An Experimental and Theoretical Study of Excited-State Absorption Processes in Conjugated Oligomers.

J.-C. Denis[1], A. Ruseckas[2], A. Matheson[2], G.J. Hedley[2], G.A. Turnbull[2], M.J. Paterson[1], I.D.W. Samuel[2] and I. Galbraith[1]

[1]School of Engineering and Physical Sciences, SUPA, Heriot-Watt University, UK
[2]School of Physics and Astronomy, SUPA, University of St. Andrews, St. Andrews, UK
Corresponding Author: I.Galbraith@hw.ac.uk

Progress in efficient opto-electronic devices based on conjugated polymers, requires an understanding of excited-state absorption (ESA) properties in active regions. Such ESA processes can limit the efficiency of photovoltaic cells, and high-brightness LEDs and lasers, or in contrast, improve the performance of current devices, when exploited for rapid modulation of laser action or incoherent control of emission wavelength.

Using modern theory tools such as the quadratic response function for time-dependent density functional theory (TD-DFT), we have computed a range of ESA spectra for fluorene, PPV, F8BT and PTB7 oligomers. Comparing to an experimentally measured ESA spectra for the fluorene pentamer (O5), we find good agreement when CAM-B3LYP is used (see Figure 1). For the homopolymers we have calculated that only one significant ESA electronic peak is present, whereas the ESA spectra of PTB7 and of F8BT consists of more than one electronic transition and is rather broad.

We also investigated the ionisation energies in these molecules. We find that these energies are situated around twice the energy of the one-photon absorption to the first excited-state. Thus exciton-exciton annihilation likely liberates sufficient energy to ionize the remaining exciton which may lead to device and performance degradation.

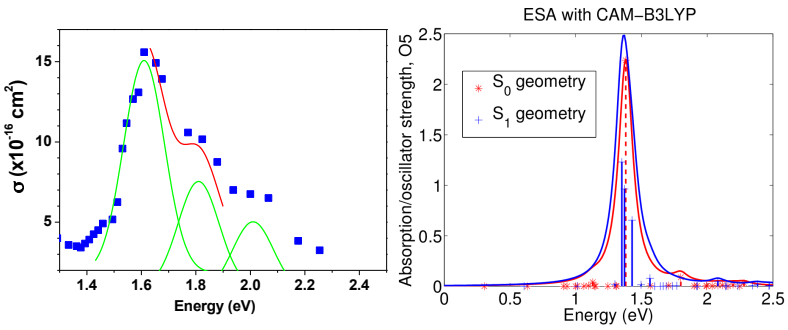

Figure 1 - Experimental (left) and theoretical (right) ESA spectra for the fluorene pentamer. Phonon replicas are indicated in green and are not included in the calculations.