Imperial College London

The Binding Energy and Dynamics of Charge Transfer States in Non-fullerene Organic Solar Cells

Yifan Dong[1], Hyojung Cha[1], Jiangbin Zhang[2], Ernest Pastor[1], Pabitra Shakya Tuladhar[1], Artem A. Bakulin[1] and James R. Durrant[1]

[1] Department of Chemistry and Centre for Processable Electronics, Imperial College London, London, UK;

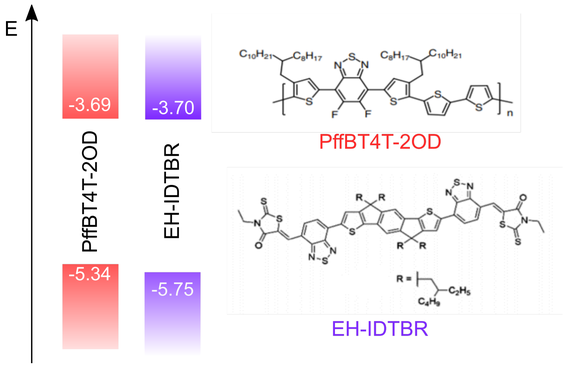
[2] Cavendish Laboratory, University of Cambridge, Cambridge, UK

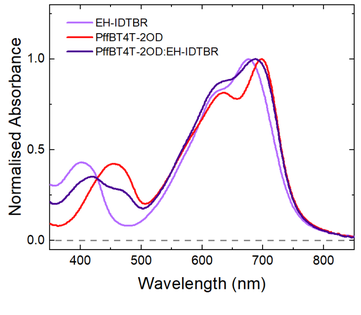
State-of-the art non-fullerene organic solar cells (OSCs) usually have a low driving force for charge separation (a low energy offset between the singlet exciton and charge transfer states).

Understanding the photophysics of charge transfer states (CTS) in such systems is essential towards understanding the whole charge separation mechanism and elucidating the recombination limit.

Here, probing the CTS dynamics with transient absorption (TA) and pump push photocurrent (PPPc) spectroscopy allows us to evaluate the binding energy and the dynamics of CTS.[1]

Materials & Energetics

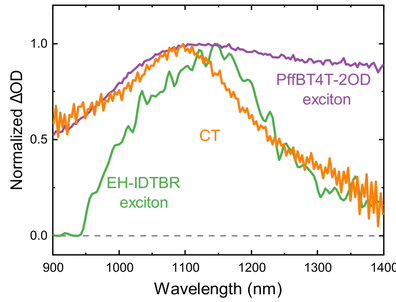




Absorption spectra for pristine PffBT4T-2OD, pristine EH-IDTBR and the blend films. Pristine PffBT4T-2OD and EH-IDTBR thin films show overlapping absorption features.

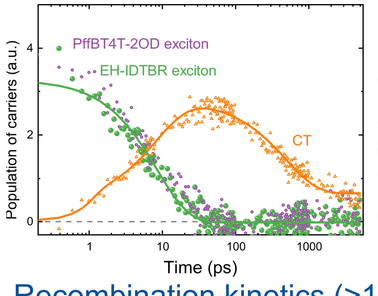
TA Spectra & Dynamics

1. Transient absorption spectroscopy can probe the dynamics of excited-state species in OSCs including excitons and CT states:



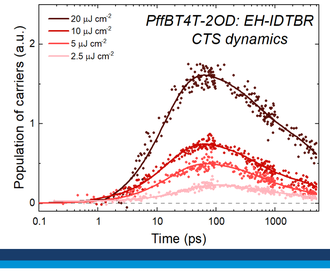
TA spectra: Global analysis deconvolutes the individual spectra features for PffBT4T-2OD exciton, EH-IDTBR exciton and CT states.

2. Donor excitons and acceptor excitons decay while CT states are formed on the same time scale with a lifetime of 15 ps:



TA kinetics: 1. Decay of PffBT4T-2OD and EH-IDTBR excitons with the same rate; 2. Generation and decay of CT states.

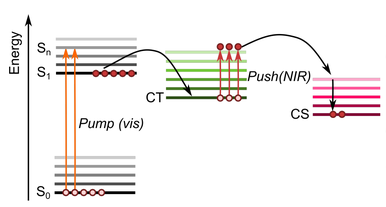
3. Recombination kinetics (>100 ps) is fluence-independent, indicating the main recombination pathway is via geminate recombination of bound CTS:



TA kinetics for CT states at different pump fluences varying from 20 to 5 μJ cm^{-2}.

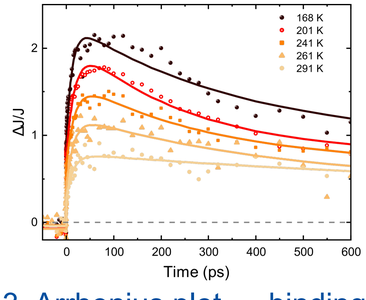
Pump Push Photocurrent

1. The amplitude of PPPc reflects the population of **bound CTS** in a device since only those states are dissociated to generate additional photocurrent:



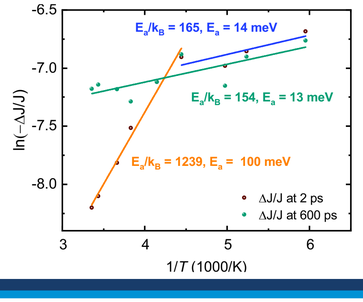
States involved in PPPc measurements: The visible pump generates singlet excitons, S_1, which can then dissociate at the interface to form CTS. The NIR push pulse excites the bound CTS and dissociates those into charges, generating additional photocurrent in the device.

2. *T*-dependent PPPc: higher amplitude at lower *T* indicates that more bound CTS are formed at a lower *T* due to less bound CTS can overcome the barrier for dissociation:



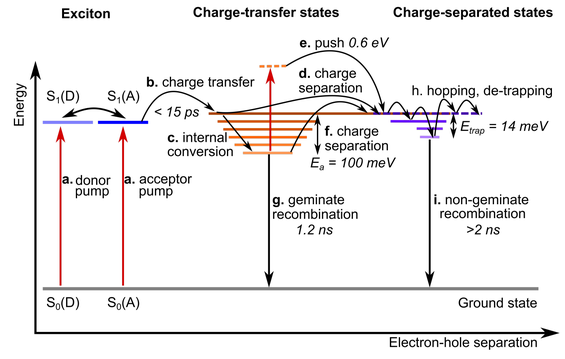
T-dependent PPPc results for a complete PffBT4T-2OD:EH-IDTBR device. The pump wavelength was 650 nm and the push wavelength was 2000 nm.

3. Arrhenius plot --- binding energy for CTS is 100 meV:



Arrhenius plot for T-dependent pump push photocurrent by taking the amplitude at 2 ps and 600 ps of the pump-push delay time, yielding an activation energy of 100 meV at early times and 14 meV at long times.

Charge Transfer Model



In summary:

- Photoexcitation generates excitons in both PffBT4T-2OD and EH-IDTBR
- Charge transfer at the donor/acceptor interface occurs with a lifetime of 15 ps
- A portion of the CT states undergo thermalisation to form bound CT states, which eventually undergo geminate recombination with a lifetime of 1.2 ns
- Utilising PPPc, the push pulse can further excite those bound CT states to a higher state and dissociate those into free charge carriers
- Measuring PPPc at various *T*, the binding energy of bound CTS is 100 meV

For further information about my work and discussion/collaboration, you can find me here:

https://www.imperial.ac.uk/people/yifan.dong12

References:

1. Dong, Y. *et al. J. Chem. Phys.* **150**, 104704 (2019).

Acknowledgements:

I would like to thank the Optoelectronics Group at the University of Cambridge for sharing the Global analysis codes.