A spectroscopic study of PCBM:P3HT heterojunctions

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Organic photovoltaic (OPV) devices [1] have the potential to provide low cost solar cells that can be made onto flexible substrates using abundant materials. At the heart of these molecular devices is an interface between regions of an electron acceptor, e.g. phenyl-C61-butyric acid methyl ester (PCBM – a functionalised fullerene), and an electron donor like poly(3-hexylthiophene) (P3HT– a conductive polymer). An exciton, created by a photon interacting with the donor molecule, diffuses to this interface where the electron and hole separate and diffuse to the electrodes of the device allowing electrical work to be done. Understanding these devices is fundamentally a surface science problem; gaining insight into the bonding, morphology and charge transfer between the interfaces is key to understanding and optimising their operation. Synchrotron based soft x-ray spectroscopies are routinely used to probe these characteristics, but the surface sensitive nature of the techniques makes it desirable to deposit the molecules in-situ in UHV, which for PCBM and P3HT is not possible via the conventional sublimation-based methods. Electrospray deposition [2] provides an attractive solution. By applying a large voltage to a dilute solution flowing through a narrow capillary tube, the liquid forms a jet that explodes into a stream of small droplets that can be fired into a differentially pumped vacuum system allowing the molecules to deposit on a surface in high vacuum (Figure 2).

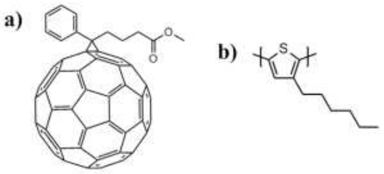

Figure 1 Structure of a) PCBM and b) P3HT.

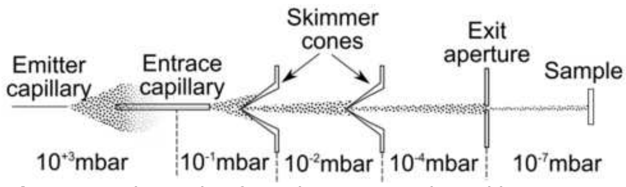

Figure 2 Schematic of an electrospray deposition system.

We present X-ray photoemission and absorption measurements of PCBM and P3HT, including both bi-layer and bulk heterojunctions of the two molecules, deposited on the Au(111) surface using electrospray. X-ray photoelectron spectroscopy (XPS) alludes to a chemical interaction between P3HT and the methoxy oxygen environment of the PCBM, see Figure 3, and we discuss the origin of this. Resonant photoemission spectroscopy allows us to probe the coupling between occupied and unoccupied orbitals. An example of this is presented in Figure 4 which shows the enhancement of occupied orbitals is very different when we measure on resonance with first three unoccupied orbitals. Through these types of measurements, we present a thorough study showing what can be learned by applying soft x-ray spectroscopies to this genre of complex molecular system.

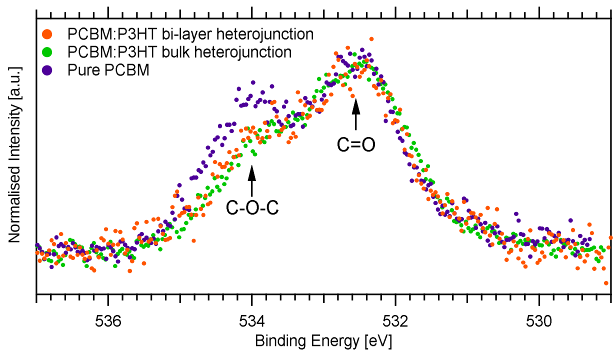

Figure 3. O 1*s* XPS showing PCBM's two chemical environments. Spectra are shown for a pure PCBM film and PCBM/P3HT bi-layer and bulk heterojunctions

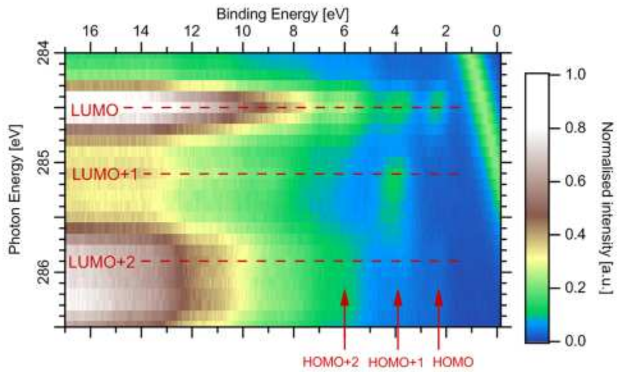

Figure 4 – C K-edge RPES map of PCBM. The positions of lowest unoccupied molecular orbitals (LUMOs) and highest occupied molecular orbitals (HOMOs) are marked.

References:
[1] Kippelen B. & Brédas J.-L. *Energy Environ. Sci.* **2,** 251 (2009)
[2] Temperton R.H, O'Shea J.N, Scurr D.J, *Chem. Phys. Lett.* **682,** 15-19 (2017)