Contact Resistance in Ambipolar Organic Field-Effect Transistors Measured by Confocal Photoluminescence Electro-Modulation Microscopy

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INTRODUCTION

An appealing perspective inherent to organic field-effect transistors (OFETs) is the opportunity to engineer truly ambipolar devices with a relatively low effort. The defining feature of these ambipolar OFETs (aOFETs) is their ability to transport both holes and electrons effectively. Single-layer ambipolar organic field-effect transistors enable the investigation of different mechanisms in hole and electron transport in a single device since the device architecture provides a controllable planar pn-junction within the transistor channel. However, a direct comparison of the injection barriers and of the channel conductivities between electrons and holes within the same device cannot be measured by standard electrical characterization. This article introduces a novel approach for determining threshold gate voltages for the onset of the ambipolar regime from the position of the pn-junction observed by photoluminescence electro-modulation (PLEM) microscopy. Indeed, the threshold gate voltage in the ambipolar bias regime considers a vanishing channel length, thus correlating the contact resistance. PLEM microscopy is a valuable tool to directly compare the contact and channel resistances for both carrier types in the same device. The reported results demonstrate that designing the metal/organic–semiconductor interfaces by aligning the bulk metal Fermi levels to the highest occupied molecular orbital or lowest unoccupied molecular orbital levels of the organic semiconductors is a too simplistic approach for optimizing the charge-injection process in organic field-effect devices.

KEYWORDS: electro-modulation microscopy, organic field-effect transistors, threshold voltages, contact resistance, photoluminescence

However, in most cases, OFETs are shown to either transport only holes (p-type device) or only electrons (n-type device) efficiently. Prevalent explanations for this discrepancy between theoretical expectation and practical implementation is due to two possible root causes: differences in charge-injection barriers and in device channel conductivities between electrons and holes. Firstly, the energy barrier for injecting holes from the contact into the highest occupied molecular orbital (HOMO) of the OSC usually are different from the energy barrier for injecting electrons into the lowest unoccupied molecular orbital (LUMO). Purely unipolar transport in OFETs occurs if only one of the charge carrier types can overcome the injection barrier into the OSC. The second cause of purely unipolar transport considers differences in the transport process of electrons and holes. Different conductivities can be caused by the differently effective orbital...
overlap of the HOMOs (hole transport) and LUMOs (electron transport) of neighboring molecules. Additionally, the amounts of trapping sites selective to only one carrier type can be different as well.\textsuperscript{2,3}

The parameters quantifying charge transport and injection in OFETs are the charge mobilities \(\mu_h\) and \(\mu_e\), and the threshold gate voltages \(V_{th,h}\) and \(V_{th,e}\) for holes (h) and for electrons (e). The threshold gate voltages express the overall device resistance, including contributions from the contact and channel resistances. An ambipolar transport regime can be observed if \(V_{th,e} < V_e < V_{th,h} + V_d\), where \(V_e\) denotes the applied gate bias and \(V_d\) the drain–source bias (Figure 1). Understanding the origin of \(V_{th(eh)}\) is therefore the key for achieving a well-balanced ambipolar transport regime.

![Figure 1](image_url)

**Figure 1.** Conditions for ambipolar transport for \(V_{th,e} < V_e < V_{th,h} + V_d\). (a) Structure of the device under investigation (b), chemical structure of NT4N (c) and energy-level diagram of the gold electrode/active layer structure. The HOMO and LUMO energy values are indicated together with the Fermi level of the gold contacts (d).

To investigate the differences between the electron and hole transport in field-effect bias conditions, ideally the contributions of the contact and channel resistances to \(V_{th,e}\) and \(V_{th,h}\) should be compared in a single device. Although \(\mu_{el(h)}\) and \(\mu_{el(e)}\) are routinely extracted from electrical transfer or locus characteristics\textsuperscript{18,19} this method cannot determine the separate contributions of contact and channel resistances. The most common approach adopted to collect the separate contributions to the gate-threshold voltages is to implement the transmission-line method.\textsuperscript{20–23} Here, the channel and contact resistances are investigated by comparing \(V_{th}\) obtained in several devices with different channel lengths. The drawback of this method is the intrinsic high variability in device fabrication, and thus, the device-to-device dependence of the extracted values of \(V_{th}\). An alternative approach for measuring the contributions of the channel and contact resistances of holes and electrons in a single device would therefore be highly beneficial for systematic investigations of the ambipolar regime.

Direct observation of the pn-junction, or a recombination zone (RZ), position in an aOFET channel as a function of \(V_{ds}\) and \(V_g\) offers an alternative method for characterizing the device electrical behavior.\textsuperscript{2,5,7,13,14,24} In the case of light-emitting OFETs (OLETs), RZ positions can be estimated by default by observing the electroluminescence (EL) originating from the RZ on an optical microscope setup.\textsuperscript{4,13,24} However, the observed light-emission region is generally broader than the RZ, as after their generation the bound electron–hole pairs (excitons) diffuse from the RZ before they recombine to emit light. The light-emission zone location is thus only an approximation of the real RZ position. Moreover, ambipolar field-effect devices neither necessarily emit light under all bias conditions, nor necessarily emit light at all, so that in many cases the observation of the EL cannot be used.

In a previous article, we presented photoluminescence electro-modulation microscopy (PLEM) as a unique optical tool for observing the charge distribution in the channel of operating OFETs.\textsuperscript{25} This technique measures the quenching of laser-generated excitons by the proximity of charges in the organic transport layer.\textsuperscript{26} The in-plane mapping of the exciton-quenching signal is directly correlated to the charge-density distribution.\textsuperscript{25} This feature enables to observe the RZ position in real-working aOFETs. Indeed, the total amount of charge carriers decreases within the RZ, given the formation of excitons and the annihilation of opposite charges. The spatial localization of the RZ is thus correlated to a negative quenching signal (i.e., increase of the active layer photoluminescence).

Here, we demonstrate the use of PLEM on a single-layer light-emitting ambipolar OFET, based on the small molecule (2,20-(2,20-bithiophene-5,50-diyl)bis(5-butyl-SH-thieno[2,3-c]pyrrole-4,6)-dione (NT4N)). This compound presents very different electrical parameters for holes and electrons in thin-film transistors,\textsuperscript{7} so that NT4N is a good candidate for studying the different charge transport mechanisms for both charge carrier types in a single device. We compared the experimental RZ position collected at different \(V_g\) values with the expected values obtained by two theoretical models published in the literature.\textsuperscript{3,28,29} Using the electrical transport parameters determined by the standard electrical characterization of the device, neither of the two models can reproduce the observed RZ positions. Conversely, the \(V_{th,h}\) and \(V_{th,e}\) values necessary to describe the experimental PLEM signals deviate strongly from those obtained by the standard electrical characteristics of the same device.

We propose that the observed difference in the \(V_{th(eh)}\) values obtained by electrical and optical methods is caused by the different bias regimes adopted during the measurements (i.e., unipolar vs ambipolar regimes). In the unipolar regime, \(V_{th(eh)}\) is determined by the overall device resistance, including the contact and channel resistances. Once the \(V_{th(eh)}\) are extracted
in the ambipolar regime as in the case of the localization of the RZ position, the $V_{th(h)}$ values define the onset of the ambipolar regime for the two different charge carriers. Indeed, the unipolar channel formed by majority charge carriers is already established at that bias conditions, and the extracted $V_{th(h)}$ value now defines the gate-threshold voltage that enables an efficient injection of the second charge carrier type, i.e., the minority charge carrier. Hence, by determining the bias-dependent RZ position, the contact resistances can be directly extracted. Moreover, comparing these values to the $V_{th(h)}$ values obtained from standard electrical characterization it is possible to determine the channel resistance of aOFETs independently. The obtained contact resistances for NT4N highlight that, contrary to what is expected by simply comparing the contact Fermi-level and OSC frontier molecular orbital energy values, hole injection into the studied OSC is strongly hindered, while electron injection only suffers from a small contact resistance. In conclusion, determining the electrical parameters from the mapping of the RZ position in the device channel enables to separate contributions from charge injection and charge transport in ambipolar field-effect transistor devices.

### METHODS

**Device Fabrication.** In our experiments, we used OFETs in a top-gate/bottom-contact geometry with a transparent glass substrate to allow the optical probing of the device from the substrate-side. Thus, investigation of the organic semiconductor beneath the injecting electrodes was possible. Consequently, an indium tin oxide-based gate electrode onto which a 450 nm-thick poly(methyl methacrylate) (PMMA) layer was spin-coated was implemented. A 15 nm-thick layer of thermally evaporated NT4N at a 0.1 Å/s deposition rate formed the active semiconductor. The injecting electrodes were realized by two 30 nm-thick gold contacts with a source−drain channel length of $L = 70 \, \mu m$. To protect the organic layer from oxygen and water during the measurements, all devices were encapsulated in a nitrogen glove box.

**Electrical Characterization.** We characterized the devices electrically by measuring their $I−V$ characteristics using a semiconductor parametric analyzer (Agilent B1500). The individual measurement points of the staircase sequences were separated by 2 V. After increasing the voltage, the current could stabilize for 200 ms. The integration time of the subsequent measurements was ca. 100 ms. In the present article, we reported the transfer and locus characteristics of the device. The former is generated by measuring the drain current for a fixed $V_{ds}$ while changing $V_g$. As the ambipolar and unipolar saturation regimes cannot be separated unambiguously, the electrical parameters were extracted from the locus curves. Here, $V_{ds}$ and $V_g$ are increased simultaneously, such that the transistor is always in unipolar saturation conditions.

**Photoluminescence Electro-Modulated Microscopy.** A confocal laser-scanning microscope (Nikon TE2000) collected the PL from a 130 μm × 10 μm area of the transistor channel, while the device is alternately switched between the biased (on-state) and in the unbiased state (off-state). The comparison between the images collected in the on- and off-states yields a measurement of the local exciton-quenching due to charge−exciton interaction according to

$$\eta(x, y) = \frac{PL(x, y) - PL_V(x, y)}{PL(x, y)}$$

Here $PL_V$ denotes that the PL from the semiconductor in on-state and $PL_0$ denotes the PL in the off-state. The quantity $\eta$ derived in this way is a measure for the charge density.\(^{2,20}\) To collect the PL, we employed a 60x objective (Nikon Plan Fluor ELWD 60x air) and a pinhole with a size of 150 μm in these measurements.

To enhance the image-contrast a scanning lock-in scheme has been used. The charge density was modulated by modulating $V_g$ with a sinusoidal waveform at a frequency of 100 Hz, which was synchronized to the scanning of the laser beam. A lock-in detection scheme is achieved by acquiring images at different phases of the alternating current (AC) signal relative to the start of the laser scanning. The desired quenching signal is then obtained by performing a Fourier-analysis of each pixel on an image-to-image basis. A more detailed description of the technique is provided in ref 30.

To monitor the possible degeneration of the semiconductor, a normal fluorescence microscopy image was taken before and after the EM-measurement. No difference in fluorescence could be measured.

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**Figure 2.** p-Type (a) and n-type (b) transfer characteristics at $V_{ds} = 100 \, \text{V}$. The V-shaped drain current in a semi-log-plot is a typical characteristic of an ambipolar OFET.\(^2\) Mobility and threshold gate voltages cannot be calculated separately from these curves, due to the simultaneous presence of electrons and holes in the active channel. Square root locus plots ($V_{th} = V_g$) for the NT4N OFET with extracted mobility and threshold voltage for the p-type (c) and n-type (d) saturation regimes.
**RESULTS**

**Electrical Characteristics.** Devices based on NT4N were shown to have both electron and hole transport characteristics and showed light emission in ambipolar bias condition. The aOFETs in this work were realized in a bottom-gate/top-contact architecture. A transparent glass substrate, gate electrode, and dielectric layer allow optical access to the OSC from the substrate-side (Figure 1b).

The electrical transfer characteristics of the devices presented a characteristic V-shape (Figure 2a,b), confirming the ambipolar behavior of the NT4N-based aOFETs. The deviation of the minimum current from lower $V_g$ as well as the differential achieved maximum currents at low and high $V_g$ clearly indicated a more efficient injection and transport of electrons with respect to holes, in line with what was previously reported in the literature.

The transfer characteristics are typically not used to extract the electrical parameters directly, as the ambipolar and saturation unipolar regimes cannot unambiguously be separated. Instead, the locus characteristics are used according to the protocol reported by Capelli et al., given that the bias conditions applied in the locus characteristics allow to operate the device always in the saturation unipolar regime (Figure 2c,d). The resulting parameters, $\mu$ and $V_{th}$ for both electrons and holes, are listed in Table 1.

**Table 1. Threshold Gate Voltages for Electron and Hole Transport and Hole-to-Electron Mobility Ratio Together with the Values of the Exponential Density of States for Electrons and Holes**

| $V_{th,e}$ (V) | $V_{th,h}$ (V) | $\mu_e/\mu_h$ | $\tau_e$ | $\tau_h$ |
|---------------|---------------|----------------|--------|--------|
| model Schmechel et al. | 6.16 | -27.67 | 0.0046 | 2 | 2 |
| model Smits et al. | 3.96 | -21.76 | 0.00432 | 3.6 | 4 |
| locus characteristics | 65.32 | -78.87 | 0.004 |

The first two rows correspond to the parameters extracted from the PLEM images using the models of Schmechel and Smits, respectively. The values in the third row were extracted from the locus curves.

Taking into consideration the very high $V_{th}$ values for both charge carriers and the mobility ratio $M = \mu_e/\mu_h$ around 0.004, it is expected that the devices do not support an ambipolar regime at $V_{th} = 100$ V, though, the transfer characteristics clearly show ambipolar behavior. Indeed, the leakage gate current ($I_g$) curves for both p- and n-polarization remain at least 1 order-of-magnitude lower than the corresponding $I_h$ in the transfer characteristics (Figure S1 in the Supporting Information).

To understand the reason for these obviously contradicting results, it is necessary to identify the origin of the very high $V_{th}$ values extracted from the standard electrical characteristics.

**PLEM Imaging of an Ambipolar OFET.** PL electroluminescence microscopy enables the direct mapping of the charge-density distribution within the channel of a field-effect transistor. In short, by comparing the PL from the OSC in biased and unbiased state of an OFET, PLEM spatially probes the quenching, $\eta$, of laser-generated excitons by the injected charges. By means of this technique, the extension of the hole and electron accumulation regions in an aOFET, and thus the position and extension of the RZ can be directly imagined.

With a maximum variation of only 3%, the relative difference in the PL intensity between the biased and unbiased states of the NT4N-based aOFET was, however, not sufficient to obtain well-resolved PLEM imaging. The measurements were further complicated by the low PL quantum yield of NT4N thin-films (around 3–4%). Therefore, the PLEM signal contrast had to be enhanced by implementing a synchronized digital lock-in detection scheme. The charge density within the channel of the transistor was periodically modulated by an AC gate bias. The desired differential PL signal, $\eta$, was then obtained by applying a lock-in detection scheme across several collected images.

Figure 3 shows the result of a series of PLEM measurements with $V_{ds} = 100$ V and $V_g$ varying between 0 and 100 V, which correspond to the n-type saturation transfer characteristic previously reported. Every horizontal line in Figure 3 represents the average charge distribution along the channel of a 130 \( \mu \)m \( \times \) 10 \( \mu \)m image for a given $V_g$. The color coding indicates the intensity of the PLEM signal. Red implies a high positive signal (fluorescence quenching) and blue a negative signal (charge depletion and fluorescence enhancement). The RZ is clearly visible as a negative signal (dark blue line) sweeping from the source to drain. The negative signal amplitude is caused by the electroluminescence originating from the radiative recombination of the injected charges.

At $V_g = 0$ V, we observe pronounced charge accumulation at the drain electrode and charge depletion at the source electrode. This behavior corresponds to the p-type saturation regime, where holes are injected as majority carriers from the drain electrode and a depletion zone forms at the opposing source electrode. The negative signal in the depletion area under the source electrode indicates that in this region an RZ is formed where holes recombine with electrons. In this case, electrons tunnel from the injection-electrode Fermi level to the semiconductor LUMO due to the energy level bending.

In contrast, when increasing $V_g$ the gate-voltage surpass the electron-threshold ($V_g > V_{th,e} > 0$, Figure 1a) and mobile electrons are injected from the source electrode. Subsequently, the device operates in the ambipolar regime and the RZ moves across the channel by further increasing $V_g$. The ambipolar
regime starts at relative low voltages around $V_g = 10\, \text{V}$, compared to the applied drain–source voltage $V_{ds} = 100\, \text{V}$, and shows its maximum around $V_g = 30\, \text{V}$. This evidence is in contrast with the much higher values of the electron and hole threshold gate voltages extracted from the locus characteristics. Interestingly, the most balanced ambipolar regime corresponds to the minimum current in the n-type transfer curve as expected. Indeed, the rapid movement of the RZ from p-type to n-type saturation region by increasing of $\Delta V_g = 5\, \text{V}$ at around $V_g = 30\, \text{V}$ is correlated to the imbalance of the threshold voltages or of the mobilities of the two charge carriers, or by both.

If $V_g$ surpasses the sum of hole-threshold and drain–source voltage ($V_g > V_{\text{th,h}} + V_{\text{ds}}$, Figure 1), the device reaches the n-type saturation regime. During the measurements in n-type bias conditions, the RZ reaches the drain electrode at $V_g = 70-80\, \text{V}$, without moving further under the electrode as effective unipolar bias conditions are reached (Figure 3). On the contrary, the RZ is located back at 65 $\mu\text{m}$ when the $V_g$ is increased up to 100 $\text{V}$.

**Modeling of the Recombination Zone Position.** We compared the optical mapping of the experimental RZ position with theoretical predictions obtained by two analytical models introduced in the literature for organic light-emitting transistors.\(^3\) The experimental RZ position, $x_0$, was extracted from the PLEM data by fitting the photoluminescence quenching signal by a Gaussian function around its minimum intensity (blue regions) for each value of $V_g$. The extracted RZ position curves reproduce qualitatively well what is already observed in the PLEM maps (Figures 4 and 5).

![Figure 4](image)

*Figure 4.* Using the values for mobility ratio and threshold voltages extracted from the electrical locus curves does not result in an adequate description of the recombination zone position (red curves) neither for the model of Schmechel (a) nor that of Smits (b).

![Figure 5](image)

*Figure 5.* Both models for the position of the recombination zone fit the experimental data reasonably well. The temperature-dependent model of Smits offers a slightly better description of the source-to-drain swing (gray areas indicate the electrodes). The deviation around 80 $\text{V}$ in Figure 3 cannot be reproduced with either model and is left out from the fitting procedure.

Without loss of generality, the drain electrode is assumed to be at $x = 0$ and consequently $x_0 = L_e$. With some algebraic transformations, the recombination zone position can be expressed as

$$x_{0,\text{Schmechel}} = L_e \frac{(V_g - V_{\text{th,e}})^2}{(V_g - V_{\text{th,e}})^2 + \left(\frac{\mu_e}{\mu_h}(V_{\text{ds}} - V_g - V_{\text{th,h}})\right)^2}$$
Zaumseil et al. successfully used this model to describe the recombination zone position in an ambipolar light-emitting organic transistor based on F8BT, which showed well-balanced electron and hole transport characteristics.

Smits et al. reported a similar expression for the determination of the recombination zone position by using a microscopic description of charge transport based on a variable range hopping model

\[ x_{0,\text{Smits}} = L \cdot \left( \frac{V_g - V_{th,e}}{V_g - V_{th,h}} \right)^{\frac{\mu_e}{\mu_h}} \] (4)

The discrepancy in the values of Schmechel and Smits is the approach in considering the energetic and spatial spread of charge-trapping sites. While Schmechel implicitly assumed a uniform distribution and occupation of trapping sites, Smits introduced an explicit distribution function for the density of states and a temperature-dependent occupation probability. Consequently, in the Smits model the square-exponent of the Schmechel model is temperature-dependent (T) with \( \tau_{e(h)}(T) = (2T_{0,e(h)}/T) - 1 \), where \( T_{0,e} \) and \( T_{0,h} \) are measures for the width of the exponential density of states for electrons and holes.

Using the electrical parameters for \( \mu_e/\mu_h \) and \( V_{th,h} \) extracted from the aOFET locus characteristics (Table 1) we could not reproduce the observed location profile of the RZ by neither model (red lines in Figure 4). In particular, the ambipolar regime was predicted at higher \( V_g \) than what we observed by PLEM mapping. Also, slightly increasing the fitting parameters \( \tau_{e(h)} \) above 2 did not improve the accordance with the experimental data.

To investigate the deviation of the optically-observed RZ position from the predicted position derived by using the electrical measurements, we fitted both analytical models to the experimentally determined \( x_0 \) (Figures 4 and 5). We initialized the fitting parameters with those obtained from the locus curves.

We note that the channel length \( L \) must be considered as a fitting parameter as well to adequately describe the data. With approximately 65 \( \mu \)m, the electrical channel length is around 7% smaller than the nominal channel length of \( L = 70 \) \( \mu \)m. Moreover, neither model could reproduce the PLEM data collected between \( V_g = 80 \) and 90 V and the fitting algorithm did not converge if these data-points were included. As we assume that the observed behavior in this bias range is untypical for a truly ambipolar OFET, the data-points in this range were left out from the fitting procedure.

With this reduced dataset, both analytical models reproduced the data in good accordance (Figure 4). Table 1 lists the resulting threshold gate voltages and mobility ratio extracted from the RZ position data for both models. The Smits model (red line, Figure 5) can be considered more precise in the description of the RZ location as a function of the applied bias compared to the Schmechel model (blue line, Figure 5). In particular, the use of additional exponential parameters leads to a faster variation in the position. Interestingly, the best fit is obtained for \( \tau_e \approx \tau_h \approx 4 \). This evidence indicates that the spread (not amount) of hopping site distribution is a factor 2 bigger than expected from the "free-carrier"-based Schmechel model. With a value of 3.6 the site distribution for electrons is marginally smaller than the site distribution for holes which is exactly 4. Thus, the largely differing mobility values for holes and electrons cannot be simply explained by a difference in the density or occupation of trapping sites.

**DISCUSSION**

The threshold gate voltages derived from both models differ strongly from those extracted from the electrical locus curves (Table 1), while the hole-to-electron mobility ratio is almost identical in all three cases. In both models, lower \( V_{th,h} \) values with respect to the ones obtained from the electrical characteristics were needed to reproduce the onset of the ambipolar regime.

The discrepancy in the \( V_{th,h} \) values obtained from the different experimental methods (electrical characteristics vs PLEM imaging) can be rationalized by recalling the physical meaning of \( V_{th} \) in OFETs. The \( V_{th} \) parameter identifies the bias conditions for the onset of charge transport. In general, two effects can contribute to \( V_{th} \): the barrier for injecting charges into the OSC leads to a contact resistance and the barrier for transporting charges across the OSC leads to a channel resistance, respectively. Misalignment of the HOMO and LUMO levels of the OSC with respect to the work-function of the metal electrodes causes an injection barrier. On the other hand, defects and impurities at the dielectric/semiconductor interface cause an effective channel resistance. In electrical measurements, charges must be injected into the device and a conducting channel between the source and drain must be established for charge transport. Thus, the extracted \( V_{th} \) value contains contributions from both resistances.

In contrast, at the onset of the ambipolar regime a unipolar channel is already formed by one charge carrier type (here holes when the device is n-polarized). The ambipolar transport now occurs, if the second charge carrier type is also injected into the channel. The effective channel length and, therefore, also the effective channel resistance for each charge carrier type crucially depends on \( V_g \). This scenario is conceptually similar to the transmission-line method, which is used for determining the contact resistance in unipolar devices. In this method, the channel resistance is varied by comparing devices with different geometrical channel lengths \( L \). The contact resistance is subsequently extrapolated from the functional dependence of \( V_{th} \) on \( L \) at \( L = 0 \). In aOFETs, the same situation of a vanishing channel length exists at the onset of the ambipolar regime. Thus, a straightforward determination of the contact resistance in ambipolar OFETs is possible, by considering the \( V_g \) values at which the RZ reaches the source (\( x_0 = 0 \)) and the drain (\( x_g = L \)) electrodes, respectively. The PLEM map in Figure 3 shows that the situation of vanishing channel length occurs at approximately the values for \( V_{th,h} \) and \( V_{th,e} \) obtained by fitting the RZ position with the models of Schmechel and Smits. From this correspondence, we conclude that in both models describing the RZ position, \( V_{th,e,h} \) represents the value for \( V_g \) at which the onset of the ambipolar regime occurs. In other words, the \( V_{th,e,h} \) extracted by this method represent only the voltage drop due to the contact resistance, \( V_{con,e,h} \), and does not contain contribution from voltage drop due to the channel resistance, \( V_{chan,e,h} \).

We assume that the voltage drop at the contact and channel resistance can be simply evaluated by considering a circuit comprising a series of resistors. Thus, the overall threshold voltage (including the contact and channel resistance) obtained from the electrical locus, \( V_{th,e,h} \), is given by the simple sum of \( V_{con,e,h} \) and \( V_{chan,e,h} \) so that \( V_{th,e,h} = V_{con,e,h} + V_{chan,e,h} \)
performance is limited by the intrinsic characteristics of the threshold voltage only for electrons, as if the hole transport based overlap of HOMOs and LUMOs in the active layer crystalline introduction of a PMMA-capped high-electrons. Indeed, we have recently reported that the contact-component of electrons, therefore, are likely related to di

Reported39 that the hole threshold voltage is almost invariant about higher density of trapping sites for holes at the semiconductor/PMMA interface was reported for unipolar regime for holes is caused by the contact resistance, while for electrons it is only 6% (4 V).

Conversely, the voltage drop in the channel is 57.1 V for holes and 61.4 V for electrons.

It is often assumed for the sake of simplicity that the contact resistance is directly correlated to the energy difference between the semiconductor HOMO level and the metal Fermi level for hole injection, and to the energy difference between the semiconductor LUMO level and the metal Fermi level for electron injection.5,35 In the case of NT4N, we can consider HOMO and LUMO levels as the energy values obtained from the cyclic voltammetry measurements of −6 and −3.4 eV,31 respectively, while the Fermi-energy value for gold is tabulated (5.5 eV)9 (see Figure 1d). According to these data, the process of hole injection is expected to be less hindered with respect to the electron injection process that must overcome an energy barrier as high as 2 eV to be effective. Though, the PLEM measurements report that the electrons are more-efficiently injected into the organic semiconductor, as also the electrical characterization partially corroborates (higher source−drain current and mobility, lower threshold voltage). It is evident that the approach of discriminating metals for efficient charge injection by minimizing the energetic misalignment between tabulated organic semiconductor molecular orbitals and the injecting metal Fermi level is too simplistic to describe real organic−metal heterointerfaces.

Moreover, we can assert that charge-trapping phenomena at the semiconductor/dielectric interface is minimized concurrently for both electrons and holes in NT4N-based OLETs. Indeed, single-layer aOFTEs show the best balance in charge carrier mobility and threshold gate voltage when the dielectric layer is PMMA, regardless if the semiconducting layer consists of polymers or small molecules.36,37 Even though evidence about higher density of trapping sites for holes at the semiconductor/PMMA interface was reported for unipolar OFETs,38 it was demonstrated that the implementation of PMMA as dielectric enables the reduction of plot hysteresis both in p- and n-type polarization (and thus, the density of trapping sites for holes and electrons) in ambipolar OFETs.37 This is confirmed by the comparable exponential factors for electrons and holes obtained by fitting the Smits model. The different mobility and channel resistance values for holes and electrons, therefore, are likely related to different orbital overlap of HOMOs and LUMOs in the active layer crystalline domains, leading to different conductivities for holes and electrons. Indeed, we have recently reported that the introduction of a PMMA-capped high-k dielectric in NT4N-based field-effect transistors considerably reduces the gate-threshold voltage only for electrons, as if the hole transport performance is limited by the intrinsic characteristics of the active layer (i.e., crystalline structures and/or morphology at the interface with the dielectric).34 Moreover, we have recently reported99 that the hole threshold voltage is almost invariant when varying the polymeric gate dielectric from PMMA to CYTOP, while the electron threshold gate voltage increases by factor 2.

Thus, we can infer that the huge difference between the contact-component of Vth for holes and electrons might be partly explained by the low μh which is only 4% of respect to μe. In a balanced ambipolar regime, the hole and electron currents within the RZ are identical (Ih = Ih). Given that μh ≪ μe the hole density needs to be higher than the electron density to reach the ambipolar regime. Indeed, in the ambipolar regime the PLEM images indicate a higher charge density in the proximity of the drain (hole-injection electrode) rather than in the proximity of the source (electron-injection electrode). However, the high charge concentration at the drain introduces an additional electrostatic barrier for the injection of further holes. This circumstance might explain the high value for Vth,h.

Evidently, the use of a high-mobility ambipolar organic semiconductor as an active material in FET is expected to reduce the accumulation of charges at the injecting electrodes, and consequently will allow us to collect PLEM images that may be straightforwardly interpreted according to the linear-channel approximation theory used in standard FET.25

Finally, it is worth pointing out that the use of the optical method based on PLEM microscopy for investigating charge-injection mechanisms in FET-based devices is possible independently from the features of the dielectric/semiconductor interface in terms of surface energy and charge-trapping state density, since the contact-resistance and channel-resistance contributions in hole and electron threshold gate voltages are decoupled.

CONCLUSIONS

In this article, we reported the first experimental demonstration of the direct optical imaging of the recombination zone location in an ambipolar OFET, without the requirement of detectable electroluminescence. We tracked the gate-bias-dependent RZ position of a NT4N-based ambipolar OFET by PLEM microscopy,25 while it is drifted across the device channel. To detect with high signal-to-noise ratio of the very low quenching signal of the active organic semiconductor, we employed the newly developed innovative scanning-probe correlated lock-in detection scheme.30

A comparison of the electrical device parameters extracted by fitting the gate-induced movement of the RZ in the channel region with those obtained by standard electrical locus characteristics suggested an evident difference in the physical meaning of the threshold gate voltages derived by the two experimental methods. In particular, when tracking the RZ position, Vth,h(e) defines the bias conditions for the ambipolar regime, according to: Vth,e < Ve < Vth,h + Vd. At the onset of the ambipolar regime the channel length of the newly injected carrier type is negligible. The “onset” bias is determined only by the contact resistance for charge injection, as injected carriers directly recombine at the contact under these bias conditions. Thus, by fitting the recombination zone position the contact resistance can be obtained separately.

In conclusion, we demonstrated a method to determine the contact resistance for electron and hole injection into an ambipolar OFET by using a single device. Moreover, by comparison to the threshold voltages obtained from standard electrical characterization, the channel resistance can also be determined. In this way, it is possible to probe independently how the different functional interfaces (such as the electrode/OSC and the OSC/dielectric) modulate the charge carrier transport properties of holes and electrons within the same device, and in principle to decouple the device-dependent and material-dependent issues that affect the electrical performance in organic field-effect transistors.
As a first step in this direction, the present study demonstrates that charge injection at the metal/organic semiconductor interface in organic field-effect transistors is far from being sketched as the simplistic charge transfer process from a bulk metal foil to the frontier molecular orbitals of the organic semiconductor.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b05518.

Leakage current related to the saturation transfer characteristics of an NT4N-based FET both in n- and p-type polarization bias conditions (PDF)

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**Notes**

The authors declare no competing financial interest.

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