

## The open-circuit voltage of organic photovoltaics

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The power conversion efficiency of organic photovoltaic (OPV) devices is governed by electronic processes at the hetero-interfaces between electron donating and electron accepting molecules. While incident-photon-to-extracted-charge conversion yields over 85%, and absorbed photon-to-extracted-charge conversion yields of 90-100% have been achieved,<sup>[1]</sup> the difference between the optical gap of main absorber and open-circuit voltage ( $V_{oc}$ ) is much larger than that of more mature technologies. This is the main reasons why OPV's currently achieved highest power conversion efficiency of 13-14%<sup>[1, 2]</sup> is still lagging behind that of inorganic and perovskite based solar cells.

The electronic states formed at the interface between electron donor and acceptor, termed charge-transfer states, are low energy recombination sites where electrons on the acceptor can meet holes on the donor.<sup>[3]</sup> Therefore, they play a critical role in determining the  $V_{oc}$ . CT states often produce weak absorption and emission bands at photon energies below the optical gap of the neat donor and acceptor material, which allows to probe their electronic structure.<sup>[4]</sup> Over the past 10 years, we have investigated these properties for more than one hundred donor-acceptor systems we have consistently found a large difference, in the range of ~0.6 eV between  $eV_{oc}$  and the energy of the intermolecular charge transfer (CT) state,  $E_{CT}$ .<sup>[3, 5, 6]</sup>

Higher  $V_{oc}$ s for organic solar cells will thus require an increase of  $E_{CT}$ , which so far has been mainly made by tailoring the frontier molecular orbitals of donor and acceptor, taking advantage of well-known principles of molecular design. Nevertheless, the voltage losses for strongly absorbed photons is often much larger than 0.7 eV, due to CT state recombination losses of about 0.6 eV and the requirement of electron transfer from donor to acceptor as well as thermalization, together often larger than 0.1 eV.

In order to understand the origin of these large losses, we have derived<sup>[7]</sup> and experimentally tested<sup>[8]</sup> an equation relating  $V_{oc}$  to molecular and interfacial properties, such as  $E_{CT}$ , the electronic coupling between electron donor and acceptor, the molecular reorganization energy, non-radiative decay pathways and the interfacial area available for free carrier recombination. This understanding has prompted us to propose a new, multilayer organic photovoltaic device architecture for which voltage losses for strongly absorbed photons are reduced to values below 0.6 eV, with non-radiative CT state decay the main loss mechanism.<sup>[9]</sup> In general, we find that the high non-radiative decay rate is fundamentally linked to the coupling of the CT state to high frequency molecular vibrations of the ground state.<sup>[6]</sup>

As these high frequency molecular vibrations are difficult to avoid in organic materials, reducing the voltage losses even further thus requires a radically different approach than has been followed up to now. Preliminary experiments on one such an approach, where we use an optical micro-cavity device architecture in the strong light-matter coupling regime, show a steepening of the absorption onset and a further reduction of the voltage losses by 50 to 100 mV.<sup>[10]</sup>

## References

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