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Universal Arrhenius Temperature Activated Charge Transport in Diodes from Disordered Organic Semiconductors

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Charge transport models developed for disordered organic semiconductors predict a non-Arrhenius temperature dependence $\ln(\mu) \propto 1/T^2$ for the mobility μ . We demonstrate that in space-charge limited diodes the hole mobility (μ_h) of a large variety of organic semiconductors shows a universal Arrhenius temperature dependence $\mu_h(T) = \mu_0 \exp(-\Delta/kT)$ at low fields, due to the presence of extrinsic carriers from the Ohmic contact. The transport in a range of organic semiconductors, with a variation in room temperature mobility of more than 6 orders of magnitude, is characterized by a universal mobility μ_0 of $30\text{--}40 \text{ cm}^2/\text{V s}$. As a result, we can predict the full temperature dependence of their charge transport properties with only the mobility at one temperature known.

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Since electroluminescence has been reported more than one decade ago, solution-processable organic semiconductors have had a significant impact in optoelectronic applications as polymer light-emitting diodes (PLEDs) [1,2]. The charge transport properties of conjugated polymers as poly(*p*-phenylene vinylene) (PPV) and its derivatives have been extensively studied in order to understand the fundamental phenomena that govern the operation of these devices. It has been demonstrated that the hole current in PLEDs is space-charge limited (SCL). At low bias voltages at room temperature the hole mobility (μ_h) is constant [3]. At high bias voltages the SCL current was described by μ_h that depends on both the temperature T and the applied electric field E of the form [4]

$$\mu_h(E, T) = \mu_0 \exp(-\Delta/kT) \exp(\gamma(T)\sqrt{E}), \quad (1)$$

with μ_0 the hole mobility at $E = 0$ and $T \rightarrow \infty$, Δ the activation energy, and $\gamma(T)$ the field activation factor. Monte Carlo simulations by Bässler *et al.* [5] showed that this type of charge transport is characteristic for a hopping process between localized sites in disordered conductors. These sites are located in different environments (disorder), and their site energies, determined mainly by electronic polarization, therefore fluctuate from site to site. These fluctuations in the on-site energy of typically 0.1 eV are assumed to be Gaussian. Since they are about 1 order of magnitude larger than the transfer integrals, the wave functions are strongly localized [5–7]. Furthermore, in order to explain the observed electric field dependence within this Gaussian disorder model an additional spatial correlated potential for the charge carriers is needed, which could arise from charge-dipole interactions [6]. However, in contrast to the empirical relation Eq. (1) the simulations showed a non-Arrhenius temperature dependence of the mobility at low fields, given by $\mu \propto$

$\exp(-(2\sigma/3kT)^2)$, where σ is the width of the Gaussian DOS [5].

Recently, also the dependence of μ_h on the carrier density in a PPV derivative has been investigated by a combined study on polymeric diodes and field-effect transistors [8]. It has been demonstrated that the hole mobility is constant for charge carrier densities typically $<10^{22} \text{ m}^{-3}$ and increases with a power law with density for carrier densities $>10^{22} \text{ m}^{-3}$. In contrast to the earlier assumption [4] the enhancement of the mobility at higher voltages in SCL diodes at room temperature has been shown to be totally due to the increase of the carrier density instead of the electric field [9]. However, at lower temperatures the field dependence of the mobility becomes increasingly more important. Therefore, a transport model has been developed that incorporates both the effect of carrier density and electric field on the mobility [10]. The occurrence of two regimes in the density dependence of the mobility is governed by the amount of charge carriers in

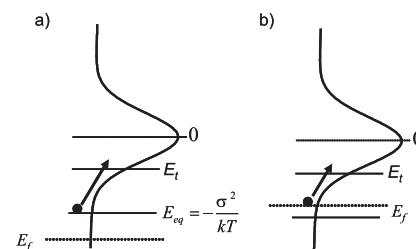


FIG. 1. (a) The hopping in a Gaussian DOS is schematically represented for low carrier densities. The equilibrium level $E_{eq} = -\sigma^2/kT$ represents the maximum of the density of occupied states and can be regarded as the starting point for the hopping process towards the transport level E_t . (b) With increasing density, the Fermi level E_f will at some point pass E_{eq} and serve as the new starting point for hopping, leading to a density dependent mobility.

the Gaussian density of states (DOS), as schematically shown in Fig. 1.

For low carrier densities [Fig. 1(a)] the Fermi level E_f is below the equilibrium level E_{eq} , which represents the maximum of the density of occupied states, given by the product of the Gaussian DOS and the Fermi-Dirac distribution. As a result, E_{eq} can be regarded as the starting point of the hopping process towards the transport level E_t , as indicated by the arrow. The transport level E_t represents the level to which carriers will hop when they are deep enough in the Gaussian DOS, because the hopping rate to this level is the fastest. As long as E_f is below the equilibrium level E_{eq} the hopping probability and mobility is independent of the position of E_f and thus independent of the carrier density. However, with increasing density [Fig. 1(b)] E_f will pass E_{eq} at a given density, and then E_f serves as a new starting point for the hopping transport. With increasing density E_f moves closer to E_t , leading to an enhanced mobility for larger densities.

The relative positions of E_f and E_{eq} are crucial to explain the temperature dependence of the charge transport [11,12]. Upon cooling down, E_{eq} moves deeper into the tail of the Gaussian DOS, leading to a non-Arrhenius temperature dependence given by $\ln(\mu) \propto 1/T^2$ in case of low densities [5]. For sufficiently high densities [Fig. 1(b)], meaning $E_f > E_{eq}$, it has been demonstrated by Coehoorn that also within the Gaussian disorder model the transport is governed by an Arrhenius-like $\ln(\mu) \propto 1/T$ behavior [12], as often observed in organic transistors [13,14]. Experimentally, the question whether the transport in organic semiconductors is better described by a $\ln(\mu) \propto 1/T^2$ or $\ln(\mu) \propto 1/T$ [Eq. (1)] behavior has been addressed by Borsenberger *et al.* [15]. From time-of-flight (TOF) measurements on vapor-deposited 1,1-bis(di-4-tolylaminophenyl)cyclohexane they convincingly demonstrated that the non-Arrhenius $\ln(\mu) \propto 1/T^2$ provides a more consistent description of the charge transport. However, in the analysis of various charge transport measurements an important aspect has been ignored: in TOF studies thick samples ($> 1 \mu\text{m}$) are used with blocking contacts to prevent charge injection. In SCL diodes, on the other hand, much thinner devices (50–300 nm) are measured, with at least one Ohmic contact to inject charge carriers. In order to align the Fermi level, charge carriers diffuse from the Ohmic contact into the device. Because of the density dependence of the mobility the hole transport in the device is strongly enhanced, for devices of only 40 nm thickness even more than 1 order of magnitude [16]. As a result, there is always a background of extrinsic charge carriers present in SCL diodes that modify the transport. In this Letter we demonstrate that the transport in SCL diodes made from a large variety of disordered organic semiconductors is governed by a universal Arrhenius-like transport.

As a first step, the temperature dependence of the hole mobility of SCL diodes made from poly(2-methoxy,5-(2'-ethyl-hexoxy)-*p*-phenylene viny-lene) (MEH-PPV)

with different layer thicknesses is investigated. The hole-only diodes were prepared on top of a glass substrate with a patterned transparent electrode, indium-tin oxide on which an anode of a hole-conducting layer of poly(3,4-ethylenedioxythiophene)/poly(styrenesulphonic acid) (PEDOT:PSS) is spin coated. Then on top of the PEDOT:PSS, MEH-PPV films ranging in thickness from 40 nm to 322 nm have been spin coated from toluene solution. The devices were finished by thermal evaporation of 100 nm of gold (Au) through a shadow mask. Temperature scans were typically made down to 200 K; because of the large activation energy of the transport, the current drops below the leakage current (as a result of local shorts) for lower temperatures.

In Fig. 2 the low-field mobilities $\mu_h(E = 0, T)$ of the samples with various thicknesses are shown in an Arrhenius plot. It is observed that the thinnest devices exhibit not only a higher mobility [16] but also weaker temperature activation. This is consistent with the fact that the thinnest devices have the largest concentration of background carriers that have diffused in from the Ohmic contact. The amount of charge that flows into a SCL diode in order to equilibrate the Fermi level can be quantified by the average charge density ρ_{av} , given by

$$\rho_{av} = \frac{\int_0^L p(x)dx}{L}, \quad (2)$$

where $p(x)$ is numerically calculated from a drift-diffusion program [16]. The simulations show that ρ_{av} typically increases from $5 \times 10^{21} \text{ m}^{-3}$ for the 318 nm device to $2 \times 10^{22} \text{ m}^{-3}$ for the 40 nm device. Furthermore, the Arrhenius plot also shows that the temperature activated transport for the various MEH-PPV layer thicknesses all originate from a single value of $\mu_0 = 30 \text{ cm}^2/\text{V s}$. Such behavior is expected since in the limit $T \rightarrow \infty$ the charge transfer rates are limited only by the wave function overlap between neighboring sites and do not depend on layer thickness or filling of the DOS. In a $\ln(\mu) \propto 1/T^2$ plot the μ_0 varies more than an order of magnitude, indicating that the Arrhenius-like $\ln(\mu) \propto 1/T$ behavior is more consistent

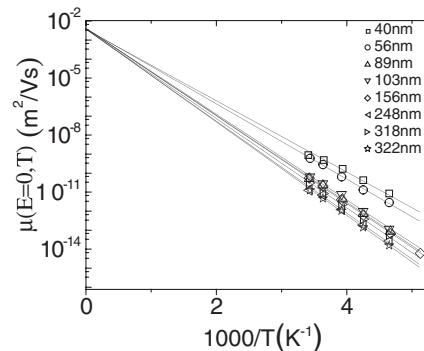


FIG. 2. Measured low-field mobilities $\mu_h(E = 0, T)$ for MEH-PPV based SCL diodes with thicknesses ranging from 40 nm to 322 nm. The solid lines are fits using the Arrhenius temperature dependence $\mu_h(E = 0, T) = \mu_0 \exp(-\Delta/kT)$.

for these SCL diodes. Using a Gaussian DOS characterized by the total number of sites $N = 3 \times 10^{26} \text{ m}^{-3}$ and $\sigma = 0.11 \text{ eV}$ [8], the equilibrium level E_{eq} is located at -0.46 eV for $T = 300 \text{ K}$. For a 40 nm diode with $\rho_{av} = 2 \times 10^{22} \text{ m}^{-3}$ the Fermi level E_f is also located at -0.46 eV . Upon cooling down E_{eq} sinks deeper into the tail of the DOS, whereas E_f is relatively temperature independent. As a result, during a temperature scan from 200 to 300 K E_f is always above E_{eq} , as indicated in Fig. 1(b). Even for the 318 nm device with $\rho_{av} = 5 \times 10^{21} \text{ m}^{-3}$, with E_f located at -0.51 eV , the equilibrium level E_{eq} will pass E_f already at $T = 275 \text{ K}$, meaning that also for the thicker diodes E_f is above E_{eq} for most of the temperature scan. This explains why an Arrhenius-like behavior is more applicable for SCL diodes that carry an extrinsic background carrier due to the presence of an Ohmic contact.

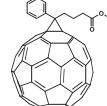
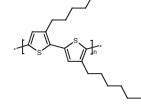
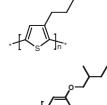
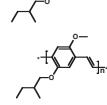
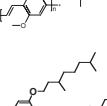
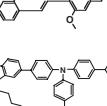
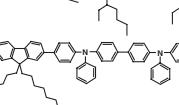
Since the observed μ_0 for $T \rightarrow \infty$ is independent of the layer thickness of the SCL diodes, it is interesting to compare the mobilities in a whole range of organic semiconductors, as summarized in Table I.

The room temperature mobilities $\mu_h(E = 0, T = 300 \text{ K})$ vary over six orders from $10^{-13} \text{ cm}^2/\text{Vs}$ to $10^{-7} \text{ m}^2/\text{Vs}$. The different mobilities for MEH-PPV and poly[2,5-bis(2-ethylhexyloxy)-1,4-phenylene vinylene] (DEH-PPV), in spite of their similar chemical structures, originates from a different morphology. From phase-imaging scanning force microscopy it has been shown by Kemerink *et al.* that PPVs with sidegroups of asymmetric length as MEH-PPV have a tendency to curl up, with the short sidegroup on the inside [21]. On the other hand, PPVs with symmetric sidegroups as DEH-PPV form more rod-like structures, which is beneficial for the charge transport. This is expressed in a higher mobility and correspondingly lower activation energy. In Fig. 3(a) the mobilities, all obtained from SCL diodes, are shown in an Arrhenius plot. As expected, the materials with a higher mobility also show weaker temperature dependence due to the reduced disorder. In Fig. 3(b) the Arrhenius plot is extrapolated to $T \rightarrow \infty$.

Remarkably, again all measured mobilities originate from nearly one point, again $\mu_0 = 30 \pm 10 \text{ cm}^2/\text{Vs}$. The occurrence of a single value for μ_0 for such a large variety of organic semiconductors is surprising since its value is expected to be governed by the amount of electronic overlap between the chain segments. This result would indicate that the packing and resulting wave function overlap would be very similar for the materials studied here. However, it should be noted that the measured mobilities for the conjugated polymers are an average between both intrachain and interchain hopping processes. For intrachain hopping the hopping distance and localization length are about equal, leading to a $T \rightarrow \infty$ mobility in a Gaussian DOS of [22]

$$\mu_0 = \frac{ea^2v_{ph}}{\sigma} \quad (3)$$

TABLE I. Room temperature mobility $\mu_h(E = 0, T = 300 \text{ K})$, activation energy Δ , and structural formula of a number of organic semiconductors.

Polymer name	Mobility $\mu_{300 \text{ K}} (\text{m}^2/\text{Vs})$ Activation energy (eV)	Chemical structure
PCBM	2×10^{-7} [17] 0.23 eV	
rr-P3HT	1.3×10^{-8} [18] 0.3 eV	
rir-P3HT	2.8×10^{-9} [8] 0.35 eV	
DEH-PPV	1.2×10^{-9} [19] 0.359 eV	
MEH-PPV	5×10^{-11} [19] 0.45 eV	
OC ₁ C ₁₀ -PPV	3×10^{-11} [4] 0.48 eV	
NRS-PPV	1.5×10^{-12} [20] 0.547 eV	
PFO-TPD 1:7	3.72×10^{-13} [18] 0.59 eV	

with a the hopping distance and v_{ph} the attempt-to-escape frequency. Using typical values of $a = 1 \text{ nm}$, $v_{ph} = 10^{14} \text{ s}^{-1}$, and $\sigma = 0.1 \text{ eV}$ yields a μ_0 of $10 \text{ cm}^2/\text{Vs}$, which is in the right order of magnitude. However, with intrachain conjugation lengths of typically 6–7 nm and interchain packing distances of $\sim 0.4 \text{ nm}$ a coupling to microscopic parameters as wave function overlap is very difficult to make.

The fact that the temperature activation is governed by one universal prefactor $\mu_0 = 30 \text{ cm}^2/\text{Vs}$ also enables us to predict the activation of charge transport with only the mobility at one temperature, for example, $\mu_h(0, 300 \text{ K})$, known. In that case Eq. (1) can be rewritten as

$$\Delta = k \times 300 \left(\frac{\mu_0}{\mu(0, 300 \text{ K})} \right). \quad (4)$$

In Fig. 4 the measured low-field room temperature mobilities $\mu_h(0, 300 \text{ K})$ are shown together with the measured activation energy Δ for the various organic semiconduc-

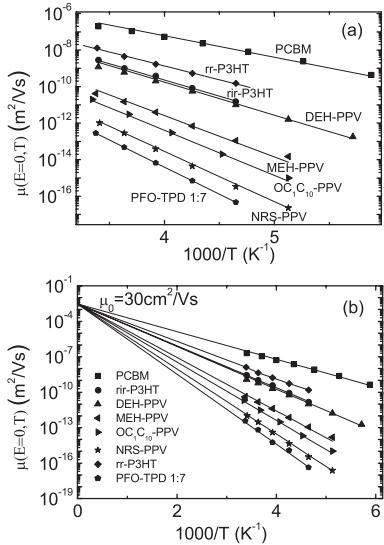


FIG. 3. Measured low-field mobilities $\mu_h(E = 0, T)$ on SCL diodes for a large range of disordered organic semiconductors (see Table I). The solid lines are fits using the Arrhenius temperature dependence $\mu_h(E = 0, T) = \mu_0 \exp(-\Delta/kT)$.

tors. The solid line is the prediction made from Eq. (4). The good agreement for semiconductors that differ by 6 orders of magnitude in $\mu_h(0, 300 \text{ K})$ shows the validity of the Arrhenius-like transport in all of these SCL diodes.

In conclusion, we demonstrate that the mobilities of a variety of organic semiconductors are consistent with an Arrhenius temperature dependent transport with a universal prefactor $\mu_0 = 30 \text{ cm}^2/\text{Vs}$. The carriers diffusing into the diodes from the Ohmic contact lift the Fermi level above the equilibrium level, resulting in an Arrhenius-like temperature dependence instead of the characteristic $\ln(\mu_h) \sim 1/T^2$ behavior as observed for blocking contacts. As a result, the temperature dependence of the charge transport can be predicted when the mobility at one single temperature is known.

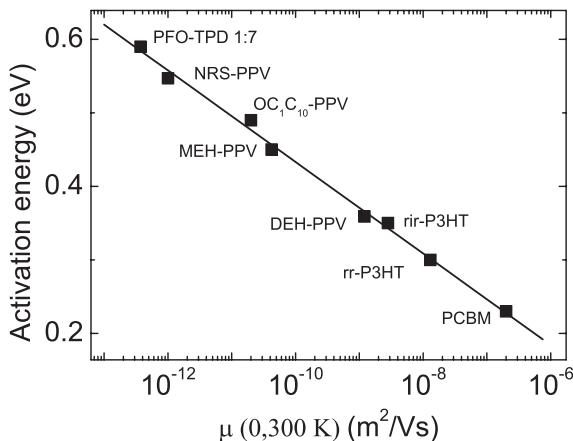


FIG. 4. Activation energy Δ as a function of the low-field room temperature mobility $\mu_h(0, 300 \text{ K})$ as obtained from SCL diodes. The solid line is the prediction from Eq. (4).

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