Charge separation at disordered semiconductor heterojunctions from random walk numerical simulations – Supporting Information

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We have focused on the role that recombination mechanism (by means of t_{r0}), absorber thickness (d_2) and initial densities (n_{0n}, n_{0p}) play in the charge separation process taking place in the heterojunction upon photoexcitation. SPV transients obtained from RW calculations for different values of t_{r0} and d_2 are shown in Fig. (1) in the main text. It can be observed that, for fixed absorber thickness, the higher the recombination time prefactor in Eq. (7) is, the later the decay appears. This is explained by the fact that as t_{r0} increases, the probability of recombination decreases with respect to transport and consequently fewer recombination events will occur. For t_{r0} = 1 s, very few carriers are recombined and the SPV signal is mainly controlled by diffusion and charge separation. Thus, a saturation effect related to the total thickness of the heterostructure seems to appear after charge separation process has been taken place. We can also see that variation of recombination frequencies affects the SPV maxima, making the maximum higher as the recombination frequency decreases. On the other hand, comparison of the three panels indicates that for a given value of the recombination frequency the SPV maxima appears at longer times as the absorber thickness (d_2) is augmented. This is a consequence of the fact that for thicker absorbers the process of diffusion with respect to electron-hole recombination is favoured.

Results of SPV maxima versus semiconductor thicknesses for various initial electron-hole densities are presented in Fig. (S1). As it can be observed, the maximum value of the SPV transients increases with respect to the width of the heterostructure according to a power law. It is interesting to note that the exponents also increase slightly with the illumination, from a slope of *1.2,* for the minimum density (n_0 = 6.25·10^{16} cm^{-3}). Likewise, it is shown that the maximum value of the SPV transients increases linearly with respect to the charge density for a given value of the total thickness in the log-log scale. The exponent is close to the unity in all cases, in accordance to experimental observations[1,2]. However, a saturation effect cannot be reproduced for larger values of illumination intensities (or initial charge densities), an observation also reported in experiments. This may be a consequence of the fact that for high charge densities the recombination mechanism changes and energy factors have to be taken into account.

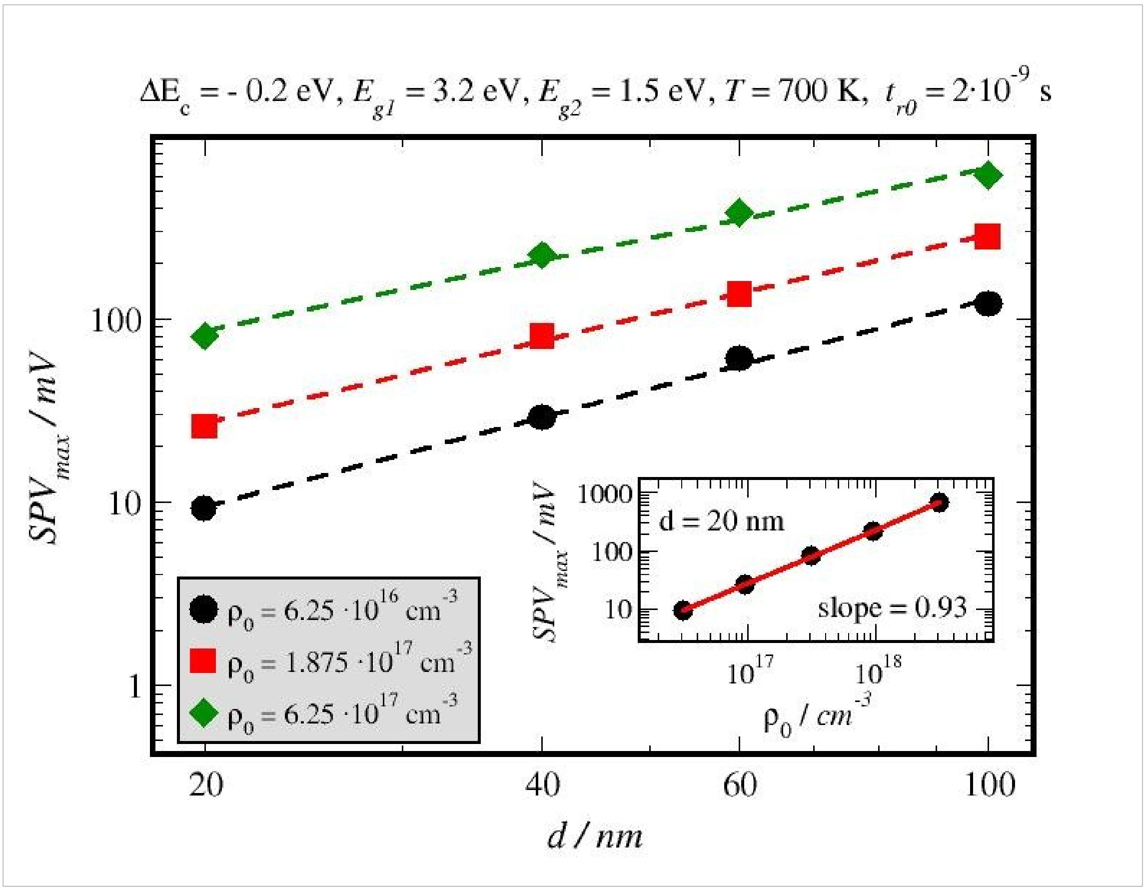

Fig. (S1). Maximum surface photovoltage of the transient versus total width of the film for several values of the carrier concentration as obtained from RW calculations with Miller-Abrahams hopping rates and a tunnelling recombination mechanism. The dashed lines stand for linear fittings of the simulation data. The inset includes the electron density dependence.

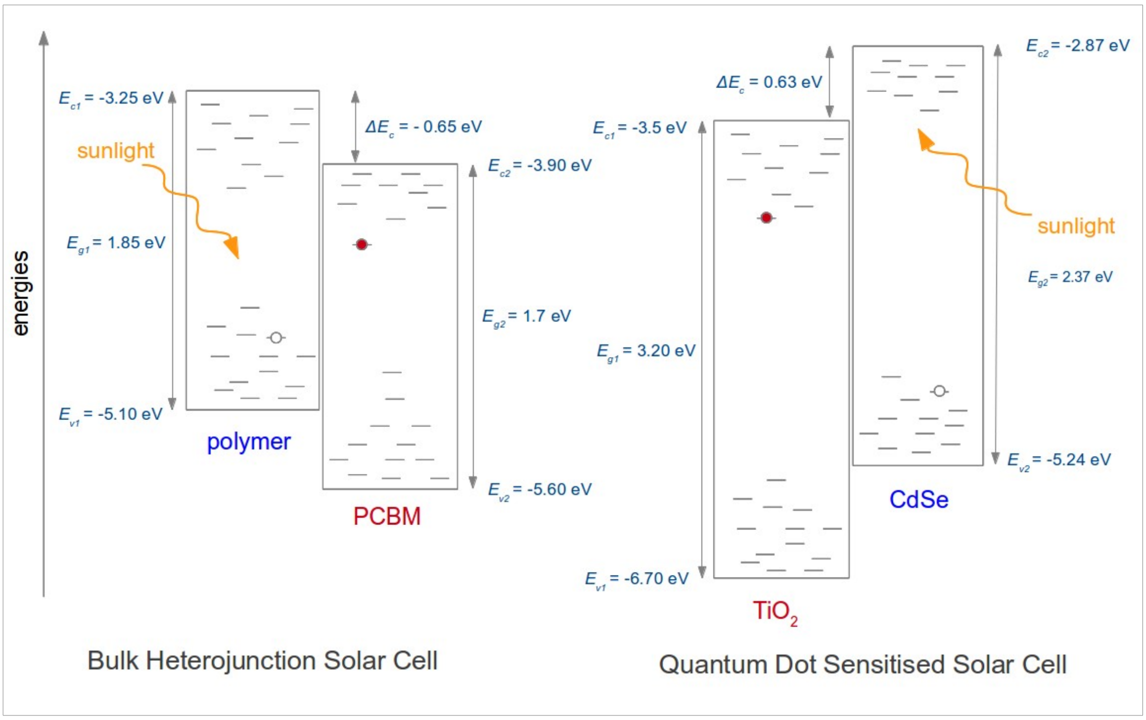

Fig. (S2). llustration of typical polymer-fullerene bulk heterojunction solar cell (left) and a QD-sensitised solar cell (right).

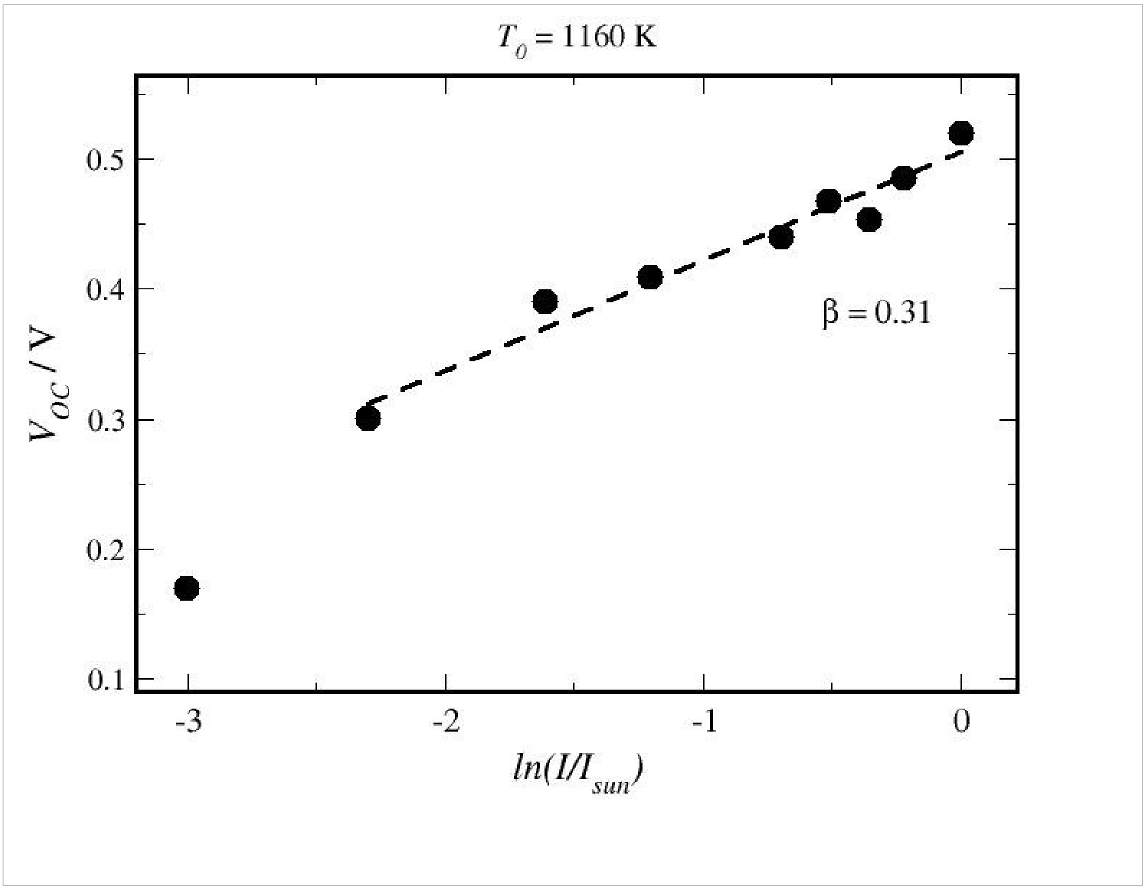

Fig. (S3). Open-circuit voltage as a function of the illumination intensity from electron Fermi level in the fullerene and hole Fermi level in the polymer as obtained by RW simulations (circles). The dashed line was obtained by fitting to Eq. (4).

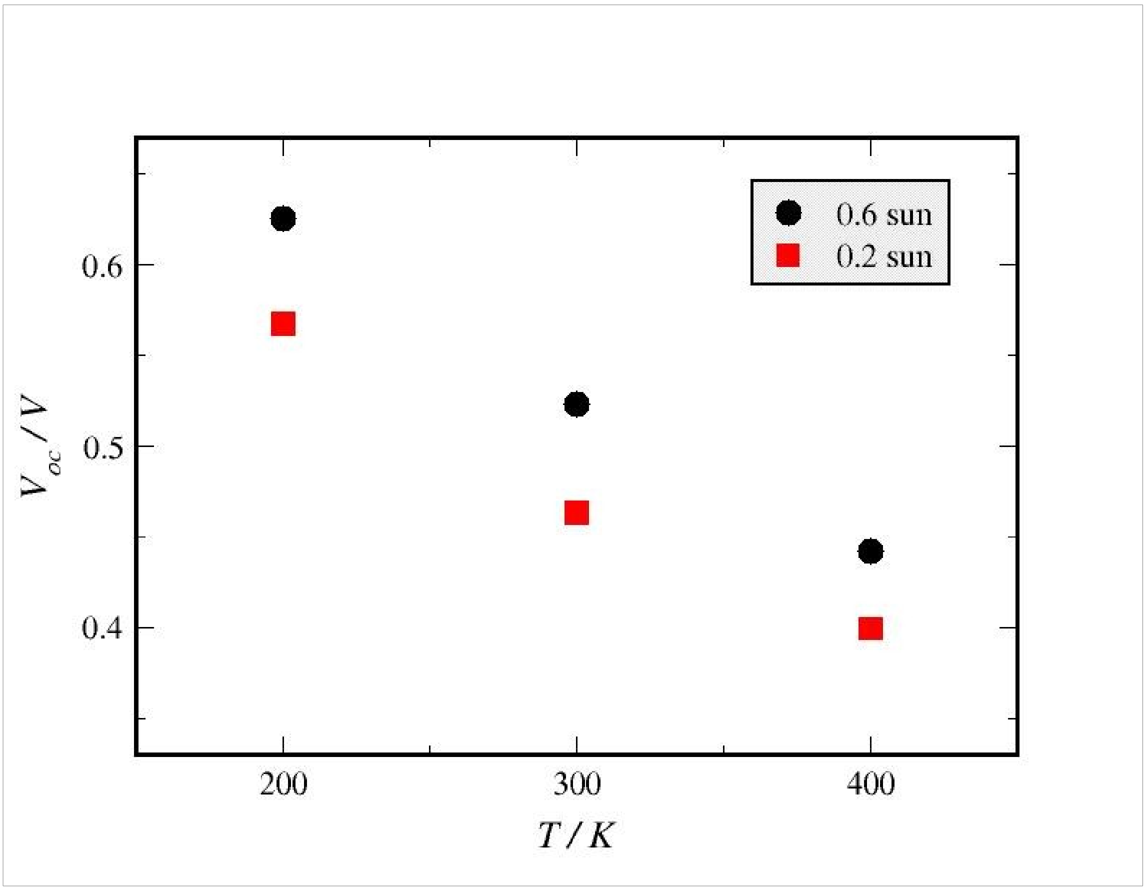

Fig. (S4). Open-circuit voltage as a function of the temperature for two degrees of illumination. The following values were used for this figure: T_0 = 500 K, T = 300 K, α_l= 2 nm and a_L = 2 nm.

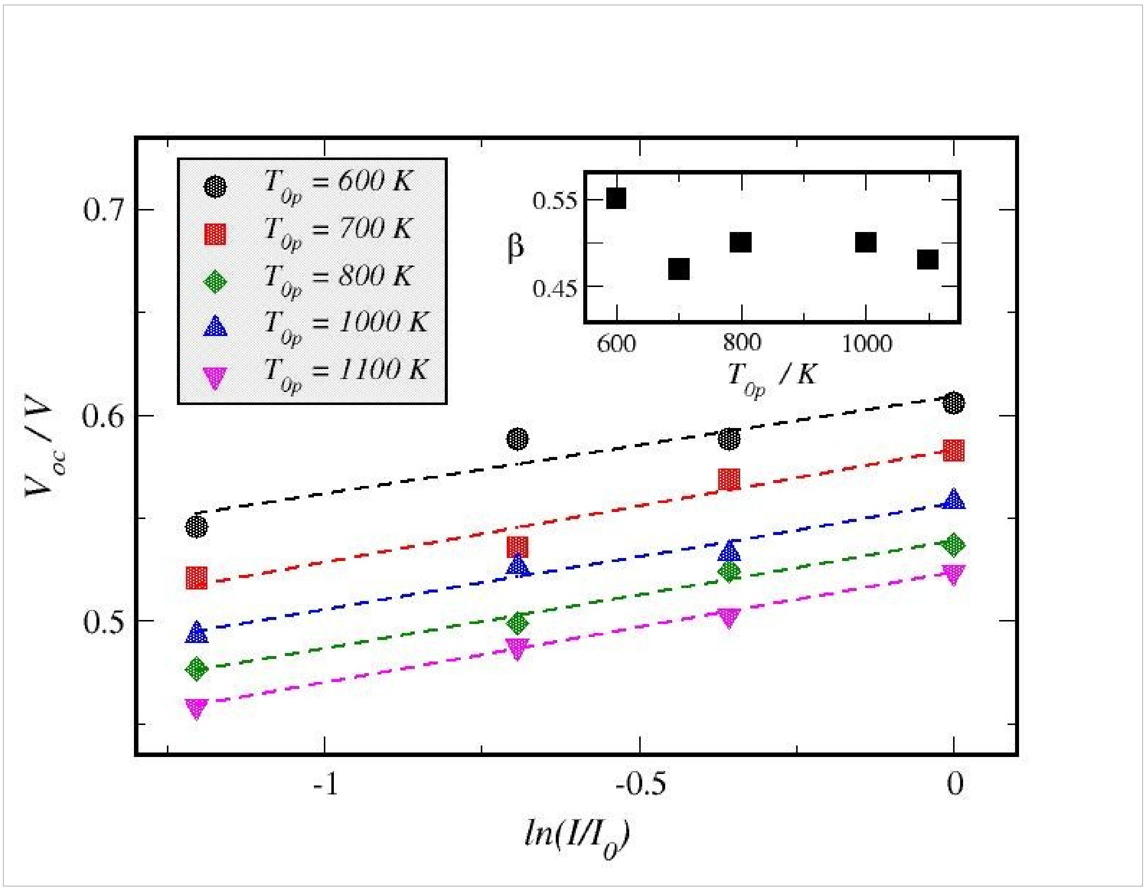

Fig. (S5). Open-circuit voltage as a function of the illumination intensity from electron Fermi level in the n-type semiconductor and hole Fermi level in the QD as obtained by RW simulations (circles). The dashed lines were obtained by fitting to Eq. (4). Extracted values of β-parameter as a function of the characteristic temperature of the QD are shown in the inset. The parameters used are shown in Table 1 in the main text.

REFERENCES

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2. Timoshenko, V. Y., Duzhko, V. & Dittrich, T. Diffusion photovoltage in porous semiconductors and dielectrics. *Physica Status Solidi a-Applied Research* **182,** 227–232 (2000).