

To the Editor — Grancini *et al.*¹ recently reported hot exciton dissociation in polymer solar cells. They performed ultrafast pump–probe spectroscopy on a low-bandgap conjugated polymer–fullerene derivative blend, PCPDTBT:PC₆₀BM. The authors interpreted the experimental findings in terms of interfacial charge-transfer states (CTS) and that polaronic species are formed on very short timescales, and conclude that the probability of dissociation of hot CTS into free charge is larger compared with thermalized CTS. To support their interpretation, the authors showed an internal quantum efficiency (IQE) spectrum obtained from a detailed characterization of a solar cell made from the same blend. They showed that the IQE increased with higher photon energies suggesting enhanced dissociation of hot states. This is not in line with our findings for other polymer–fullerene blends^{2,3}.

Therefore, we determined the optical properties and the IQE of the same blend that was investigated by Grancini *et al.* Experimental details and the refractive indices of all the materials used are provided in the Supplementary Information. Measured and calculated spectra of two devices are shown in Fig. 1. Despite the complex structure and potential imperfections of the layers composing the device, agreement between the calculated and measured spectra is very good. For the external quantum efficiency (EQE) calculations for all the devices studied, we found that a constant IQE across the spectral range investigated allows an excellent reproduction of the experimental data. This is in contrast to the findings of Grancini *et al.*

who mention in their Supplementary Information that they considered cavity effects but found a negligible contribution from optical interference to the IQE. However, in our work, we found a strong

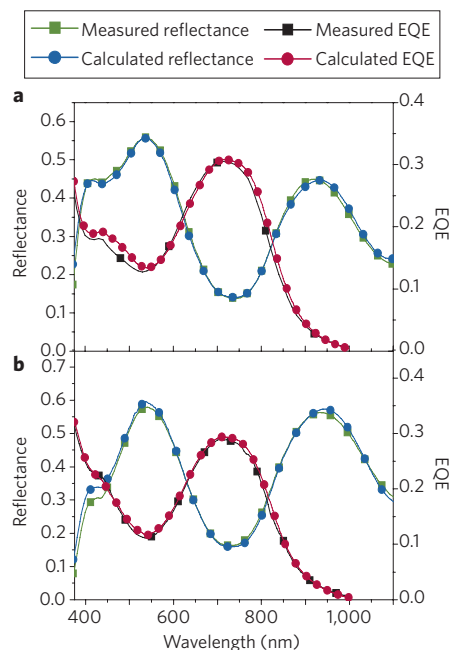


Figure 1 | Measured and calculated reflectance and EQE spectra of two different PCPDTBT:PC₆₀BM solar cells. **a**, The thickness of the hole-transport layer is 49 nm and the active-layer thickness is 107 nm. **b**, The thickness of the hole-transport layer is 25 nm and the active-layer thickness is 128 nm. By using constant IQE values of 46% (**a**) and 40% (**b**) to simulate the EQE spectra, a good agreement with the measured EQE curves is obtained.

signature of interference, and that small variations in the thickness of the hole-transport layer or active-layer led to pronounced changes especially in the reflectance properties of the device. Recently, Albrecht *et al.*⁴ published a study on PCPDTBT/PC₇₀BM blends synthesized using diiodooctane as a processing additive. An optical analysis of the layers and devices revealed an essentially constant IQE across the absorption spectrum of the blend supporting our results.

On the basis of our findings, the experimental results presented by Grancini *et al.* may need to be interpreted differently. It seems that the dissociation of hot excitons observed at very short times after photoexcitation does not have any impact on the overall charge-generation efficiency of a PCPDTBT:PC₆₀BM (1:4 wt%) solar cell operated under steady-state illumination. This suggests that other processes that occur on the pico- to millisecond timescale may actively quench the effects observed immediately after photoexcitation. □

References

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Additional information

Supplementary information is available in the [online version of the paper](#).

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Grancini *et al.* reply — In our work¹ we included the internal quantum efficiency (IQE) of a PCPDTBT:PC₆₀BM active layer to show that hot exciton dissociation influences the performance of an operating photovoltaic device. To specifically reveal the physics of the interface governing the charge photogeneration mechanism, we measured the IQE in a simple vertical device architecture consisting of fluorine-doped tin oxide (300 nm)/active layer (200 nm)/silver (150 nm). Our results demonstrated a rising trend in the IQE with increasing photon energy¹.

As Armin *et al.*² point out, measuring the IQE of an optimized device, which usually has additional stacking layers (for example, selective charge-extracting layers), is difficult and could be affected by a

number of artefacts such as light scattering, parasitic absorption in layers other than the active layer and/or interference effects. Indeed, Scharber *et al.*³ show that simply tuning the thickness of the polyethylene dioxythiophene:polystyrene sulphonate (PEDOT:PSS) layer can dramatically change the reflectance spectrum of the active layer. Furthermore, in some cases, the thin-film approximation based on the transfer matrix approach for calculating the active-layer absorption may not be adequate for reproducing the measured absorption. In particular, at energies above 2.2 eV, which are rarely considered, discrepancy between the measured and the calculated external quantum efficiency (EQE) spectra can be observed³. For these reasons, correctly evaluating the

IQE in the high-energy spectral range is particularly tricky.

To overcome these technical obstacles we measured the IQE of a device with a lateral geometry based on a finely dispersed PCPDTBT:PC₆₀BM blend (see Supplementary Information for experimental details). We also simulated, by means of the transmission-line analysis approach, the absorption of the active layer, and found that it closely matches the experimental absorption (see Supplementary Information for details). Figure 1 shows the IQE obtained by dividing the measured EQE spectrum by the measured (blue curve) and simulated (black curve) absorption spectrum of the active layer. Our new measurements confirm our previous results. The observation of the same