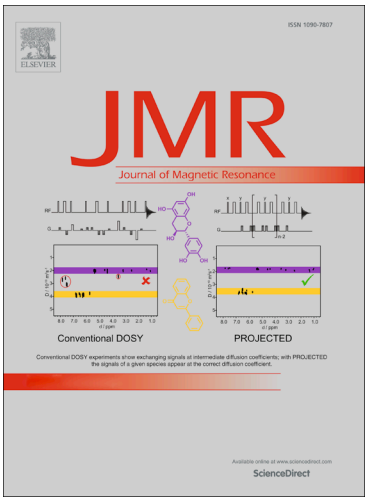

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Melissa Van Landeghem, Wouter Maes, Etienne Goovaerts, Sabine Van Doorslaer

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Disentangling overlapping high-field EPR spectra of organic radicals: Identification of light-induced polarons in the record fullerene-free solar cell blend PBDB-T:ITIC

Melissa Van Landeghem[a], Wouter Maes[b], Etienne Goovaerts[a,*], Sabine Van Doorslaer[a,*]

[a] *Department of Physics, University of Antwerp, Universiteitsplein 1, 2610 Antwerpen, Belgium*
[b] *Institute for Materials Research, Design & Synthesis of Organic Semiconductors, Hasselt University, Agoralaan 1, 3590 Diepenbeek, Belgium*

Abstract

We present a combined high-field EPR and DFT study of light-induced radicals in the bulk heterojunction blend of PBDB-T:ITIC, currently one of the highest efficiency non-fullerene donor:acceptor combinations in organic photovoltaics. We demonstrate two different approaches for disentangling the strongly overlapping high-field EPR spectra of the positive and negative polarons after charge separation: (1) relaxation-filtered field-swept EPR based on the difference in T_1 spin-relaxation times and (2) field-swept EDNMR-induced EPR by exploiting the presence of ^{14}N hyperfine couplings in only one of the radical species, the small molecule acceptor radical. The approach is validated by light-induced EPR spectra on related blends and the spectral assignment is underpinned by DFT computations. The broader applicability of the spectral disentangling methods is discussed.

1. Introduction

Solution-processed organic solar cells (OSCs) are considered a highly promising technology due to their low manufacturing costs and compatibility with flexible substrates allowing for innovative photovoltaic applications. For two decades, the research efforts into increasing the power conversion efficiencies (PCEs) of OSCs mainly relied on bulk heterojunction (BHJ) blends of a conjugated polymer and a fullerene acceptor such as [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). In the last few years, however, OSCs with non-fullerene acceptors have attracted considerable research interest due to their enhanced absorptivity and chemical tunability as compared to conventional fullerenes [1–3]. Careful molecular design of the acceptor materials allows OSCs to surpass the 11.7% certified record efficiency of single-junction polymer-fullerene solar cells [4]. The donor-acceptor combination studied in this work, poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-*b*:4,5-*b*']dithiophene))-*alt*-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-*c*:4',5'-*c*']dithiophene-4,8-dione))] (PBDB-T) with 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-*d*:2',3'-*d*']-*s*-indaceno[1,2-*b*:5,6-*b*'] dithiophene (ITIC), was the first fullerene-free OSC to recently achieve >11% efficiency, challenging the state-of-the-art polymer-$PC_{71}BM$ devices [5, 6]. To the best of our knowledge, this work presents the first EPR characterization of charge-transfer radicals in a blend of PBDB-T and ITIC.

Charge transfer and separation in the donor-acceptor contact regions are essential steps of the photovoltaic process in BHJ OSCs, which lead to the production of positive and negative free charges, called polarons. These are radical states in the blend localized on the donor and acceptor molecules, respectively. Also other paramagnetic species, such as coupled radical pairs and triplet excitons are important for understanding of the device operation and optimization of its efficiency. Over the past decades, light-induced EPR has played a crucial role in the study of OSCs because of its selectiveness in detecting the different paramagnetic species created in the BHJ blend under illumination. As such, EPR can distinguish between polarons in the donor or acceptor regions. Characterization of the photogenerated charge car-

*Corresponding author
Email addresses:
melissa.vanlandeghem@uantwerpen.be (Melissa Van Landeghem), wouter.maes@uhasselt.be (Wouter Maes), etienne.goovaerts@uantwerpen.be (Etienne Goovaerts), sabine.vandoorslaer@uantwerpen.be (Sabine Van Doorslaer)