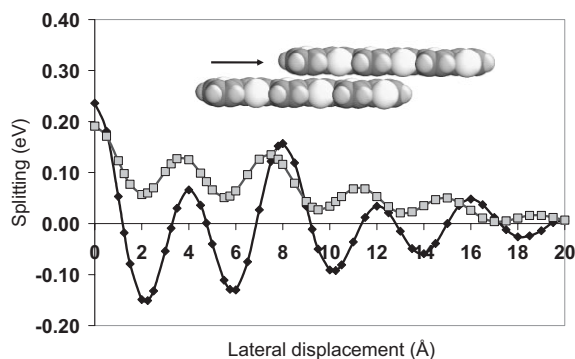
The internal reorganization part ( $\lambda_i$ ) reflects the changes in the geometry of the two molecules when going from the initial to the final state. This term originates from the fact that the geometry of a charged  $\pi$ -conjugated molecule differs significantly from that of the corresponding neutral molecule, owing to a marked redistribution of the  $\pi$ -electron bond densities. The reorganization energy  $\lambda_i$  can be estimated as the sum of two terms, see Figure 1b:<sup>[20]</sup> i) the difference between the energy of the charged molecule in its fully relaxed geometry and that in the geometry characteristic of the ground state, and ii) the difference between the energy of the neutral molecule in its equilibrium geometry and that in the geometry characteristic of the charged system. In general, these two contributions are nearly equal to one another. For the sake of illustration, Figure 1a shows the evolution of the internal

reorganization energy for oligoacenes containing from 3 to 5 rings as a function of the inverse number of rings, as calculated for holes and electrons at the density functional theory (DFT) level (with the B3LYP functional and a 6-31G\* basis set) and as extracted from gas-phase UV photoelectron spectroscopy (UPS) spectra for holes.<sup>[21]</sup> We observe a very good quantitative agreement between theory and experiment for holes; importantly, the  $\lambda_i$  values have globally the same order of magnitude for electrons and holes. In general, in our experience,  $\lambda_i$  varies in the range 0.1–0.5 eV; the smaller values are obtained, as expected, when the extent of geometric deformations is minimal when going from the neutral to the charged state. This is the case, for instance, for oligoacenes<sup>[21]</sup> or phthalocyanines.<sup>[22]</sup> Clearly, the molecular reorganization energy values do not provide markedly different contributions to hole and electron transport in organic conjugated materials.

We now turn to the transfer integral. This parameter proves to be very sensitive to the relative positions of the two interacting molecules, as illustrated in Figure 2. There, we have plotted the evolution of the transfer integral for holes and electrons in a cofacial dimer made of two sexithienyl molecules, upon translation of one molecule along its long axis, as calculated at the semi-empirical Hartree–Fock intermediate neglect of differential overlap (INDO) level.<sup>[20]</sup> The results show major fluctuations in the amplitudes of the transfer integrals. These fluctuations can be fully rationalized from the orbital shape (bonding–antibonding pattern) of the HOMO and LUMO levels. Maxima are observed for holes [electrons] when there is a dominant bonding interaction in the HOMO–1 [LUMO] level of the dimer in the overlapping region and a dominant antibonding interaction in the HOMO [LUMO+1] level; minima are obtained when there is a near compensation between the bonding and antibonding interactions. Importantly, these results contradict the often-expressed idea that



**Figure 1.** a) Evolution of the internal reorganization energy in oligoacenes as a function of the inverse number of rings, as calculated at the density functional theory level for holes (●) and electrons (■), and estimated as twice the relaxation energy extracted from gas-phase UV photoelectron spectroscopy measurements (○) for holes. Adapted from [21]. Copyright 2002 American Physical Society. b) The four energy values to be calculated in the ground (0) and charged (+/-) states to deduce the two components of the internal reorganization energy.



**Figure 2.** Intermediate neglect of differential overlap (INDO) calculated evolution of the HOMO (diamonds) and LUMO (squares) splittings in a dimer formed by two sexithienyl molecules separated by 4 Å when translating one molecule along its long axis and keeping the molecular planes parallel. The full chemical structure of the molecule is shown in Figure 5.

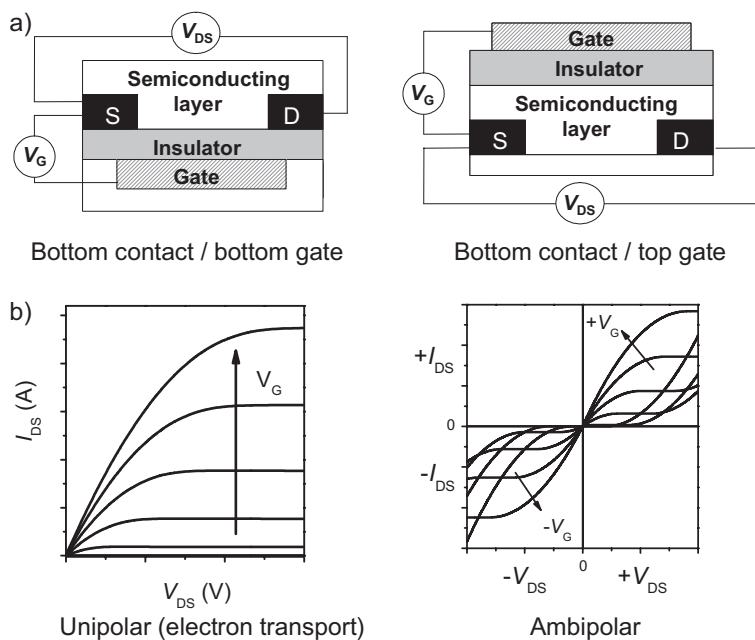
there is a direct relationship between the degree of *spatial* overlap of the two interacting molecules and charge mobility. If this were true, the transfer integral would decrease monotonically with the degree of translation. These results further demonstrate that a very small change in the relative positions of the interacting molecules can switch the relative amplitudes of the HOMO and LUMO splittings. However, in our experience, most of the packing geometries yield transfer integrals for holes and electrons that differ by less than one order of magnitude. Thus, our analysis shows that intrinsically organic materials can be as good electron conductors as hole conductors. However, there is no reason for the electron mobility to be exactly the same as the hole mobility, because each process is governed by molecular parameters that are somewhat different for the two charge carriers.

### 3. Experimental Studies

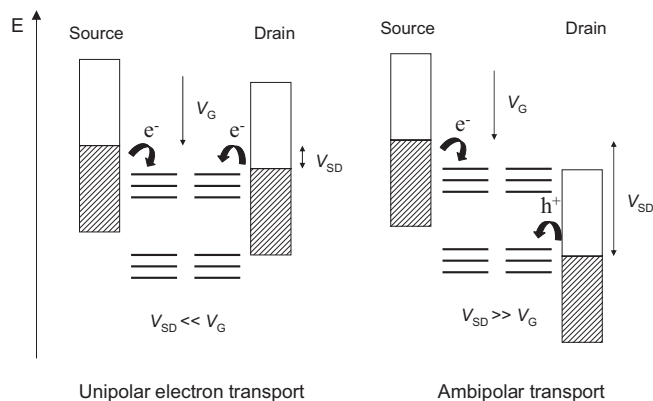
Since a great deal of knowledge on charge transport has been accumulated from the analysis of  $I/V$  characteristics of FETs, we will first describe the working operation of such devices in both unipolar and truly ambipolar modes. In a FET, an organic semiconducting layer is connected to two metallic electrodes (source, S, and drain, D) and is separated from a third electrode (gate, G) by an insulating layer (Fig. 3). When a positive [negative] bias is applied between the gate and the source (generally grounded), electrons [holes] accumulate at the interface between the organic layer and the insulator. At the molecular level, the role of the positive [negative] gate potential is to stabilize [destabilize] the electronic levels and promote a resonance between the Fermi energy of the electrodes and the lowest unoccupied [highest occupied] molecular orbitals, which leads to electron [hole] injection (Fig. 4). The application of a second bias between

the source and drain electrodes induces the migration of the charges and, hence, a unipolar current along the channel. Generally, the gate potential has to exceed a given threshold voltage to observe a rise in current; this is because of the presence of barriers for charge injection in the absence of Ohmic contacts or because of the presence of traps that have to be filled before generating mobile carriers in the channel. The  $I/V$  characteristics of the device are displayed by plotting the current in the channel ( $I_{SD}$ ) versus the applied potential ( $V_{SD}$ ) for various gate potentials ( $V_G$ ) (Fig. 3). Two regimes can be distinguished and are described hereafter in the case of a positive gate bias (i.e., electron accumulation in the channel): i) when  $V_G > V_{DS}$ , there occurs a linear regime, yielding a linear relationship between  $I_{SD}$  and  $V_{SD}$ ; here, the charge carriers are injected from the two electrodes and the charge density profile is uniform throughout the channel (Fig. 4); ii) when  $V_{DS} \geq V_G$ , a saturation regime is obtained in which the channel is “pinched off”; in that case, the larger stabilization of the drain potential compared to the gate potential prevents the occurrence of resonance between the Fermi energy and the unoccupied levels and, hence, the injection of electrons at the drain. This leads to a nonuniform density profile with a depletion region next to the drain. However, if the drain potential is large enough, so that the Fermi energy gets in resonance with the occupied levels, holes can be injected at the drain (Fig. 4); this leads to a situation where electrons and holes are injected simultaneously at the source and drain electrodes, respectively (provided that the source and drain potentials exceed the corresponding threshold voltages  $V_T$ ). The resulting  $I/V$  curves are illustrated in Figure 3.

The frequent lack of observation of efficient unipolar electron transport in the channel of organic transistors upon appli-



**Figure 3.** a) Architecture of an organic FET in two different geometries. b)  $I/V$  characteristics of such a device in the unipolar and ambipolar modes.

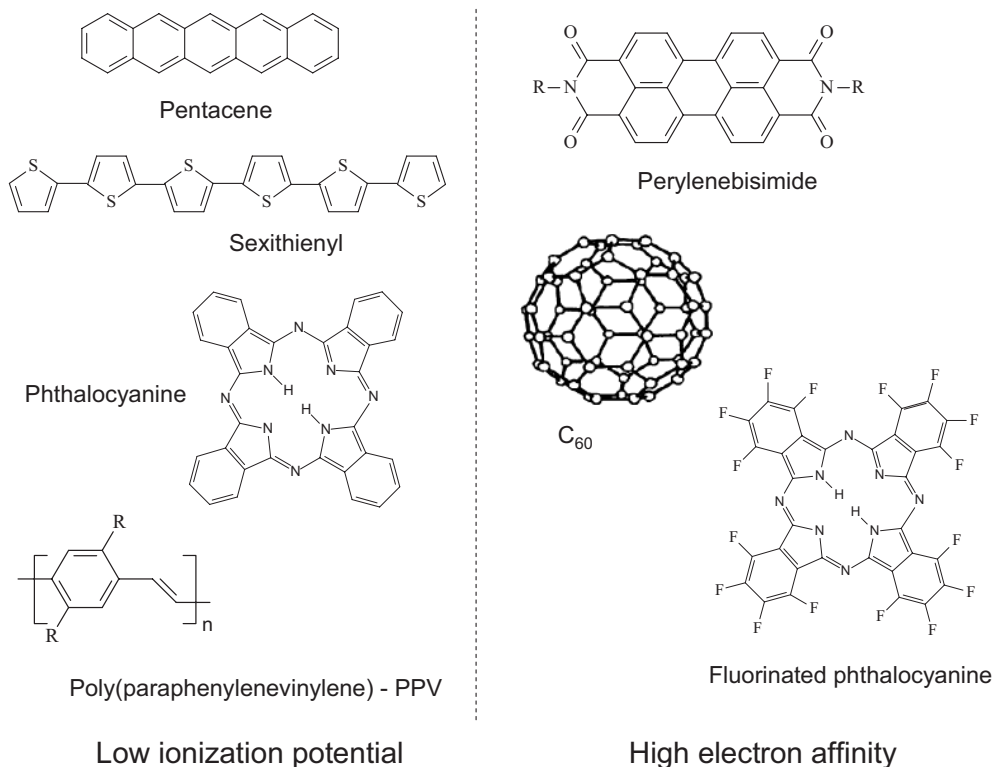


**Figure 4.** Electronic structure diagrams showing the injection of electrons from the source and drain electrodes in the linear regime for unipolar transport (left) and the simultaneous injection of electrons from the source and holes from the drain in the ambipolar regime (right).

cation of a positive gate bias has several origins. For example, in many commonly used device configurations the injection of holes in the organic layer is more favorable than that of electrons. The barrier for hole injection corresponds to the energy difference between the ionization potential of the semiconducting material deposited onto the metal and the work function of the electrode (which actually differs from the bulk Fermi energy when interface dipole effects are taken into account).<sup>[23]</sup> Because the ionization potential of many organic

conjugated systems (on the order of 5–6 eV) has the same order of magnitude as the work function of gold (around 5 eV), which is generally used as electrode material, the barrier for hole injection is small. However, the barrier for electron injection is generally much larger, because the HOMO–LUMO separation is typically on the order of 3–4 eV. Electron injection can be improved by using low-work-function metals such as calcium or magnesium (which are, however, not environmentally stable); another strategy is to use organic molecules with a high electron affinity,<sup>[24]</sup> for example, fullerene derivatives, fluorinated compounds (oligothiophenes, phthalocyanines), or molecules containing carbonyl groups such as perylenebisimide derivatives (see chemical structures in Fig. 5).

Another origin of the poor electron transport is preferential electron trapping at the interface between the semiconducting layer and the gate dielectric. In this respect, recent experimental works have clearly demonstrated that the SiO<sub>2</sub> layers generally used as dielectric exhibit a large number of silanol groups that can capture electrons via their OH moieties, which in turn considerably shifts the threshold voltage.<sup>[25]</sup> Such trapping events can be avoided by using dielectric layers without hydroxyl groups, for example, insulating trapping-free dielectric polymers or SiO<sub>2</sub> layers covered with a self-assembled monolayer. This has enabled the general observation that, in a broad class of conjugated polymer semiconductors, electron and hole mobilities are of comparable magnitude, as expected from the theoretical considerations of their electronic structure outlined above. Observation of electron transport



**Figure 5.** Chemical structures of some widely studied organic semiconductors.

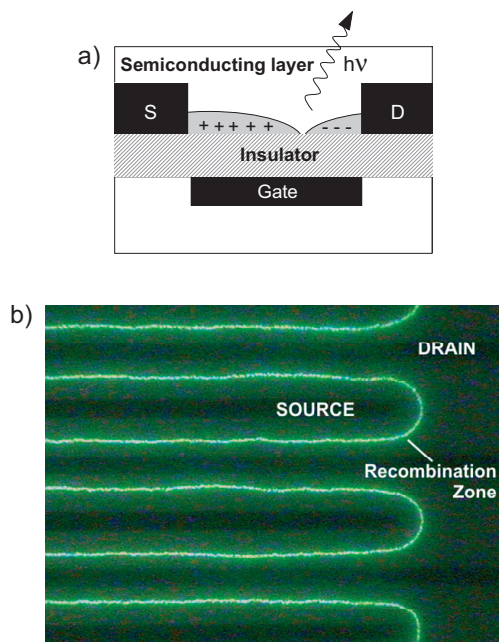
at SiO<sub>2</sub> or other gate dielectrics containing electron-trapping groups that can be easily reduced has only been reported for organic semiconductors with electron affinities larger than about 3.7–4 eV,<sup>[26]</sup> which are expected to be less sensitive to electron trapping. For organic semiconductors with lower electron affinities, either no electron transport or device characteristics with high threshold voltages and poor device stability have been reported at SiO<sub>2</sub> interfaces. It appears clear that similar electron trapping processes can also occur as a result of chemical impurities in the bulk of the organic semiconductor. Therefore, another criterion for the observation of electron transport is a sufficiently low concentration of electron-trapping chemical impurities.

A third problem is related to the fact that the reduction potential of most conjugated molecules is lower than that of water and oxygen,<sup>[27]</sup> which implies that the latter can easily capture electrons from radical anions. Electron transport is thus generally observed only in inert atmosphere, which is an unattractive feature at the technological level. The sensitivity of organic molecules to ambient conditions is partly reduced when the organic thin films can act as an impermeable layer against oxygen and water diffusion; this appears to be the case with fluorinated compounds because of the larger size of the fluorine atoms compared with hydrogen atoms.<sup>[28]</sup> Again, stable electron transport under atmospheric conditions can also be expected in most materials with sufficiently high electron affinities.<sup>[27]</sup> All together, when the proper actions are undertaken, it is clear that whether a particular organic semiconductor exhibits n-type or p-type conduction depends more on the device configuration and environmental conditions employed; when suitable injecting contacts, trapping-free dielectrics, and suitable environmental conditions are provided most organic semiconductors are capable of either electron or hole transport with mobilities of similar magnitude.<sup>[25]</sup>

The next logical step was to explore ambipolar transport, and to uncover systems that can transport electrons and holes alternatively or even simultaneously. This has been demonstrated in many recent experimental studies by means of different approaches that we briefly describe hereafter; a more detailed description can be found in a recent review.<sup>[29]</sup> We depict in Figure 5 the chemical structures of some of the (macro)molecules that have been the most widely investigated in this context. A first strategy is to deposit in the channel a bilayer consisting of a material with a low ionization potential (as hole transporter) and one with a high electron affinity (as electron transporter).<sup>[30–33]</sup> In such a device, the accumulation of electrons and holes is expected to occur in different layers; note that transport in the top layer can be impeded by the roughness of the organic/organic interface, which points to the key role played by the growth conditions.<sup>[32]</sup> The bilayer is often fabricated via vacuum deposition; solution processing is less straightforward because it requires the use of orthogonal solvents to prevent solubilization of the first layer when depositing the second one.

A second approach is to deposit the two materials in the channel under the form of an organic blend by co-evaporation<sup>[34,35]</sup> or by solution processing.<sup>[36,37]</sup> In general, the interpenetration of the two phases leads to a reduction in the hole and electron mobilities compared to the pure phases. Ambipolar transport has also been reported for transistors built from a single material, in particular fullerene<sup>[38,39]</sup> and phthalocyanine<sup>[40]</sup> derivatives and pentacene.<sup>[41]</sup> However, the injection of one type of charge carrier is less optimal because of the large HOMO–LUMO separation. This can be improved by using a narrow-bandgap semiconductor, as exemplified with low-bandgap polymers<sup>[36]</sup> or near-infrared absorbing dyes,<sup>[42]</sup> or two metallic electrodes with different work functions at the source and drain (for instance gold for hole injection and calcium for electron injection).<sup>[43]</sup> The *I*/*V* characteristics can be further optimized by changing the geometry of the device, for example from a bottom contact/bottom gate to a bottom contact/top gate configuration (Fig. 3); the latter is attractive for devices with high injection barriers because charges are not only injected from the edge of the source/drain electrodes but also from the part of the upper surface overlapping the gate electrode.<sup>[44]</sup>

Some ambipolar organic semiconductor FETs have recently been shown to be capable of operating as light-emitting FETs (LFETs), which visualize in a spectacular manner the ambipolar transport properties of organic semiconductors. In these devices, under biasing conditions  $V_G > V_T^e$  and  $V_G - V_{DS} < V_T^h$ , electron and hole accumulation layers are simultaneously present in different portions of the channel, extending from the source and drain contacts into the channel. Light emission originating from recombination of electrons and holes is observed from the boundary between the electron and hole accumulation layer (see Fig. 6). Such light-emitting organic FETs integrate the switching characteristics of transistors and the emission properties of electroluminescent diodes. They offer advantages over the traditional two-terminal light-emitting devices because i) a much higher current density can be injected,<sup>[45]</sup> which should translate into a higher brightness and might open the way to the fabrication of electrically pumped lasers; ii) the location of the emission zone can be controlled and centered away from the electrodes by tuning the concentration profile of holes and electrons in the channel via modulation of  $V_G$  and/or  $V_{DS}$ ;<sup>[44,46,47]</sup> and iii) there occur well-balanced electron and hole injections, because it is very unlikely that one charge carrier can cross the accumulation layer built with the opposite charges. Another advantage, at the fundamental level, is that the geometry of the transistor allows for the potential and emission profiles across the channel to be resolved using local probe microscopy techniques, in contrast to an LED structure. Such ambipolar light-emitting transistors have been fabricated with a horizontal bilayer structure (the two materials are deposited side-by-side by angle evaporation),<sup>[48]</sup> an organic blend,<sup>[34]</sup> or a single component phase.<sup>[44,46,47]</sup>



**Figure 6.** a) Illustration of the formation of two oppositely charged accumulation layers and of light emission upon charge recombination in light-emitting organic field-effect transistors (LFETs). b) Optical image of light-emission from an LFET based on green-emitting poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT) chains.

#### 4. Conclusions and Perspectives

While theoretical calculations have suggested for a long time that organic conjugated materials can be good hole and electron transporters, it is only recently that experimental works have evidenced the signature of ambipolar transport in field-effect transistors. We have discussed in this Progress Report the reasons for which ambipolar transport is expected on the basis of theoretical considerations, and the strategies that can be exploited to observe such transport in actual devices. It is clear now that most organic semiconductors of adequate chemical purity can exhibit n-type, p-type, as well as ambipolar transport properties, provided that suitable injecting contacts, trapping-free dielectrics and environmental conditions are selected. Ambipolar transport fuels many interesting prospects at both fundamental and technological levels. Indeed, it offers a good opportunity to compare electron versus hole mobility in a given material under the same experimental conditions, and to assess their dependence on electric field, temperature, and charge carrier density. Moreover, this should open new device advances through the design of device architectures that make use of these ambipolar transport properties.

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