Charge Separation in Organic and Amorphous Silicon Solar Cells probed by Transient EPR

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Using transient electron paramagnetic resonance (trEPR) and electrically detected magnetic resonance (EDMR) spectroscopy we analyse and compare the process of free charge carrier generation and separation in organic and hydrogenated amorphous silicon (a-Si:H) solar cells. In both types of solar cells charge transport and recombination is dominated by local disorder. One of the main advantages of transient EPR spectroscopy is that it is possible to follow the charge separation process on a nanosecond to millisecond time scale and, at the same time, identify the microscopic origin of the participating paramagnetic states through their EPR signatures. While trEPR has previously been applied to polymer/fullerene blends, no reports so far are available for a-Si:H although many of the models used to describe transport and recombination in organic solar cells originate from a-Si:H research. We here will try to shed light on one of the still open questions after even more than 40 years of intensive a-Si:H research: the role of spin-correlated geminate states in the charge separation process. We here present a first direct experimental proof for the existence of spin-correlated electron-hole pairs in a-Si:H and compare the observations to recent results achieved on prototypical P3HT:PCBM blends. In polymers, prior to dissociation of photogenerated excitons into separated charges, bound polaron pairs (also referred to as charge transfer states) form at the donor/acceptor interface as shown in Figure 1. These states can be observed in the tEPR spectrum as also shown in Fig. 1. There is consensus that such charge transfer states may critically influence the yield of free charge carriers, but their exact role is being controversially discussed at the moment [1,2].

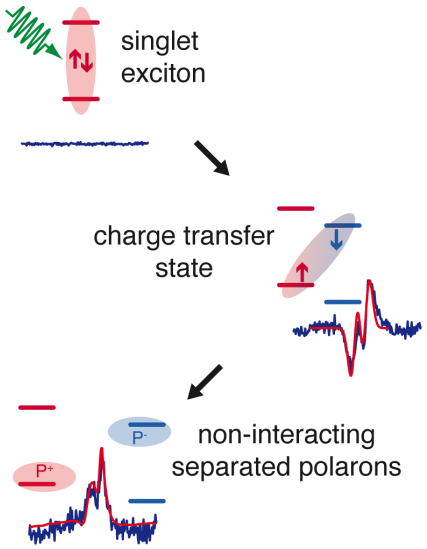

Figure 1. Free charge-carrier generation from singlet excitons via charge transfer states as detected by transient EPR. The respective tEPR signals obtained for P3HT:PCBM blends are shown.

Here we report trEPR measurements with sub-microsecond time resolution performed on polymer:fullerene blends and undoped device-grade a-Si:H. We show that the trEPR spectrum immediately following photoexcitation reveals signatures of spin-correlated charge carrier pairs in both types of solar cell materials and thus decisively differs from

the spectrum of separated charge carriers commonly observed in light-induced cwEPR. The pair partners (positive polarons on the donor and negative polarons on the acceptor in polymers and localized electron-hole pairs in the band tails of the respective bands in a-Si:H) can be identified by their characteristic *g* values. The fact that the population of the pair states strongly deviates from Boltzmann equilibrium unambiguously shows that both constituents of each pair are geminate, i.e., originate from the same exciton in polymer blends [3] as well as in a-Si:H.

In this presentation we discuss the role of coupled charge carrier pairs in mediating the conversion from excitons into separated charges as probed by trEPR. Particular emphasis will be given to triplet excitons, which are encountered in some donor:acceptor systems and in a-Si:H used in high-efficiency solar cells. Such triplet exciton states in a-Si:H can be the origin of the genesis of metastable defect states that are recently shown to exist in distinctively different local configurations [4].

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[2] K. Vandewal *et al.*, *Efficient charge generation by relaxed charge-transfer states at organic interfaces*, Nature Mater., **2014** (13) 63.

[3] J. Behrends, A. Sperlich, A. Schnegg, T. Biskup, C. Teutloff, K. Lips, V. Dyakonov and R. Bittl, *Direct detection of photoinduced charge transfer complexes in polymer fullerene blends*, Phys. Rev. B, **2012** (85) 125206.

[4] M. Fehr, A. Schnegg, B. Rech, O. Astakhov, F. Finger, R. Bittl, C. Teutloff, and K. Lips, *Metastable Defect Formation at Microvoids Identified as a Source of Light-Induced Degradation in a−Si:H*, Phys. Rev. Lett, **2014** (112) 066403.