

# Spin-dependent Processes of Interfacial Charge Transfer Excitons in Polymer-fullerene Solar Cells

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Efficient solar energy conversion in bulk hetero-junction (BHJ) organic photo-voltaic devices relies on photo-generation of charges at the donor and acceptor hetero-interfaces. An important requirement in further improving device efficiency is our understanding of the photo physics of interfacial charge transfer (CT) states - the precursors for charge generation, and their contributions to both charge generation and energy losses. Earlier studies have shown that spin and localization of the interfacial CT states play crucial roles in ultrafast charge generation and the subsequent recombination loss in polymer/fullerene blend systems. However, a direct proof for such roles on the microscopic level is still lacking.

In this work, we focus on the direct probing of the optically-excited lowest CT exciton states ( $CT_1$ ) and their associated spin-dependent processes in a model polymer/fullerene solar cell based on TQ1/PCBM blends. By combining selective optical excitation and detection with the optically detected magnetic resonance (ODMR) technique, we are able to identify the triplet  $CT_1$  states and the associated spin-spin interaction. With this, we estimate the electron-hole separation of the  $CT_1$  exciton to be about 1 nm, within the physical dimension of a one-polymer-one-fullerene unit. The size of the  $CT_1$  exciton is found to be identical in the blends regardless of the fullerene load and aggregation that are known to affect the degree of delocalization of CT excited states. We therefore conclude that the exciton localization of the  $CT_1$  state is not responsible for the observed different efficiency of the solar cells with different fullerene loads. In addition, we provide direct evidence that  $CT_1$  can mediate charge loss by facilitating intersystem crossing between the singlet and triplet of  $CT_1$ , trapping and bimolecular recombination of separated charges via  $CT_1$ , and electron back transfer from  $CT_1$  to the polymer triplet. Interestingly, we also observe at the same time efficient charge generation via the  $CT_1$  state. As such, we propose a dual role of  $CT_1$  in both charge loss and charge generation. We furthermore suggest the physical principle and possible pathways to turn  $CT_1$  from a loss channel into a charge generation channel.

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