

ORGANIC PHOTOVOLTAICS

Pushing the knowledge of interfaces

The use of a spectroscopy technique called pump-push-probe electro-absorption provides insight into the energetic landscape of nanostructured donor-acceptor interfaces in bulk-heterojunction organic solar cells.

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Charge transfer at solid–solid interfaces plays a primary role for solid-state electrochemistry, energy storage, catalysis and photovoltaic energy conversion. It is therefore of utmost importance to understand the behaviour of charges and the electronic landscape near the interface, which can be significantly different from the bulk of the materials. This is particularly challenging when the interface is nanostructured, disordered and buried away from the surface. In this case, more conventional techniques such as electron microscopy, photoelectron spectroscopy, X-ray measurements and even surface-specific nonlinear optical techniques tend to fail. Now, writing in *Nature Materials*, Andreas Jakowetz and colleagues overcome this limitation by developing a spectroscopic method known as pump–push–probe electro-absorption (PPP-EA), which allows

probing the dynamics of photogenerated charges and the electronic properties near disordered solid–solid interfaces¹.

They apply this technique to the nanostructured interface formed between an electron donor and an electron acceptor in organic photovoltaic (OPV) blends. In these systems, the donor (typically a conjugated polymer) and the acceptor (typically a fullerene derivative) are mixed in solution and cast into ~100-nm-thick films, forming a solid-state blend of the two components, arranged into a rich phase morphology with inhomogeneous interfaces at the molecular to nanometre scale (Fig. 1a)^{2–3}. This cheap, large-scale and flexible photovoltaic technology yields a power conversion efficiency of almost 12%⁴. Light absorption by the donor or acceptor gives rise to the formation of excitons (bound electron–hole pairs),

which dissociate to charges at the interface. Those positive and negative charges are either initially still bound in an interfacial charge-transfer state, or are already long-range separated at ultrafast times, according to opposing views that have fuelled a rich scientific debate about the mechanism of charge separation in organic solar cells^{5–8}.

The ultrafast optical approach developed by Jakowetz and collaborators provides key elements to the understanding of those complex charge dynamics. It combines two concepts that have individually already brought significant advances to the field of organic photovoltaics: the Stark effect and pump–push spectroscopy. The Stark effect describes the shift of spectroscopic transitions in the presence of an electric field. When charges are photogenerated in OPV blends, the electric field

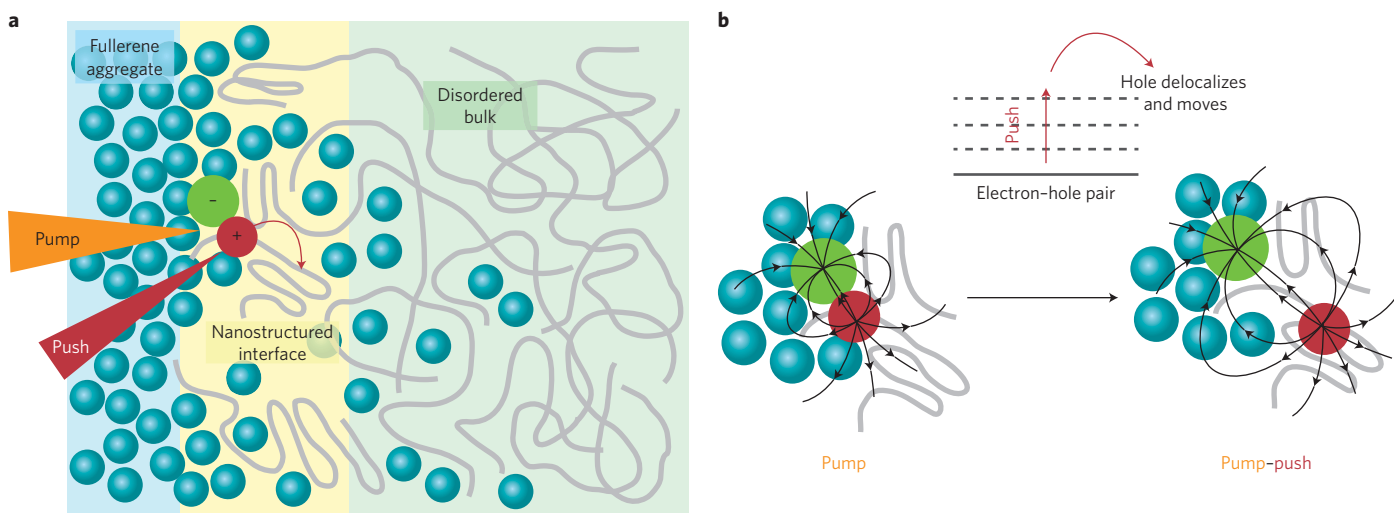


Figure 1 | Monitoring charge separation with PPP-EA. **a**, Nanostructured interface formed in a high-efficiency organic solar cell blend containing an excess of fullerenes (blue spheres), which aggregate into neat clusters. The results reported by Jakowetz and colleagues¹ show that there is enhanced ordering of the conjugated polymer chains (grey lines) near the interface compared to the disordered bulk of the amorphous polymer. Electrons (green spheres) and holes (red spheres) are photogenerated near the interface following excitation of the donor or acceptor with a pump pulse. The holes have the possibility to move into highly ordered, low-energy sites on ultrafast time scales, which assists spatial charge separation and leads to enhanced photovoltaic efficiency. **b**, In PPP-EA spectroscopy, the electron-hole pair generated by the pump pulse (left) is re-excited by the push pulse into slightly higher-lying delocalized states (dashed lines in the energy-level diagram), allowing the hole to move by subsequently localizing on an adjacent polymer segment (right). This leads to a redistribution of the electric field (black lines) around the photogenerated charges, which can be followed by measuring the change in the electro-absorption signal recorded with a third laser beam (the probe).

surrounding them causes Stark shifts in the neighbouring molecules (Fig. 1b). In femtosecond pump–probe spectroscopy, this leads to the appearance of an electro-absorption (EA) signal, defined as the difference between the absorption spectrum with and without the field⁹. The phenomenon has been used to probe the local environment of the charges, and to estimate the electron–hole separation with high time resolution^{5,6}. In pump–push spectroscopy, the sample is excited with a visible femtosecond pump pulse, and then the photogenerated species are re-excited to slightly higher-lying states using a near-infrared push pulse. The impact of the push pulse on the photocurrent extracted from organic solar cells has been recently evaluated, showing that re-populating short-lived delocalized states enhances the photocurrent by assisting the spatial electron–hole separation⁸. The effect is more pronounced for poor OPV materials, which particularly benefit from the additional push.

In their combined PPP-EA approach, Jakowetz and colleagues isolate the effect of the push pulse on the EA signal from polymer chains surrounding the photogenerated charges. In conjugated polymers, the Stark effect is generally dominated by polarizability effects and the shape of the EA is well described by the first derivative of the absorption spectrum. By integrating the isolated EA signal, the authors obtain the local absorption

spectrum of the polymer environment near the interface after the hole carrier is moved away from the interface by the push pulse at different times following pump excitation (Fig. 1b). They thus trace the energetic landscape along the pathway of the hole during charge separation. The technique is applied to the well-known polymer PCDTBT¹⁰, blended in two different ratios with the fullerene derivative PCBM, in order to yield a poorly performing and a well-performing OPV blend. The first important conclusion of the research team is that the polymer chains surrounding the charges near the interface have an extremely redshifted absorption spectrum compared to the bulk, probably due to strong ordering effects induced by the proximity of ordered fullerenes (Fig. 1a). In fact, the low-energy sites involved in the interfacial charge transfer make up only 1% of the total polymer chains. Moreover, they show that in the well-performing blend, the holes move to even more ordered regions within 150 fs, which contributes to favourable charge separation and high efficiency (Fig. 1b).

Jakowetz and colleagues provide the community with an exciting tool to directly visualize how the local electronic landscape allows charges to separate across nanostructured interfaces in organic solar cell materials. While the results reported in this work emphasize the essential role played by the molecular-scale arrangement of the donor and acceptor near the interface, their implications for

the validation or refutation of previous hypotheses involving interfacial energy cascades, local charge mobility, or electron delocalization into fullerene clusters must be discussed further^{3,6,11}. More generalized results for a variety of different polymer materials and complementary methods, such as terahertz spectroscopy or ultrafast optical techniques on operational OPV devices, will be particularly useful in this respect. Beyond organic photovoltaics, it will be interesting to assess the impact of PPP-EA on the understanding of different solid heterojunctions for other applications, including photo-catalytic and energy-storage systems. □

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References

1. Jakowetz, A. C. *et al. Nat. Mater.* <http://dx.doi.org/10.1038/nmat4865> (2017).
2. Westacott, P. *et al. Energy Environ. Sci.* **6**, 2756–2764 (2013).
3. Sweetnam, S. *et al. J. Am. Chem. Soc.* **136**, 14078–14088 (2014).
4. Green, M. A. *et al. Prog. Photovoltaics: Res. Appl.* **25**, 3–13 (2017).
5. Causa, M. *et al. Nat. Commun.* **7**, 12556 (2016).
6. Gélinas, S. *et al. Science* **343**, 512–516 (2014).
7. Vandewal, K. *et al. Nat. Mater.* **13**, 63–68 (2014).
8. Bakulin, A. A. *et al. Science* **335**, 1340–1344, (2012).
9. Lanzani, G. *The Photophysics Behind Photovoltaics and Photonics* (Wiley, 2012).
10. Park, S. H. *et al. Nat. Photon.* **3**, 297–302 (2009).
11. Burke, T. M. & McGehee, M. D. *Adv. Mater.* **26**, 1923–1928 (2014).