Supporting Information to: " V_{oc} from a Morphology Point of View: the Influence of Molecular Orientation on the Open Circuit Voltage of Organic Planar Heterojunction Solar Cells"

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Supporting Information Available

Molecular orientation from NEXAFS

The relative intensities of the 6T π^* resonance contributions to the recorded C1s-edge NEX-AFS spectra are shown in Figure 1 as a function of incident angle. The general result is in agreement with the bulk analysis by X-ray scattering and confirms a mixture of lying and standing 6T at the interface for RT and only standing 6T for HT samples. Yet, 6T grown at $100 \,^{\circ}\text{C}$ exhibits a weak tendency towards a slightly larger molecular angle at the free surface and at the interface to C_{60} than in the bulk. A common fit yields an angle of 84° to the substrate plane. At the 6T(HT)/DIP interface a relaxation of the 6T angle to about 72° is observed. The expected average angle of the conjugated plane (not the long molecular axis), estimated from the crystal structure, of standing 6T is approx. 78°, and thus in between the two extracted angles.¹ The same trends are visible for RT samples but the experimental error is close to the observed individual fit differences. Therefore a common fit for all three 6T interfaces was performed and yields an average molecular angle of about 64°. This is significantly lower than what is expected for standing 6T and may thus be interpreted as a superposition of contributions from standing and lying 6T molecules. Note that apart from the experimental error of $\pm 3^{\circ}$ additional uncertainties are introduced by the deconvolution procedure and the fit itself. The latter error is expected to be larger for molecular angles far away from 55° and is estimated to $\pm 5^{\circ}$ for the neat 6T(HT) film but drastically reduced for the other films (cf. gray lines in Figure 1).

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Figure 1: Angular dependence of the NEXAFS C1s- π^* transitions of the 6T molecules in the investigated films. The data points are corrected for angle misalignment and normalized to an angle of incidence of 55°. The solid lines correspond to the respective fits 6T(HT) and 6T(HT)/C₆₀ (common fit, red), 6T(HT)/DIP (orange) as well as 6T(RT) (common fit of all three samples, blue). The individual fits of the RT 6T samples are shown as the dashed blue lines. The gray lines illustrate the calculated behavior at the angles indicated right of the graph.

Simulation of the $V_{\rm oc}(T)$ behavior of the 6T/DIP system

An extention of the Shockley-Queisser limit to organic heterjunction solar cells was discussed in detail in Ref. 2. This model starts from the radiative limit, where the ideal solar cell is regarded as a black body radiator weighted by the absorption spectrum α of the semiconductor. The dark saturation current $j_{0,\text{rad}}$ then relates to the number of emitted photons N:²

$$j_{0,\text{rad}} = eN(\alpha, T) = e \int_0^\infty \alpha(E) n(E, T) dE$$

= $e \int_0^\infty \alpha(E) \frac{2\pi}{h^3 c^2} \left[\exp\left(\frac{E}{k_{\text{B}}T}\right) - 1 \right]^{-1} E^2 dE,$ (1)

where e is the elementary charge, E the photon energy and T the temperature. h, c and $k_{\rm B}$ denote Planck's constant, the speed of light and the Boltzmann constant, respectively.

In the original considerations by Shockley and Queisser a step function was assumed for the absorption spectrum with complete absorption of photons with an energy above the (optical) band gap E_{opt} and zero absorption otherwise.³ For organic heterojunctions this concept is typically extended to a bi-step function in order to account for the additional but weak charge transfer (CT) absorption at the donor-acceptor interface (α_{CT}) for energies above the energy of the CT state $E_{D/A}$:^{2,4,5}

$$\alpha(E) = \begin{cases} 0 & : E < E_{\text{D/A}} \\ \alpha_{\text{CT}} & : E_{\text{D/A}} < E < E_{\text{opt}} \\ \alpha_0 \equiv 1 & : E > E_{\text{opt}} \end{cases}$$
(2)

This is illustrated in Figure 2(a).

With this formulation of $\alpha(E)$ Eq. (1) yields:

$$j_{0,\text{rad}} = eA \left[\alpha_{\text{CT}} \chi_{\text{CT}} \exp\left(\frac{-E_{\text{D/A}}}{k_{\text{B}}T}\right) + (\alpha_0 - \alpha_{\text{CT}}) \chi_{\text{opt}} \exp\left(\frac{-E_{\text{opt}}}{k_{\text{B}}T}\right) \right], \tag{3}$$

where $A = \frac{2\pi k_{\rm B}T}{h^3 c^2}$ and $\chi_{\#} = E_{\#}^2 + 2k_{\rm B}T E_{\#} + 2k_{\rm B}^2 T^2$ for $E_{\rm D/A}$ and $E_{\rm opt}$, respectively.

Note that the two summands in Eq. (3) both take the form

$$j_0 = j_{00} \cdot \exp\left(\frac{-\Delta E}{nk_{\rm B}T}\right),\tag{4}$$

with an ideality factor of n = 1. This identifies recombination via the CT state at the donor-acceptor interface and recombination across the optical gap of the absorber as two competing processes contributing to the dark saturation current.⁶ The relative strength of the individual contributions depends on temperature. At low temperatures the CT term is dominant; with increasing temperature the second term becomes more and more important

and, after a small transition regime, outweighs the contribution of the first term. The exact transition temperature depends on the intermolecular electronic coupling as expressed by the absorption coefficient of the CT state $\alpha_{\rm CT}$ as well as on the absolute values of $E_{\rm D/A}$ and $E_{\rm opt}$.

For real world devices additional, non-radiative recombination needs to be taken into account. In Ref. 2 a factor $\gamma = j_{0,\text{non}}/j_{0,\text{rad}}$ was introduced that relates non-radiative and radiative contributions to the dark saturation current thus that the total dark saturation current is given by $j_0 = j_{0,\text{rad}} \cdot (1 + \gamma)$. For the simulations of the 6T/DIP solar cells investigated here, the ideality factor n as in Eq. (4) was additionally introduced. Note that both γ and n further affect the dark saturation current compared to the radiative limit. Since the individual contributions can usually not be separated in the measurement, this directly influences the effective overall value of j_{00} of a device.

As expressed by the relation $eV_{\rm oc} = nk_{\rm B}T \cdot \ln(j_{\rm sc}/j_0 + 1) \approx \Delta E - nk_{\rm B}T \cdot \ln(j_{00}/j_{\rm sc})$ the open circuit voltage depends critically on the dark saturation current. A linear extrapolation of the measured temperature dependence of $V_{\rm oc}$ will discriminate the two energy gaps $E_{\rm D/A}$ and $E_{\rm opt}$ and thus identify the dominant process in the temperature range where the device was operated.

The temperature dependent behavior of V_{oc} of both 6T/DIP solar cells presented in the main article can be simulated with identical values of $E_{D/A} = 1.8 \text{ eV}$ and $E_{opt} = 2.1 \text{ eV}$ but extremely different intermolecular electronic coupling for both cells, if the above model is applied. As shown in Figure 2(b), the simulation matches the measurement in the linear temperature dependence regime but yields a severe deviation from linearity at low temperatures. It is important to note that this flattening of the *simulated* curves does *not* originate from transport limitations or injection barriers. The cause is rather the afore mentioned temperature dependent competition between recombination processes via the intermolecular gap and the optical gap of the absorber. In agreement with Ref. 2, a linear extrapolation in a temperature regime sufficiently far away from the transition regime (i.e. the "kink") in the

simulated curve yields the energy gap of the dominating process. For the high temperature prepared 6T/DIP device this energy matches well with the optical gap of DIP (2.1 eV).⁷

The anisotropic intermolecular coupling between 6T and DIP manifests itself in strongly different effective overall j_{00} values extracted for the two different devices from the simulation at a cell temperature of 300 K. These are $j_{00,\text{RT}} = 4.8 \times 10^6 \text{ mA/cm}^2$ and $j_{00,\text{HT}} = 9.7 \times 10^3 \text{ mA/cm}^2$, respectively. Note, however, that the quantities α_{CT} and γ as specified in the figure caption, which affect the coupling, are experimentally unknown and have to be estimated.



Figure 2: (a) Schematic illustration of the idealized absorption spectrum of an organic heterojunction. (b) Simulation of $V_{\rm oc}(T)$ of both 6T/DIP devices according to a modified Shockley-Queisser model (Ref. 2) with identical intermolecular gaps of 1.8 eV but different coupling. Ideality factors of $n_{\rm RT} = 1.55$ and $n_{\rm HT} = 2.0$ have been chosen, the optical gap of the absorber was set to 2.1 eV. The relative absorption strengths of the CT state were set to $\alpha_{\rm CT}(\rm RT) = 1 \times 10^{-3}$ and $\alpha_{\rm CT}(\rm HT) = 6.5 \times 10^{-4}$. Scaling factors to compensate for additional non-radiative recombination were $\gamma_{\rm RT} = 2 \times 10^3$ and $\gamma_{\rm HT} = 0.5$.

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