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Supplementary Information

Validity of the Einstein Relation in Disordered Organic Semiconductors

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I. Simulation parameters

The relevant simulation parameters and procedures for the simulations in Figs. 3 and 4 in the article are provided here.

A. Simulations Fig. 3

The simulations were carried out using a numerical drift-diffusion model [S1] that next to Langevin recombination includes an additional Shockley-Read-Hall (SRH) recombination mechanism, for which the recombination rate is given by

$$R_{SRH} = C_n C_p N_t (np - n_i p_1) / [C_n (n + n_i) + C_p (p + p_1)], \quad (S1)$$

with C_n and C_p the capture coefficients for electrons and holes, respectively, N_t the density of electron traps, n and p the electron and hole density and $n_i p_1 = n_i^2$ their product under equilibrium conditions in the case that the Fermi level coincides with the position of the recombination centers, where n_i denotes the intrinsic carrier concentration in the sample. The expression for the Langevin recombination rate reads

$$R_L = \frac{q}{\epsilon} (\mu_n + \mu_p) (np - n_i^2), \quad (S2)$$

with ϵ the dielectric constant and μ_n and μ_p the electron and hole mobility, respectively. The sum of both recombination rates enter the continuity equations according to

$$\frac{1}{q} \frac{\partial}{\partial x} J_n = -\frac{1}{q} \frac{\partial}{\partial x} J_p = R_L + R_{SRH}, \quad (S3)$$

where J_n and J_p denote the electron and hole current-density, respectively.

The capture coefficients and trapping parameters for the simulations in Fig. 3 are $C_n = C_p = 5 \times 10^{-19} \text{ m}^3/\text{s}$ and $N_t = 1 \times 10^{23} \text{ m}^{-3}$, with a trap depth of 0.7 eV. The trap depth is determined from the energy difference between the red and blue emission peaks, whereas the amount of traps results from studying the electron transport in these materials by electron-only devices.

The strength of the SRH recombination is mainly determined by the product of the electron trap density and the capture coefficient. The choice of the capture coefficient follows from a best fit to the experiment. Using these parameters, the total Langevin and SRH recombination rates are about equal, in agreement with the fact that intensity of the blue and red component of the white emission are similar. It should be noted, however, that the choice of these parameters is not critical in our case: Langevin and SRH recombination were measured independently, so that it does not matter whether either of the two is dominant. For a sufficiently deep trap, SRH recombination will give an ideality factor of 2 and Langevin recombination an ideality factor of 1.

Langevin recombination was applied using Eq. (S2), without any modification [S2].

Values for the charge carrier mobility were obtained by fitting the low-field space-charge-limited current of a single-carrier diode with the conventional Mott-Gurney square law. The obtained mobility of $1 \times 10^{-11} \text{ m}^2/\text{Vs}$ was directly used as input parameter for the electron and hole mobility.

B. Simulations Fig. 4

The experimentally deduced simulation parameters for the PPV:PCBM solar cell can be found in Ref. [S1] and are also listed in Table S1. Since recombination in such a solar cell arises predominantly from free charge carriers, only Langevin and geminate recombination were taken into account. Also for these simulations it should be noted that the slope of the V_{oc} -intensity characteristics in Fig. 4 is not dependent on any of the parameters listed below in Table S1.

Parameter	Numerical value
HOMO(D)-LUMO(A)	1.34 eV
Electron mobility	$2.5 \times 10^{-7} \text{ m}^2/\text{Vs}$
Hole mobility	$3.0 \times 10^{-8} \text{ m}^2/\text{Vs}$
Eff. density of states	$2.5 \times 10^{25} \text{ m}^{-3}$
Generation rate	$2.7 \times 10^{27} \text{ m}^{-3} \text{ s}^{-1}$
Dielectric constant	$3.0 \times 10^{-11} \text{ F/m}$
e/h pair distance	1.3 nm
Decay rate of e/h pairs	$1.5 \times 10^6 \text{ s}^{-1}$

Table S1. Input parameters for the device simulations depicted in Fig. 4. HOMO(D) denotes the highest occupied molecular orbital of the donor material, and LUMO(A) the lowest unoccupied molecular orbital of the acceptor material.

II. Influence of leakage current

In Fig. S1a the temperature-resolved η - V characteristics of an rr-P3HT hole-only diode are shown. The ideality factor, obtained from the minimum value, shows no significant variation over the whole temperature regime. In contrast, the characteristics of a second device (Fig. S1b) show a clear temperature dependence of the apparent ideality factor, due to a higher leakage current. In that case, the leakage current masks the diffusion regime as the drift current reduces upon cooling, due to the temperature dependence of the mobility, and the plateau cannot be discerned anymore.

Fig. S1. Temperature dependent η - V characteristics of rr-P3HT hole-only diodes for a device with a particularly low leakage current (a) and a device with a higher leakage current (b), showing the influence of the leakage current on the apparent temperature dependence of the ideality factor. The inset in (a) shows that the leakage current is even below the sensitivity of the measurement set-up for this device.

III. Current-density–voltage characteristics

Fig. S2. Temperature dependent J - V characteristics of a tbi-PCBM electron-only diode with a thickness of 280 nm.

Fig. S3. Temperature dependent J - V characteristics of a PCPDTBT hole-only diode with a thickness of 175 nm.

Fig. S4. Temperature dependent J - V characteristics of a rr-P3HT hole-only diode with a thickness of 140 nm.

Fig. S5. Temperature dependent J - V characteristics of a BEH/BB-PPV hole-only diode with a thickness of 77 nm.

Fig. S6. Temperature dependent J - V characteristics of a BEH-PPV hole-only diode with a thickness of 104 nm.

Fig. S7. Temperature dependent J - V characteristics of a PTAA hole-only diode with a thickness of 96 nm. Note that at low temperatures a leakage contribution obscures the exponential diffusion regime.

Fig. S8. Temperature dependent J - V characteristics of a PFO hole-only diode with a thickness of 80 nm.

Fig. S9. Temperature dependent J - V characteristics of a MEH-PPV hole-only diode with a thickness of 70 nm.

Fig. S10. Temperature dependent J - V characteristics of a rir-P3HT hole-only diode with a thickness of 65 nm.

Fig. S11. Temperature dependent J - V characteristics of a NRS-PPV hole-only diode with a thickness of 60 nm.

References

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