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Electron Trapping in Conjugated Polymers

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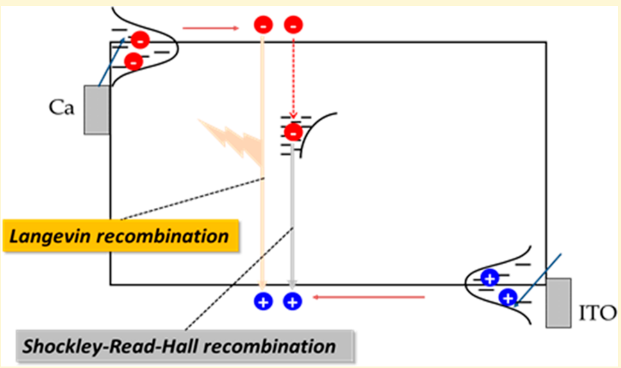
ABSTRACT: Electron trapping is a well-recognized issue in organic semiconductors, in particular in conjugated polymers, leading to a significant electron mobility reduction in materials with electron affinities smaller than 4 eV. Space-charge limited current measurements in diodes indicate that these traps have similar molecular origin, while calculations show that hydrated molecular oxygen is a plausible molecular candidate, with the tail of the solid-state electron affinity distribution reaching values as high as 4 eV. By decreasing the trap density by mixing conjugated polymers with an insulating polymer matrix, one can fill the traps with charges and hence eliminate their effect on electron mobility. Trap dilution not only improves transport but also reduces trap-assisted recombination, boosting the efficiency of polymer light emitting diodes.



1. INTRODUCTION

In 1977, polyacetylene was made electrically conductive upon doping.[1] Unstable and brittle, this polymer was not suitable for flexible and lightweight optoelectronic devices. The discovery, however, encouraged scientists to search for novel polymeric semiconducting materials: flexible, chemically and mechanically resistant, and solution-processable. Envisioned was the possibility of the roll-to-roll deposition, similar to newspaper printing systems, which would allow designing large-area devices, such as solar cells, lighting panels, sensors, and screens. A new field was born: *plastic electronics*.

In conducting polymers, atomic orbitals of carbon atoms hybridize into three sp^2 and one p_z orbital. sp^2 orbitals form σ-bonds with the adjacent atoms, while p_z orbitals, aligned perpendicular to the σ bonds, are responsible for the π-bonding. They form *delocalized* π (occupied) and π^* (unoccupied) molecular orbitals. In a π-stacked molecular dimer, these delocalized orbitals overlap, providing comparatively large electronic couplings between the monomers. In addition, the free energy barrier for an extra charge to move between the monomers of a dimer, which is proportional to the free energy change upon charging of a molecule, is small. These peculiar molecular properties ensure sizable rates of (thermally activated) charge-transfer reactions, responsible for the semiconducting properties of conjugated materials.[2] The molecular π orbital, filled with electrons, is termed the highest occupied molecular orbital (HOMO), whereas the π^*, being the first empty energy level, is the lowest unoccupied molecular orbital (LUMO). Though commonly used in the literature, these two orbitals and their respective energy levels do not represent the transport levels of a material. Solid-state ionization energy (IE) and electron affinity (EA) are the relevant energy levels where the transport of holes and electrons, respectively, takes place. Both are comprised of a gas phase and solid-state contributions[3,4] and, for conjugated polymers, vary in the range of 1 to 4 eV (EA) and 4.5 to 6.5 eV (IE) with respect to the vacuum level.

The transport gap largely influences the optical gap of conjugated polymers, though the two of course differ by the (screened) excited state electron−hole binding energy.[5] The optical gap of conjugated polymers covers a spectral range from ultraviolet, through visible, to infrared light. The possibility of visible light emission makes these polymers suitable materials for optoelectronic devices, such as polymer light-emitting diodes (PLEDs),[6] in which a layer of conjugated polymer is sandwiched between two electrodes. The first PLEDs were based on poly(*p*-phenylenevinylene) (PPV) that was formed after annealing of a deposited film of a (unconjugated) precursor polymer. Later on, by addition of solubilizing side chains to the PPV backbone, conjugated polymers like poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) could be directly deposited from solution, without the necessity of a conversion step.[7] In these bipolar devices, injected electrons and holes are transported toward each other and recombine subsequently.

To investigate the charge-transport properties of conjugated polymers, three types of devices are typically used: hole- and electron-only devices, which are used to determine the

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mobility of one type of carrier, and bipolar LEDs, where next to charge transport also recombination takes place.[8] In pristine conjugated polymers, countercharges do not neutralize injected charges, leading to a formation of a charged layer (space charges). The presence of this charge limits (electrostatically) the current: The current–voltage dependence for the space-charge-limited current (SCLC) was first derived by Mott and Gurney[9]

$$J = \frac{9}{8}\epsilon_0\epsilon_r\mu\frac{V^2}{L^3} \quad (1)$$

where ϵ_r is the relative permittivity of the semiconductor, μ is the charge mobility, V is the applied voltage, and L is the device thickness. It has been demonstrated that eq 1 applies to the trap-free hole transport in PPV derivatives like poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and MEH-PPV, but only at low applied voltages and room temperature.[10] The hole mobility is then conveniently obtained by fitting the current density–voltage characteristics with eq 1. At higher voltages the experimental data deviate from eq 1, since the mobility can no longer be regarded as constant, as will be outlined below.

The low mobility of PPV derivatives, in the order of 10^{-11} $m^2/(V\ s)$, as obtained from the SCLC, originates from the presence of *energetic disorder*. The structure of these polymers is often highly disordered, practically amorphous. Structural disorder manifests itself in defects (kinks) along the polymer backbone, which break the conjugation. A polymer chain becomes therefore a sequence of conjugated segments. Segments of different lengths have different ionization energies and electron affinities (recall an electron energy spectrum in a periodic box),[11−14] leading to broad distributions of IEs and EAs, or density of states (DOS).

In a material with energetic disorder, thermal energy is required to transfer an electron to a segment with lower electron affinity. Conwell and Mott suggested such thermally assisted transport already in 1956, for impurity conduction in inorganic semiconductors.[15,16] Consequently, Miller and Abrahams proposed a simple expression for the charge transfer rate, which penalizes uphill transfers by a Boltzmann prefactor and accounts for the separation-dependent electronic overlap by an exponential decay with molecular separation.[17] Using these rates, Bässler explained the observed dependence of mobility on temperature, which is non-Arrhenius, as well as its field dependence at high electric fields in systems with a Gaussian DOS distribution.[18] The so-called Gaussian disorder model (GDM) also predicted the dependence of charge mobility on charge density and electric field,[19] addressed experimentally by combining measurements on diodes and transistors.[20] In field-effect transistors (FETs), filling of the tail of the density of states upon application of a gate bias led to an increase of the mobility according to a power law.[21] GDM simulations of organic SCL diodes by Pasveer et al. showed that at room temperature the enhancement of the mobility at high voltages is due to the increased carrier density, whereas at low temperatures the mobility is mainly enhanced directly by the electric field, which increases the hopping rates by lowering the barrier for uphill jumps.[22]

2. RESULTS AND DISCUSSION

2.1. Trap-Limited Electron Transport. While the GDM was very successful in rationalizing hole transport in PPV-based polymers, *electron* transport turned out to be more difficult to get a grip on. As shown in Figure 1, the electron

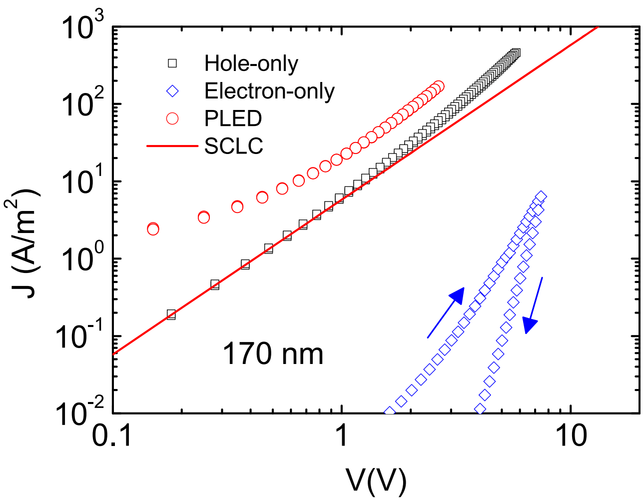

Figure 1. Log–log plot of the current density versus voltage for a MEH-PPV based hole-only device (black squares), electron-only device (blue diamonds), and bipolar PLED device (red circles). The red line is the quadratic trap-free SCLC fit according to eq 1.

transport for MEH-PPV is reduced by at least 3 orders of magnitude as compared to the quadratic SCL hole current. A further distinctive feature of the electron current is its strong voltage dependence, typically $J \sim V^6$. Furthermore, the downward J–V sweep does not follow the initial upward sweep but is much lower. In fact, the steep voltage dependence and hysteresis are typical fingerprints of *trap-limited* currents.

Already in 1956, Lampert evaluated the effect of a discrete trap level on the device current.[23] In disordered semiconductors, however, it is more likely that trap levels are distributed in energy. Mark and Helfrich in 1962 studied the case of an exponential distribution of trap states.[24] In this case, the density of trap sites decreases exponentially with energy, according to

$$n_t(E) = \left(\frac{N_t}{k_B T_t}\right)\exp\left(\frac{E - E_c}{k_B T_t}\right) \quad (2)$$

with $n_t(E)$ the trap density of states at energy $E < E_c$, E_c the energy of the conduction band, N_t the total density of traps, and $k_B T_t$ an energy characterizing the steepness of the exponential tail of the trap distribution. For such a trap distribution with a total trap concentration N_t the trap-limited current reads

$$J = Nq\mu_e\left[\frac{\epsilon_0\epsilon_r}{qN_t}\exp\left(-\frac{E_{tc}}{k_B T_t}\right)\right]^r\left[\left(\frac{2r+1}{r+1}\right)^{r+1}\left(\frac{r}{r+1}\right)^r\right]\frac{V^{r+1}}{L^{2r+1}} \quad (3)$$

where N is the density of transport sites, q is the elementary charge, μ_e the free electron mobility, T_t the characteristic temperature of the trap distribution, E_{tc} the energy of traps measured from the top of the valence band (hole traps) or bottom of the conduction band (electron traps), and $r = T_t/T$, respectively. According to eq 3, the value of r, representing the shape of the trap DOS, can directly be derived from the slope of log J versus log V. The magnitude of this slope was investigated for a wide range of conjugated polymers, and a

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correlation was found with the electron affinity.[25] Figure 2 shows this relation for the polymers investigated; it appears

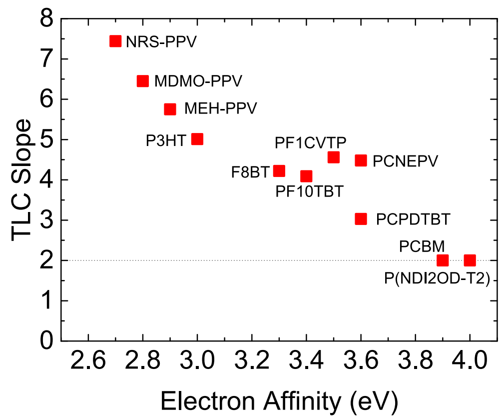

Figure 2. Slope of log J vs log V of the trap-limited electron current versus electron affinity shown for different polymers. The figure is adapted with permission from ref 25. Copyright 2012 Springer Nature. Here MEH-PPV has been added.

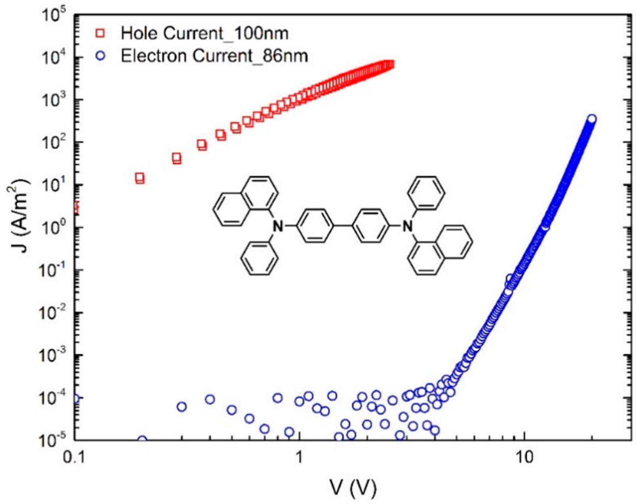

Figure 3. Log–log plot of the current density versus voltage for α-NPD hole only (red squares) and electron-only (blue circles) devices. Data from ref 28.

that for polymers with higher electron affinity the slope of log J vs log V is decreasing from 7.5 to about 3 at an EA of 3.6 eV, corresponding to a decrease in trap temperature from 1950 to 600 K at room temperature. For an EA of 3.8 eV or lower it becomes equal to 2, which is the signature for trap-free SCLC.

The electron currents of the whole series of conjugated polymers could be described by assuming a *universal* electron trap centered around 3.6 eV with a density of $3{-}5 \times 10^{23}$ m^{-3}. A universal energy level for electron trapping in conjugated polymers indicates that it has an extrinsic origin, for example, related to water and/or oxygen impurities.

An intriguing question is whether severe electron trapping also occurs in organic small molecules. In contrast to solution-processed conjugated polymers, small molecules are deposited in high vacuum, are monodisperse, have no end groups, and are easier to purify. Electron transport has previously been characterized in electron-only devices based on the aluminum complexes Alq3 and BAlq, showing that electron trapping does occur.[26,27] However, it was not clear whether electron trapping is specific to Alq-based materials or if it also occurs in other evaporated small molecules. Figure 3 shows the hole and electron current in the evaporated small molecule *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (α-NPD).

Similar to PPVs (Figure 1), the hole current is space-charge-limited and depends quadratically on voltage. In contrast, the electron current is orders of magnitude lower and shows a much stronger voltage dependence, $\sim V^6$. The steep voltage dependence combined with a strong dependence on sample thickness indicates that also in α-NPD the electron current is strongly trap-limited. In fact, electron currents are well described by a model with Gaussian-distributed trap density of 1.3×10^{24} m^{-3} at a depth of 0.67 eV below the center of EA, similar to PPV-based conjugated polymers.[28] The observed thickness dependence of V^{r+1}/L^{2r+1} confirms that the low electron current is due to trapping and not the result of a large electron injection barrier, which would give rise to a current scaling with the electric field, V/L. This result supports the conclusion that electron trapping is not specific to solution-processed conjugated polymers only but can also occur in an evaporated small molecule as α-NPD, also with comparable traps densities. As trapping sites not only limit charge transport, but can also act as nonradiative recombination centers, it is important to understand the molecular origin of these defects.

2.2. Origin of Electron Trapping. Combined photoelectron spectroscopy and quantum-chemical studies indicated that water molecules complexed with polyphenylenevinylene (PPV) chains can modify the polymer ionization energies.[29] To further quantify the role of water and/or oxygen as possible electron traps in organic semiconductors, a series of quantum-chemical calculations were performed by Brédas and co-workers.[25] Water and hydrated oxygen complexes between chains as well as defects on the chains due to photo-oxidation products and halogen termination were probed as potential origins of trap states. A major conclusion of the calculations was that water molecules induce relatively small changes, about 0.1 to 0.2 eV, to the oligomer vertical electron affinity, which is not sufficient to create trap depths of 0.6–0.7 eV, found experimentally for a series of PPV derivatives.

Another candidate, namely, hydrated oxygen complexes, was suggested as a potential universal electron trap by Ho and co-workers.[30] In order for hydrated oxygen complexes to exhibit an electron affinity of around 3.6 eV, a shift in electron affinity of around 1.5 eV from the gas phase would be required. To evaluate the effect of polarization stabilization, vertical electron affinities of $O_2{\cdot}H_2O$ complexes[31,32] were evaluated in a continuum dielectric using the polarizable continuum model.[33] The results confirmed that the surrounding dielectric can lead to a stabilization of the electron affinity by up to 1.5 eV, indicating that $O_2{\cdot}H_2O$ complexes are indeed potential candidates for electron trapping.

More accurate calculations, which are based on the explicit atomistic morphologies and hence also account for a nonuniform electrostatic field created by the organic host,[3,4,34,35] predict that electron affinity of molecular oxygen can indeed be lowered from 0.45 eV[36] to 4 eV. Different sizes of the hydration shell as well as orientations of molecular dipoles of water molecules broaden the density of states of molecular oxygen in a way that the DOS tail can easily reach 4 eV (see Figure 4). Hence, hydrated oxygen can definitely serve

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as a source of universal electron traps in all organic semiconductors.

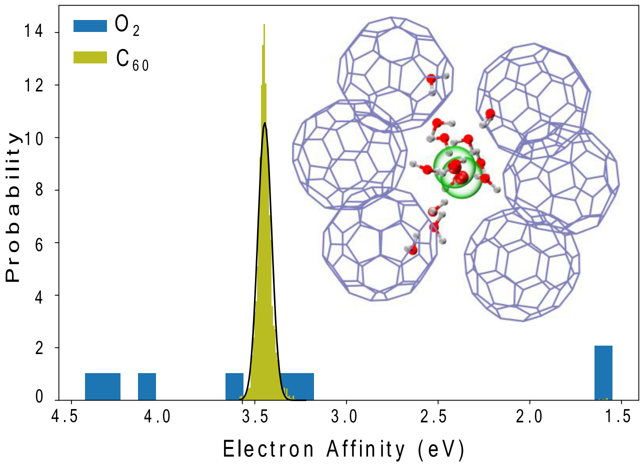

Figure 4. Electron affinities of clusters of hydrated molecular oxygen in a C_{60} crystal (blue) as well as C_{60} molecules (yellow). Electron affinity of molecular oxygen is very sensitive to the cluster size and orientation of molecular dipoles of water molecules in the hydration shell, leading to a broad distribution of the density of states with the tail around 4 eV. Inset shows a molecular dynamics snapshot of a hydrated O_2 cluster in a C_{60} crystal. Solid-state ionization contributions are performed in a perturbative way, by adding electrostatic and induction contributions to the gas-phase EA of C_{60} (2.65 eV) and O_2 (0.45 eV). These contributions are evaluated using the polarizable Thole model and distributed atomic multipoles.

2.3. Elimination of Electron Trapping.

It might seem that purification of conjugated polymers during and/or after synthesis is the most practical and straightforward procedure which could help to get rid of electron trapping. While purification could partially remove trapping, reducing the hysteresis,[37] attempts in this direction were not successful until now. Alternatively, one can fill traps by doping[38,39] or by injecting large numbers of carriers. For example, in field-effect transistors (FETs) concentrations induced by the gate carriers are typically 2 orders of magnitude higher than the concentration of bulk electron traps. A complete trap filling leads to a similar electron and hole transport in FETs for many conjugated polymers.[40] In diodes like PLEDs, where charge-carrier densities are typically an order of magnitude lower than the trap concentration, electron traps can reduce the transport by several orders of magnitude.

The fact that the electron traps are energetically distributed allows a (counterintuitive) approach to suppress trapping, based on device physics. Indeed, eq 3 shows that the trap-limited current for an exponential distribution of traps scales with N/N_t^r. Consequently, a simultaneous reduction of N and N_t would, for $r > 1$, lead to a strong increase of the trap-limited current. As an example, for a semiconductor with $r = 4$ a 10-fold dilution of N and N_t will lead to a thousand times increase of the trap-limited current. The physics of the concept of trap dilution arises from the relation between free n and trapped electron density n_t, which for an exponential trap distribution is given by

$$\frac{n}{N} = \left(\frac{n_t}{N_t e^{E_{tc}/kT_t}}\right)^r \qquad (4)$$

This relation shows that the ratio between free (n) and trapped (n_t) electrons depends on N and N_t in a nonlinear fashion. A simultaneous reduction of N and N_t enhances this ratio, meaning that the fraction of injected electrons that are free increases, thereby enhancing the current. Conjugated polymers are ideal systems for utilizing such a *trap-dilution* effect. Solution processability helps blend conjugated polymers with other large band gap semiconductors or insulators; for example, MEH-PPV can be blended with the large band gap host polymer poly(vinylcarbazole) (PVK).[41] The IE and EA of MEH-PPV are 5.3 and 2.9 eV, respectively,[42] while for PVK the IE amounts to 5.8 eV and the EA to 2.2 eV.[43] As a result, in electron-only devices with Ba/Al cathodes with work function 2.9 eV, electrons are selectively injected into the MEH-PPV. Due to the high IE of PVK, also the hole transport takes place exclusively on the PPV, so that PVK does not take place in the electrical conduction.

In Figure 5 the comparison of the hole and electron currents is shown for various MEH-PPV:PVK blend concentrations.

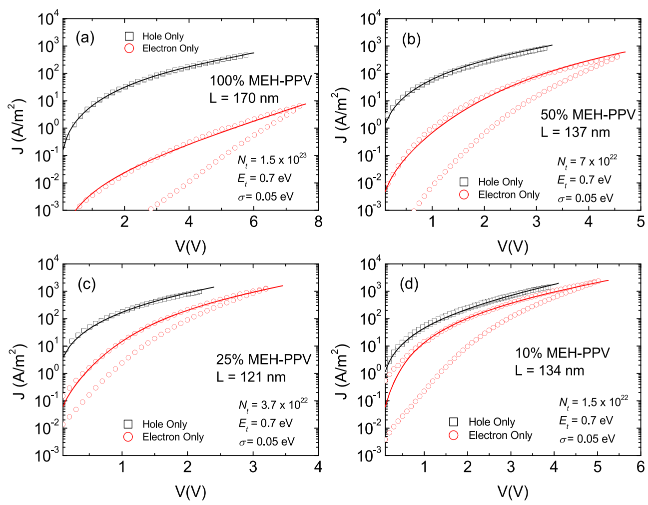

Figure 5. Hole and electron transport in hole-only and electron-only devices of (a) the MEH-PPV reference device, (b) 50:50% MEH-PPV:PVK, (c) 25:75% MEH-PPV:PVK, and (d) 10:90% MEH-PPV:PVK. The electron trap density in the blends is extracted from numerical simulations (solid lines). Reprinted with permission from ref 41. Copyright 2016 Springer Nature.

For pristine MEH-PPV (see Figure 1) the electron current is 3−4 orders of magnitude lower than the hole current, due to trapping. For the 25:75 MEH-PPV:PVK blend the difference between the electron and hole current is reduced to an order of magnitude, whereas for the 10:90 blend there is only a small difference at low voltages. For a bias larger than 3 V the electron and hole currents are almost on top of each other, indicating that above 3 V all traps are filled and electron transport is trap-free.

As can be also observed in Figure 5, the hole current in the MEH-PPV:PVK blends is nearly independent of the addition of PVK, up to a weight fraction of 90%. The reduction of the energetic disorder in the MEH-PPV clearly compensates the loss of the charge-conducting volume, and consequently the hole mobility is not compromised. By modeling the electron currents, a linear relation between the trap density and the MEH-PPV fraction is obtained, consistent with the concept of trap dilution.

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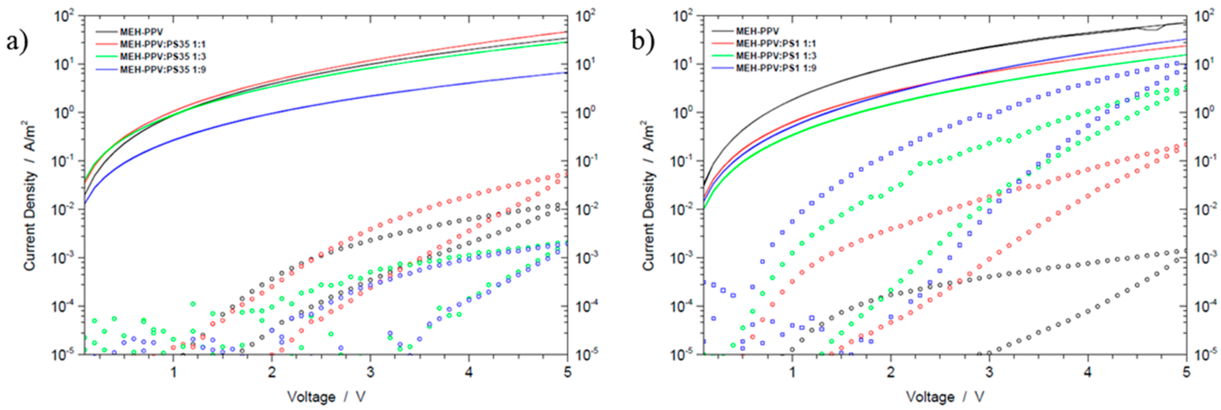

Figure 6. Current density (J) of positive (lines) and negative (dots) charges plotted as a function of applied voltage (V), measured on single carrier devices based on (a) MEH-PPV:PS35 and (b) MEH-PPV:PS1. The colors represent different MEH-PPV:polystyrene weight ratios: 1:0 (black), 1:1 (red), 1:3 (green), and 1:9 (blue). Reprinted with permission from ref 44. Published by the Royal Society of Chemistry, http://creativecommons.org/licenses/by/3.0/.

As a prerequisite for efficient trap dilution, one would expect the intimate mixing of semiconductor and host at the segmental level. This implies that the phase domains comprise mixed phases containing both polymers. To verify the effect of intermixing on trap dilution, polystyrene (PS), which is available in a wide range of molecular weights, has been used as a polymeric insulator. For this blend, trap-dilution can be predicted from the phase diagram, calculated using Flory—Huggins theory.[44] As shown in Figure 6, trap dilution is not observed when high molecular weight PS (M_w = 35 kDa) is used as host. In this case, the blend shows pronounced liquid—liquid demixing during solution casting. By contrast, for low molecular weight (M_w = 1.1 kDa) the mixing between MEH-PPV and PS is sufficient to allow for spatial separation of transport and trap sites within the semiconductor, resulting in the removal of the trap-limited nature of the MEH-PPV electron current.

2.4. PLED Efficiency. Apart from reducing the electron transport, traps can facilitate recombination of electrons and holes, as schematically indicated in Figure 7. In PLEDs, for example, an important loss process is the nonradiative recombination of trapped electrons with free holes. A dilution of trapping sites can therefore help to reduce trap-assisted recombination.

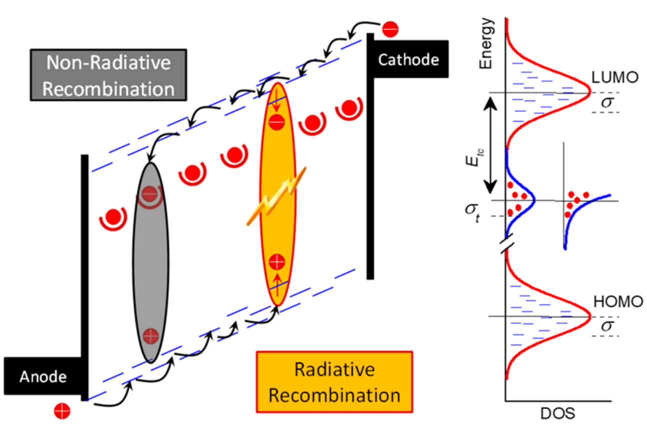

Figure 7. Schematic representation of a PLED with trap-free hole transport and trap-limited electron transport (traps are indicated as red circles below the LUMO). The traps are distributed in energy, typically represented by an exponential Gaussian distribution (right figure). With the existence of trap states, two types of recombination are possible: Langevin radiative recombination between free holes and electrons and Shockley—Read—Hall (SRH) trap-assisted recombination between trapped electrons and free holes.

To quantify the effect of trap-assisted recombination, a numerical device model[45] has been used that includes drift and diffusion of holes and electrons, space charge effects, a density-dependent carrier mobility, and a trap distribution for electrons, as well bimolecular Langevin and trap-assisted Shockley—Read—Hall (SRH) recombination between trapped electrons and free holes. The simulation results shown in Figure 8 demonstrate that the presence of electron traps strongly limits the PLED efficiency for a device with a layer thickness of 60 nm. When the trap density is higher than 10^{24} m^{-3}, the efficiency is almost zero, due to dominance of trap-assisted recombination. With a reduction of the trap density, the efficiency rapidly increases and reaches its maximum at about 10^{22} m^{-3} trapping density. Further decrement of trapping density does not enhance the efficiency. Exciton-quenching losses at the cathode typically amount to 20% when the trapping density is high and decrease to 10% for balanced transport when the trap density is low. In that case, a symmetric recombination profile will be formed throughout

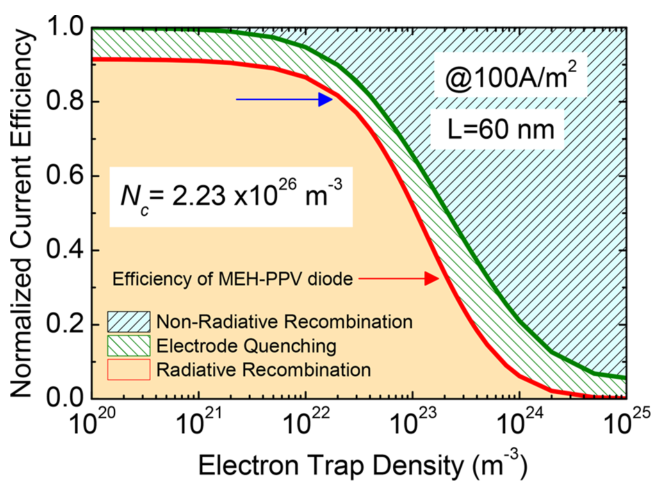

Figure 8. Simulation of contribution of loss effects to the PLED efficiency for a 60 nm MEH-PPV diode as a function of trap density.

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the emissive layer, where each electrode contributes to half (5%) of the total quenching losses. The trapping density for conjugated polymers is of the order of $\sim 10^{23}-10^{24} m^{-3}$, and in particular for MEH-PPV it is $\sim 2 \times 10^{23}$ m^{-3}, indicated by the red arrow in the Figure 8. Due to the steep dependence on trap density, elimination of traps can have a big effect on the PLED efficiency. The blue arrow in the figure demonstrates that a ten times reduction of traps in the polymer would increase the efficiency of PLED by more than two times. Since the trapping density is about 0.1% of the density of transporting sites, their identification and elimination is a challenging and time-consuming task, far more complicated than trap dilution.

As a proof of concept, we have compared the efficiency of a typical MEH-PPV PLED with a device using trap dilution by a 10:90 MEH-PPV:PVK blend. Figure 9 compares efficiencies of

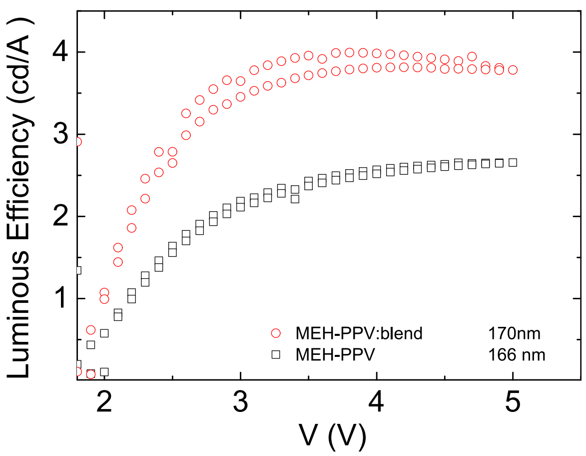

Figure 9. Luminous efficiency (light-output divided by current) vs applied voltage for reference MEH-PPV and 10%:90% MEH-PPV:PVK PLED. Reprinted with permission from ref 41. Copyright 2016 Springer Nature.

both devices: the blend PLED efficiency has nearly doubled, in line with the calculated losses due to electron trapping (Figure 8). Apart from higher efficiency, diluted blends also offer a reduction of material costs, since the price of insulators such as polystyrene is negligible compared to organic semiconductors.

3. CONCLUSIONS

In summary, trap-free hole transport and trap-limited electron transport are typical for a wide range of solution-processed conjugated polymers and are also observed in the evaporated small molecule α-NPD. The electron trap densities typically vary in the range of $10^{23}-10^{24}$ m^{-3}, and their universal energetics suggests common extrinsic defects that exist even in a nitrogen-filled glovebox. Suitable candidates for these defects are, for example, hydrated oxygen molecules, whose gas-phase electron affinity is stabilized by the molecular dipoles of surrounding water molecules. The electron trapping can be suppressed by a simultaneous dilution of the transport and trapping sites, which is illustrated by blending semiconducting polymers with insulators, such as polystyrene. Polymer light-emitting diodes based on the intermixed blends double their efficiency due to the suppression of trap-assisted recombination. Balanced transport, enhanced efficiency, and reduced material costs of PLEDs are, without a doubt, very much desired properties for large-area electronic applications.

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Notes

The authors declare no competing financial interest.

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