Comment on "Charge Carrier Extraction in Organic Solar Cells Governed by Steady-State Mobilities"

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Comment on:

Vincent M. Le Corre et al. “Charge Carrier Extraction in Organic Solar Cells Governed by Steady-State Mobilities” (DOI: 10.1002/aenm.201701138)

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Introduction

Photo-generated carrier extraction in conventional bulk-heterojunction organic photovoltaic (OPV) devices typically spans the sub-picosecond to microsecond temporal range. Ultrafast time-resolved experiments show an increasing amount of evidence[1,2] that the sub-microsecond regime in polymer/fullerene[3], polymer/polymer[4] and small molecule[5] OPVs can be explained only if non-equilibrium effects, related to the gradual thermalization of the photogenerated carriers[6–8], are accounted for when modelling the experimental data.[9–12] On the other hand, slower (> 1µs) time-resolved and steady-state techniques, which probe the charge motion of mostly thermalized charge carriers, can, in most cases, be adequately described by (near) equilibrium charge transport models.[4] In principle, all of these time scales should be taken into account when modelling steady-state OPV device operation, e.g. during current-voltage (IV) measurements. This has been achieved in 1D continuum models.[13–15] To the best of our knowledge, a 3D (quasi) atomistic model, which would be needed to account for percolation and entropy effects,[16] that can successfully and simultaneously (using the same parameter set) fit both time-resolved sub-picosecond to microsecond transient kinetics and steady-state IV data, has not yet been demonstrated.

In a recent article by Le Corre et al.[17], its authors use transient photocurrent measurements with sub-microsecond time resolution (slower than ~10-100 ns) to conclude that ultrafast non-equilibrium processes (faster than ~10-100 ns) are unimportant when modelling steady-state device operation. Specifically, the mobility enhancement by several orders of magnitude at <0.1-1 µs time scales that was recently observed in multiple ultra-fast transport experiments[13] and reproduced by kinetic Monte Carlo simulations (kMC)[1,3–5,10] was argued to be unimportant for carrier extraction, on basis of a single measurement.

Here, we have repeated the transient experiments of Ref. [17] and fitted the data by kinetic Monte Carlo simulations to show that the observed slow (~0.1-10 µs) transients in the experiment by Le Corre et al. are not representative of actual steady-state extraction rates as (a) they are dominated by the limited temporal resolution of the used experimental technique and (b) they actually show that extraction is dispersive, i.e. indicate non-equilibrium transport.
Results

The transient photocurrent response to a step-wise decrease in white light-emitting diode (LED) intensity (~1.0 to ~0.5 Sun) under short-circuit conditions for a) PTB7:PC71BM and b) TQ1:PC71BM is shown in Figure 1. For these measurements, we avoid working at bias equal to built-in voltage as promoted by Le Corre et al. since under these “flatband” conditions there is either no driving field or the field is ill-defined. Since diffusion is undirected, in the absence of a driving field there should be no visible current transient — any net current transient at apparent “flatband” conditions must therefore be due to ill-defined remaining electric fields and unknown contact selectivity. For reliability, we have therefore performed our measurements under short-circuit conditions.

We have used a larger step size than 1.0 to 0.9 Sun in Ref. [17] to obtain a sufficient signal/noise ratio in our kMC simulations. The kinetics are independent of step size as stated in Ref. [17]. The temporal resolution of our measurement setup was evaluated by measuring the response of a reference Si photodiode (Fig. 1a red trace). The temporal resolution of our setup is ~0.3 µs and similar to the one in Ref. [13]. The input pulse driving the LED as well as complementary details on the time resolution of the experiment are included in the Supporting Information (SI).

Kinetic Monte Carlo simulations successfully reproduce the experimental data in Figure 1. For TQ1:PC71BM, we use simulation parameters from previous work (SI Table S1), where we have successfully fitted several time-resolved experiments spanning the full sub-picosecond to microsecond temporal range,[5,10] assuring that we consistently describe also the experiment in Figure 1. For PTB7:PC71BM we have used the same electron hopping parameters as for TQ1:PC71BM, while the hole parameters were independently obtained from temperature-dependent space-charge limited conduction (SCLC) experiments (SI Figure S2). The used parameters correspond to balanced steady-state electron and hole mobilities $\mu = 3 \times 10^{-8}$ m$^2$/Vs in PTB7:PC71BM.[17,18]

In contrast to the claim in Ref. [17], the transient photocurrent decay is not necessarily exponential. More concretely, the response for TQ1:PC71BM to a step-wise (~1.0 to ~0.5 Sun) decrease in LED intensity is not mono-exponential, cf. the orange line in Figure 1b, but is composed of a very steep part.
at short times (below \( \sim 1 \mu s \)) which cannot be fully resolved, followed by a slower response at longer times. This suggests that the transients could be bi-exponential, with electrons and holes each giving a (roughly) exponential contribution, in line with recent transient photocurrent measurements with high (ca. ns) temporal resolution by Ullbrich et al.\[^{[19]}\] The response of PTB7:PC71BM on the other hand seems to be fitted adequately by a mono-exponential decay which we attribute to the balanced electron and hole mobilities and, possibly, to the limited temporal resolution of the experimental setup (bi-exponential decay cannot be adequately resolved). This highlights the main drawback of electrical transient photocurrent measurements – limited temporal resolution. Figure S3 plots the data on semi-log scale, revealing that for both material systems a mono-exponential fit does neither capture the slow dispersive decay beyond \( \sim 1 \mu s \) that is observed experimentally.

Both PTB7:PC71BM and TQ1:PC71BM photocurrent transients are accurately reproduced by kinetic Monte Carlo simulations as shown in Figure 1a, b. As the raw simulated kMC photocurrent transients have a low signal-to-noise ratio, a phenomenological model, assuming exponential decays for electrons and holes was calibrated on the (much less noisy) integrated photocurrent from kMC as described in the SI (green solid lines). The inset in Figure 1b shows that for TQ1:PC71BM the steep current decay at short times is due to the very fast extraction of electrons, followed by a slower extraction of holes. This is confirmed by the different 1/e time constants in the phenomenological fits (0.2 \( \mu s \) for electrons, 1.5 \( \mu s \) for holes, see SI Table S2). The corresponding 1/e time constants for PTB7:PC71BM are 0.3 \( \mu s \) for electrons and 0.6 \( \mu s \) for the holes. Nevertheless, as we will show below, in view of the strong dispersion in disordered media,\[^{[20,21]}\] these extraction times are not particularly relevant.

It is crucial that neither the experiment nor the (representation of) the simulations shown in Figure 1 allow making statements about the extraction kinetics of the full charge population. This is due the simple reason that any signals on 0.2-0.3 \( \mu s \) or shorter time scales are washed out by the setup – this experimental technique reliably probes only the fraction of charges remaining in the device longer than the temporal resolution of the setup, e.g. \( \sim 0.2-0.3 \mu s \). As such, Figure 1 serves only to show that our kMC simulations can reproduce the experimental findings. Nevertheless, as we will demonstrate below, these findings are fully consistent with our earlier results showing that under steady-state device operation the majority of photo-generated charges have already been extracted at time scales of the order of \( \sim 100 \) ns or faster that are not accessible in this experiment\[^{[3]}\]; the exact time scale depends on material and device parameters, see refs. \[^{[4]}\], \[^{[5]}\] and \[^{[7]}\].

The limitations mentioned above are highlighted in Figure 2a,c where the simulated charge extraction time distributions (histograms) are plotted and compared to the histogram obtained from the experimental \( j(t) \) curve – see ref. \[^{[3]}\] and SI for details. Clearly, there is an excellent match in the time window that can be probed by the used experiment, i.e. from a few hundreds of ns onward. However, the experiment is blind to a significant fraction of, mainly, photo-generated electrons, especially for the thinner TQ1:PC71BM device (100nm, whereas PTB7:PC71BM is 140nm). In other words, depending on the specifics of the investigated system, the transient photocurrent measurement resolves only a subset of the photo-generated charge carrier population, namely the subset of charges that have relaxed sufficiently to have an extraction time beyond the experimental time resolution. While it is not surprising that these slowest tails, that correspond to the subset of most relaxed charges, can be phenomenologically fitted with parameters corresponding to an equilibrium model, the conclusion that the equilibrium mobility describes the extraction of all charges clearly cannot be drawn. In addition to experimental problems, the 1/e extraction times are of limited relevance due to dispersion, as highlighted by comparing them to the charge extraction histograms, c.f. vertical lines in Figure 2a and c. Most of the charges are extracted at much earlier time scales than predicted by 1/e extraction.
times, as can be seen by comparing the latter to the histogram peak positions, see Ref. \([3,4]\) for full details.

Figure 2b,d shows the calculated photo-generated carrier thermalization kinetics during the charge extraction experiment. In contrast to what is suggested in Ref. \([17]\), the relaxation rate is independent of photo-generated carrier density as shown experimentally and supported by kMC simulations.\([2,3,10]\) The thick traces correspond to mean electron and hole energies in their respective disorder broadened density of states (DOS). For an infinite device, electrons would relax to the highest (holes to the lowest) of the equilibrium energy \((\sigma^2/k_B T)\) (marked by dotted lines) and the quasi-Fermi energy (thin solid lines). Clearly, for the finite devices considered here, relaxation does not complete before extraction, showing that dispersive and faster than quasi-equilibrium extraction kinetics are important for both types of charges. This is in agreement with the convex tailing edge (long times) of the extraction histogram obtained from the experimental data, which can only originate due to dispersive transport, as we have demonstrated previously;\([3]\) the leading edge (early times) is determined by the setup and therefore virtually identical for both systems. As such it contains no physically meaningful information. Therefore, transient photocurrent measurements, such as those shown here or in Ref. \([17]\), unless specifically optimized for high temporal resolution,\([19,22]\) probe only a subset of the total photo-generated carrier population (Fig. 2a,c). In addition, the fact that one can phenomenologically describe transient photocurrent measurements with a quasi-equilibrium model does not justify the conclusion that relaxation is fast compared to the time needed for extraction, i.e. it does not justify that extraction rates can be meaningfully described by non-dispersive equilibrium mobilities.

Figure 2. a) Extraction time histogram (blue line) corresponding to the transient photocurrent experiment of PTB7:PC\(_{71}\)BM under short-circuit conditions plotted together with electron and hole extraction time histograms from kinetic Monte Carlo simulations (red lines); c) The same for TQ1:PC\(_{71}\)BM; b), d) Corresponding calculated relaxation kinetics vs. time after photogeneration (thick solid lines), quasi-Fermi energies (thin solid lines), equilibrium energies (thin dotted lines), according to the Gaussian Disorder model (GDM),\([6]\) and HOMO/LUMO
energies (dashed lines). Vertical bars in panels a and c indicate the electron and hole 1/e extraction times, respectively (Table S2 in the SI).

To conclude, explicit kinetic Monte Carlo simulations accurately reproduce the transient photocurrent response to a step-wise change in continuous light intensity for PTB7:PC71BM and TQ1:PC71BM OPV devices. In contrast to the conclusions by Le Corre et al., we demonstrate that for both systems fast and dispersive transport is quite important. This is the reason why Time-Resolved Electric-Field-Induced Second Harmonic generation (TREFISH) was initially selected as the probing technique[3–5]. We wish to point out that our current findings should not come as a surprise since we had previously shown that pulsed and steady-state excitations yield identical relaxation and extraction kinetics[3], and that steady-state IV curves also successfully match those recorded by pulsed laser measurements. Finally, it is important to note that due to slow relaxation and dispersion, the detrimental effects of disorder are not as bad as they would have been in case of instantaneous carrier thermalization, but that enhancing disorder is evidently a bad design rule, as pointed out in our earlier publications.

Experimental

See Supporting Information for details on device fabrication, measurements and simulations.

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