Bipolaron Formation at Room Temperature in Organic Bulk Heterojunction Solar Cells Observed by Pulsed Electrically Detected Magnetic Resonance

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Organic semiconductors provide a range of commercial optoelectronic display devices, and show great promise in the field of photovoltaics (PV) if improved efficiency, combined with low cost and ease of production, can be achieved. In addition, the weak spin-orbit coupling of organic semiconductors is attractive for carrier spin transport and manipulation, and is driving efforts to develop spintronic devices. All these applications depend upon detailed knowledge of the relevant transport processes, in particular, those influenced by spin selection rules. The observation of large magnetoresistance (MR) has, for example, attracted a range of explanations, but aspects of the proposed mechanisms remain controversial.

Conduction in disordered organic semiconductors is dominated by hopping of charge carriers between localized states. Because of strong electron-phonon coupling the carriers are polarons. Oppositely charged polarons can form excitons and eventually recombine; the process normally depends on the spin state of the coupled pair immediately prior to exciton formation. In addition, the strong coupling between carriers and the environment can markedly reduce the energy cost of doubly occupying states. Two like-charge polarons can form a bipolaron, the correlation energy between the pair and the lattice deformation lowering the formation energy. However, the on-site exchange requires that the final state is a spin singlet, and bipolaron formation will be ‘‘spin-blocked’’ if two polarons have the same spin component along the common axis of quantization.

Organic PV devices have advanced dramatically with the development of bulk heterojunction materials, which comprise a π-conjugated polymer blended with an electron acceptor such as a fullerene derivative. The two phase-separated components give interpenetrating networks with vastly increased interfacial regions. The PVeffect is due to photoexcitation of the polymer, followed by highly efficient electron transfer to the fullerene phase. Positive polarons (P+) are transported through the polymer matrix, negative polarons (P-) through the fullerene phase, efficiently suppressing carrier loss by P+P- recombination. However, unipolar transport to the electrodes may be influenced by bipolaron formation. Gaining insight into this process, which affects charge carrier collection efficiency in solar cells and which may be responsible for MR, cannot be achieved on the basis of the electrical properties alone. Here we detect resonant changes in charge transport through organic heterojunction solar cells, which can be attributed to spin-dependent bipolaron formation during hopping transport through the polymer, using electrically detected magnetic resonance

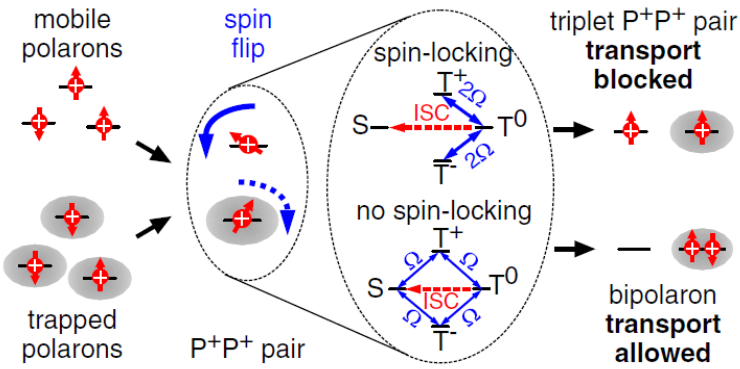

Figure: Bipolaron formation under resonant microwave excitation. In the scheme polaron charge and spin are indicated by + and arrow, respectively. Gray shaded ellipses indicate trap sites accommodating P+ or bipolarons. From left to right polarons form weakly coupled spin pairs in a mixed singlet (S) triplet (T) state upon encounter of mobile and trapped polarons. Resonant mw excitation alters the S and T content, with an oscillation frequency Ω (no spin locking) or 2Ω (spin locking). Inter system crossing (ISC) transfers population from T_0 to S. Depending on the S and T content of the pair, either triplet P+P+ pairs (transport blocked) or bipolarons (transport allowed) are formed.

(EDMR). EDMR has the potential to fulfill this task because it actively manipulates spin pair recombination or hopping rates and probes the resulting change in conductivity. Benefiting from the long spin relaxation times in organic materials and the high sensitivity of EDMR, coherent effects may be exploited to analyze the spin-dependent processes in great detail at room temperature.

The probability for bipolaron formation depends on the spin symmetry of the weakly coupled precursor P+P- pair (see Figure). An increase in the singlet content of the pairs, caused by a spin-resonant excitation, leads to an enhanced bipolaron formation probability, and thus facilitates the hopping transition of one P+ to the site of the other. This process enables the previously blocked transport path and, in consequence, provides a resonant change in the detected current (the EDMR signal). Room temperature measurements on poly (2-methoxy-5-(2'-ethyl)-hexyloxy-p-phenylene) vinylene (MEH-PPV) : [6,6]-phenyl C61-butyric acid methyl ester (PCBM) devices operated in forward bias exhibit a continuous wave (cw) EDMR spectrum that can be resolved into two components. The resonance position (g = 2.0028) is in agreement with that for positive polarons, and precludes any significant involvement of PCBM centers (g = 1.9995). Pulsed EDMR (pEDMR) measurements at high microwave (mw) field intensities exhibit spin locking and show that the resonant spin-dependent transport process involves coupled S = 1/2 pairs. Spin-coherent Rabi oscillations are also detected and quantify spin locking, giving further insight into the mechanism of bipolaron formation.

The observation of spin locking at high mw field values shows that weakly coupled S = 1/2 spin pairs are responsible for the spin-dependent current. The g value of the resonance indicates that the transport process is due to polarons in the MEH-PPV phase, and rules out the involvement of PCBM. The negligible population of negative polarons in MEH-PPV excludes recombination mechanisms. It is concluded that the EDMR spectrum is due to spin-dependent formation of positive bipolarons in MEH-PPV, where the spin-pair partners originate from different polaron populations.

Reference

Bipolaron formation in organic solar cells observed by pulsed electrically detected magnetic resonance, J. Behrends, A. Schnegg, K. Lips, E.A. Thomsen, A.K. Pandey, D.W. Samuel, D.J. Kneeble, Phys. Rev. Lett. 105, 176601 (2010)