

## Charge-separated states in fullerene- and non-fullerene-based organic photovoltaics probed by EPR

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Organic photovoltaics hold promise as a flexible, cost-efficient, and sustainable solution to the challenges posed by an ever-growing energy demand. Organic solar cells are based on an active layer consisting of a blend of electron donating and accepting organic semiconductors. Photoexcitation generates strongly bound excitons that diffuse to the donor-acceptor interface to form an interfacial charge-transfer state, followed by separation into positive and negative charge carriers, which can then be extracted to generate electricity.

In recent years, the development of new electron acceptor molecules, to replace the fullerene-based ones traditionally used, has led to significant increases in power conversion efficiencies, which are now close to reaching the 20% threshold.<sup>1</sup> Despite this remarkable progress, a detailed mechanistic understanding of the energy conversion process is still missing, with the charge separation step at the donor-acceptor interface being the least well understood aspect of organic photovoltaics. Recent evidence based mainly on optical spectroscopies points towards significant differences in this crucial step between solar cells based on fullerene acceptors and on novel fused-ring electron acceptors.<sup>2</sup>

We are using EPR spectroscopy to investigate the nature and dynamics of paramagnetic species generated upon photoexcitation in blends of fullerene acceptors (PC<sub>61</sub>BM) or fused-ring electron acceptors (ITIC, Y6) with matching donor polymers (PBDB-T, PBDB-T-2F). At short times after laser excitation, the transient EPR spectra show the clear signatures of spin-correlated pairs of charges on donor and acceptor molecules, followed by evolution of the initially spin-polarised signal to fully absorptive spectra of the donor and acceptor radicals at long times. Analysis of the time- and temperature-dependence of this evolution reveals distinctly different behaviours for different donor:acceptor blends, hinting at differences in the charge separation process.

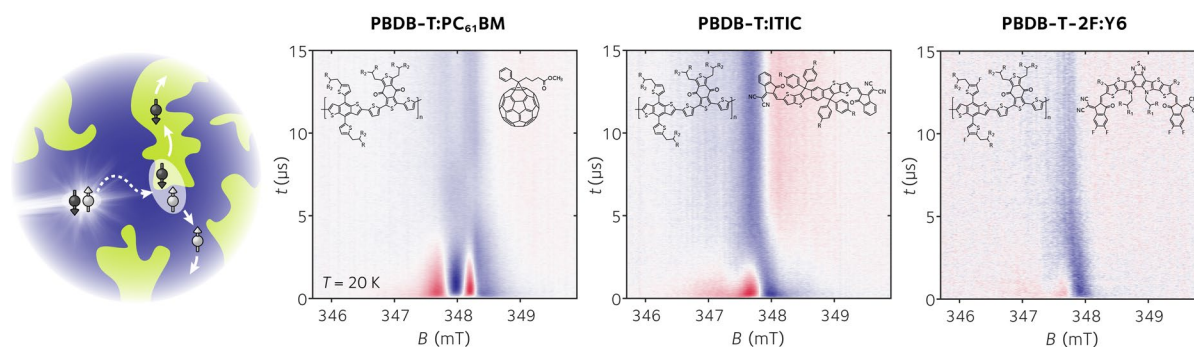


Figure 1. X-band transient EPR spectra recorded on blends of PBDB-T:PC<sub>61</sub>BM, PBDB-T:ITIC and PBDB-T-2F:Y6 at 20 K after photoexcitation at 532 nm.

[1] M. Moser, A. Wadsworth, N. Gasparini, I. McCulloch, *Adv. Energy Mater.* **11**, 2100056 (2021).

[2] A. Armin, A., W. Li, O.J. Sandberg, Z. Xiao, L. Ding, J. Nelson, D. Neher, K. Vandewal, et al. *Adv. Energy Mater.* **11**, 20003570 (2021).