Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Effect of a large hole reservoir on the charge transport in TiO_2/organic hybrid devices

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Analytic expression for SCLC in linearly increasing voltage

The current equation of a hole reservoir at the TiO_2 contact in a linearly increasing voltage can be written as[1]

$$j(t) = e\mu_p p(x,t)E(x,t) + \varepsilon\varepsilon_0 \frac{dE(x,t)}{dt} \qquad (1)$$

where μ_p is the mobility and $p(x,t)$ the density of the holes, respectively; $E(x,t)$ is the electric field, ε_s the electric permittivity of the organic semiconductor blend and ε_0 the permittivity in vacuum. By integrating Equation 1 over the sample thickness (here E=At/d) as

$$j(t) = \frac{1}{d}\int e\mu_p p(x,t)E(x,t)dx + \frac{\varepsilon\varepsilon_0}{d}\frac{d(At)}{dt} \qquad (2)$$

and noting that the thickness of TiO_2 $\ll$ thickness of P3HT:PCBM layer, with the boundary condition $E(0,t)=0$ we obtain:

$$j(t) = \frac{\varepsilon\varepsilon_0 A}{d} + \frac{\mu_p\varepsilon\varepsilon_0}{d}\frac{E^2(d,t)}{2} = \varepsilon\varepsilon_0\frac{dE(d,t)}{dt} \qquad (3)$$

where d is the thickness of the device and $A = U/t$ is the voltage rise speed. By solving Equation 3 we get $E(d,t)$ and noting that $j(0) = \varepsilon_s\varepsilon_0 A/d$ we obtain at $t < t_{sc}$ (the time needed for the charge carriers to reach the opposite contact):

$$\frac{\Delta j}{j(0)} = \tan^2\left(\frac{t}{t_{tr}}\right) \qquad (3a)$$

$$t_{tr} = d\sqrt{\frac{2}{\mu A}} \qquad (3b)$$

This is the behaviour of the current as shown in Fig. S1 in area 1. Here $t_{sc} = 0.92t_{tr}$ and t_{tr} is the small-charge transit time in a linearly increasing voltage. When $t \gg t_{tr}$, the current will grow quadratically as (area 2 in Fig. S1):

$$\frac{\Delta j}{j(0)} = \frac{9}{4}\frac{t^2}{t_{tr}^2} \qquad (4)$$

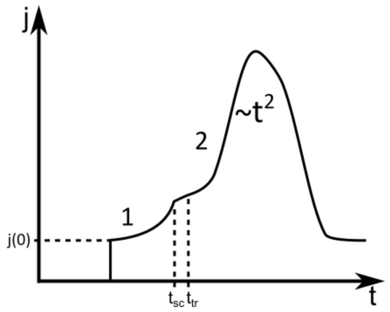

Fig. S1. Schematic representation of the parameters introduced in the text.

Modeling of a device with reduced extraction

The device is described with a 1D drift-diffusion model[2]. The equations to be solved are the carrier continuity equations for electrons $n(x,t)$ and holes $p(x,t)$,

$$\frac{dn}{dt} = \frac{1}{e}\frac{\partial j_n}{\partial x} + G - R \quad (5a)$$

$$\frac{dp}{dt} = -\frac{1}{e}\frac{\partial j_p}{\partial x} + G - R \quad (5b)$$

coupled to the Poisson equation for the electric field $E(x,t)$

$$\frac{dE(x,t)}{dx} = \frac{e}{\varepsilon\varepsilon_0}(p(x,t) - n(x,t)) \quad (6)$$

where the electron and hole current densities j_n and j_p, respectively, are given by

$$j_n(x,t) = en(x,t)\mu_n E(x,t) + \mu_n kT\frac{dn}{dx} \quad (7a)$$

$$j_p(x,t) = ep(x,t)\mu_p E(x,t) - \mu_p kT\frac{dp}{dx} \quad (7b)$$

here the classical Einstein relations have been used.

The net recombination is assumed to be given by

$$R - G = \beta\left(np - n_{eq}p_{eq}\right) - G_L \quad (8)$$

where β is the bimolecular recombination coefficient, G_L is the photo generation rate of free electrons and holes under illumination (G_L = 0 in dark), and n_{eq} (p_{eq}) is the electron (hole) concentration at thermal equilibrium. The bimolecular recombination coefficient is given by

$$\beta = \zeta\beta_L \ , \quad (9)$$

where β_L is given by Langevin's theory as

$$\beta_L = \frac{e}{\varepsilon\varepsilon_0}(\mu_p + \mu_n) \tag{10}$$

and ζ is a reduction factor, typically in the order of ~10^{-3} for P3HT:PCBM[3]. It is, however, noted that due to the large amount of holes (compared to electrons) in this case, the recombination is negligible.

The charges generated at the contacts, according to thermionic emission theory, are given by[4]:

$$n_{Cu} = N_{LUMO}\exp\left[-\frac{\phi_{Cu}}{kT}\right] \tag{11a}$$

$$p_{Cu} = N_{HOMO}\exp\left[-\frac{(E_g-\phi_{Cu})}{kT}\right] \tag{11b}$$

$$n_{ITO} = N_{LUMO}\exp\left[-\frac{(E_g-\phi_{ITO})}{kT}\right] \tag{11c}$$

$$p_{ITO} = N_{HOMO}\exp\left[-\frac{\phi_{ITO}}{kT}\right] \tag{11d}$$

where N_{LUMO} and N_{HOMO} is the effective density of states at the LUMO and HOMO levels, respectively, E_g is the energy difference between the HOMO of P3HT and LUMO of PCBM and ϕ_{Cu} (ϕ_{ITO}) is the energy difference between the LUMO (HOMO) and the copper (ITO) Fermi-level. To describe the electron and hole transfer at the electrodes in a more general way, the extraction rate of carriers is described as a surface recombination velocity. The boundary conditions for the hole current density at the electrodes is thereby given by

$$j_p\big|_{electrode} = eS_p^{electrode}(p - p_{electrode}) \;, \tag{12}$$

where $p_{electrode}$ is the thermal hole concentration at the respective electrode given by Equations 11a-11d and $S_p^{electrode}$ is the surface recombination velocity interpreted as an extraction rate. Similar expressions are valid for electrons. In the case of ideal electrodes, $S_p^{electrode}$ is infinite and the hole concentration at the electrode reduces to $p_{electrode}$. In the developed model, the P3HT:PCBM layer is assumed to behave as an effective semiconductor, sandwiched between two electrodes: ITO and Cu. The thin layer of TiO_2 is effectively replaced by a significantly reduced extraction rate for holes at the ITO-electrode. The other carrier extraction rates are assumed to be infinite.

The boundary condition for the electric field is given by:

$$\int_0^d E(x,t)dx = U - U_{bi} \tag{13}$$

where U_{bi} is the built-in potential given by the difference between the electrode work functions.

Finally, the total current density is given by:

$$\mathrm{j(t)} = \frac{1}{d}\int_0^d (j_n + j_p)dx + \frac{\varepsilon\varepsilon_0}{d}\frac{dU}{dt} \tag{14}$$

where U is the applied potential.

The parameters used for the modeling of the CELIV transients in Fig 4a, are shown in Table S1

Table S1

T	300 K
ε (dielectric constant)	4
N_{LUMO}, N_{HOMO}	10^{18} cm^{-3}
E_{gap}	1.2 eV
φ_{Cu} , φ_{ITO}	0.77, 0.37 eV
d	800 nm
μ_{n}, μ_{p}	10^{-3} , $3x10^{-4}$ $cm^2V^{-1}s^{-1}$
S_n^{ITO} , S_n^{Cu} , S_p^{Cu}	10^{48} cm/s
S_p^{ITO}	$3x10^{-4}$ cm/s
A	4 V/1 ms

References

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