

THE EXTERNAL BIAS-DEPENDENT ELECTRIC FIELD AT HOLE-INJECTING ELECTRODE/ α -NPD JUNCTION AND ITS RELATIONSHIP TO GAUSSIAN DISORDERED INTERFACE STATES

OD ZUNANJE NAPETOSTI ODVISNO ELEKTRIČNO POLJE OB STIKU VRZELI VBRIZGAJOČE ELEKTRODE/ α -NPD IN POVEZAVA Z NEUREJENIMI ENERGIJSKIMI STANJI VMESNE PLASTI

Bruno Cvikl ³³

Keywords: electrode/organic electric field, contact affected hole mobility, organic interface disorder parameters

Abstract

An alternative interpretation of two different sets of published temperature-dependent current-voltage α -NPD (i.e. N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine) organic semiconductor data is presented. The measurements are described in terms of the hole drift current density expressed with two parameters: the electric field at the hole-injecting interface, E_{int} , and, μ_{max} , the hole mobility determined by the measured current density at the maximum value of the externally applied electric field, E_a , in a given experiment. The former parameter, depending on the contact resistance, may be a function of E_a but the latter is E_a independent. The fixed value of E_{int} signifies the occurrence of the space charge limited current, SCLC, within the electrode/ α -NPD structures

³³ Corresponding author: Professor Emeritus Bruno Cvikl, PhD., University of Maribor, Maribor, Slovenia and Jožef Stefan Institute, Ljubljana, Slovenia, E-mail address: bruno.cvikl@ijs.si

and the contact is ohmic. Then, the calculated weak bias-dependent hole drift mobility, a function of E_{int} , equals the well-known exponential bias-dependent mobility, and saturates. The data not displaying SCLC characteristics are used for the calculation of E_{int} dependence on the applied field, E_a . It is shown that the quasi-ohmic contacts cause E_{int} to become a strong double-valued function of the externally applied electric field, E_a , described in terms of the distorted, inverted, high order parabola. The corresponding bias-dependent hole drift mobility is non-exponential and evolves on a considerably lower level than in SCLC cases. It is found that a sufficiently increased E_a alters the quasi-ohmic contact/ α -NPD region into the ohmic one. A simple model of a thin, net hole charged, electrode/ α -NPD interface enables the relationship between the deduced interfacial electric field, E_{int} , and the E_a dependent Gaussian width, σ , as well as the energy shift of its peak, ϕ , along the negative binding energy is to be investigated. The current-voltage method appears to be a helpful expedient for the investigation of the electric field at hole-injecting electrode/organic interfaces.

Povzetek

Članek podaja alternativno fizikalno interpretacijo dveh primerov v literaturi objavljenih temperaturno odvisnih meritev gostote toka v odvisnosti od pritisnjene napetosti na vzorcih α -NPD (i. e. N,N'-Di(1-naftil)-N,N'-difenil-(1,1'-bifenil)-4,4'-diamin) organskega polprevodnika. Meritve gostote toka vrzeli so v pričujočem članku popisane z dvema parametroma: z jakostjo električnega polja, E_{int} , na vmesni plasti elektroda/organski polprevodnik kjer se vrzeli vbrizgavajo v organski medij in, μ_{max} , mobilnost vrzeli, ki je določena z izmerjeno gostota toka pri maksimalni vrednosti zunanje električne poljske jakosti, E_a , danega eksperimenta. Parameter, E_{int} , ki je funkcija kontaktne napetosti, lahko zavisi še od E_a , toda drugi parameter je od E_a neodvisna konstanta. Nespremenjena vrednost E_{int} z vrednostjo E_a podaja obstoj t. im. omejenega toka zaradi prostorskega naboja, SCLC, v vzorcu α -NPD s čimer je tedaj električni kontakt opredeljen kot ohmski stik. V tem primeru je izračunana, šibko E_a , odvisna mobilnost vrzeli podana z dobro poznano eksponentno odvisnostjo, ki vodi do nasičenja mobilnosti vrzeli. Eksperimentalni podatki, ki ne zadoščajo merilom SCLC so uporabljeni za izračun odvisnosti E_{int} od zunanjega polja E_a . Izkaže se, da zaradi kvazi-ohmskega kontakta postane E_{int} dvolična funkcija zunanjega pritisnjenega polja E_a , ki zavzame obliko skrivljene in invertirane parabole višjega reda. Temu ustrezna mobilnost vrzeli se izraža v ne-eksponentni formi is zavzame vrednosti, ki so bistveno pod nivojem vrednosti izračunane v primerih opredeljenih z SCLC značilnostmi. V delu je pokazano, da je mogoče z dovolj velikim zunanjim poljem, E_a , preoblikovati kvazi-ohmski kontakt v ohmskega. Poenostavljeni model tenke, z vrzeli nasičene, vmesne plasti elektroda/ α -NPD omogoča proučevanje vzajemnega odnosa med električnim poljem vmesne plasti E_{int} in od E_a odvisno širino Gaussove funkcije razmazanosti energijskih stanj vrzeli v organskem polprevodniku in pa energijski pomik le-te vzdolž negativne vezavne energije. Eksperimentalna metoda gostota toka - napetost se izkaže, kot nadvse ustrezna metoda za raziskave električne poljske jakosti z vbrizganimi vrzeli odlikovane vmesne plasti stika elektrode/organski polprevodnik.

1 INTRODUCTION

All organic semiconductor electrical devices are developed with the aim that the resistance between the injecting (and ejecting) charges from the suitable electrode into the organic is minimized. Improvements in the resistance of the electrode/organic semiconductor contact result in considerably improved device performances on account of advances of the charge carrier mobility. The science of so-called contact engineering [1-7] crucially contributes to the optimized performance of the distinct organic devices that are in use. The charge mobility μ is an involved function of the externally applied electric field, E_a , the temperature T , and the charge carrier density, ρ , providing that the injection barrier between the charge-injecting electrode and the contacting organic semiconductor is as small as possible. The charge mobility is most commonly inferred by the current-voltage, $j - V_a$, experiments in which the steady-state current density, j , through the electrode/organic/metal structures as a function of the externally applied DC electric field, $E_a = V_a/L$, is measured. Here V_a is the applied voltage over the two electrodes and L is the thickness of the organic medium between them. The prerequisite for its successful determination is the existence of ohmic contacts between the charge injecting electrode/organic interfaces. The current through such a structure is then the space charge limited current, SCLC, and only under this condition the data then provide the fully reliable charge-carrier mobility [3, 8, 9]. The criteria for the occurrence of SCLC are based on the effects of the electric field-dependent charge mobility, organic layer thickness and charge-injection barrier height as extensively discussed by Wang et. al. [8, 9]. It was concluded that these condition should be fulfilled prior to the measurements; otherwise the obtained results apparently “have no meaning” [9]. In cases of non-ohmic contacts the current density no longer exhibits the SCLC behavior. A thorough investigation into the reproducibility problem of the mobility measurements in organic semiconductors that concludes with the recommendations regarding the device preparation, fabrication, measurement and analyses in order to ensure the most trustworthy results has been reported recently by Blakesley et al. [10].

The above-stated works and others that have followed provide evidence that under identical conditions the hole mobility of a given organic substance is a function of the electrode material utilized for injection of holes. Evidently, the cause that influences the hole mobility ought to be related to the electric field at the hole-injecting interface. This expectation is explicitly expressed in the form of the steady-state non-zero electric field at the charge-injecting electrode/organic interface, E_{int} , that is a parameter in the extended Mott-Gurney space charge limited current model [11]. The second parameter of the stated law is the maximum value of the charge mobility, μ_{max} , (in [11] inappropriately termed effective mobility μ_{eff} as will be discussed later) that is in a given current-voltage experiment determined from the current density measured (exclusively) at the maximum value of E_a . The parameter μ_{max} is consequently bias independent. It should be stressed that both parameters are related to the charge drift mobility, μ_d , which is the quantity of great practical interest. As shown in [11], the SCLC fits in various organic samples based on the extended Mott-Gurney law are characterized by the external bias independent, parameter E_{int} , see for instance Fig. 1 and Fig. 2 of [11]. In cases of poor ohmic contacts the current density is no longer of the SCLC type, which commonly occurs (at least) within the initial part of the interval of the externally applied electric field $E_a \geq 0.1$ MV/m say, see Figs. 3, and 4 of [11]. The SCLC is in the extended Mott-Gurney formulation described in terms of a non-zero constant E_{int} , which is independent of the externally applied electric field, E_a . This was empirically verified by the independent SCLC analyses based upon the well-known Mott-Gurney expression incorporating

the exponential bias dependent mobility [11]. As seen, there the SCLC predictions of Eqs. (1), and (2) considerably overshoot the j - V data within the initial part of the respective E_a interval. In contrast to this, it was found that in cases of a non-ohmic metal/organic contact, the concave SCLC curve formulated by the extended Mott-Gurney model can always be made to intersect (at least) the first and the last current-voltage measuring point of a given E_a interval.

Recently, a particularly interesting current-voltage temperature and thickness dependent hole transport measurements within the various electrode/ α -NPD (i.e., N,N' -Di(1-naphthyl)- N,N' -diphenyl-(1,1'-biphenyl)-4,4'-diamine) organic thin diode devices have been published by Rohloff et al. [12] and van Mensfoort et al. [13]. In [13] it was determined that Mott-Gurney law with the exponential bias-dependent mobility could not account for their data. Consequently, the given set of current density measurements, [13], on a ITO/ α -NPD/Pd hole only organic structure, offers the information related to the current density deviation from the expected SCLC behavior. In contrast to this, for the hole only PEDOT:PSS/ α -NPD/ TCTA/MoO₃/Al organic structures the occurrence of SCLC has been determined by j - V measurements as reported by Rohloff et al. [12]. Here PEDOT:PSS denotes poly(3,4-ethylenedioxythiophene):polystyrene sulfonate and TCTA is an abridged notation for tris(4-carbazoyl-9-ylphenyl)amine. It is evident that in case of the stated organic structures prepared with chemically identical organic semiconductor α -NPD that the observed difference in the hole current density (between the samples of equal thickness and at similar temperature) should be related to the different hole injecting electrodes. The data of [12], and [13] then provide an opportunity to arrive at some additional information of not-yet understood processes that occur at the hole-injecting electrodes/ α -NPD interfaces. In this respect, the investigation of the electric field at the hole-injecting electrodes/ α -NPD interface, E_{int} , a parameter of the extended Mott-Gurney law [11], seems to be most convenient.

This is the purpose of the presented work. Namely, as written above, E_{int} is in an organic structure related to the charge drift mobility, μ_d and no detail knowledge exists in the literature about its relationship to the non-SCLC current density, j . The later process occurs due to the non-ideal electrode/organic contact. The explicit knowledge of E_{int} dependence on the externally applied field E_a (note that in SCLC cases E_{int} , is a constant, [11]) should then provide additional illumination of the charge transport processes and by this on the expected performance of a given organic structure. It will be shown that the current density deviation from the SCLC behavior in α -NPD hole transporting electrode/organic structures occurs on account of the external bias dependence of the electric fields, E_{int} , at hole injecting contacts, which detrimentally affects the hole drift mobility.

It is known, and [12] and [13] offer support to the claim that the interface between the electrode and the organic substance plays a crucial role in the charge transfer between the stated two media. It primarily depends on the relative alignment of molecular energy states in the organic to the Fermi level of the electrode giving rise to the energy barrier at the interface.

On account of a low density of free charge within the organic bulk, the electric field applied between the two electrodes results in a charge imbalance at the organic side of the charge injecting interface. The imbalance may be particularly large if the electrical contacts are ideal ohmic. The SCLC, the space charge limited current through the metal/organic/metal structure at a given applied electric field, E_a , is determined by the ability of the charge injecting electrode to continuously supply excess charges to the interface in the amount exceeding the steady current through the organic that is limited by space charge in its interior [14, 15]. On account of the interaction between the adsorbed organic molecules and the electrode the additional energy

states develop at the contact that depend on the method of the organic deposition, the organic crystallinity, and on number of other possible factors, The complex array of resultant energy barriers on the interface represents a cause that a portion of injected charges, the ones with insufficient energies accumulate (become trapped) in it. The free excess charge supplied by the contact the net trapped holes on those parts of α -NPD molecules that constitute the interface the charge on the organic side of the interface that compensate the built-in voltage, the charge at the electrode/organic contact and other possible sources of charge all contribute to the resultant electric field within the α -NPD organic.

The electrode/organic interface charging, i.e. the charge transient processes, before the steady state current is established is most suitable investigated by the time-resolved electric-field-induced optical second-harmonic generation, EFISHG, method [16, 17]. With the stated technique the electric fields in organic layers can be selectively and directly probed [16, 17]. In comparison to the EFISHG method it will be shown that the current-voltage method is suitable for the investigation of the steady state electric field at the charge injecting interface. It will be shown that the electric field at the hole injecting interface, E_{int} , as used in this paper represents the magnitude of the resulting vector $\vec{E}_{int} = \vec{E}_a + \vec{E}_{ch}$ at the position of the interface. Here E_{ch} stands for the magnitude of the (steady state) electric field due to all other, unspecified, sources of charge and E_a , is the externally applied (steady state) electric field over the device.

It is noted that the authors of [12] and [13] have successfully interpreted their measurements in terms of the drift-diffusion theory of the hole mobility subjected to the charge hopping among the energy states described by the static, uniform, Gaussian energetic disorder in α -NPD organic bulk [18]. Assuming the hopping hole transport within the Gaussian distribution of disordered energy levels in the organic the authors have shown that the Gaussian disorder model (GDM) [19], reproduces the measurements well. This model takes into account the hole mobility described as a known function of the hole density, the electric field, the temperature, and the Gaussian width, σ . Likewise, it was shown that the correlated Gaussian disorder model (CDM) [20] also accounts for the data well. The CDM model contains additional description of the site energy correlated disorder due to the randomly oriented dipoles and may be viewed as an upgrade of the GDM description. No direct interaction between the hole-injecting electrodes and the α -NPD organic has been considered.

In [21] the charge transfer from the electrode into the density of states within the organic bulk has been considered and suggested that the spread of the disordered energy states near the interface appeared to be correlated with the charge mobility. This important question is presently also addressed and the relationship between the bias-dependent E_{int} (the principle cause of affecting the hole drift mobility) and the disordered energy states within the organic part of the interface is established on the basis of a simple interface model constructed upon the findings of Oehzelt et al., [22].

This paper is organized as follows:

In Sec. 2, a brief presentation of the extended Mott-Gurney law is given and the method of E_{int} extraction is presented. It is shown that the original Mott-Gurney law describing SCLC is valid for $E_{int} = c E_a$, where c is an electrode/organic specific constant. A simple model is presented by which the compatibility of the deduced results with Gaussian energetic disorder in organic is established. In Sec. 3.1, the predictions of the hole drift current density, j , are compared to the published current-voltage data of [12]. It is shown that the forward biased (i.e. Al at the positive

potential) PEDOT:PSS/ α -NPD(100 nm)/TCTA(5 nm)/MoO₃/Al structure displays SCLC characteristics only for E_a exceeding a given temperature-dependent threshold value within the respective E_a interval of measurements. Within the SCLC region, characterized by the constant E_{int} , the calculated E_a dependence of the hole drift mobility, μ_d , coincides with the prediction of the well-known exponential dependent hole mobility. This is the region of good ohmic contact. The small current density deviation from the SCLC characteristic is used to calculate the E_a dependence of E_{int} , and to investigate its effect on the hole drift mobility. Based upon the simple model the relationship between the deduced E_{int} and the hole transport within the Gaussian distribution of disordered energy states within the organic side of the interface is demonstrated and characterized. In Section 3.2 the absence of SCLC characteristics for all temperature-dependent current-voltage measurements on the ITO/ α -NPD/Pd organic structure of [13] is determined. The strong bias dependence of E_{int} is evaluated and the detrimental effect of its E_a dependence on the drift hole mobility is demonstrated. In Sec. 4 the conclusions drawn are presented.

On the basis of the results presented here the current/voltage method might be of interest also in the area of contact engineering.

2 THE EFFECT OF THE ELECTRODE/ORGANIC CONTACT ON CURRENT-VOLTAGE DATA

It was shown in [11] that the extended Mott-Gurney law describes the steady state current density within the single layer metal/organic structure that originates due to the externally applied DC electric field, E_a , and reflects the complicated electrode/organic processes, which directly govern the charge transport. These processes have generally been neglected in the analyses of current-voltage measurements from which the charge mobility is most often extracted.

Throughout this work, the hole-injecting electrode at the positive potential, V_a , is considered at the origin of the frame of reference and the cathode is placed at the position $x = L$, where L is the thickness of the organic layer. The general expression of the hole drift current density is then expressed by the extended Gurney-Mott law, [11], that explicitly considers the charge-injecting interface of a given metal/organic structure and reads,

$$J = \varepsilon\varepsilon_0\mu_d\frac{E_a^2}{L} \quad (2.1)$$

where, j is the (steady state) current density, ε , is the relative permittivity of the organic layer, ε_0 is the permittivity of vacuum, $E_a = V_a/L$, is the externally applied DC electric field over the organic structure and μ_d is E_a dependent charge carrier drift mobility, defined as,

$$\mu_d = \frac{\mu_{max}}{2}$$

$$\left\{ \frac{9}{8} - \frac{3}{2} \left(\frac{E_{int}}{E_a} \right)^2 + \left[\frac{81}{64} - \frac{3}{4} \left(\frac{E_{int}}{E_a} \right)^4 + 3 \left(\frac{E_{int}}{E_a} \right)^3 - \frac{27}{8} \left(\frac{E_{int}}{E_a} \right)^2 \right]^{\frac{1}{2}} \right\} \quad (2.2)$$

The charge drift mobility, μ_d , depends on the organic morphology, intrinsic and extrinsic impurities, method of deposition, strengths of the charge-phonon interactions that determine the charge drift transport among the disordered energy states of the organic bulk, etc.

The stated model is characterized by two distinct, independent physical parameters; (a) the nonzero electric field at the charge injecting electrode/organic interface, E_{int} , [11] that is in this work investigated as a function of the externally applied electric field, E_a , and (b) the maximum value of the charge mobility μ_{max} as measured in a given experiment. Evidently, in the (forbidden limit) $E_{int} = 0$, see [11], Eq. (2.1) would have reduced into the original Mott-Gurney law, [14]. It is characterized by the charge density singularity, [14] at the charge-injecting interface. By postulating the existence of the non-zero electric field at the charge-injecting electrode/organic interface, $E_{int} \neq 0$, this deficiency is remedied, [11]. It can be noted, however, that for the ratio $E_{int}/E_a = c$, where c is a given constant $0 < c < 1$ the charge drift mobility Eq. (2.2) is E_a independent. Simple rearrangements of terms then result in the expression,

$$j = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V_a^2}{L^3} \quad (2.3)$$

where the so called effective charge mobility, μ , [14], identified as $\frac{8}{9} \mu_d$, is bias V_a independent. Eq. (2.3) represents the original version of Mott-Gurney law that describes the SCLC condition of the drift current density within the given organic semiconductor. As seen, Eq. (2.3) is in fact valid when the non-zero ratio E_{int}/E_a is a given constant, i.e. $E_{int} \neq 0$, and represents a particular example of Eq. (2.1).

However, it has been realized that the charge mobility, μ , Eq. (2.3) is in fact on the externally applied electric field, E_a , dependent parameter, [23]. With the current-voltage measurements of large number of organic semiconductors it was empirically determined that μ may be suitably formulated in terms of the phenomenological exponential bias-dependent charge mobility given by,

$$\mu = \mu_0 e^{\beta \sqrt{E_a}} \quad (2.4)$$

The last two expressions taken together traditionally describe the SCLC (i.e. the maximum steady current density that a given electrode/organic structure may sustain) and are very often used in current-voltage experiments for experimental determination of the charge mobility, [8-10]. It was shown, [11] that the general expression for hole current density j , Eq. (2.1), leads to SCLC only under the condition that E_{int} is E_a independent quantity in which case the contact is defined as ohmic. The deviation of the given current density from the shape of SCLC curve is then reflected in a bias dependence of E_{int} (remember that μ_{max} is fixed since it is for a given organic structure extracted from the maximal value of the current density, j_{max} , as obtained at maximum E_a). The bias dependence of E_{int} is determined in two steps. Initially, the (fixed) parameters $E_{intSCLC}$, and μ_{max} , are determined so that the trial SCLC fit, Eq. (2.1), intersects the first and the last current

density points of the given E_a interval of measurements. With μ_{max} known the bias dependence of E_{int} is then described by the (positive) roots of Eq. (1) evaluated successively for each experimentally determined pair (j, E_a) . Note that the first and the last current density points are measured at two different values of E_a . Both points are characterized by identical value of $E_{int} = E_{intSCLC}$. Consequently, E_{int} is a double valued function of the parameter E_a in all cases in which the current density defies the SCLC description.

The relationship exist among the electric field at the charge-injecting electrode/organic interface, E_{int} , the externally applied electric field, E_a , and the electric field at the site of the interface due all other charges present within the organic, E_{ch} . It is deduced by observing that the resultant electric field within the organic layer is, $\vec{E} = \vec{E}_a + \vec{E}_{ch}$ see [16]. Written explicitly for the (thin) charged electrode/organic interface placed at the coordinate origin $x = 0$ the spatial dependent internal electric field, $E(x)$, is then equal to

$$E(x) \equiv \left[E_{int}^2 + 2 \frac{j(E_a)}{\varepsilon \varepsilon_0 \mu_{max}} x \right]^{1/2} = E_a + E_{ch}(x) \quad (2.5)$$

Note that the interfacial electric field, E_{int} , is incorporated within the left term. Consequently, $E_{ch}(x)$ then represents the resultant electric field within organic due to all other sources except E_{int} . Since the hole-injecting interface is at the position $x = 0$, it immediately follows that,

$$E_{int} = E_a + E_{ch} \quad (2.6)$$

where $E_{ch}(x=0) = E_{ch}$. Consequently, current-voltage experiments directly provide the interfacial electric field, E_{int} , see Eq. (2.1), and with Eq. (2.6) its relation to the electric field at the site of the interface that results from the distribution of other charges existing within the organic is presented.

The compatibility of the current-voltage data analyses using the above-presented method with the notion of the charge transport within the Gaussian disordered energy states in the organic is illustrated by virtue of a simple model described below.

Lange et al. [21], have reported that the band bending in organics may be explained by the transfer of charge from the electrode into the tail of Gaussian distribution of energy states, DOS, which extends into the organic charge transport gap. The space charge formed by occupation of tail states strongly modulates the width of Gaussian energetic disorder at the electrode-organic contact and in such a way appears to affect the charge mobility. Since, as shown presently, the bias dependence of the hole drift mobility is greatly influenced by the electric field at the hole-injecting electrode/ α -NPD interface it remains to show that the hole drift mobility (or equivalently the electric field E_{int}) and the Gaussian energetic disorder at the electrode/ α -NPD contact are mutually interrelated. To show this, a simple physical model is constructed. It is assumed that the interface may be represented as a plane sheet of uniformly distributed holes that occupy the disordered energy states at the organic side of the contact. Specifically, Oehzelt et al. [22], have determined that in thermal equilibrium in absence of the externally applied electric field, $E_a = 0$, the nonzero charge density is spontaneously induced at the metal/organic contact. This fact triggers a shift of the central position of the Gaussian energetic disorder in the direction of the increased (negative) binding energy [22]. The prediction has been verified by Whitcher et al. [24, 25], and Khoshkho et al. [26]. More specifically, Beck et al., [27], have with

the infrared spectroscopy method determined (at $E_a = 0$) that the charge at the Mo3/CBP interface where CBP denotes (4,4'-bis(N-carbazolyl)-1,1'-biphenyl) organic semiconductor decays to a very small value already within about 3 nm into the CPB organic bulk.

With an extension of the ideas of [22] to cases in which the externally applied electric field is non-zero, $E_a \neq 0$, it was already possible: (a) to show that the room temperature linearly increasing electric field at the hole-injecting ITO/P3HT (i.e. poly(3-hexylthiophene)) interface leads to the negative field hole mobility, [28], and (b) to provide the evidence of the relationship between the linearly dependent interfacial electric field and the Gaussian energetic disorder, σ , within the narrow region of the P3HT organics close to the hole-injecting metal/organic interfaces [28].

In order to investigate the relationship between the E_a dependent electric field at the hole-injecting electrode/organic interface and the Gaussian energetic disorder in the organic a simple model has been constructed, [28]. Considering the interface as a thin, laterally infinite, uniformly charged plane (in presence of steady electric fields) than from the Gauss law $\epsilon \epsilon_0 \oint \vec{E}_{int} d\vec{S} = q(p_t + p_f)$ it follows that $E_{int} = \gamma_{int}/(2\epsilon \epsilon_0)$. Here p_t , and p_f are the (number) densities of trapped and free charge on the interface and γ_{int} denotes the interface charge density per unit area. In parallel to [28] and elaborating the approach of [22] and [27], it is now assumed that L^* nm thick, laterally unlimited, organic layer in contact with an electrode is covered by an excess hole (areal) density that is in the first approximation equal to $q \rho L^* P(E) = 2 \epsilon \epsilon_0 E_{int}$, where $P(E)$ is the probability that the disordered interfacial energy states are populated. The width L^* chosen in this work, is the distance from the electrode/organic contact into the organic bulk at which the induced interface charge density is reduced to a small value, see Fig. 2a of [22], and Fig. 2 of [27]. The holes within the layer represent the seat of the interfacial electric field, E_{int} . The holes populate the disordered energy states within the organic interface, which are described in terms of Gaussian distribution function characterized by its width, σ , and the energy shift, φ . The stated relationship then reads,

$$E_{int} = \frac{q \rho L^*}{2 \epsilon \epsilon_0 \sigma \sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\exp\left[-\frac{1}{2} \left(\frac{E-E_H+\varphi}{\sigma}\right)^2\right]}{1+\exp\left[\frac{-E+E_F}{kT}\right]} dE \quad (2.7)$$

where E_H is the highest occupied molecular orbital (HOMO), and E_F is the Fermi level. In this work the energy shift, φ , and the width of the Gaussian, σ , are assumed to be implicit functions of the externally applied electric field, E_a . Evidently, the stated two parameters are fixed for constant E_{int} (SCLC conditions) but in case of the external bias-dependent E_{int} their bias dependence should vary in a particularly coordinated way on account that E_{int} is then a double-valued function of E_a . It is noted that Eq. (2.7) is: (a) independent of the hole mobility, and (b) that the product $q \rho L^*$, the interface (areal) hole charge density plays the role of the scaling factor only. For reference the number of charged molecules per unit area the (saturation) value of $\rho L^* = 8 \times 10^{13} \text{ cm}^{-2}$ is in [27] deduced from the measurements.

3 RESULTS AND DISCUSSION

3.1 The PEDOT: PSS/ α -NPD(100 nm)/TCTA(5 nm)/MoO₃/Al current-voltage data of Ref. [12]

The room temperature *j*-*V* measurements of the PEDOT:PSS/ α -NPD(100 nm)/MoO₃/Al organic structure of [12] were reported to exhibit unexpected behavior. The work functions of PEDOT:PSS is 5.1 eV, the HOMO level of the amorphous α -NPD is at 5.4 eV (i.e., the hole barrier between the two is then 0.3 eV) and the work function of MoO₃ is placed at 6.86 eV, [12]. Contrary to the expectations it was found that the hole current density in the reverse direction (Pedot:PSS contact at the positive potential) exceeds the hole current in forward direction of bias, i.e., when the Al contact is at a positive potential. The authors report, [12] that the current density symmetry in the forward and backward direction of current is established by the deposition of 5 nm thick tris(4-carbazoyl-9-phenyl)amine (TCTA) interlayer between the α -NPD and the MoO₃/Al electrode.

The stated current density asymmetry effect will now be tentatively explained. In the reverse direction of bias, the barrier at PEDOT:PSS/ α -NPD junctions appears to be small enough for the hole SCLC to take effect. However, the Al contact at the positive potential results in an unexpectedly weak current density, an effect that may be explained by the finding of Matsushima et al., [29]; in their study of the effect of the molybdenum trioxide layer placed between the ITO and α -NPD organic on the hole current transport the authors of [29] provide evidence that, under the stated polarity, the α -NPD/MoO₃ interface becomes charged. Specifically, it is claimed that α -NPD boundary layer of the interface is charged positively while the MoO₃ one negatively. Such a charged layer then detrimentally affects the hole injection from the MoO₃/Al electrode. It is a fact that with the 5 nm thick TCTA layer between the α -NPD organic and the positively biased MoO₃/Al electrode, [12], the SCLC regime is activated in the stated organic structure. This observation evidently supports the conjecture of Matsushima et al., [29], that in the forward direction of bias the α -NPD/MoO₃ interface becomes charged. If this is indeed so, it may be clarified by the time-resolved electric-field-induced optical second-harmonic generation, EFISHG, investigation in combination with the steady current voltage measurements of the type as reported recently by Nishi et al. [16].

The forward hole current (positive potential at Al) within the PEDOT:PSS/ α -NPD(100 nm)/TCTA(5 nm)/MoO₃/Al organic structure was reported to be of the SCLC type, [12]. Then it is expected that from calculated curve with the bias-independent electric field, E_{int} , Eq. (2.1), at the hole-injecting TCTA/ α -NPD interface, should describe the data well. Consequently, the room temperature $T = 295$ K measurements, [12], are compared to the SCLC fit predicted by Eq. (2.1) (solid triangles) that connects the first and the last data point of the $L = 100$ nm thick sample (solid hexagons). In all calculations reported here the relative dielectric constant $\epsilon = 3$. The parameters of this initial (trial) SCLC fit are found to be: the maximum hole mobility is $\mu_{max} = 3.7 \times 10^{-8}$ m²/Vs and the interfacial electric field is $E_{int} = 1.5$ MV/m, see Fig. 1. As seen in Fig. 1 an excellent fit to the $T = 295$ K data of [12] is indeed obtained but only within the range say, $E_a \geq 1.0 \times 10^7$ V/m, Fig. 1. Thus, within the interval $10.0 \text{ MV/m} \leq E_a \leq 25.0 \text{ MV/m}$ the electric field at the hole-injecting interface ($E_{int} = 1.5$ MV/m), is constant and the bias dependence of the current density, j , is governed by the product $\mu d E_a^2$. The hole drift mobility μd is weakly bias-dependent within the stated interval, as will be shown later. The fact that a clear disagreement between the SCLC fit and the data is observed within the interval of the applied electric field, $0.194 \times 10^7 \text{ V/m} \leq E_a$

$\leq 1.0 \times 10^7$ V/m, Fig. 1, signifies that the Al/MoO₃/TCTA/5 nm)/ α -NPD(100 nm)/PEDOT:PSS organic structure (Al at the positive bias V_a) is not barrier-free within the stated E_a interval.

For the Al electrode (at the origin of the frame of reference) at positive bias, $V_a > 0$ then follows that within the interval $1.94 \text{ MV/m} \leq E_a \leq 25.0 \text{ MV/m}$ the interfacial field $E_{int} < E_a$, see Fig 2. This fact demonstrates that the (organic side of) the hole-injecting interface is exposed to an additional (steady) electric field in the opposite direction of E_a . This electric field due to the space charge and other charge sources (E_{int} is excluded) is denoted as E_{ch} . In fact, it will be observed that the relationship $E_{int} < E_a$, is valid for all cases reported here even for non-SCLC current density conditions. Consequently, for the particular structure under investigation TCTA/ α -NPD is identified as the hole-injecting interface, and it is feasible that the space charge and perhaps also the α -NPD/PEDOT:PSS interface represent a positively charged source of the (steady-state) interfacial electric field, E_{ch} , acting in the opposite direction to E_a . The stated organic structure represents then a particular example of an organic bilayer, [16]. The resulting steady-state electric field at the hole-injecting interface TCTA/ α -NPD is equal to $E_{int} = E_a - E_{ch}$, see Eq. (6), in agreement with the experimental fact that $E_{int} < E_a$. The E_{int} represents the electric field at the TCTA/ α -NPD contact that is directed towards the cathode in the positive direction of the x-axis.

The stated difference between the trial SCLC fit and the data within $1.94 \text{ MV/m} \leq E_a \leq 10.0 \text{ MV/m}$ interval will now be analyzed. As seen, Fig. 1, the initial current density point $j_{init} = 15.75 \text{ A/m}^2$ at $E_a = 1.94 \text{ MV/m}$ and likewise $j = 1079.35 \text{ A/m}^2$ at $E_a = 10.0 \text{ MV/m}$, are both characterized by already deduced SCLC parameters $E_{int} = 1.5 \text{ MV/m}$, and $\mu_{max} = 3.7 \times 10^{-8} \text{ m}^2/\text{Vs}$. Following the procedure described in Sec. 2 the bias-dependent interfacial electric field, E_{int} , within the stated E_a interval is evaluated and the resulting electric field at the hole-injecting interface, E_{int} , is exhibited on Fig 2 (circles). Within the stated narrow E_a interval, it attains the shape of the distorted, inverted high order parabola that is analytically described by the approximation function presented in Table 1. It is noted that E_{int} is double-valued function of the argument E_a . The parameters of the SCLC curve well describing the data for $E_a \geq 10 \text{ MV/m}$ are shown in Table 2. Inserting the deduced bias-dependent E_{int} and the maximum hole mobility, μ_{max} back into Eq. (2.1), the newly calculated fit practically coincides (as it should) with the data throughout the remaining part of the measuring interval (the crosses over the measuring points, i.e., solid hexagons), Fig. 1.

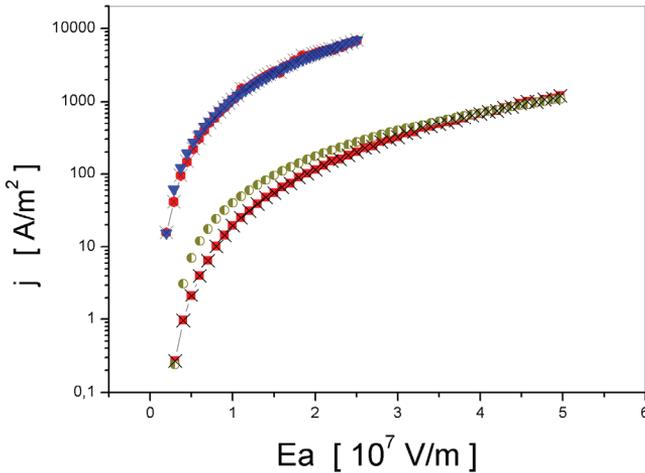


Figure 1: Top curves: the comparison of the calculated trial SCLC curve (filled triangles) to the PEDOT:PSS/ α -NPD(100 nm)/TCTA(5 nm)/MoO₃/Al hole $j - E_a$ data of [12] measured at $T = 295$ K (filled hexagons) reveals the existence of SCLC regime at values of the externally applied electric field $E_a \geq 10$ MV/m. Bottom curves: the calculated trial SCLC curve (half-filled circles) to the data at $T = 213$ K (filled squares) of [12] exhibits the narrow SCLC regime only for $E_a \geq 41.8$ MV/m. Crosses joined by the thin curve that in both examples coincide with the measurements denote the predictions of Eq. (2.1), when incorporating the deduced and for each temperature appropriate E_a dependent electric field at the hole-injecting α -NPD(100 nm)/TCTA interface, E_{int} , see Fig. 2. The data are redrawn from Fig. 2b of Ref. [12].

Viewing the $T = 295$ K curve (Fig. 1) the slow continuous merger of the SCLC fit to measurements that is taking place within the certain narrow range of E_a is noted. Consequently, Fig. 1 provides evidence that the quasi-ohmic contact may transit into a good ohmic one by an appropriate increase of the externally applied electric field, E_a . It is, however, unclear if this process is reversible. At this point, it should be stated that as seen in Fig. 1 the transition occurs continuously and it is not feasible that this interval could be univocally determined. For this reason such an interval is in this work replaced by a single current density point (here defined at $E_a = 10.0$ MV/m) at which both curves still coincide. This simplification affects the obtained results in two ways: (a) the calculated values of E_{int} are progressively scattered with increasing E_a , and (b) the derivative of the function $E_{int} = E_{int}(E_a)$ with respect the argument E_a is then discontinuous at the point of merger, see Fig. 2. It should be emphasized that the magnitude of the $T = 295$ K resulting (bias-dependent) interfacial electric field, E_{int} , within the initial part of the E_a interval, i.e., within the quasi-ohmic region, $1.94 \text{ MV/m} \geq E_a \geq 10 \text{ MV/m}$, considerably exceeds the one that characterizes the SCLC regime (i.e., $E_{int} = 1.5 \text{ MV/m}$), see Fig. 2 (circles).

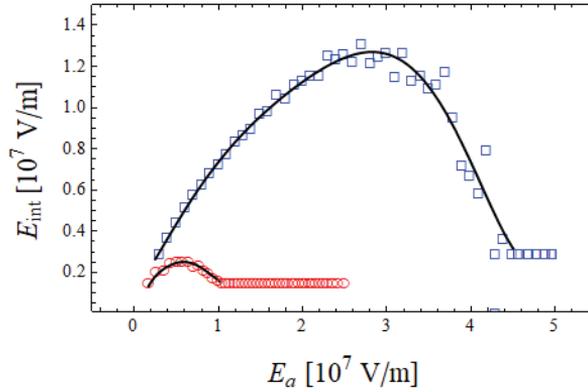


Figure 2: The calculated electric fields at the hole-injecting electrode/ α -NPD(100 nm) interface, E_{int} , as a function of the applied electric field, E_a , are exhibited for cases of the hole j - E_a data of [12]. The deduced interfacial electric field at $T = 295$ K (circles) and $T = 213$ K (squares) are represented by the approximation functions given in Table 1, and are shown by thin curves in Fig. 2. The constant E_{int} , characterize the E_a regions of SCLC regime indicating the ohmic resistance at the hole-injecting contact.

Inserting the two parameters $\mu_{max} = 3.7 \times 10^{-8} \text{ m}^2/(\text{Vs})$, and $E_{int} = 1.5 \text{ MV/m}$ into Eq. (2), the calculated bias-dependent SCLC hole drift mobility, μ_d , at $T = 295$ K is exhibited in Fig. 3 (stars). For comparison with Eq. (2.3) the predicted fit with the exponential bias-dependent mobility, Eq. (2.4), (empty squares) is also included in Fig. 3. The parameters of the stated mobility are found to be: $\mu_0 = 3.6 \times 10^{-8} \text{ m}^2/(\text{Vs})$, and $\beta = 0.4 \times 10^{-4} (\text{m/V})^{1/2}$. As shown in Fig. 3 the evaluated mobility, μ , Eq. (2.4), and μ_d , Eq. (2.2) considerably differ within the initial part of the E_a interval. The calculated curves within SCLC region practically coincide, a behavior similar to the one reported; see Fig. 4 of [11]. However, the correct bias dependence of the hole drift mobility is obtained only when Eq. (2.2) is calculated with the bias-dependent E_{int} ; see Fig. 2 (circles). The result is exhibited in Fig. 3 (solid points) and the strong E_a dependence of μ_d , at small values of the externally applied electric field, Fig. 3, within the range of disagreement between the data and the (trial) SCLC curve is evident. The calculated curve is characterized by the relatively slower increase of the hole drift mobility with E_a (solid points) occurring entirely within the quasi-ohmic region, Fig. 3. Consequently even at $T = 295$ K the sample of [12] was not absolutely barrier-free. Over $E_a > 10 \text{ MV/m}$ the ohmic region is attained that is characterized by the constant value of $E_{int} = 1.5 \text{ MV/m}$. This is the region within which the hole drift mobility, Eq. (2.2), exhibits very weak E_a dependence as evidenced on Fig. 3. The bias-dependent exponential hole drift mobility, Eq. (2.4), is at $E_a = 25.0 \text{ MV/m}$ then equal to $\mu_d = 4.4 \times 10^{-8} \text{ m}^2/(\text{Vs})$. The stated interval represents the saturation region of the electric field at the hole-injecting electrode/organic interface. Consequently, the SCLC region is the region within which the parameter, E_{int} , the interfacial electric field is independent of the externally applied electric field, E_a . Then the hole drift mobility, Eq. (2.2), is itself only weakly E_a dependent and for this reason the current density, Eq. (2.1), within the saturation region is almost proportional to E_a^2 .

Table 1: Approximation functions for the temperature dependent electric field at the hole injecting TCTA/ α -NPD organic interface of the form $E_{int} = a + b E_a + c E_a^2 + d E_a^3 + e E_a^4 + f E_a^5 + g E_a^6$ are shown. E_a denotes the externally applied electric field.

T [K]	a [V/s]	b	c [(V/s) ⁻¹]	d [(V/s) ⁻²]	e [(V/s) ⁻³]	f [(V/s) ⁻⁴]	g [(V/s) ⁻⁵]
PEDOT:PSS/α-NPD(100 nm)/TCTA/MoO₃/Al Ref. [12]							
213	-1.039×10 ⁶	1.733	-1.826×10 ⁻⁷	1.392×10 ⁻¹⁴	-5.750×10 ⁻²²	1.172×10 ⁻²⁹	-9.450×10 ⁻³⁸
295	-1.232×10 ⁶	2.618	-9.311×10 ⁻⁷	2.009×10 ⁻¹²	-2.469×10 ⁻²⁰	1.527×10 ⁻²⁷	-3.693×10 ⁻³⁵
ITO/α-NPD(100 nm)/Pd Ref. [13]							
189	-1.872×10 ⁷	4.287	-2.354×10 ⁻⁷	8.897×10 ⁻¹⁵	-1.814×10 ⁻²²	1.939×10 ⁻³⁹	-8.607×10 ⁻³⁹
295	2.815×10 ⁸	-88.586	1.136×10 ⁻⁵	7.349×10 ⁻¹³	2.564×10 ⁻²⁰	-4.609×10 ⁻²⁸	3.348×10 ⁻³⁶

Table 2: The temperature dependent maximum hole mobility, μ_{max} , of the electrode/ α -NPD(100 nm) thick organic entity and the associated electric field at the hole-injecting interface, E_{int} , are presented. Both quantities, based on published measurements of Rohloff et al., [12], and van Mensfoort et al., [13], are deduced by Eq. (2.3) at the maximum value of the externally applied electric field, E_a^{max} .

T [K]	μ_{max} [10 ⁻⁸ m ² (Vs) ⁻¹]	E_{int} [10 ⁷ Vm ⁻¹]	E_a^{max} [10 ⁷ Vm ⁻¹]	Ref.
PEDOT:PSS/α-NPD(100 nm)/TCTA/MoO₃/Al [12]				
213	0.15	0.29	5.0	
295	3.7	0.15	2.5	
ITO/α-NPD(100 nm)/Pd [13]				
189	0.013	2.20	7.5	
295	0.08	1.41	3.1	

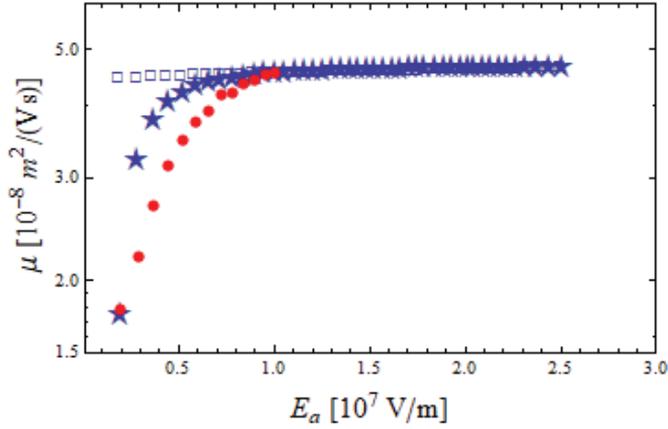


Figure 3: The E_a dependence of the room temperature hole drift mobility within the α -NPD structure of [12] is shown. Assuming the SCLC regime to exist within the entire interval of measurements then: (a) the exponential bias-dependent hole mobility, Eq. (2.3), with the parameters, $\mu_0 = 3.6 \times 10^{-8} \text{ m}^2/(\text{Vs})$, and $\beta = 4.0 \times 10^{-5} (\text{m/V})^{1/2}$ is described by empty squares, and (b) the hole drift mobility, μ_d , calculated from Eq. (2.2) with the constants $E_{int} = 1.5 \text{ MV/m}$, and $\mu_{max} = 3.7 \times 10^{-8} \text{ m}^2/(\text{Vs})$ is shown by stars. The μ_d curve denoted by solid points represents the predictions (within the non-SCLC region) of Eq. (2.2) evaluated with bias-dependent E_{int} of Fig. 2 (circles). Within the SCLC interval of bias, all three curves coincide.

At this point it has to be emphasized that μ_{max} depends on the coordinate (E_{amax} , $j(E_{amax})$) of the measured current-voltage end point. Consequently, μ_{max} is evidently E_{amax} sensitive, and so are the deduced bias-dependent E_{int} values. The initial, i.e., the first current density point with coordinates (E_{amin} , $j(E_{amin})$) defines the initial intersection with the calculated (trial) SCLC curve and, consequently, this point is primarily related to the value of the second SCLC parameter, the bias-independent interfacial electric field, E_{int} . Discarding some given number of measurements within the highest range of the E_a interval (i.e. narrowing the given E_a interval) then the value of μ_{max} , the maximum hole mobility is decreased and, consequently, the set of bias-dependent interfacial fields calculated within the narrow E_a interval (relative to the narrowed SCLC curve) is also correspondingly changed. However, the bias-dependent hole drift mobility curves, Eq. (2.2), calculated for each data set separately are found to coincide (within the shorter E_a interval) and thus prove that the magnitude as well as the bias-dependence of the hole drift mobility, μ_d , is invariant to the width of the E_a interval. Thus, the auxiliary parameters the bias-independent μ_{max} and the bias-dependent set of evaluated E_{int} then via Eq. (2.2) define the bias-dependent hole drift mobility as a unique material property of the electrode/organic entity under the investigation.

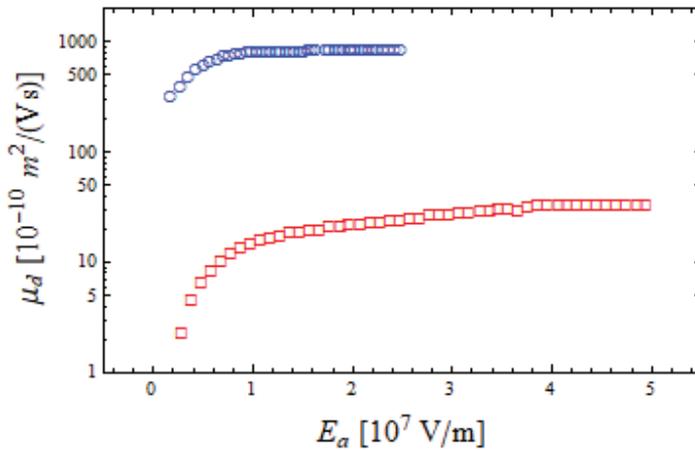


Figure 4: The E_a dependence of the calculated hole drift mobility, μ_d , Eq. (2.2) incorporating the deduced bias dependence of E_{int} at $T = 295$ K (circles) and $T = 213$ K (squares), within the α -NPD(100 nm) structure of [12] is shown. The growing part of the curves denotes the quasi-ohmic contact region that with the increasing E_a continuously evolves into the ohmic region of (almost) the constant values of μ_d (compare Fig. 2).

The results of the similar analyses as above of the data measured at $T = 213$ K, [12], are also shown on Fig. 1 (filled squares). It is immediately evident that the initial ($E_{int} = 2.9$ MV/m and $\mu_{max} = 1.5 \times 10^{-9}$ m²/Vs) SCLC fit calculated from Eq. (1) (half filled circles) exhibits within the interval (e.g. 3.0 MV/m $\leq E_a \leq 41.8$ MV/m) a noted disagreement to the data set. However, beyond that, i.e., within 41.8 MV/m $\leq E_a \leq 50$ MV/m interval the agreement between this initial (trial) SCLC curve and the measurements is evident. It is noted that the calculated SCLC curve using the above two bias-independent parameters again intersects the first and the last current-density data point. This is then a clear indication that the SCLC regime within the given structure (at the stated temperature) occurs within the highest range of the E_a interval only. Thus it is confirmed that the ohmic region of the PEDOT:PSS/ α -NPD(100 nm)/TCTA(5 nm)/ MoO₃/Al structure is temperature dependent and may be induced by the external bias, E_a . The ohmic region at $T = 213$ K has considerably narrowed in comparison to the one at $T = 295$ K. In addition the measuring E_a interval has substantially widened. Following the previously described steps, the bias-dependent interfacial electric field, E_{int} , is calculated, and together with the approximation function, Table 1, is exhibited in Fig. 2 (squares). Within the interval 41.8 MV/m $\geq E_a \geq 45.0$ MV/m the calculated values of E_{int} are considerably scattered. This occurs due to the fluctuations in reading off the (finite sized) data points that almost coincide with the SCLC fit, see Fig. 1. However, when the calculated bias-dependent E_{int} is inserted into Eq. (2.2), then the fit, Eq. (2.1) to the measured data is once again excellent (represented by the thin line passing through the crosses), Fig. 1. Once again it is observed that the magnitude of bias-dependent E_{int} considerably exceeds the corresponding (but bias-independent) value within the (narrow) SCLC region, Fig. 2. The E_a dependence of the hole drift mobility, Eq. (2.2), at $T = 213$ K is presented in Fig. 4, (empty squares).

Thus far, the emphasis has been on the dependence of the electric fields, E_{int} , at hole-injecting TCTA/ α -NPD interfaces, as a function of the externally applied electric field, E_a , and an excellent agreement with the published data has been obtained. Quite similar quality fits are presented in

[12], and [13], but their calculations were based on the drift-diffusion hole transport using the well known models of the hole mobility characterized by hopping between the disordered energy states of the organic bulk as described by the Gaussian distribution function [18 - 20]. In particular, their results have shown that the half widths, σ , of the Gaussian disordered states, depending on the particular case investigated, should be placed within the interval $0.08 \text{ eV} \leq \sigma \leq 0.14 \text{ eV}$. It is noted that σ is independent of the applied electric field and describes an average over the organic sample.

The essential difference between the results reported in the literature and the findings presented here is the fact that at all temperatures the (temperature dependent) electric field at the hole-injecting TCTA/ α -NPD interface is non-zero and definitely non-exponential. In addition, the resulting findings are obtained devoid of any phenomenological parameters. It is interesting that the data of [12], and [13], are in the present work also interpreted to an excellent approximation but seemingly on wholly unrelated basis. Consequently, it appears that the Gaussian disorder model and this work might be somehow related. The cause that different studies of hole mobility performed under similar conditions on chemically identical α -NPD organic semiconductor provide rather inconsistent results (compare for instance Figs. 4 and 8) is, in this work, attributed to unequal conditions at the hole-injecting interfaces, see Fig. 2, and Fig. 8.

In [21] the charge transfer from the electrode into the density of states within the organic bulk has been identified and it was suggested that the spread of the disordered energy states near the interface appeared to be correlated with the charge mobility. Consequently, it now remains to show that the above derived bias-dependent electric field at the hole-injecting TCTA/ α -NPD interface, $E_{int} = E_{int}(E_a)$, is related to the Gaussian energetic disorder at the organic side of the interface in conjunction with findings described in [18 - 20].

The deduced E_{int} , the inverted and distorted high order parabolas, are (for non-ohmic contacts) all double valued functions of the argument E_a , see Fig. 7. The calculations based on Eq. (2.7) are performed in the reverse order starting with E_{int} at the maximum value of the applied field, E_a , and proceed in a step-wise fashion towards its initial value. With the decreasing E_a , the corresponding value of the (bias-dependent) interfacial electric field, E_{int} , increases, attains its relative maximum and then decreases, as seen in Fig. 7. In the calculations the following parameters were used: $\rho = 1.4 \times 10^{27} \text{ m}^{-3}$, see [13], $L^* = 5 \text{ nm}$, $\epsilon = 3$, $E_H = 5.4 \text{ eV}$, $E_F = 5.1 \text{ eV}$, [12]. The thickness $L^* = 5 \text{ nm}$ of the hole charged interface is chosen such that the (areal number) density ρL^* of charged molecule is comparable with the similar value quoted in [27]. However, since this factor is just a scaling factor its exact magnitude is not crucial for the discussion that follows.

In the analyses of the lowest temperature $T = 213 \text{ K}$ data reported, [12], taking into consideration E_{int} shown on Fig. 2 (filled squares), the value for σ was set to $\sigma = 0.11 \text{ eV}$ (squares), ($E_{int} = 2.9 \text{ MV/m}$ at $E_{amax} = 50.0 \text{ MV/m}$) and the energy shift was then found $\varphi = 0.7197 \text{ eV}$ (crossed circles). The bias dependence of the pair (σ , φ) exhibits shapes similar to the ones above and are shown in Fig 5. Despite the particular precaution taken by authors of [12] to eliminate the potential barrier at the hole-injecting TCTA/ α -NPD interface, the barrier is nevertheless still present within the interval $2 \text{ MV/m} < E_a < 42.0 \text{ MV/m}$ as evidenced by the bias dependent interfacial electric field, Fig. 2.

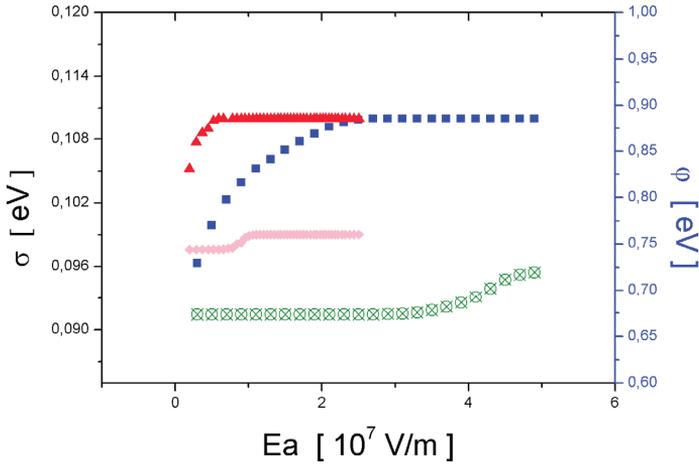


Figure 5: The E_a dependence of the Gaussian width, σ , (left scale) calculated from Eq. (2.7) for the values of E_{int} that are shown on Fig. 2: $T = 213$ K (filled squares), and $T = 295$ (filled triangles) is exhibited. The E_a dependence of the energy shift, ϕ , (right scale) of Gaussian peak is presented for $T = 213$ K (crossed circles) and $T = 295$ K (diamonds).

As seen, the interfacial electric field deduced from $T = 295$ data of [12] is bias-dependent within the initial interval $2 \text{ MV/m} \leq E_a \leq 10 \text{ MV/m}$, see Fig. 2 (circles), while above it the SCLC regime prevails and E_{int} attains a constant value $E_{int} = 1.5 \text{ MV/m}$ (squares). The constant value of E_{int} is according to Eq. (2.7) reflected in bias-independent pair (σ, ϕ) and E_{int} then indicates the existence of a stationary, bias-independent, small potential barrier against the injection of holes at the respective interface.

A comment about the nature of the double valued inverted parabolas E_{int} with the increasing E_a is now in order. The increasing part of the E_{int} curve is related to the diminishing value of σ keeping the constant value of ϕ , while the decreasing part of E_{int} illustrates the increasing energy shift ϕ , at the constant value of the Gaussian width, σ . Consequently, in this way the meaning of the apparent double valued E_{int} with the increasing E_a is clarified.

In this section, a relationship of E_{int} with the Gaussian disorder energy states at the interface is thus established. It is well-known that the GDM model, [18], describes the charge hopping transport within the Gaussian disordered states in organics that is characterized by the constant width. It is demonstrated above that at given temperature the bias-independent interfacial electric field, E_{int} , is related not only to the bias-independent Gaussian width but also to the bias-independent energy shift of its peak. Such a specific case occurs only under the SCLC condition characterized by the (relative) highest attainable values of the hole drift mobility, μ_d , that then exhibit a weak monotonic increase with the externally applied electric field, see Fig. 3. As presented here, none of the samples investigated in [12] and [13] has been truly barrier-free within the investigated E_a interval of measurements.

3.2 The ITO/ α -NPD(100 nm)/Pd current-voltage data of Ref. [13]

Taguchi et al., [17], have investigated the room temperature IZO/ α -NPD(200 nm)/Al organic structure by EFISHG method, in which IZO is the indium zinc oxide. Independently of the polarity of bias, it was determined that the electric field within the α -NPD organic is directed from anode to cathode (as expected) with the electrodes being charged accordingly. No other phenomena have been reported. This observation is here interpreted as the evidence that the so-called built-in voltage between the anode and cathode is compensated by a suitable collection of charge on the appropriate interface. The evidence that such compensation of the built-in voltage is also taking place in bilayer organic structures has been provided by Nishi et al., [16].

Van Mensfoort et al., [13] have reported the $j - V$ results of the temperature and thickness dependent hole transport measurements in the amorphous small-molecule organic semiconductor α -NPD. The diode structures of the type ITO/ α -NPD(L)/Pd, the organic thicknesses being $L=100$ nm and 200 nm are described in [13] in terms of the well-known charge transport models. The ITO contact was assigned as the anode.

In the previous section, it was shown that the fit to the SCLC data enables the two parameters, E_{int} , as well as μ_{max} of Eq. (2.2) to be simultaneously deduced. It is observed that the current density data at low E_a are weakly displaced from the SCLC curve. Using the previously determined μ_{max} , such data then enable the bias dependence of E_{int} to be determined from Eq. (2.1). However, in examples of strong deviation of data from the SCLC characteristics, the bias-independent parameter μ_{max} ought to be evaluated separately. This is accomplished by using the trial SCLC curve that intersects the first and the last current density point within the appropriate interval of E_a . The procedure is illustrated as follows.

The data of [13] are again tested for the SCLC regime characterized by the two bias-independent parameters: E_{int} , and μ_{max} . The disagreement between the data and the (trial) SCLC curve represents a measure of the contact deficiency. According to [11] and as shown above, the maximum hole mobility, μ_{max} , is determined from the fit of Eq. (2.1) through the current density point at the maximum E_a , within its respective interval while in the first approximation is E_{int} represented by the initial, but slightly decreased value of E_a . In the next step, E_{int} is refined so that the calculated, postulated SCLC current density curve also intersects the first current-density data point at the initial value of the E_a interval. The experimental data of [13] and the calculated, E_a dependent, trial SCLC current density curves intersecting the data at corresponding abscissa values E_{amin} and E_{amax} are shown in Fig. 6 for $L = 100$ nm sample of [13]. The SCLC parameters for the room temperature $T = 295$ K measurements are $E_{int} = 14.1$ MV/m, and $\mu_{max} = 7.5 \times 10^{-10}$ m²/Vs determined within 14.12 MV/m $\leq E_a \leq 31.4$ MV/m (experiment – solid diamonds, calculations – solid triangles). At the lowest temperature $T = 189$ K the corresponding (trial) SCLC values obtained are $E_{int} = 21.96$ MV/m, and $\mu_{max} = 1.3 \times 10^{-10}$ m²/Vs within 22.0 MV/m $\leq E_a \leq 74.9$ MV/m (experimental data – filled squares, calculations – tiny diamonds), see Fig. 6.

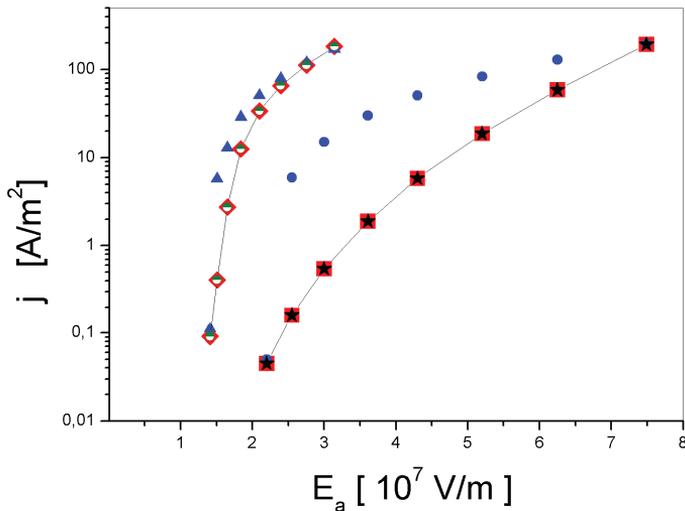


Figure 6: The ITO/ α -NPD(100 nm)/Pd hole $j - E_a$ data measured at $T = 295$ K (diamonds) and at $T = 189$ K (squares) of [13] are compared to the calculated trial SCLC curves (triangles at $T = 295$ K, and tiny diamonds at $T = 189$ K). It is shown that by using the relevant temperature deduced bias dependent electric field, E_{int} , see Fig. 7, at ITO/ α -NPD interface then by Eq. (2.1) calculated fits ($T = 295$ K, half filled circles, and $T = 189$ K, stars) fully merge with measurements. The data are redrawn from Fig. 3b of [13].

Evidently, the curves calculated under the SCLC assumption (solid triangles: $T = 295$ K, and solid points: $T = 189$ K), apart for the first and the last data points, strongly deviate at both temperatures from the data of [13] (solid diamonds and solid squares), see Fig. 6. The disagreement indicates the complete absence of the SCLC regime within the ITO/ α -NPD/Pd structure; consequently the contact in question is at most quasi-ohmic.

Eq. (2.1) in conjunction with the measured current density, j , [13], is then used to calculate E_{int} as a function of E_a . The obtained bias dependence of E_{int} is to a very good approximation described by the temperature-sensitive, 6-th order (inverted) distorted parabola, Table 1, see Fig. 7 ($T = 295$ K solid dots, and $T = 189$ K filled diamonds). Then, using the extracted E_a dependent interfacial electric field, E_{int} , see Fig. 7, together with the appropriate value of the (constant) maximum hole mobility in Eq. (2.1) the recalculated hole current density, j , at each temperature practically coincides with the measured data. This is shown in Fig. 6 exhibited by the thin curve through the calculated points that all coincide with the measurements.

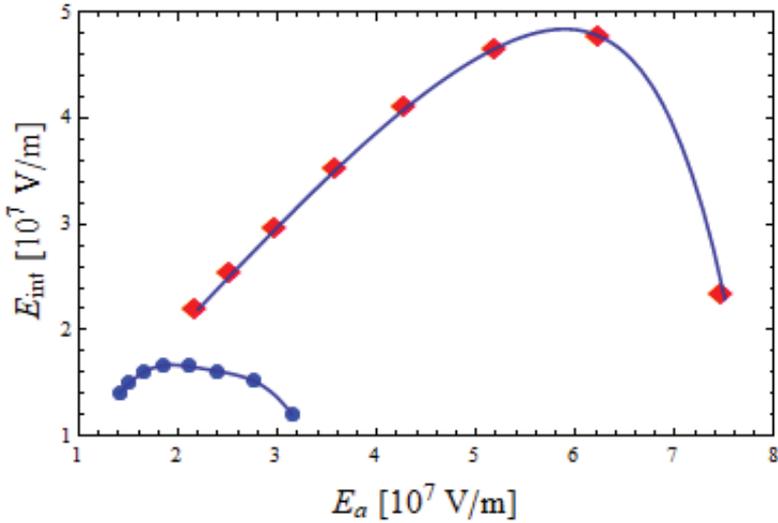


Figure 7: The calculated electric field at the hole-injecting ITO/ α -NPD interface, E_{int} , as a function of the applied electric field, E_a , is exhibited for cases of the ITO/ α -NPD(100 nm)/Pd hole j - E_a data of [13]. The approximation functions of the calculated interfacial field at $T = 295$ K (solid dots) and $T = 189$ K (diamonds) are given in Table 1, and are represented by thin curves in Fig. 7. No traces of SCLC can be observed.

The room temperature zero-field mobility at $T = 295$ K of approximately $\mu_0 \sim 1 \times 10^{-9}$ m²/Vs but for $L = 200$ nm sample is reported in [13]. The maximum hole mobility for the stated sample analyzed using Eq. (2.2), turns out to be $\mu_{max} = 7.0 \times 10^{-10}$ m²/Vs (initial $E_{int} = 5.6$ MV/m). Consequently, μ_{max} and the zero-field prefactor, μ_0 , of the conventional exponential mobility remain comparable, [11] even in cases of a minor deviation from the ideal SCLC condition. Consequently, the zero-field prefactor, μ_0 , and the maximum hole mobility, μ_{max} , appear to be closely related under the SCLC occurrence. Since the latter parameter is strongly temperature-dependent and of the electrode/organic deposition method dependent quantity (as reflected in E_{int} , see Fig. 7) it is clear that the attempts of fitting various temperature-dependent current-density spectra by the single zero-field prefactor should be unsuccessful, [13].

In Fig. 8, the hole drift mobility for the room temperature structure of [13] is shown (solid dots). In comparison to Fig. 4, its E_a dependence evolves on considerably lower level on account of the smaller value of the maximum hole mobility, μ_{max} , due to the non-ohmic contacts. This occurs despite the fact that the bias-dependent interfacial electric field, E_{int} , (solid dots, Fig. 7) is about an order of magnitude above the one determined at the room temperature; compare Fig. 2.

For $L = 200$ nm organic at $T = 192$ K (the bias independent) maximum hole mobility is found to be $\mu_{max} = 5 \times 10^{-11}$ m²/Vs at $E_{amax} = 75$ MV/m (the postulated SCLC curve is calculated with fixed $E_{int} = 15.1$ MV/m). As seen, the maximum hole mobility in α -NPD organic is thickness dependent in agreement with [11], but bias independent.

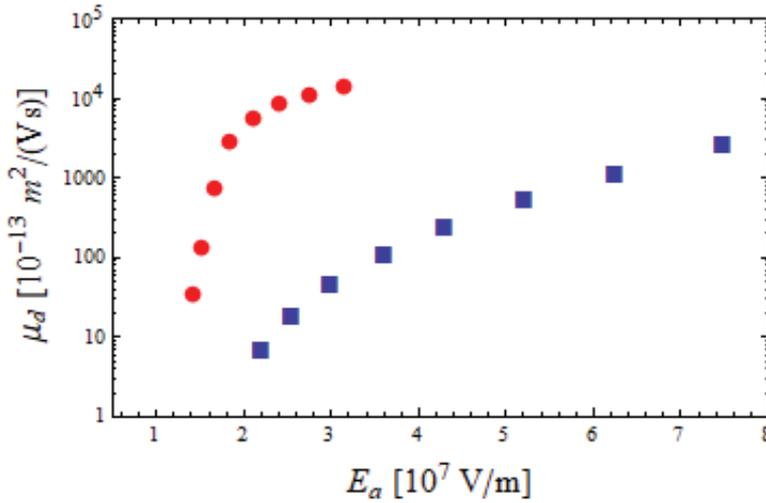


Figure 8: The E_a dependence of the calculated hole drift mobility, μ_d , Eq. (2.2) at $T = 295$ K (solid dots), and $T = 189$ K (solid squares) within the ITO/ α -NPD(100 nm)/Pd structure of [13] is shown.

Based on the analyses above and in conjunction with [11] it is seen that the current density to be characterized as SCLC then the measurements should satisfy Eq. (2.1) where the parameter E_{int} , the electric field at the hole-injecting electrode/organic interface, ought to remain constant over the wide span of the applied electric field E_a . If a pair of suitably determined bias independent parameters E_{int} and μ_{max} cause the calculated curve, Eq. (2.1), to intersect just the first and the last data point in the $j - E_a$ diagram this indicates: (a) that the electric field at the hole-injecting interface is bias-dependent, (b) that the operation of a given organic structure is limited to the quasi-ohmic region, and (c) that the maximum hole mobility would necessarily be smaller than the (optimal) one deduced under the SCLC conditions. This is well illustrated in Figs. 4, and 8.

As seen, compare Figs. 4, and 8, the (relatively) highest level of the E_a dependent hole drift mobility, μ_d , that is then accompanied by the minimal value of the interfacial electric field for a given electrode/organic structure is obtained for SCLC regime at room temperature. The above-presented examples and other similar observations point out the facts that the decrease in temperature is accompanied by the decrease of the hole drift mobility for over one order of magnitude that is simultaneously accompanied by the strong increase in the magnitude of the electric field at the hole-injecting electrode/ α -NPD interface. The large electric field at the hole-injecting interface then implies the existence of a considerable hole barrier.

Consequently, on this account, it is claimed that the hole-drift mobility within α -NPD bulk at $T = 295$ K is $\mu_d = 4.4 \times 10^{-8}$ m²/(Vs) (at $E_a = 25.0$ MV/m). It may now be claimed that the value $\mu_d = 7.0 \times 10^{-10}$ m²/(Vs) (at $E_a = 31.4$ MV/m) determined from the data of [13] at similar temperature, points to the contact incapability to attain the regions of mobility saturation. Similar observations are valid for measurements obtained at other temperatures.

The excellent agreement between the temperature and bias-dependent measurements of [13] and the predictions of Eq. (2.1), see Fig. 6 (thin curves), is a confirmation that the electric field at the hole-injecting ITO/ α -NPD organic interface is at all temperatures strongly E_a dependent. The E_a dependence of electric fields at the stated interfaces, E_{int} , are all distinct and suitably described in terms of the different (inverted, higher order) parabola-like curves, see Table 1. No real SCLC can be detected in the data of [13] for any thickness and temperature.

At this point it should be emphasized that the data of [12], and [13] are to an excellent approximation described by Eq. (2.1) in terms of two physical clearly defined parameters E_{int} , and μ_{max} . The stated data are also well- interpreted in terms of the hole transport among the disordered energy states within α -NPD organic medium described in terms of the Gaussian distribution, characterized by its width σ [12, 13]. Consequently, it remains to show that a relationship exists between Eq. (2.1) and the disordered energy states within the organic side of the interface at the hole-injecting electrode/organic junction. This will be accomplished on the basis of a simple model as expressed by Eq. (2.7).

Eq. (2.7) is applied to E_{int} deduced at $T = 189$ K, Fig. 6 (the starting value $E_{int} = 23.37$ MV/m at maximum $E_a = 74.9$ MV/m, see Fig. 7 (diamonds), with σ initially set to $\sigma = 0.10$ eV. This choice enables the direct comparison with results of [13] to be made. From Eq. (2.7) calculated corresponding energy shift turns out to be $\varphi = 0.719$ eV. In the next step the higher value of $E_{int} = 47.64$ MV/m evaluated at the lower $E_a = 62.5$ MV/m, Fig. 7 (diamonds), is balanced by keeping σ unchanged (filled squares) and allowing φ (filled stars) to decrease, see Fig. 9. Then the new value of the (decreased) energy shift $\varphi = 0.697$ eV is obtained in the calculation. In subsequent steps this value of the energy shift was kept constant. Namely, it appears unlikely that Gaussian peak could undergo an additional energy shift at still lower values of E_a . Consequently, in the subsequent calculations the parameter φ is kept constant but σ then decreases. The value of $E_{int} = 21.96$ MV/m corresponds to the initial $E_a = 21.99$ MV/m, see Fig. 7 (diamonds) for which $\sigma = 0.0915$ eV is found at constant $\varphi = 0.697$ eV. The results are presented on Fig. 9.

Starting once again with an arbitrary selected $\sigma = 0.10$ eV for Gaussian width, and $L^* = 5$ nm, then similar results are obtained in the analyses of the E_{int} at $T = 295$ K, see Fig. 7 (solid dots) that exists at ITO/ α -NPD organic structure. The results of the calculations are exhibited in Fig. 9. As seen at $\sigma = 0.10$ eV (diamonds) the energy shift φ (triangles) is at $T = 295$ K equal to $\varphi = 0.763$ eV and both parameters are considerably greater than the corresponding values calculated at lowest T . Both parameters are monotonically dependent on the externally applied electric field, E_a , and are single-valued functions of E_a , within the entire experimental region.

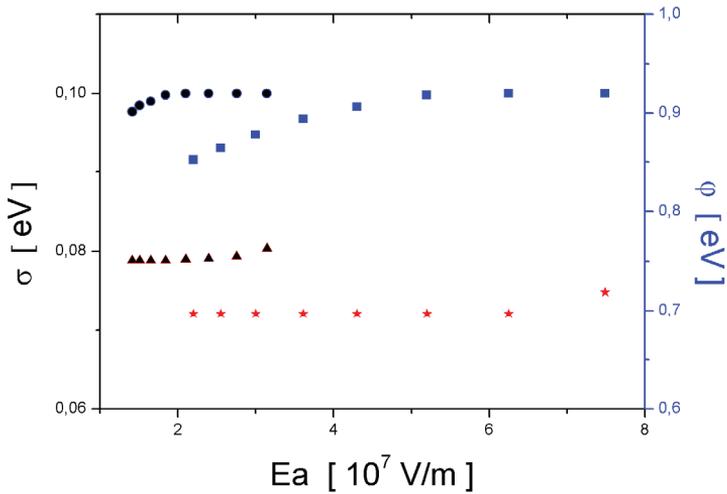


Figure 9: The E_a dependence of the Gaussian width σ , (left ordinate) calculated from Eq. (2.7) for the values of E_{int} that are shown on Fig. 7: $T = 189$ K (filled squares), and $T = 295$ (diamonds) is exhibited. The E_a dependence of the energy shift ϕ (right scale) of Gaussian peak is presented for $T = 189$ K (filled stars) and $T = 295$ K (triangles).

It is seen that the parameter $\sigma = 0.10$ eV for Gaussian width that has been determined by CDM results in [13] provides through Eq. (2.7) a self-consistent description of the double-valued E_{int} as a function of E_a under the condition that the Gaussian width, σ , and the energy shift of its peak, ϕ , are bias-dependent. Consequently, under the stated constraint the compatibility of Gaussian model derived parameter of [13] to the predictions of Eq. (2.7) has been demonstrated.

Their analyses have shown that the data cannot be consistently interpreted in terms of the drift-diffusion model incorporating the conventional exponential bias-dependent hole mobility. This inability was attributed to the fact that the dependence of the hole mobility on charge density is neglected in the stated model.

In this section, the hole drift transport within the disordered organic states has also been indirectly verified. It was shown that the experimentally determined interfacial electric field at the hole-injecting interface, E_{int} , is on the basis of a simplified model, well interpreted by the (E_a dependent) parameters of [22] that characterize Gaussian distribution of the disordered energy states within the α -NPD organic as reported [12, 13]. It was shown that such relationship exists irrespective of the current density being of SCLC type or not. Since by Eq. (2.2) the interfacial field, E_{int} , critically affects the hole drift mobility, μ_a , compare Figs. 4 and 8, the relationship between the hole drift mobility, μ_d , and Gaussian disordered states is revealed.

Returning to Figs. 4, and 8 the minimum value of the evaluated room temperature hole drift mobility for TCTA/ α -NPD interface of [12] turns out to be $\mu_{dmin} = 3.8 \times 10^{-8}$ m²/(Vs) at $E_{amin} = 1.94$ MV/m. The corresponding (minimum) value of μ_d determined for ITO/ α -NPD interface of [13] is found to be $\mu_{dmin} = 1.7 \times 10^{-12}$ m²/(Vs) at $E_{amin} = 14.12$ MV/m. Evidently, the effect of the electrode/ α -NPD electrical contact on the hole drift mobility is most instructive. The reason

for almost four orders of magnitude between the two is traced to the existence of considerably different electric fields at the stated contacts as exhibited in Fig. 2, and Fig. 7.

As seen, Eq. (2.1) enables that the interfacial electric field, E_{int} , be determined directly from the measured current-voltage data. This implies that the hole current density, j , as a function of E_a implicitly incorporates the hole density E_a dependence and, for this reason, the stated effect on the deduced hole drift mobility is redundant. Likewise, the effect of the built-in voltage is at all times expected to be compensated by the corresponding part of the charge density induced at the interface and, consequently, it is expected not to have any specific role in the steady-state current-voltage determination of E_{int} as a function of bias, E_a .

4 CONCLUSIONS

In the present work, based upon the published current-voltage data, the influence of the electric field at the hole-injecting electrode/ α -NPD organic structure on the hole transport has been investigated. It is shown that the (steady-state) hole drift current density within the organic structure crucially depends on two experimentally deduced parameters: the electric field at the hole-injecting electrode/organic interface, E_{int} , and the so-called maximum drift mobility, μ_{max} . It is empirically verified that, in a given experiment, μ_{max} , is a fixed constant, but the interfacial electric field, E_{int} , could be a function of the externally applied electric field, E_a . It is argued that hole drift SCLC occurs whenever the stated electric field, E_{int} , is over a given interval of the externally applied electric field, E_a a fixed small constant (with respect to E_a). Then, the hole drift mobility is prone to attain (weakly) bias-dependent saturation that represents an optimum for the organic structure under the investigation. If the data cannot be described by the constant E_{int} then its bias dependence may be calculated, and its detrimental effect on the hole drift mobility is clearly exhibited. It is revealed that merely by increasing externally applied electric field, the non-SCLC occurring due to the quasi-ohmic contact of the electrode/ α -NPD interface may transcend into the ohmic one. It is shown that the different electric fields that originate at the hole-injecting electrode/ α -NPD interfaces are closely related to vastly different values of the hole drift mobility within the chemically identical α -NPD organic.

On the assumption that the interface may be described in terms of an infinite thin uniformly charged sheet, then the relationship between E_{int} and the Gaussian distribution of the disordered energy states within the α -NPD organic interface is established. It is shown that the Gaussian width and the energy shift of its central position along the negative binding energy are E_a dependent.

Based on the described findings, it appears that the current-voltage method might serve as a useful tool for probing the electric fields at charge injecting/organic interfaces.

References

- [1] **K. H., S. Y. Yang, C. Yang, S. H. Kim, D. Choi, C. E. Park:** *Reducing the contact resistance in organic thin-film transistors by introducing a PEDOT:PSS hole-injection layer*, *Org. Electron.* **9**, 864, 2008
- [2] **Z. Liu, M. Kobayashi, B. C. Paul, Z. Bao, Y. Nishi:** *Contact engineering for organic semiconductor devices via Fermi level depinning at the metal-organic interface*, *Phys. Rev. B*, **82**, 035311, 2010
- [3] **N. B. Kotadiya, H. Lu, A. Mondal, Y. Ie, D. Andrienko, P. W. M. Blom, G.-J. A. H. Wetzelaer:** *Universal strategy for Ohmic hole injection into organic semiconductors with high ionization energies*, *Nature Materials*, **17**, 329, 2018
- [4] **A. A. Günther, M. Sawatzki, P. Formánek, D. Kasemann, K. Leo:** *Contact Doping for Vertical Organic Field-Effect Transistors*, *Adv. Funct. Mater.* **26**, 768, 2016, DOI: 10-1002/adfm.201504377
- [5] **W.-L. Seah, C. G. Tang, R.-Q. Png, V. Keerthi, C. Zhao, H. Guo, J.-G. Yang, M. Zhou, P. K. H. Ho, L.-L. Chua:** *Interface Doping for Ohmic Organic Semiconductor Contacts Using Self-Aligned Polyelectrolyte Counterion Monolayer*, *Adv. Funct. Mat.* **27**, 1606291, 2017
- [6] **C. Liu, Y. Xu, Y.-Y. Noh:** *Contact engineering in organic field-effect transistors*, *Materials Today* **18**, 79, 2015
- [7] **S. Liu, P. Billig, A. Al-Shadeedi, V. Kaphle, B. Lüssem:** *Doped bottom-contact organic field effect transistors*, *Nanotechnology* **29**, 284001, 2018
- [8] **Z. B. Wang, M. G. Helander, M. Greiner, J. Qui, Z. H. Lu:** *Analysis of charge-injection characteristics at electrode-organic interfaces: Case study of the transition-metal oxides*, *Phys. Rev. B* **80**, 235325, 2009
- [9] **Z. B. Wang, M. G. Helander, M. T. Greiner, J. Qui, Z. H. Lu:** *Carrier mobility of organic semiconductors based on current-voltage characteristics*, *J. Appl. Phys.* **107**, 034506, 2010
- [10] **J. C. Blakesley, F. A. Castro, W. Kylberg, G. F. A. Dibb, C. Arantes, R. Valaski, M. Cremona, J. S. Kim, J.-S. Kim:** *Towards reliable charge-mobility benchmark measurements for organic semiconductors*, *Org. Electron.*, **15**, 1263, 2014
- [11] **B. Cvikl:** *The electric field at hole injecting metal/organic interface as a cause for manifestation of exponential bias-dependent mobility*, *Thin Solid Films* **573**, 56, 2014
- [12] **R. Rohloff, N. B. Kotadiya, N. I. Craciun, P. W. M. Blom, G. A. H. Wetzelaer:** *Electron and hole transport in the organic small molecule α -NPD*, *Appl. Phys. Lett.* **110**, 073301, 2017
- [13] **S. L. M. van Mensfoort, V. Shabro, R. J. de Vries, R. A. Janssen, R. Coehoorn:** *Hole transport in the organic small molecular material α -NPD; evidence for the presence of correlated disorder*, *J. Appl. Phys.* **107**, 113710 2010
- [14] **M. A. Lampert:** *Simplified Theory of Space-Charge-Limited-Currents in an Insulator with Traps*, *Phys. Rev.* **103**, 1648, 1956
- [15] **P. Mark, W. Helfrich:** *Space-Charge-Limited Currents in Organic Crystals*, *J. Appl. Phys.* **33**, 205, 1962

- [16] **S. Nishi, D. Taguchi, T. Manaka, M. Iwamoto:** *Analysis of current-voltage characteristics of Au/pentacene/fluorine polymer/indium zinc oxide diodes by electric-field-induced-optical second-harmonic generation*, J. Appl. Phys. **117**, 245502, 2015
- [17] **D. Taguchi, L. Zhang, J. Li, M. Weis, T. Manaka, M. Iwamoto:**, *Analysis of Carrier Transients in Double-Layer Organic Light Emitting Diodes by Electric-Field-Induced Second-Harmonic Generation Measurement*, J. Phys. Chem. C, **114**, 15136, 2010
- [18] **W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, M. A. J. Michels:** *Unified Description of Charge-Carrier Mobilities in Disordered Semiconducting Polymers*, Phys. Rev. Lett. **94**, 206601, 2005
- [19] **M. M. Mandoc, B. de Boer, G. Paasch, P. W. M. Blom:** *Trap-limited electron transport in disordered semiconducting polymers*, Phys. Rev. B **75**, 193202, 2007
- [20] **M. Bouhassoune, S.L.M. van Mensfoort, P.A. Bobbert, R. Coehoorn:** *Carrier-density and field-dependent charge-carrier mobility in organic semiconductors with correlated Gaussian disorder*, Org. Electron. **10**, 437, 2009
- [21] **I. Lange, J. C. Blakesley, J. Frisch, A. Vollmer, N. Koch, D. Neher:** *Band Bending in Conjugated Polymer Layers*, Phys. Rev. Lett. **106**, 216402, 2011
- [22] **M. Oehzelt, N. Koch, G. Heimel:** *Organic semiconductor density of states controls the energy level alignment at electrode interfaces*, Nat. Commun. **5** 4174, 2014
- [23] **Y. Shen, M. W. Klein, D. B. Jacobs, J. C. Scott, G. G. Malliaras:** *Mobility-Dependent Charge Injection into an Organic Semiconductor*, Phys. Rev. Lett. **86**, 3867, 2001
- [24] **T. J. Whitcher, W. S. Wong, A. N. Talik, K. L. Woon, N. Chaniek, H. Nakajima, T. Saisopa, P. Songsiritthigul:** *Electrostatic model of energy-bending within organic semiconductors: experiment and simulation*, J. Phys.: Condens. Matter **28**, 365002, 2016
- [25] **T. J. Whitcher, W. S. Wong, A. N. Talik, K. L. Woon, N. Chaniek, H. Nakajima, T. Saisopa, P. Songsiritthigul:** *Investigation into the Gaussian density of states widths of organic semiconductors*, J. Phys. D: Appl. Phys. **49**, 325106, 2016.
- [26] **M. S. Khoshkhoo, H. Peisert, T. Chassé, M. Scheele:** *The role of the density of interface states in interfacial energy level alignment of PTCDAs*, Org. Electron. **49**, 249, 2017
- [27] **S. Beck, D. Gerbert, T. Glaser, A. Pucci:** *Charge Transfer at Organic/inorganic Interfaces and the Formation of Space Charge Regions Studied with Infrared Light*, J. Phys. Chem. C **119**, 12545, 2015
- [28] **G. Jecl, B. Cvikl:** *The density-of-states contributions to the negative field charge drift mobility effect in poly(3-hexylthiophene) organic semiconductor*, Thin Solid Films, **646**, 190, 2018
- [29] **T. Matsushima, Y. Kinoshita, H. Murata:**, *Formation of Ohmic hole injection by inserting an ultrathin layer of molybdenum trioxide between indium tin oxide and organic hole-transport layer*, Appl. Phys. Lett. **91**, 253504, 2007