



# Charge transport characterization in a squaraine-based photodetector by means of admittance spectroscopy



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## ABSTRACT

Thanks to their strong absorption in the near infrared, squaraine dyes have raised interest in the field of organic photovoltaics and photodetection. We develop photodetectors based on the bulk heterojunction of an indolic squaraine and of a fullerene derivative, obtaining an external quantum efficiency as high as 12% at 590 nm. To gain insight into carrier transport and recombination phenomena, devices are characterized in the dark by means of admittance spectroscopy. At low applied voltages carrier transport is dominated by holes, which show dispersive transport and an electric field dependent mobility of about  $10^{-5}$ – $10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. At higher voltages electron injection occurs as well and a bipolar, recombination-limited regime sets in. The modeling of the low-frequency negative capacitance contribution suggests a trap-mediated carrier recombination mechanism.

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## 1. Introduction

Squaraine compounds have recently gained a renewed interest due to the emergence of their application potential in several fields [1,2] such as NIR-emitting fluorescent probes for bioimaging and chemosensing applications [3], sensitizers for photodynamic therapy [4,5], and low-cost electro-optic devices based on non-linear phenomena [6]. Additionally, squaraine dyes find useful applications in optoelectronic devices, namely field effect transistors [7], organic photovoltaics [8], dye-sensitized solar cells [9], and organic photodetectors [10–13]. Despite the number of possible and promising applications, a complete characterization of transport properties in squaraine-based devices is still missing. Here we characterize the charge transport properties of a squaraine/fullerene thin film. The characteristics of blends based entirely on small molecules can be different from the more widely studied polymer/fullerene systems as far as nanoscale morphology is

concerned, and they are likely characterized by a higher density of charge-trapping sites, “cul-de-sacs”, and dead ends [14].

The understanding of charge carrier transport in disordered molecular or polymeric materials and the measurement of charge carrier mobility have traditionally been based on a variety of different methods [15–17]. These include time of flight (TOF), charge extraction by linearly increasing voltage (CELIV), dark-injection space-charge-limited current (DI-SCLC), electroluminescence transient (ELT), field effect transistor (FET), pulse radiolysis time-resolved microwave conductivity (PR-TRMC), and photoinduced transient Stark spectroscopy (Pi-TSS). Every technique has its own requirements in terms of setup and device structure, and its own application range in terms of charge density, electric field, timescale, and dispersive transport. For example: TOF requires the use of thick films (in the range of micrometers), efficient blocking layers, films with low dark conductivity, and without strongly dispersive transport; CELIV is usually limited to highly conductive materials and does not allow measurement of mobility at fixed electric field since the applied voltage is linearly increasing; DI-SCLC often requires models accounting for a specific distribution of trap states in the presence of hopping transport; ELT is limited to electroluminescent semiconductors; charge transport in FETs typically occurs in a very high density regime and is influenced by the semiconductor–insulator interface (depending on the

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chemical structure of the dielectric surface); PR-TRMC provides useful information about AC intra-chain mobility, but it cannot account for the DC mobility which is mainly ruled by inter-chain transport; Pi-TSS is limited to materials which exhibit strong Stark features and requires a sophisticated experimental set-up. To obtain reliable information, it is important to study transport phenomena directly on working devices in operational conditions, without having to introduce modification of the geometries. To this end we opt for admittance spectroscopy (AS), which is a purely electric technique and can be applied without any changes in device geometries or the need for a complex experimental setup. In addition, it can account for the presence of trap states and permits the evaluation of dispersive effects and relaxation processes under strong bias conditions in a straightforward way. Besides providing a characterization of squaraine-based photodetectors, our results demonstrate that AS, hitherto adopted only in a limited number of polymer-based blends with relatively high mobility [18–23], is also an effective tool in the study of small organic molecules.

## 2. Materials and methods

The organic photodetectors were fabricated using a vertical geometry on glass substrates precoated with an ITO anode and pretreated by oxygen plasma. Three types of bottom electrodes were tested: bare ITO, ITO covered with poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, Clevios P VP Al 4083), and ITO covered with poly(3,4-ethylenedioxythiophene)-block-poly(ethylene glycol) doped with perchlorate (PEDOT:PEG(PC), Sigma Aldrich). PEDOT:PSS was spin-coated from aqueous solution at 2000 rpm for 30 s. PEDOT:PEG(PC) was spin coated from a filtered 1 wt% nitromethane solution at 5000 rpm for 60 s.

Following the deposition, the samples were thermally treated at 110 °C for 15 min under nitrogen. The active material is a bulk heterojunction layer, given by an indolic squaraine with alkylic chains (Sq) [2] as electron donor component, blended with phenyl-C<sub>61</sub>-butyric-acid-methyl-ester (PC<sub>61</sub>BM) as the electron acceptor in 1:3 ratio (by weight). The blend was dissolved in chloroform (19.2 mg/ml) and spin-coated at 100 rpm in ambient atmosphere for 1 min, followed by a second step at 1000 rpm for 1 min, giving a film with a thickness of about 130 nm as deduced by profile measurement (KLA TENCOR, Alpha Step 500). Thermal evaporation of the aluminum top electrode (ca. 100 nm) completed the process, giving devices with an active area of 1 mm<sup>2</sup>.

Optical absorption was measured by a PERKIN ELMER Spectrophotometer (Lambda 1050). Cyclic voltammetry measurements, performed with a Metrohm Autolab PGSTAT302N, served to derive the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energetic levels of squaraines (0.1 mM in tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>)).

DC electrical characterization was performed in air and at room temperature. Current density–voltages (*J*–*V*) curves were measured by means of a semiconductor parameter analyzer (Agilent B1500), keeping the Al contact grounded. External quantum efficiency (EQE) measurements were performed in vacuum (*p* < 10<sup>−5</sup> mbar) by biasing the ITO contact at −1 V and keeping the Al contact grounded. The photodetectors were irradiated at a light intensity of approximately 1.5 mW/cm<sup>2</sup> by a set of light emitting diodes, and the resulting photocurrent was measured by means of a low-noise transimpedance amplifier connected to an oscilloscope. Impedance measurements were conducted in air using an E4980A Precision LCR meter (Agilent) in dark conditions. AC signal amplitude was set at 20 mV and the frequency was swept between 1 and 100 kHz.

## 3. Theory

In the following we give a brief account of the theoretical background of AS.

We start with unipolar charge injection giving rise to the space-charge limited current (SCLC) regime. For a one dimensional device operating in trap-free SCLC, the analytical expression for steady-state (DC) response is expressed by the Mott–Gurney square law [24]:

$$j = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_{DC} \frac{(V_{\text{appl}} - V_{\text{bi}})^2}{L^3} \quad (1)$$

where  $\mu_{DC}$  is the steady state mobility,  $V_{\text{appl}}$  is the applied potential,  $V_{\text{bi}}$  is the built-in potential which is approximately equal to the difference between the work functions of the two electrodes, and  $L$  is the thickness of the active layer. In the presence of charge transport by a hopping mechanism,  $\mu_{DC}$  can be field-dependent according to the Poole–Frenkel relation [25]:

$$\mu_{DC} = \mu_0 \exp(\beta \sqrt{E}) \quad (2)$$

where  $\beta$  is called Poole–Frenkel coefficient,  $\mu_0$  is the zero-field mobility and  $E$  is the electric field.

In this case Eq. (1) has to be corrected by using an effective mobility given by:

$$\mu_{DC} = \mu_0 \exp \left[ 0.89 \beta \sqrt{(V_{\text{appl}} - V_{\text{bi}})/L} \right]. \quad (3)$$

In the case of application of an external, time dependent potential, in a perturbative approximation the current density signal can be expressed by the sum of three different contributions. These describe, respectively, the response of the DC charge density to the AC field, the current due to the additional time-dependent injected charge density, and the displacement current, as explained in Refs. [26,27]:

$$j(t) = e \mu(t) \rho_{DC}(x) E_{AC}(x, t) + \varepsilon_0 \varepsilon_r \mu(t) E_{DC}(x) \frac{\partial E_{AC}(x, t)}{\partial x} + \varepsilon_0 \varepsilon_r \frac{\partial E_{AC}(x, t)}{\partial t} \quad (4)$$

with  $e$  the electron charge,  $\rho_{DC}(x)$  the DC charge density,  $\mu(t)$  the time dependent mobility, and  $E_{AC}(x, t)$  and  $E_{DC}(x)$  the AC and DC electric field components, respectively.

By applying a Fourier transform to Eq. (4) one obtains the admittance, expressed as:

$$Y_{SC}(\omega) = G_{SC}(\omega) + i\omega C_{SC}(\omega) = \frac{C_g}{\tau_t} \left\{ \frac{(\omega \tau_t)^3}{2i\bar{\mu}^2 [1 - \exp(-i\omega \tau_t/\bar{\mu})] + 2\bar{\mu}\omega \tau_t - i(\omega \tau_t)^2} \right\} \quad (5)$$

where  $G_{SC}(\omega)$  and  $C_{SC}(\omega)$  are the conductance and the capacitance of the system,  $C_g$  is the geometrical capacitance defined as  $C_g = \varepsilon_0 \varepsilon_r \frac{A}{L}$  (with  $A$  denoting the active area), and  $\tau_t$  is the transit time defined as:

$$\tau_t = \frac{4L^2}{3\mu_{DC}(V_{\text{appl}} - V_{\text{bi}})} \quad (6)$$

where  $\bar{\mu}$  is a normalized dimensionless mobility defined as  $\bar{\mu}(\omega) = \mu(\omega)/\mu_{DC}$ .  $\mu(\omega)$  is the frequency dependent mobility accounting for the effect of traps.

In the ideal *trap-free* case, viz.  $\mu(\omega) = \mu_{DC}$ ,  $C_{SC}$  is equal to  $\frac{3}{4}C_g$  at low frequency (where the space charge can keep up with the modulating voltage), and tends to  $C_g$  at high frequency; the boundary between low and high frequency is given by the reciprocal of the carrier transit time ( $\tau_t^{-1}$ ).

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