

## Research



**Cite this article:** Yaghoobi Nia N, Méndez M, di Carlo A, Palomares E. 2019 Energetic disorder in perovskite/polymer solar cells and its relationship with the interfacial carrier losses. *Phil. Trans. R. Soc. A* **377**: 20180315. <http://dx.doi.org/10.1098/rsta.2018.0315>

Accepted: 2 April 2019

One contribution of 13 to a discussion meeting issue 'Energy materials for a low carbon future'.

**Subject Areas:**

chemical physics, materials science, nanotechnology, physical chemistry, spectroscopy

**Keywords:**

perovskite solar cells, poly(3-hexylthiophene), charge extraction, photo-induced transient photovoltage, energetic disorder

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Electronic supplementary material is available online at <https://dx.doi.org/10.6084/m9.figshare.c.4513301>.

Energetic disorder in  
perovskite/polymer solar cells  
and its relationship with the  
interfacial carrier losses

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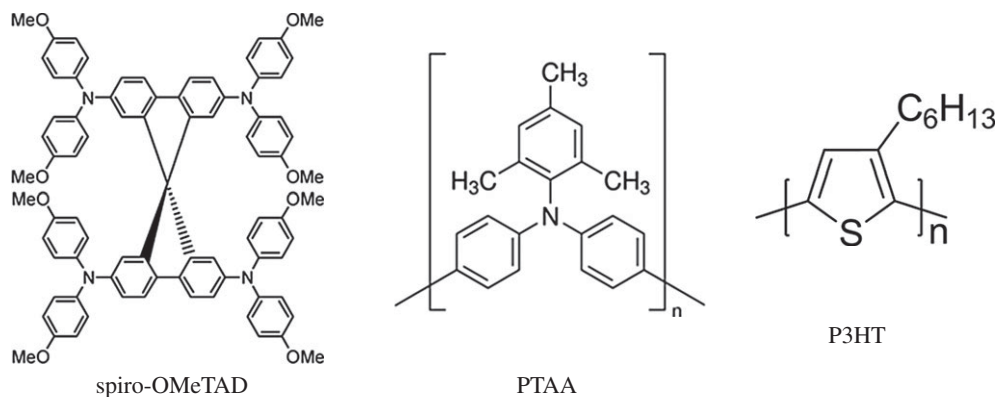
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Previous reports have observed a direct relationship between the polymer poly(3-hexylthiophene) molecular weight (MW) and the perovskite solar cell (PSC) efficiency. Herein, we analyse how the differences in MW and the differences in energetic disorder influence the interfacial carrier losses in the PSCs under operation conditions and explain the observed differences.

This article is part of a discussion meeting issue 'Energy materials for a low carbon future'.

**1. Introduction**

In efficient hybrid perovskite solar cells (PSCs), spiro-OMeTAD (scheme 1) (2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene) is widely used as a small molecule hole transport material (HTM) [1–3]. Nonetheless, a myriad of alternative HTMs have been designed and synthesized to replace spiro-OMeTAD. Only a few materials have been able to match or overpass the solar cell efficiency of spiro-OMeTAD [4–6], for instance, semiconductor polymers such as PTAA (poly-[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]) (scheme 1) have been reported to match the performance



**Scheme 1.** The most common HTMs (molecular and polymeric) used in perovskite solar cells.

of the spiro-OMeTAD-based PSCs [1]. Notwithstanding this, PTAA shows great batch-to-batch variation and high price that prevent its use in large-scale fabrication which convince researchers to choose other semiconductor polymers. An example is the poly(3-hexylthiophene) (P3HT, scheme 1) which has been thoroughly studied and represents a standard in organic polymer and PSCs [7–9].

Some intrinsic physico-chemical properties of P3HT, such as high hole mobility values of approximately  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [10], good solubility and reproducibility [11], high thermal stability [12] and commercial availability with proper price [13] make this polymer a potential alternative compared to PTAA and spiro-OMeTAD. Furthermore, the P3HT properties can be tuned by varying the length of the side chains, which creates different polymeric regions depending on the degree of crystallinity (order) or the number of amorphous regions [14]. The understanding of the carrier hopping through these crystalline and amorphous regions in semiconductor polymers has attracted a lot of interest in the organic electronic community [13,15,16]. Seminal papers on this matter have been reported, and had changed the paradigm that better crystallinity leads to better solar cell efficiency [14,16]. In fact, the knowledge of the energetic disorder in the organic material and its relation with the carrier transport and carrier recombination is a key factor for improvement of the photovoltaic performance of the PSCs that are equipped with polymers and other organic semiconductor molecules as selective contacts.

We have previously studied the performance of PSCs using different P3HT molecular weights (MWs) [8]. Direct relationships between the MWs of polymers and their solar cell performances have been investigated [3]. Recently, Dixon *et al.* showed that the recombination rate decreases by increasing of the MW from 14 to 331 kDa and that the most efficient charge collection occurs for P3HT with a MW of 48 kDa, having  $5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}$  as hole mobility [14]. In these studies, the carriers' mobility is attributed to the P3HT morphology changes from a paraffinic microstructure to a semi-crystalline structure. Accordingly, at higher MWs, the entanglement density increases, leading to a large fraction of amorphous regions. One could think that these molecularly disordered domains limit the inter-lamellar transport and carrier mobility. The presence of higher energetic disorder in polymers with higher MW is one of the hypotheses for the lower solar cell performance due to the increase of the interfacial recombination kinetics of free carriers at the perovskite/HTM interface [17]. However, the studies on the interfacial carrier recombination processes in PSCs, which differ in the degree of crystalline packing of the organic semiconductor selective contact, are scarce and no direct evidence has been reported.

Interfacial recombination kinetics can be studied by the combination of the dark current density-voltage ( $J$ - $V$ ) characteristic, the open circuit voltage decay (OCVD) and the electrical impedance spectroscopy (EIS) measurements [8,18]. However, to carry on all these experiments, in different sets of PSCs, requires a large amount of time under different illumination environments, which compromises the steady-state condition of the solar cell during the

measurements. Hence, the use of faster measurements (time scale of minutes) that allow extracting information of the device parameters such as (i) charge accumulated under light irradiation and (ii) carrier's lifetime, is recommendable. In this work, we propose the use of photo-induced charge extraction (PICE) and photo-induced transient photo voltage (PI-TPV) techniques to address the study of efficiency losses in PSCs. In this way, we can analyse the influence of the P3HT MW and the inherent differences in their nanomorphology over the interfacial carrier losses under operando conditions, fast enough to ensure that the solar cell steady-state condition has not changed during the measurement.

For our studies described herein, our perovskite-based devices were fabricated with the archetypal structure of FTO/TiO<sub>2</sub>-c/TiO<sub>2</sub>-m/PSK/P3HT/Au as reported previously [8]. The 44, 77 and 124 kDa P3HT MWs were used for this investigation.

## 2. Results and discussion

The characterization of fabricated PSCs (table 1; electronic supplementary material, figure S1) shows that the higher the P3HT MW the better the power conversion efficiency, mainly owing to the increase of the fill factor (FF). The comparison of PICE and PI-TPV decay values are also shown in table 1, moreover, electronic supplementary material, figure S2 shows the Voc (open circuit voltage of the solar cell) stability tracking measurement that was recorded during the spectroscopic analysis to monitor the steady-state condition of the solar cell during the experiments.

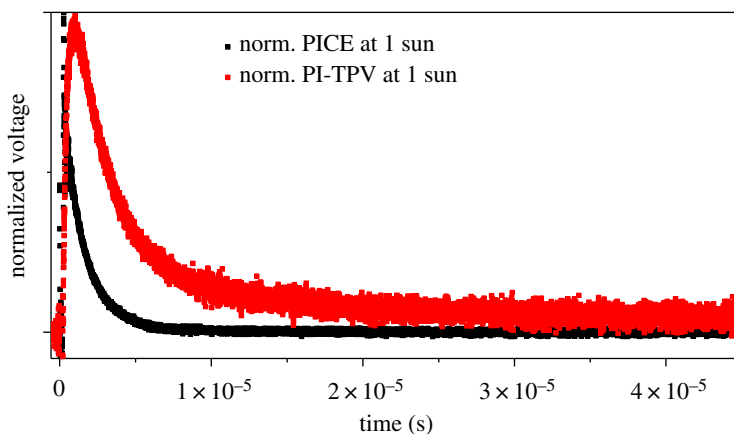
As we have previously detailed [19–21], the PICE technique allows the measurement of the accumulated charges and the PI-TPV permits registering the carrier recombination decay under different light biases (solar cell voltage as a result of light irradiation). In molecular solar cells, such as the full-organic or the dye-sensitized solar cells, the photo-generated carriers are extracted before they recombine. In other words, the PICE decay is always much faster than the PI-TPV at the same light bias. However, in PSCs, a PICE decay similar or even slower than PI-TPV decay transients may occur due to the kinetics of the ion migration under illumination. As we have shown previously, this depends on the perovskite composition [22]. Figure 1 illustrates the PICE and PI-TPV decays for one of the PSCs analysed in the present study.

The PICE decay kinetics shows faster dynamics when compared with the PI-TPV, which means that both electronic carriers and mobile ions are extracted before the carriers' recombination takes place [22]. Hence, we can use the PICE technique to evaluate the charge present at the devices under different light biases and other alternative techniques such as differential capacitance [23] measurements are not necessary.

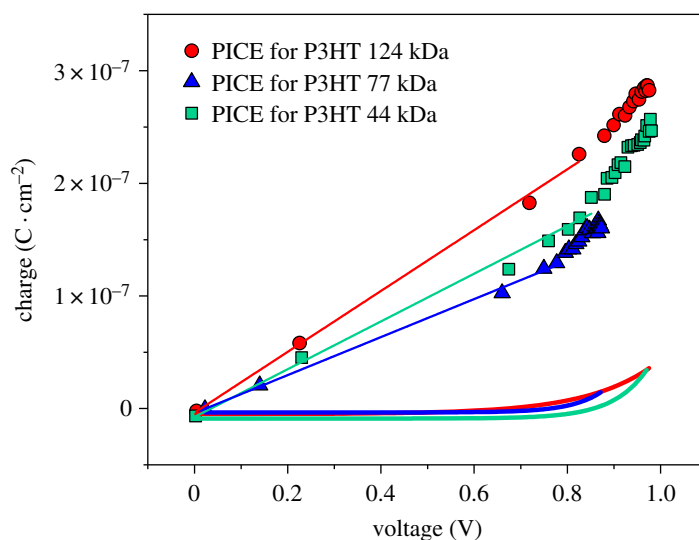
The results of PICE measurements for PSCs with several P3HT MWs as selective contacts, obtained with different light biases, are illustrated in figure 2.

To carry on the comparison between PSCs with different P3HT MWs, we have taken care that the film thickness is equal in all devices within the measurement error and with a P3HT thickness of  $130 \pm 10$  nm. From the average of the PICE measurements, we can see that the PSC with higher MW P3HT, and expected larger energetic disorder, shows a higher amount of charges for a given voltage when compared with the other P3HT MWs samples. Interestingly, the sample with MW = 77 kDa shows similar charge accumulation—within the measurement error—than the lower MW P3HT (44 kDa) sample. Although there is not any clear linear correlation between the P3HT MW and the amounts of storing charge under illumination, there exists a different charge accumulation depending on the P3HT length chain. As was observed in previous work [24], in all P3HT cases there appeared an extended linear relationship between the measured charge and the light bias for values from 0 V (dark conditions) to 0.8–0.9 V. This means that under open circuit conditions and far from 1 sun conditions, the charges are accumulated at the selective contact electrodes (geometrical capacitance).

Once the PICE measurements were finished, we focused on the PI-TPV decays for the different devices. The results of the different PI-TPV decays at different light biases are depicted in figure 3.



**Figure 1.** The PICE and PI-TPV decays under 1 sun illumination conditions for PSC with 44 kDa P3HT.

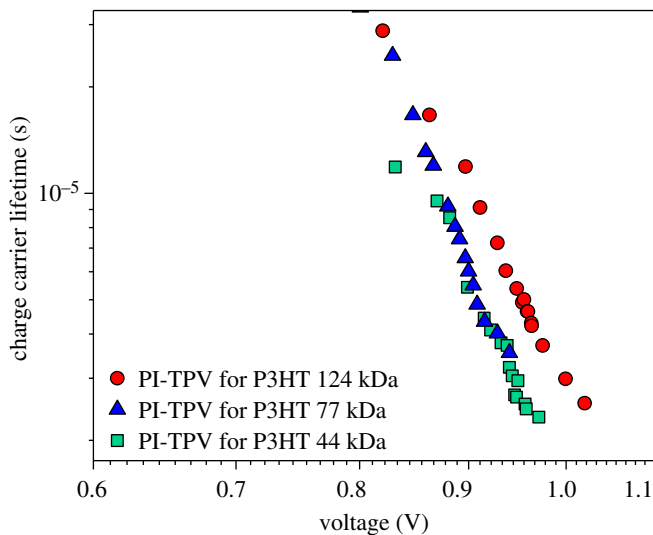


**Figure 2.** Charge measured at different light biases for PSCs with the different P3HT polymers as selective contacts for electronic holes. The linear solid lines are the data fits using a linear model. The solid lines at the graph's bottom represent only the exponential part of the fits:  $y = Be^{Cx}$  (chemical capacitance).

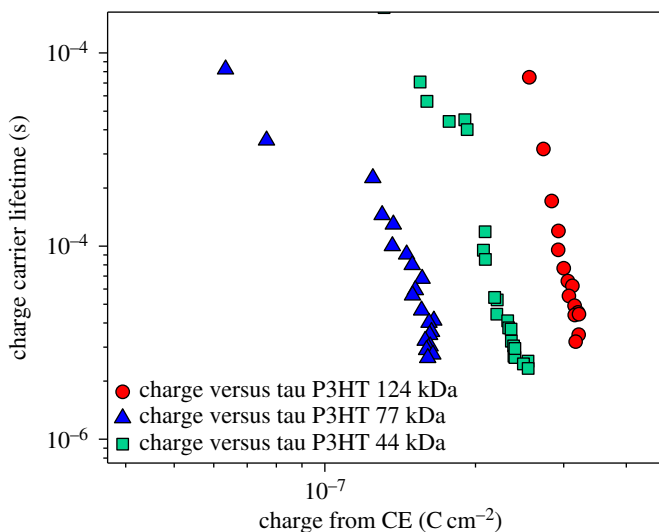
**Table 1.** Solar cell parameters measured at 1 sun (AM1.5G), PICE and PI-TPV decay lifetimes for PSCs fabricated using several P3HT with different MWs.

P3HT molecular weight (kDa)	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF	PCE (%)	$\tau_{\text{PICE}}$ ( $\mu\text{s}$ )	$\tau_{\text{PI-TPV}}$ ( $\mu\text{s}$ )
44	$0.993 \pm 0.07$	$18.7 \pm 1.2$	$0.61 \pm 0.01$	$11.37 \pm 1.3$	$2.1 \pm 0.6$	$2.4 \pm 1.1$
77	$0.952 \pm 0.01$	$19.78 \pm 0.2$	$0.73 \pm 0.05$	$13.65 \pm 0.1$	$1.9 \pm 0.3$	$2 \pm 0.6$
124	$1.026 \pm 0.03$	$19.72 \pm 0.3$	$0.79 \pm 0.1$	$16.04 \pm 0.05$	$2.2 \pm 0.3$	$2.4 \pm 0.7$

At first sight, it would seem that the P3HTs with lower MWs (44 and 77 kDa) show similar carrier recombination–voltage dependence. Yet, the carrier recombination kinetics depends on the charge ( $n$ ). Therefore, it is convenient to plot the data extracted from the PI-TPV measurements versus  $n$  for an appropriated comparison between different devices, as shown in figure 4.



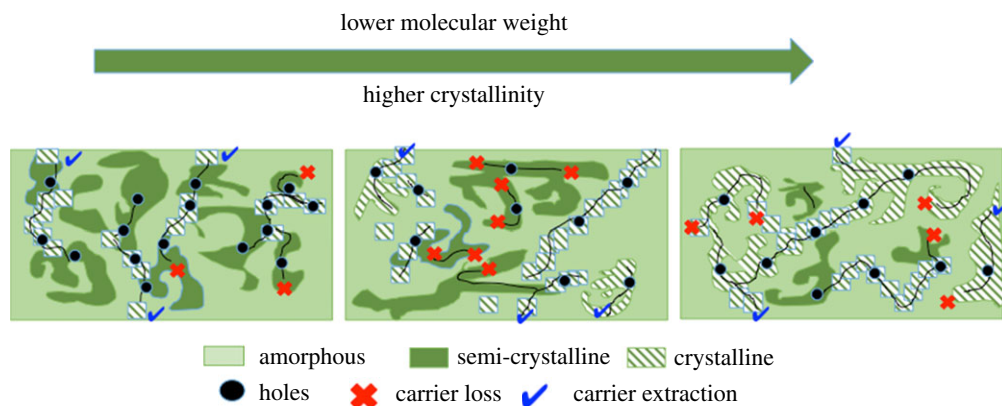
**Figure 3.** Average measurements of the PI-TPV decays for the PSCs with the different P3HT semiconductor polymers used as selective contacts.



**Figure 4.** Charge ( $n$ ) measured using PICE versus the carrier lifetime measured using PI-TPV, both measurements under the same light bias for the different P3HT MWs.

Taking into account the charge present in the solar cells under the same light bias, it is evident that there are noticeable differences between PSCs with different P3HT MWs. The higher P3HT MW shows the slowest interfacial recombination dynamics, followed by the samples with the lower MW, while the P3HT with a MW of 77 kDa shows the fastest recombination. Note also that the slope for the  $\tau$  versus  $n$  curves for all samples is alike, which implies that the carrier recombination order is similar in all devices independently of the P3HT MW.

The above results suggest that for the P3HT semiconductor polymer the use of high MW is desirable when used as selective contact in PSCs. This is in good agreement with previous studies in organic solar cells, where P3HT samples were analysed in detail using electroluminescence, X-ray diffraction and charge mobility measurements [16]. Our results suggest that in the polymer



**Figure 5.** Illustration to show the interplay between crystallinity, MW, different polymer domains and carrier recombination and carrier extraction.

with higher MW the number of intermolecular pathways (figure 5) for carriers percolation is sufficient to achieve better charge collection before carriers can recombine. Moreover, the best FF values corresponded to those devices with higher P3HT, which can be directly related to better charge transport and extraction at the perovskite/HTM interface. It is also noticeable that the  $V_{oc}$  variation matched perfectly with the different recombination rate obtained for the different MW. Although the amount of amorphous domains and the presence of higher energetic disorder is expected to be larger in polymers with higher MW, for P3HT, which is a known semi-crystalline polymer, the presence of interconnected crystalline phases suffices to collect the charges from these amorphous regions. In the case of the P3HT with a MW of 77 kDa, these ordered phases are unlikely to be as present as in the 124 kDa P3HT sample, which leads to faster carrier recombination kinetics of the carriers trapped in the amorphous regions of the polymer. By contrast, for the low MW sample (44 kDa), the number of rich ordered phases within the film would be larger but the degree of energetic disorder seems to be greater or at least there are less favourable domains for intermolecular carrier transport that influences both the photocurrent and the FF of the solar cells.

### 3. Conclusion

We have analysed a series of PSCs using different MWs of semiconductor polymer P3HT used as hole selective contact. We have focused on the differences observed in the overall efficiency of the solar cells under standard conditions and the fact that the P3HT polymer with higher MW leads to the highest efficiency despite the fact that the use of high MW implies the presence of less ordered polymeric domains and less crystallinity. An analysis in depth of the solar cell charge under different light biases and the interfacial carrier recombination kinetics shows that the efficiency of the solar cells with the 124 kDa P3HT polymer is due to slower carrier recombination when compared with the other two lower MWs of P3HT polymer. In good agreement with previous experimental work, we have observed that the crystallinity of the polymer is not as essential as had been previously considered, but that the balance between the interconnections of crystalline domains and amorphous polymer phases results are key for the creation of percolation ways for efficient carrier extraction.

**Data accessibility.** This article has no additional data.

**Authors' contributions.** A.D.C., E.P. and M.M. conceived the work. A.D.C. contributed to the discussion of the results and critically revised the manuscript. N.Y.N. designed and fabricated the solar cells and performed IV. N.Y.N. contributed to the writing of the manuscript. M.M. performed the  $V_{oc}$  stability, PICE and PI-TPV measurements.

**Competing interests.** We have no competing interests.

**Funding.** M.M. and E.P. would like to acknowledge MINECO for the Severo Ochoa Excellence Accreditation 2014–2018 SEV- 2013–0319. E.P. is also grateful for the CTQ2016-80042-R project and Generalitat de Catalunya for the AGAUR funding. A.D.C. acknowledges the financial support of the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST ‘MISiS’ (no. K2-2019-13), implemented by a governmental decree dated 16 March 2013, N 211.

**Acknowledgements.** N.Y.N. and A.D.C. gratefully acknowledge the project PERSEO-‘PERovskite-based Solar cells: towards high Efficiency and lOnG-term stability’ (Bando PRIN 2015-Italian Ministry of University and Scientific Research (MIUR) Decreto Direttoriale 4 novembre 2015 no. 2488, project no. 20155LECAJ) for funding.

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