Organic semiconductors offer many advantages for energy conversion, saving and storage applications. Low temperature and flexible processing of the semiconducting layer enables production at low cost and energy expenditure, and integration on non-heat resistant substrate materials such as plastics and textiles. A critical limitation of organic semiconductors in devices, however, is the poor electrical properties. To avoid substantial electrical losses, very thin active layers are utilised in state-of-the-art solar cells. We recently demonstrated that the thin active layer (< 100 nm) in high performance polymer solar cells limits the maximum achievable photocurrent via limited absorption, and therefore the power conversion efficiency [1].

Molecular doping is an interesting and versatile strategy for enhancing the electrical properties of organic semiconductors [2]. Recently we demonstrated that molecularly p-doping the active layer of polymer solar cells can increase the photocurrent by increasing hole mobility in the polymer phase[3] and decreasing recombination[4] losses. Blends of the low bandgap polymer poly[2,6(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b0]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and the fullerene derivative PC$_{60}$BM were doped via co-solution with the strong electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ). At low concentrations of F4-TCNQ (≤ 10 molar %), both hole conductivity and mobility are observed to increase. Saturation in the hole conductivity at higher doping concentrations could be correlated with clustering of the F4-TCNQ in the polymer [5].

However a correlation between microscopic variations in polymer conformation and morphology and the macroscopic changes in electrical performance in devices remains unclear. Vibrational spectroscopy have been shown to be a useful tool for elucidating dopant-polymer interactions at low dopant concentrations [6]. In this talk, I will present a novel approach which combines Raman and impedance spectroscopies to explore structure-function relationships in organic photovoltaic systems. Using impedance spectroscopy, we study dopant-dependent variations in the dielectric properties of PCPDTBT doped with F4-TCNQ. We combine these measurements with Raman spectroscopy in order to identify the influence of charged species on the vibrational spectrum of the polymer. We observe shifts in
the Raman spectra which are correlated with the change in conductivity of the semiconductor. This approach gives insight into material interactions and the subsequent effects on device efficiencies.


