



Project 01: Scientific Progress – Fall 2009 to Fall 2015

Polymer:carbon nanotube (CNTs) systems have been studied, CNTs have been chemically functionalized and devices studied. Some enhancements in the stability as well as in the open-circuit voltage of the cells have been observed. The full potential of the CNTs as IR absorbers has not been realized; the reason may be that full separation of the CNTs between metallic and semiconductor bands was not realized appropriately.

Alternative nanomaterials like TiO₂ and ZnO have been incorporated successfully in the polymer cells; they also improve performances like J_{sc}.

Plasmonics for Photon Trapping has been explored and implemented successfully. It was published early in the project.

We have addressed directly, with ultrafast time resolution and molecular specificity, the dynamics of photoinduced charges at polymer:fullerene heterojunctions with an ultrafast optical probe that is sensitive to molecular conformation dynamics as well as electronic population, which allows us to establish unambiguously that the photoproducts of ultrafast charge separation are unbound polarons. We concluded that following ultrafast polaron generation, the structure of the polymer backbone hosting it does not evolve significantly over < 50 ps, which suggests that the initial exciton separation produces charges that are sufficiently far apart to escape their mutually binding Coulomb potential. This was published last year (Provencher Nat. Comms. 2014).

We probed charge photogeneration and subsequent recombination dynamics in neat regioregular poly(3-hexylthiophene) films over six decades in time by means of time-resolved photoluminescence spectroscopy. Exciton dissociation at 10 K occurs extrinsically at interfaces between molecularly ordered and disordered domains. Polaron pairs thus produced recombine by tunnelling with distributed rates governed by the distribution of electron-hole radii. Quantum-chemical calculations suggested that hot-exciton dissociation at such interfaces results from a high charge-transfer character.

This was published earlier in the project (Paquin Phys. Rev. Lett. 2011).

We have constructed a novel non-linear coherent spectroscopy, photocurrent-detected two-dimensional spectroscopy (2DPC), which is an ultrafast optical technique belonging to a family of 2D Fourier-domain spectroscopies that allows measurement of correlations between optical transitions induced by short optical pulses. In our implementation, spectral correlations are detected via the time-integrated photocurrent produced in a photovoltaic diode. Four collinear ultrashort laser pulses (10 fs, centered at 600 nm in our experimental setup) excite the semiconductor polymer in the solar cell, with a variable delay that is independently controlled between each pulse in the sequence. Each pulse separately excites a quantum wavepacket with spectral phase and amplitude imparted by that pulse, while the effect of the pulse sequence is to collectively excite multiple quantum coherences. Interferences between the various combinations



of the wavepackets determine linear and non-linear contributions to the material optical response. The fourth-order signal terms of the detected photocurrent are read using phase-sensitive detection schemes with reference waveforms corresponding to a modulation of specific phase combinations of the four femtosecond excitation pulses. By scanning the time delay between the pulses 1 and 2, as well as that between pulses 3 and 4 (coherence times), at a fixed delay between pulses 2 and 3 (population waiting time), one measures a two-dimensional coherence decay function that is Fourier transformed to produce a 2D photocurrent correlation excitation spectrum. Measurement of such spectra at different population waiting times provides insight into the role of spectral correlations and state coherence in photocurrent generation in such complex functional materials. We have thus far focused on solar cells produced by blends of a common carbazole-thiophene-benzothiadiazole polymer, PCDTBT (the donor polymer), and PCBM (the fullerene acceptor), in which we analyse the dynamics of total photocurrent generation via the time evolution of diagonal and off-diagonal spectral correlations. We are currently addressing the role of vibronic coherence as well as resonant tunnelling in charge separation pathways on ultrashort timescales. This will be a technique used extensively during the next few years.