Organic photovoltaics

How To Split an Exciton

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Non-fullerene acceptors have enabled record power conversion efficiencies in organic solar cells, but it is unclear how they achieve efficient electron/hole separation. New research shows that extremely long exciton lifetimes are essential to ensure charges are generated efficiently.

Recent increases in organic solar cell power conversion efficiencies are due to the advent of non-fullerene electron acceptors, which have largely replaced the more conventional fullerene (C_{60}) acceptors. Several of these non-fullerene acceptors can undergo efficient charge separation with a minimal energetic offset between the donor and acceptor materials (Figure 1a). Such small offsets maximise the open circuit voltage produced by the cell. However, a sufficiently large offset is typically required to provide a driving force to split the photogenerated excited state – or exciton – efficiently into free charges and thus ensure high device short circuit current. Nevertheless, efficient charge separation in non-fullerene acceptor solar cells with a small energetic offset is often reported.[2]

There is a lack of understanding of the factors that enable both efficient free charge generation and reduced voltage losses at negligible energetic offset in non-fullerene acceptor solar cells. Writing in *Nature Energy*, Classen et al. show that a long exciton lifetime is key to achieving efficient charge separation in non-fullerene acceptor solar cells.[3]

The researchers study a series of polymer/non-fullerene blends with a range of energetic offsets. They measure exciton lifetimes for both pristine and blend films by time-resolved photoluminescence spectroscopy, determining their exciton splitting efficiency. They observe a strong correlation between exciton splitting efficiency and the solar cell's external quantum efficiency (EQE), which is related to the device's current (Figure 1b). For some blends, they note that the exciton splitting is so slow that it exceeds the lifetime of the exciton itself, and this limits the EQE. For other blends such as those based on Y6, one of the most efficient non-fullerene acceptors currently known, the exciton splitting efficiency is almost unity even at minimal energy offsets, thus enabling high short circuit current. The researchers relate this efficient exciton splitting to Y6's exceptionally and unusually long exciton lifetime of 1 ns.

The experimental findings are corroborated by a two-state model with local excitons in equilibrium with charge transfer (CT) states. Such an equilibrium exists when the CT state energy approaches the exciton energy, as occurs in a minimal energy offset system. The researchers show that the exciton splitting efficiency is dictated by both the energetic offset and, crucially, the exciton lifetime.

The researchers demonstrate that the small non-radiative voltage losses observed are a result of a shift in the CT-exciton equilibrium towards the exciton that occurs only at negligible energy level offsets (Figure 1b). The exciton state has a higher radiative oscillator strength compared to the CT state, which minimises detrimental non-radiative recombination. Negligible energy level offsets are

therefore essential to achieve high voltages but also inhibit the efficiency of exciton splitting. High currents can only be retained if exciton splitting remains efficient by employing acceptors with an exciton lifetime longer than the exciton splitting lifetime.

Classen et al. offer a clear principle for material design, but ensuring long exciton lifetimes is not as simple as it appears. To maximise photocurrent, materials are designed to cover the full solar spectrum by pushing bandgaps further into the near-infrared (NIR). Indeed, Y6 has its absorption maximum around 800 nm. However, the bandgap and thus exciton energy decrease when moving towards the NIR, which increases non-radiative relaxation: this is the energy gap law.[4-5] This internal conversion can become very fast, precluding long exciton lifetimes in low-bandgap materials. It is therefore especially intriguing that Y6 has such a long exciton lifetime, and a key future development will be on understanding why this is the case. Consequently, we will be able to design materials that break the energy gap law. The NIR light-emitting diode field already offers a guiding light in this respect, with recent ground-breaking research into exciton-vibration decoupling.[6]

The equilibrium behaviour observed by Classen et al. is not exclusive to non-fullerenes. If a fullerene is matched with a very low bandgap polymer (thereby also yielding a negligible energy offset), the exciton and CT states hybridise and form an equilibrium. This minimises non-radiative voltage losses in much the same way as non-fullerene acceptors can.[7-8] Despite this, such low offset fullerene devices still show substantially smaller power conversion efficiencies compared to many non-fullerene systems.

An important future step, then, is to decouple the magnitude of the energy offset from the identity of the acceptor to truly understand what makes these non-fullerene acceptors so special. The work of Classen et al. has taken a significant step in this regard by identifying a long exciton lifetime as one key criterion for efficient charge separation at minimal energy offsets.

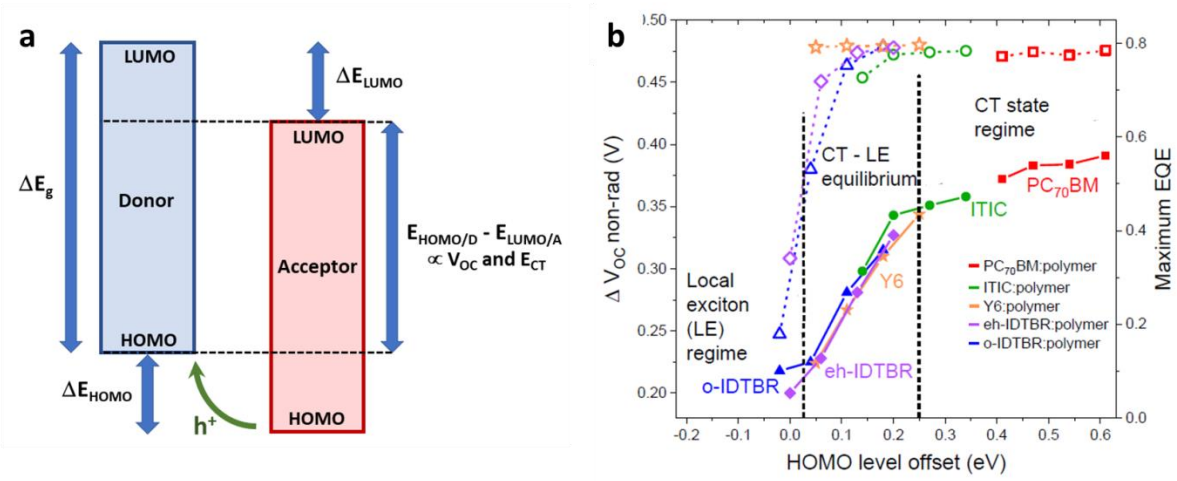

Figure 1. Energy level alignment in electron donor and acceptor pairs and its correlation with non-radiative voltage loss and external quantum efficiency. (**a**) Shown are the bandgap of the donor (ΔE_g), and the relative position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for each component. The driving force for exciton splitting and charge separation is either ΔE_{HOMO} or ΔE_{LUMO}, depending on whether the acceptor or donor is photoexcited respectively. Classen et al. consider ΔE_{HOMO}, and the concomitant exciton splitting via hole (h+) transfer when the acceptor is photoexcited. A key parameter is the energy difference

between the HOMO of the donor and LUMO of the acceptor ($E_{HOMO/D} – E_{LUMO/A}$), as this is directly proportional to both the open circuit voltage (V_{OC}) and the energy of the charge transfer state (E_{CT}). (**b**) The non-radiative voltage losses ($\Delta V_{OC,non\text{-}rad}$, filled symbols/ solid line) and EQE (empty symbols/dashed lines) with respect to the energy level offset and at various CT-local exciton (LE) regimes (distinguished with vertical dashed black lines). Y6 has both high EQE and minimal non-radiative voltage losses at negligible energy level offsets. The coloured lines in between data points are guides to the eye. Panel b is adapted from ref. [3].

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