Ultrafast Long-Range Charge Separation in Organic Semiconductor Photovoltaic Diodes

Simon Gelinas[1], Akshay Rao[1], Abhishek Kumar[1], Samuel L. Smith[1], Alex W. Chin[1], Jenny Clark[1], Tom S. van der Poll[2], Guillermo C. Bazan[2], Richard H. Friend[1]

1 Cavendish laboratory, University of Cambridge, Cambridge, UK
2 Center for Polymers and Organic Solids, University of California, Santa Barbara, USA
Email: sg559@cam.ac.uk

Abstract: By tracking the modulation of the optical absorption due to the electric field generated between the charges, we are able to observe the ultrafast electron-hole separation process in organic photovoltaic materials.

OCIS codes: (320.7130)　Ultrafast processes in condensed matter, semiconductors; 300.6530　Spectroscopy, ultrafast;

Organic photovoltaic cells (OPVs) consist of a nanostructured blend of donor (D) and acceptor (A) semiconductors. Photons absorbed in either material create molecular excitons, which can dissociate at the D-A heterojunction into holes on D and electrons on A. The hole and electron are still subject to their mutual Coulomb interaction and can self-trap at the heterojunction, giving rise to charge transfer (CT) excitons. However, in efficient OPV blends that use fullerenes as the acceptor, electron and hole escape from the heterojunction and long-range charge separation is efficient (figure 1A). The motion of charges away from the heterojunction had been generally attributed to diffusion; however recent results have suggested that delocalized states may play a role in this process [1-4]. Here we directly measure the electron-hole separation process at the heterojunction and find that the Coulomb barrier is surmounted at times as short as 40 fs, suggesting that rapid charge motion away from the interface through delocalized band states is a necessary ingredient for long-range charge separation.
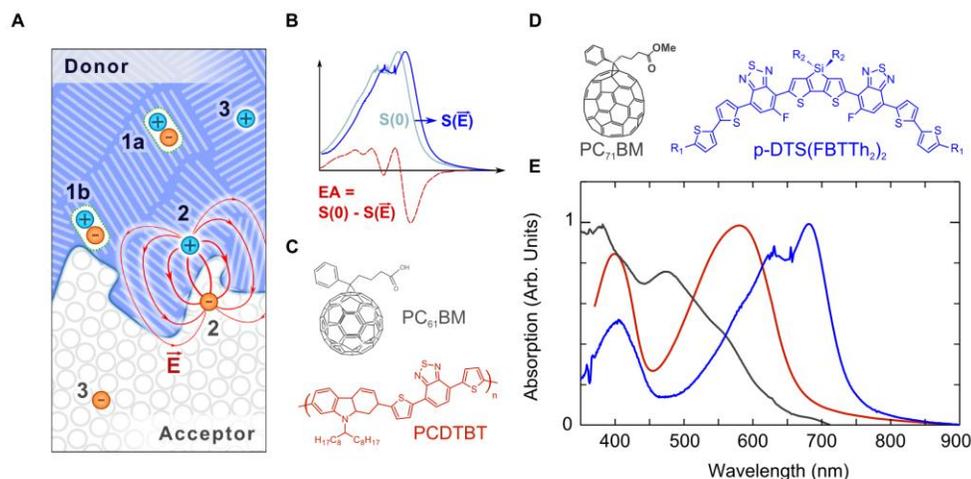

Figure 1. (a) Overview of charge photogeneration at a heterojunction; (b) Stark shift of the absorption results in an electro-absorption signature; (c,d) Chemical structures of the molecules studies; (e) Absorption spectra of the molecules in c,d.

In order to temporally resolve the electron-hole separation process we require a probe that is sensitive to the distance between these charges. The electric field generated as the charges separate (figure 1A) serves this purpose by shifting the energy levels of neighboring molecules, causing a change in their electronic transition energies and an associated optical electro-absorption (EA) signature, represented schematically in figure 1B. We measured these EA signals with sub 30fs precision using transient absorption (TA) spectroscopy. This allows us to calculate the energy stored in the electric field as the charges separate and hence the mean electron-hole distance as a function of time, as we can calibrate the time-resolved data against steady state EA measurements.

We perform this analysis on two systems, presented in figure 1 C-E, and use a global analysis method to extract the spectra of the excited states present each material as well as their kinetics (figure 2A-D). Using a steady-state EA calibration, we convert the transient EA amplitude of figure 2B and 2C to a spatially-averaged value of the square of the electric field. We calculate that the RMS field strength and hence that the energy stored in the electric field.

Figure 2E shows the energy stored in the electric field per charge pair as a function of time for the various blends studied. For the 60:40 p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM the energy per charge pair reaches more than half its maximum value by 300fs and for the 1:4 PCDTBT:PCBM blends it attains its saturation value by 40fs.
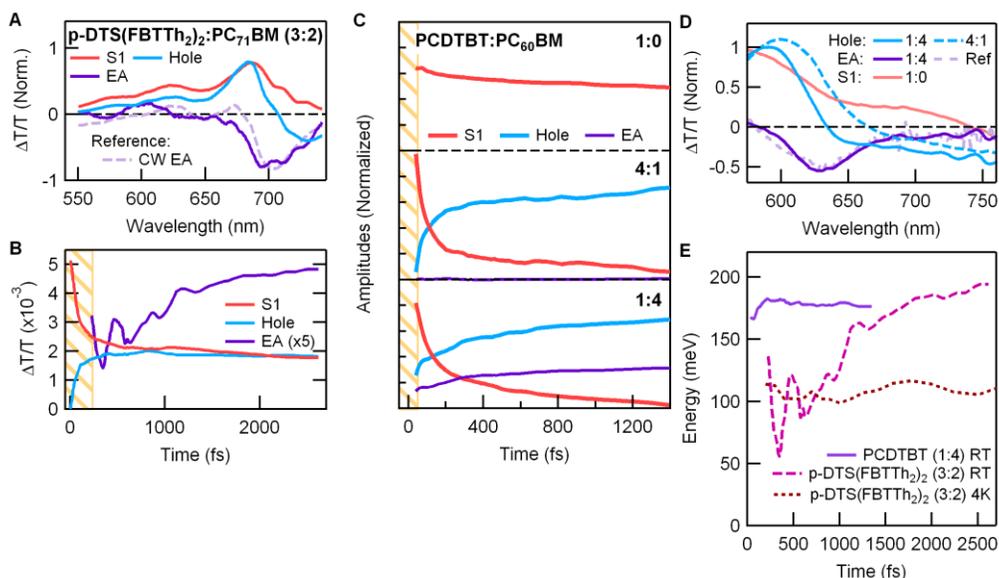

Figure 2. Optical spectra of excited states (a,d) and their temporal evolution (b,c) for the systems presented in figure 1 c,d respectively. (e) Energy stored in the electric field per electron-hole pair as they separate into free charges.

The energies involved are substantial, well above k$_B$T, and provide direct evidence that considerable work must be done to overcome the Coulomb attraction between the separating electron hole pairs in these low dielectric constant materials. Crucially, the majority of this work against the Coulomb interaction is done on ultrafast timescales. This requires that charges underdo rapid spatial separation on these timescales.

With simple electrostatic modelling and the assumption that the initial step of photoinduced electron transfer just across the heterojunction causes an average separation of electron and hole by 1.5nm in the absence of fullerene aggregation, we find that charges reach a separation of 4 to 5 nm in both systems at the earliest times measured.

Our results rationalize the apparent asymmetry between efficient electron-hole capture in organic light-emitting diodes and near-unity photo-conversion quantum efficiencies in OPVs by revealing that ultrafast charge separation through delocalized band-like states in fullerene aggregates is key to efficient charge separation. Moreover, the fast timescale for this process indicates that efficient charge separation requires no excess energy beyond that needed to overcome the Coulomb interaction. This is in contrast to Onsager-like models that require excess energy in hot states. Our results suggest that the real energy loss during charge separation lies elsewhere, for instance in later energetic relaxation of charges through polaron formation or the presence of defect-mediated gap states and that such energy losses are not fundamental for efficient charge separation.

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