

How To Make Ohmic Contacts to Organic Semiconductors

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The process of charge injection plays an important role in organic semiconductor devices. We review various experimental techniques that allow injection to be separated from other competing processes, and quantify the injection efficiency of a contact. We discuss the dependence of the injection efficiency on parameters such as the energy barrier at the interface, the

carrier mobility of the organic semiconductor, its carrier density (doping level), the presence of mobile ions, and the sample geometry. Based on these findings, we outline guidelines for forming ohmic contacts and present examples of contact engineering in organic semiconductor devices.

1. Introduction

Organic semiconductor devices are on the verge of widespread commercialization. Organic light emitting diodes (OLEDs), developed for applications in flat panel displays and solid-state lighting, can already be found in consumer electronic products such as car stereos, cell phones, and other appliances.^[1] Organic thin film transistors (OTFTs) are being developed for applications in display backplanes and disposable electronics, such as smart tags.^[2] During the past decade, dramatic advances have been accomplished in their performance, which currently rivals that of amorphous silicon transistors.^[2] Dramatic advances have also been achieved in the performance of organic photovoltaic cells (OPVs), which are currently at levels worthy of consideration for applications in low-cost modules for the production of domestic electricity.^[3, 4]

In all these devices, metal electrodes are utilized to inject charge into (or extract charge from) the organic semiconductor layer(s). In OLEDs, for example, metal electrodes inject electrons and holes into opposite sides of the emissive organic layer(s). As shown in the energy level diagram of Figure 1, electron injection takes place from the Fermi level of the cathode into the manifold of the lowest unoccupied molecular orbitals (LUMO) of the organic layer. An energy barrier φ_e has to be overcome. At the

same time, hole injection (or electron extraction) takes place from the Fermi level of the anode into the manifold of highest occupied molecular orbitals (HOMO) of the organic layer. The two carriers then recombine in the bulk of the organic layer to produce light.^[1]

The process of charge injection dominates the performance of organic semiconductor devices. In OLEDs, for example, charge injection was found to be the most critical factor in determining the device efficiency.^[5] The lifetime of OLEDs was also found to depend on the efficiency of the injection processes.^[6] Despite its importance, the physics of charge injection in organic semiconductors remains poorly understood. One difficulty in extending our knowledge from crystalline to amorphous molecular semiconductors arises because the latter are not conventional semiconductors: Charge transport is no longer by free propagation in extended states, but rather by hopping in a manifold of localized states. A few early models that capture some of the identifying characteristics of organic semiconductors have been developed,^[7–11] and are currently being tested.^[12–14] This Review is not meant to be an exhaustive review on charge injection—this has been the scope of recent review articles.^[15–16]

Another difficulty in understanding injection in organic semiconductors arises from the lack of experimental data. Many injection studies have been carried out in OLEDs where an interfacial layer was inserted between the organic layer and one of the electrodes, and the changes in the device current and radiance were monitored. Such experiments provide, at best, only qualitative information regarding charge injection. OLEDs are bipolar devices and their current and radiance reflect a cascade of multiple processes. For example, inserting a layer between the organic layer and the cathode affects not only the injection of electrons, but also affects other processes, such as

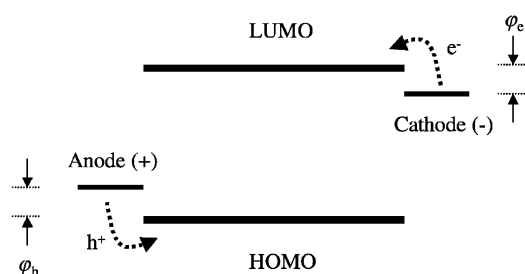


Figure 1. Energy level diagram of a single layer organic light emitting diode. Shown are the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) of the organic semiconductor and the Fermi levels of the anode and cathode. Energy barriers for hole and electron injection (φ_h and φ_e , respectively) are indicated.

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the extraction of holes, the quenching of excitons, and the efficiency of photon extraction from the device.^[1] Techniques that allow the separation of injection from these other processes are needed in order to generate reliable data and help our understanding of the dependence of injection on various materials parameters.

This is the essence of this Review. In it, we discuss the factors that influence the efficiency of the charge injection at a metal/

organic semiconductor contact. We begin by identifying a figure-of-merit for contact performance and use that to define what an ohmic contact is. We then follow a phenomenological approach, where degrees of freedom available to the experimentalist (such as the energy barrier at the contact, the mobility of charges in the organic semiconductor, and so on) are tuned, and the resulting changes in the performance of a contact are discussed. One reason for the phenomenological approach is necessity: Some of the effects that are described in this Review are understood only qualitatively, as a detailed microscopic picture of the injection process is not yet available. As a result, no quantitative analysis of the data is presented here. Rather, emphasis is given on techniques available to the experimentalist for separating the process of charge injection from other competing processes. In addition, a few demonstrations of how one can capitalize on the outcome of injection studies to improve the performance of organic electronic devices are presented. This Review is not meant to be a review of all the interface modification schemes that have been reported in the literature. Rather, we opted to follow a didactic approach, where a small number of examples is discussed in order to illustrate the connection between the fundamentals of injection and device engineering.

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2. What is an Ohmic Contact?

The first step in quantifying the charge injection properties of a metal/semiconductor contact is to define an appropriate figure-of-merit. Let us consider the simple case of a metal electrode injecting electrons in a trap-free semiconductor. The first question we ask is "what is the maximum (electron) current that can flow through the semiconductor"? This is depicted as a solid line in Figure 2. At lower voltages (and neglecting diffusion), the current is determined by the motion of free

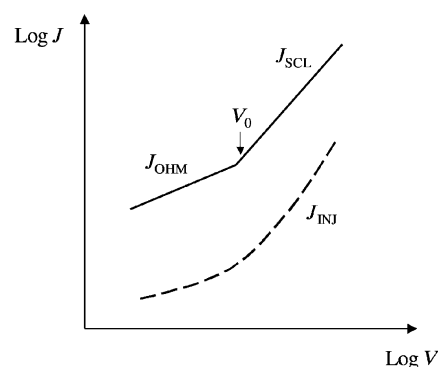


Figure 2. Bulk-limited (solid line) and injection-limited (dashed line) current density versus voltage characteristics for a trap-free semiconductor. The threshold voltage V_0 at which the bulk-limited current turns from ohmic to space charge limited is indicated.

electrons that are present in the semiconductor and the current density is given by Ohm's law,^[17] Equation (1),

$$J_{\text{OHM}} = eN_q\mu \frac{V}{L} \quad (1)$$

where e is the charge of an electron, N_0 is the number of free electrons per unit volume, μ is their mobility, V is the applied voltage, and L is the sample length.

As the voltage increases, electrons injected from the contact begin to outnumber the ones that are initially present inside the semiconductor. This happens when the number of electrons becomes approximately equal to $C \cdot V$, where C is the capacitance of the sample. This is the space-charge-limited (SCL) regime, where the current density is given by the Mott–Gurney law,^[17] Equation (2)

$$J_{\text{SCL}} = \left(\frac{9}{8}\right) \epsilon \epsilon_0 \mu \frac{V^2}{L^3} \quad (2)$$

where $\epsilon \epsilon_0$ is the dielectric constant. The threshold voltage V_0 at which the current turns from ohmic to SCL can be found by equating the two currents and it is given by Equation (3).

$$V_0 = \left(\frac{8}{9}\right) e N_0 \frac{L^2}{\epsilon \epsilon_0} \quad (3)$$

The above discussion assumes that the injecting contact does not pose any limitation in the flow of current through the semiconductor. Therefore, the solid line in Figure 2 represents the density of the *bulk-limited current*, J_{BULK} , which is either ohmic, or space-charge-limited in this example.

However, in many cases, the contact ends up limiting the amount of current that flows through the sample. This is depicted with the dashed line in Figure 2. The current is now smaller in magnitude than that of the bulk-limited current and it is called an *injection-limited current*, with a density J_{INJ} . Its functional dependence is, in the general case, unknown, as it depends on the mechanism of injection. A figure-of-merit for contact performance is the injection efficiency, defined by Equation (4).

$$\eta = \frac{J_{\text{INJ}}}{J_{\text{BULK}}} \quad (4)$$

The injection efficiency measures the “ohmicity” of a contact. According to the above, an *ohmic contact is a contact that satisfies the demands of the bulk for current*. By definition, an ohmic contact supplies the semiconductor with a current density equal to J_{BULK} and has an injection efficiency of one. Studying charge injection means determining how far a contact is from being ohmic. This involves a) finding a way to measure (or estimate) the bulk-limited current and b) measuring the injected current and comparing it to the bulk-limited one.

In Figure 2, one can distinguish two regimes for carrying out injection efficiency measurements: In the first, V_0 is small and the bulk-limited current is space-charge limited—see Equation (2). This regime is of relevance to contacts in OLEDs, where the organic layer is depleted (charge densities of the order of 10^{13} cm^{-3}) and the sample length is of the order of 100 nm.^[1] In such cases, V_0 (of the order of a millivolt) is much smaller than the typical driving voltage for an OLED (a few volts). In the second regime, V_0 is large and it is the ohmic current—see Equation (1)—that represents the bulk-limited current. This regime is of relevance to contacts in OTFTs, where the distance between the source and drain electrodes is tens to hundreds of microns and the organic layer is doped by the field effect. Different ways

of measuring the injection efficiency are required in these two regimes.

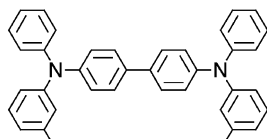
The above discussion was limited to the ideal case of a trap-free semiconductor. Although trap-free transport (especially for holes) has been observed in numerous organic semiconductors,^[18] the presence of traps in many organic semiconductors of interest to applications makes the evaluation of injection efficiency a bit more challenging. A discussion of these cases is beyond the scope of this Review. An additional complication arises from the fact that mobilities in organic semiconductors are electric field dependent.^[18] For example, the density of the SCL current is not given by Equation (2), but rather by a more complex (yet, still analytical) expression.^[19, 20]

As far as experimental considerations are concerned, one needs to be careful about built-in potentials, especially in thinner samples. Current–voltage curves that look like the solid line in Figure 2 should not be taken as evidence for bulk-limited current. Often, the inflection observed in these curves is an artifact, arising from a failure to account for a built-in potential.^[21] Moreover, contacts where the metal is deposited on the organic (top contact) layer often behave differently than contacts where the organic layer is deposited on the metal (bottom contact). Top contacts are usually found to have a lower injection efficiency, attributable to damage of the organic layer during the deposition of the metal.^[22] Furthermore, the injection efficiency of certain top contacts was found to evolve in time, which implies healing of the deposition-induced damage.^[22] Finally, oxidation of the metal, reactions between the metal and the organic layer, contamination at the interface, delamination of the metal, and other such phenomena will certainly influence the injection efficiency. Of course, one could use injection efficiency measurements to follow such phenomena. However, for understanding the fundamentals of charge injection in organic semiconductors, it is important to use trap-free organic semiconductors (typically hole transport materials) and bottom contacts made with air-stable metals. These are the cases discussed in this Review.

Keeping these caveats in mind, we are now ready to begin turning knobs and observing the dependence of injection efficiency on the various materials parameters.

3. Interface Energetics

By looking into Figure 1, one might expect that the heights φ_e and φ_h of the energy barriers at the cathode and anode play a critical role in controlling electron and hole injection, respectively. Abkowitz et al.^[23–24] were the first to propose a technique for measuring injection efficiency, which they used to study the influence of interface energetics on hole injection. The technique is applicable in the regime where V_0 is small, and the SCL current represents the bulk-limited current. It was applied to study the efficiency of hole injection from various metals in the organic semiconductor *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1'-bis-phenyl]-4,4'-diamine dispersed into polycarbonate (PC:TPD). This material, which is the “fruit fly” of charge-transport experiments in organic semiconductors, is a solid solution of the aromatic molecule TPD (structure shown in Scheme 1) in the



Scheme 1. Structure of TPD.

inert host PC. It can transport holes^[25] which move via hopping among TPD molecules.

The essence of this elegant technique is shown in Figure 3. The PC:TPD layer is sandwiched between two electrodes. The one on the left forms the contact-under-test, the one on the

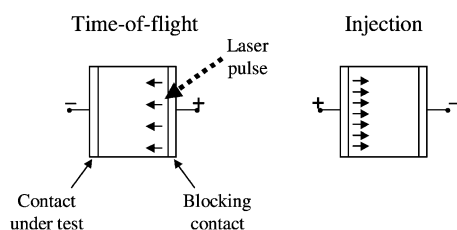


Figure 3. Layout of an experiment for the measurement of injection efficiency. The bias indicated is appropriate for a hole-transporting organic semiconductor.

right forms a “blocking” contact, that is, a contact that does not inject holes.^[26] The measurement is performed in two steps. In the first step (left hand side of Figure 3), the polarity of the applied voltage is selected to be such that the contact-under-test is under reverse bias. Since the other contact is blocking and PC:TPD is only capable of transporting holes, there is very little current flow. This allows one to perform a time-of-flight experiment (TOF)^[18] and measure the hole mobility. TOF involves shining a nanosecond laser pulse from a nitrogen laser, which enters the PC:TPD from the side of the blocking contact and is strongly absorbed within a short distance. The sheet of photo-induced holes created near the blocking contact is made to transverse the sample under the influence of the applied bias. The motion of holes produces a photocurrent, which is measured as a function of time. When the holes arrive at the opposite electrode, the photocurrent drops to zero. The hole mobility is obtained from the transit time, which is the time it takes the holes to transverse the sample. With knowledge of the mobility, the SCL current can be calculated. In the second step (right hand side of Figure 3), the polarity of the applied bias is reversed and the current injected from the contact-under-test is measured directly. The ratio of the two currents gives the injection efficiency.

This technique allows the easy measurement of the injection efficiency in organic semiconductors with a low charge density. Apart from a straightforward determination of mobility, the TOF experiment is very sensitive to the presence of traps and can be used to check the purity of a material. One of the difficulties associated with this technique is that it requires fairly thick samples (of the order of a few microns), so that TOF can be performed. This is difficult to do with certain small molecules, which tend to crystallize and give films that crack at these

thicknesses. As an alternative, transient SCL injection can be used to measure the mobility and perform injection efficiency measurements in thinner films.^[27]

Figure 4 shows the injection efficiency of various contacts as a function of the energy barrier at the contact. The latter was estimated by assuming the Schottky–Mott picture for interface

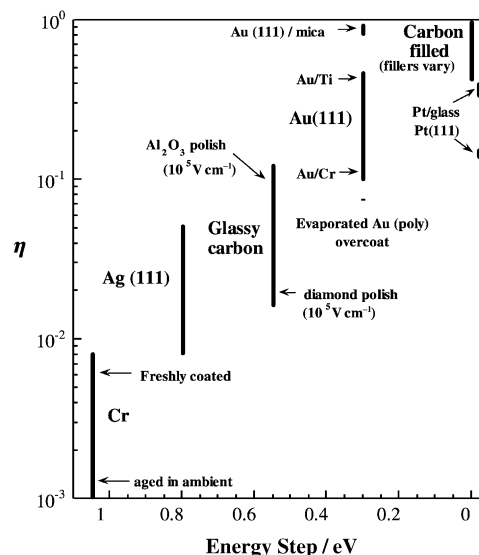


Figure 4. Injection efficiency versus energy barrier at the contact. Reproduced from ref. [23] with permission.

energetics, that is, by subtracting the work function of the metal from the ionization potential of TPD (holes are injected into the HOMO manifold of the TPD molecules^[28]). Overall, the injection efficiency was shown to increase dramatically as the barrier height at the interface decreased. The contacts became ohmic for low barrier heights. Therefore, *minimizing the energy barrier at a metal/organic semiconductor interface helps make a contact ohmic*. This is a well-known designer rule in organic semiconductor devices, in which low (high) work function metals are used for electron (hole) injection. The data of Figure 4 were the first direct experimental confirmation of this rule.

The fact that the injection efficiency scales with the work function of the metal indicates that the interactions between the organic semiconductor and the metals are not severe enough to cause pinning of the Fermi level. This is unlike the case of silicon, where surface states usually result in pinning of the Fermi level.^[29] It also shows that interface dipoles^[30] are negligible in these contacts. This topic is currently at the center of a debate in the organic electronics community.^[31] Energy barriers (measured with photoelectron spectroscopy) of contacts prepared under ultrahigh vacuum (UHV) show a large interface dipole that invalidates the Schottky–Mott picture.^[32, 33] On the other hand, in addition to the data of Figure 4, there is substantial evidence from device studies,^[1] as well as photoelectron spectroscopy measurements,^[34] that contacts prepared under realistic manufacturing conditions (glove box, high vacuum) show negligible dipoles. The discrepancy has probably to do with extrinsic factors. For example, it is possible that polar solvent molecules,

or water molecules from the ambient surroundings, are trapped at the interface during sample preparation and orient in such a way that they cancel the interface dipole. This is in line with recent photoelectron spectroscopic measurements, where interface dipoles in contacts prepared under UHV conditions were found to decrease upon exposure of the contacts to ambient conditions.^[35] Clearly, more experiments are required to settle this important issue.

In certain devices, there is limited freedom in the choice of electrode materials. For example, indium tin oxide (ITO) is often used as the anode in OLEDs due to its combination of transparency and conductivity.^[11] Several ways have been developed to engineer the interface energetics and decrease the energy barrier for hole injection in these cases. These include the use of self-assembled monolayers,^[36–37] various treatments of the surface of the electrode,^[38] and the insertion of thin layers of other organic,^[6, 39] and inorganic layers.^[40–43] An example of using injection efficiency measurements to optimize contacts in OLEDs was discussed by Shen et al.^[44] These measurements revealed that contact between ITO and TPD creates a bottleneck in current flow, due to the presence of a sizeable energy barrier. By depositing a 5 Å film of Pt on ITO, it was possible to increase the ITO work function by 0.6 eV and make an ohmic contact to TPD. This led to a dramatic improvement in the current and radiance of OLEDs using an ITO/TPD contact (Figure 5). A similar study was performed by Forsythe et al.,^[45] to elucidate the role of copper phthalocyanine (CuPc) between ITO and a TPD derivative.

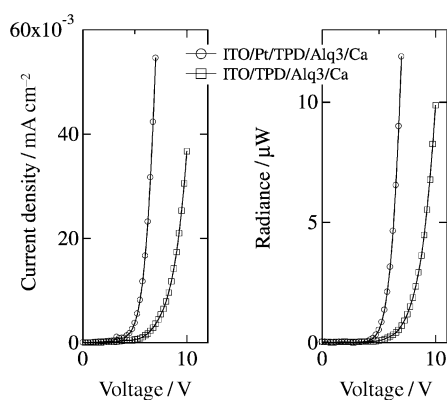


Figure 5. Current density and radiance versus voltage characteristics of ITO/TPD/Alq₃/Ca/Al devices with (open circles) and without (open squares) the Pt modified ITO. Reproduced from ref. [44] with permission.

4. Charge Carrier Mobility

In the early literature on OLED, it was implied that charge injection in these devices was problematic due to the low carrier mobility of organic semiconductors. Shen et al.^[46] used the organic semiconductor PC:TPD, to investigate the dependence of injection efficiency on the hole mobility. By changing the relative concentration of TPD and PC (thereby changing the distance between hopping sites), samples with mobilities

ranging from 10^{-6} to 10^{-3} cm² V⁻¹ s⁻¹ were prepared. ITO was used as the hole-injecting electrode. The Abkowitz technique^[23] was used to measure the injection efficiency.

In Figure 6, the SCL current density and the injected current density are shown for six samples with different mobilities. The former is shown to be proportional to the mobility, in agreement

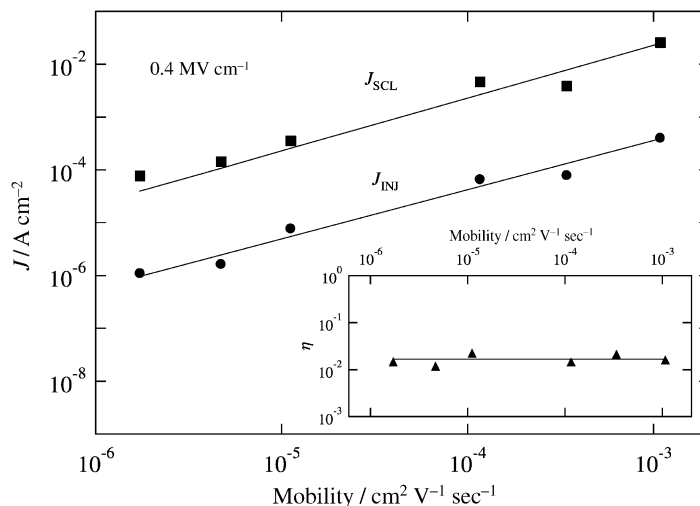


Figure 6. Mobility dependence of the space charge limited and the injection-limited current densities for six PC:TPD samples at 0.4 MV cm⁻¹. The relative TPD concentration in PC was equal to 30, 40, 50, 60, 80, and 100 %, respectively. The solid lines are fits with slopes of 1 and 0.91 ± 0.07 , respectively. Inset: Mobility dependence of the injection efficiency in the PC:TPD samples at 0.4 MV cm⁻¹. Reproduced from ref. [46] with permission.

with Equation (2). The injected current was also found to be proportional to the mobility, which results in an injection efficiency that is independent of mobility (inset of Figure 6). The current remained injection-limited in all samples, regardless of mobility. Therefore, *changing the mobility of an organic semiconductor does not help to make the contact ohmic*. The reason for this behavior was first discussed in 1966.^[47] In low mobility materials, injected carriers spend a long time near the contact before escaping into the bulk, and are therefore subject to recombination with their image charge.^[10] A different interpretation for this effect has also been proposed.^[9]

5. Charge Density

Recent experiments indicate that the presence of a high charge density near the interface with organic semiconductors improves charge injection.^[48–50] The majority of evidence comes from OLED studies, where the introduction of a doped organic layer between the metal and an (undoped) organic semiconductor improved device performance. Understanding this effect requires a direct measurement of the injection efficiency in contacts between metals and doped organic semiconductors. This is difficult to do with the Abkowitz technique. First, the TOF technique is not suitable for doped materials.^[18] Second, in highly doped samples, V_0 is large and the bulk-limited current under typical voltages might be ohmic. Estimating the ohmic

current requires knowledge not only of the mobility, but also of the carrier density.

A technique that allows the measurement of the injection efficiency in this case involves preparing two samples that have different metal electrodes, but are otherwise identical.^[51] The first sample has electrodes that make ohmic contacts to the organic semiconductor, and it is used to measure the bulk-limited current. The second sample has electrodes that form the contact under test, and it is used to measure the injected current. The ratio of the currents in the two samples gives the injection efficiency of the contact under test. This, however, sounds like a "chicken and egg" problem: An ohmic contact is needed in order to define the ohmicity of a contact.

Luckily, there is an additional way to probe contact ohmicity. This is shown in Figure 7. The sample geometry, shown in the inset, consists of a quartz substrate, two metal electrodes (shown

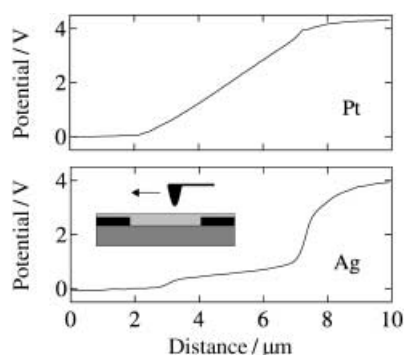


Figure 7. Scanning Kelvin probe traces on PC:TMTPD samples with Pt and Ag contacts. The sample configuration is shown in the inset. The distance between the two electrodes was 5 μm .

in black), and an organic layer deposited on top. The current here flows in the plane of the substrate. The organic semiconductor PC:TMTPD (where TMTPD is a TPD derivative) was used for these experiments and was doped p-type as discussed below. Using electric force microscopy in the Kelvin probe configuration, one can profile the potential drop across the sample.^[52] In the case of the sample with Pt electrodes, the potential dropped linearly in the PC:TMTPD (top panel in Figure 7). This is the behavior expected when an ohmic current flows through a sample. On the other hand, in a similar sample with Ag electrodes, a large potential drop was observed at the injecting contact (bottom panel in Figure 7).^[53] This potential drop reflects a high contact impedance and confirms the nonohmicity of the Ag/PC:TMTPD contact. As expected, the current in the sample with the Ag contacts was found to be lower than that in the sample with the Pt electrodes. The ratio of the two currents gave the injection efficiency for the Ag/PC:TMTPD contact.

This comparative technique was used to measure the injection efficiency of the Cr/PC:TMTPD contact as a function of p-type doping of the PC:TMTPD.^[51] Doping was performed by replacing a fraction x of the TMTPD molecules with their salt TMTPD⁺:SbF₆⁻.^[54] The results are shown in Figure 8. The injection

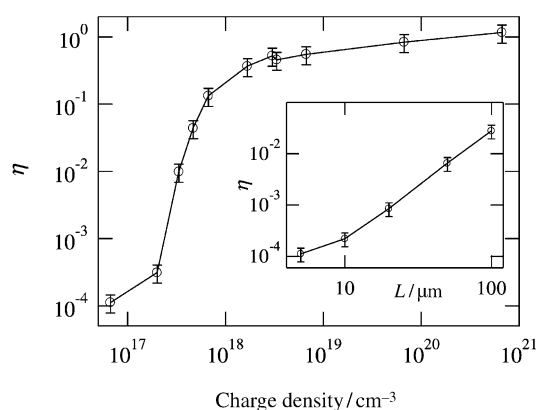


Figure 8. Evolution of the injection efficiency of the Cr/PC:TMTPD contact as a function of doping, for $L = 5 \mu\text{m}$ and $E = 10^5 \text{ V cm}^{-1}$. Inset: Evolution of the injection efficiency of the Cr/PC:TMTPD contact as a function of distance between the two electrodes L , for $E = 10^5 \text{ V cm}^{-1}$. The TMTPD sample was p-doped with a hole density of $6.7 \times 10^{16} \text{ cm}^{-3}$.

efficiency increased dramatically with doping and the contact became ohmic at higher hole densities. The exact amount of doping required to make the contact ohmic depended on the exact value of the energy barrier at the contact, as well as on the applied electric field and other parameters, but the trend was universal. Therefore, *doping an organic semiconductor helps to make a contact ohmic*. Photoelectron spectroscopy at metal/doped organic semiconductor contacts suggests that a mechanism similar to band bending in crystalline inorganic semiconductors is at work.^[55–57] This means that doping enhances injection by decreasing the height and width of the energy barrier at the contact. However, a quantitative description of this effect is presently not available.

A demonstration of using doping to improve contacts in OLEDs is shown in Figure 9. Au (work function of 5.1 eV^[58]) is a bad electron injector in the conjugated polymer poly[2-methoxy, 5-(2-ethylhexoxy)-1,4-phenylene vinylene] (MEH-PPV). As a

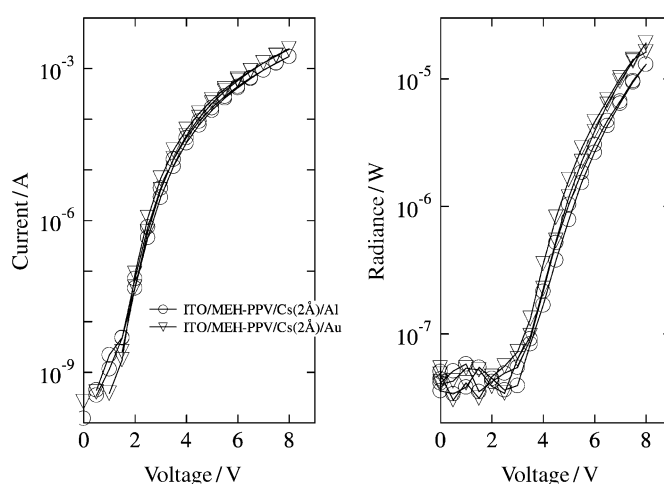


Figure 9. Current versus voltage and radiance versus voltage characteristics of two MEH-PPV light emitting diodes with Al and Au cathodes. The MEH-PPV layer was doped by evaporating 2 Å of Cs before depositing the cathodes. Reproduced from ref. [59] with permission.

result, OLEDs utilizing Au cathodes emit very little light.^[21] On the other hand, Al (work function of 4.2 eV^[58]) is a considerably better electron injector than Au. MEH-PPV based OLEDs with Al cathodes show relatively intense emission.^[21] However, when MEH-PPV is doped, both Al and Au form ohmic contacts for electron injection.^[59] This is shown in Figure 9, where two OLEDs with Au and Al cathodes, respectively, show the same performance. Doping of the MEH-PPV was achieved by evaporating approximately 2 Å of Cs just before depositing the cathode, a procedure known to lead to n-type doping in organic semiconductors.^[60–61]

6. Presence of Mobile Ions

The presence of mobile ions can have beneficial effects to charge injection. This is the idea behind the so-called light emitting electrochemical cells (similar to light emitting diodes, but with an organic layer that has a large quantity of mobile ions).^[62] These devices show a high efficiency, indicating that injection of both electrons and holes is very efficient. The mechanism is believed to involve the accumulation of mobile ions near the contact, which creates a very large electric field and decreases the barrier to charge injection.^[63]

A direct measurement of the injection efficiency in such systems can be obtained with the comparative method described in the previous section. However, there is a simpler measurement one can perform in order to demonstrate contact ohmicity. The measurement relies on the fact that a bipolar device, such as the OLED shown in Figure 1, is expected to show a higher current and radiance in the forward than in the reverse bias. This rectification is due to the fact that the anode injects holes more efficiently than it does electrons (and the opposite is true for the cathode).

This is clearly not the case for the data shown in Figure 10, where a lack of rectification is observed. The data were recorded in a device made from the organometallic semiconductor $[\text{Ru}(\text{bpy})_3]^{2+}(\text{PF}_6^-)_2$ (bpy is 2,2'-bipyridine) sandwiched between a Pt anode and a Au cathode. The PF_6^- ions in this material are mobile at room temperature and drift under the influence of an applied bias.^[64] Under forward bias, they accumulate near the anode (Pt electrode), creating a strong electric field that enhances hole injection. At the same time, $[\text{Ru}(\text{bpy})_3]^{2+}$ ions are left uncompensated near the cathode (Au electrode), which enhances electron injection. When the bias is reversed, the ions accumulate near the cathode (Au electrode) and the situation is reversed. The ionic space charge near the contacts enhances hole injection from Au and electron injection from Pt. The absence of rectification seen in Figure 10 indicates that under the influence of the ionic space charge, Au and Pt become capable of injecting both electrons and holes, with identical efficiency. In other words, both contacts become ohmic, for both electron and hole injection.^[65] Therefore, *introducing mobile ions into an organic semiconductor helps to make a contact ohmic*. It should be noted that for this enhancement in injection to take place, a high density of mobile ions is required. The reader is referred to ref. [63] for a discussion on this issue. Related

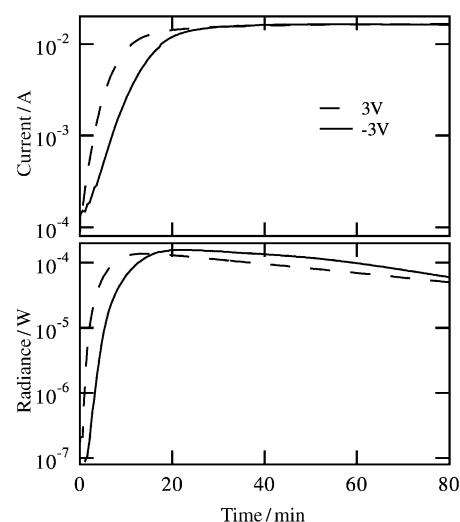


Figure 10. Temporal evolution of current and radiance in a Au/ $[\text{Ru}(\text{bpy})_3]^{2+}(\text{PF}_6^-)_2/\text{Pt}$ device under forward (dashed line) and reverse (solid line) bias.

synergistic effects between ionic and electronic carriers have been observed in inorganic materials.^[66]

Of note is the transient response of the current and radiance. Under forward bias, the device reaches the maximum current and radiance faster than it does under reverse bias. This has to do with the asymmetry between the two electrodes. Since Pt has a higher work function than Au, the initial barriers for hole and electron injection (from Pt and Au, respectively) are lower under forward bias. Therefore, fewer PF_6^- ions need to migrate near the Pt electrode in order to make the contacts ohmic. On the other hand, under reverse bias, the barriers for hole and electron injection (from Au and Pt, respectively) are larger. Therefore, more PF_6^- ions need to migrate (now near the Au electrode) to make the contacts ohmic. This is an interesting effect where the contact behavior evolves in time, from current-limiting, to ohmic.

7. Sample Geometry

The geometry of the sample affects the properties of a contact. A simple demonstration of this effect is shown in the inset of Figure 8. The injection efficiency of the Cr/PC:TMTPD contact was measured as a function of the distance between the two Cr electrodes (the sample configuration is presented in the inset of Figure 7). The injection efficiency was shown to increase with L .^[51] Therefore, *increasing the distance between the two electrodes helps to make a contact ohmic*. This brings home a very important point: Contacts are device parameters, hence their performance is not only determined by the physics (energetics, doping, etc.) at the contact, but always needs to be considered in the context of the whole device. The explanation for the length dependence is simple: Consider two resistors in series, one that corresponds to the contact (R_C) and one that corresponds to the bulk of the organic semiconductor (R_B). In

this context, by rewriting Equation (4), the injection efficiency can be expressed by Equation (5).

$$\eta = \frac{R_B}{(R_C + R_B)} \quad (5)$$

As the distance L between the two contacts increases, the resistance of the semiconductor bulk increases proportionally. When $R_B \gg R_C$, the contact becomes ohmic ($\eta \approx 1$).

Equation (5) describes the relationship between contact resistance, which is often used in traditional semiconductor devices to describe contacts, and injection efficiency. Whereas the former expresses an absolute property of the contact, the latter expresses how well the contact performs in the context of the whole device, that is, it directly measures contact ohmicity. One should keep in mind that due to the field dependence of mobility,^[18] the bulk resistance R_B of organic semiconductors is electric field dependent. As a result, the contact resistance (which is also field dependent) is not such a practical figure-of-merit for organic semiconductor contacts.

8. Towards Molecular Electronics

A few comments are in order regarding the ultimate limits of contact behavior. In the previous section, we saw that as the distance between the two electrodes becomes smaller, a nonohmic contact will increasingly act as a bottleneck in the flow of current. This has obvious implications for the field of molecular electronics, where L can be as small as a single molecule.^[67] In devices based on chemisorbed monolayers of organic semiconductors, bonding leads to strong interactions between the organic layer and the metals. As a result, metal/molecule/metal devices are often treated as a single entity, without explicit separation between contact and “bulk”.^[68] However, recent transport measurements on aliphatic self-assembled monolayers of varying length revealed a clear separation between contact and “bulk” resistance.^[69] Given the interest in molecular electronic devices, the question arises as to how far down towards this regime do concepts such as injection efficiency, ohmic, and SCL current extend.

Klein et al.^[70] discussed the scaling of current and contact behavior down to the regime where the device consists of just a few hopping sites between two electrodes. Figure 11 shows the results of a simulation of current flow in a sample with $L = 5$ molecular layers. The open circles represent the current from an ohmic contact. The current shows an overall SCL behavior—the solid curve represents the Mott–Gurney law of Equation (2)—but with a threshold voltage that corresponds to Coulomb blockade and a Coulomb staircase. The “jumps” in the current correspond (roughly) to the addition of the first, second, third, and so on, electron in the device. In the regions between these jumps, the current is ohmic.

In this regime, the contact consists of the metal electrode and the first molecular layer inside the organic semiconductor. What makes the contact ohmic is the availability of charge in the first molecular layer. If enough charge is available to move upon request, then the contact is ohmic. In contrast, if there is not enough charge in the first molecular layer, the current is injection

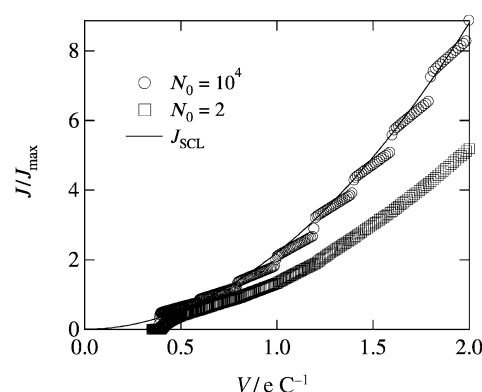


Figure 11. Calculated current density versus voltage for a sample that consists of five molecular layers between two metal electrodes, at $T = 1$ K. Two curves, for different amounts of charge at the first molecular layer inside the organic semiconductor, are shown. The solid line is the prediction of the Mott–Gurney law, Equation (2). As in ref. [70].

limited (shown in Figure 11 as the open squares). Extending the concept of injection efficiency to this regime is, therefore, straightforward.

9. Conclusions

In conclusion, the injection efficiency, defined as the ratio of injected to bulk-limited current, is a good figure-of-merit for metal/organic semiconductor contacts. A contact is ohmic if it is able to supply the semiconductor with bulk-limited current. By definition, the injection efficiency of an ohmic contact is equal to one. The injection efficiency is independent of the mobility in organic semiconductors. It increases when the barrier height at the interface is lowered; when the organic layer is doped; and when mobile ions are introduced. It was demonstrated that these observations can be applied to optimize contacts in organic electronic devices. Finally, it was discussed that contacts are device parameters, hence their injection efficiency increases with the distance between the two electrodes.

It is important to realize that our understanding of the fundamentals of injection in organic semiconductors is still in its infancy. A great deal of work is required in order to obtain a quantitative understanding of the observations discussed above. We hope this article will stimulate further work in this exciting field along these lines.

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