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## TRESR study of the photo-induced electron transfer in P3DDT/maleic anhydride blend in THF solution under UV flash photolysis

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### ABSTRACT

Photo-induced electron transfer (PET) between a poly(3-dodecylthiophene) (P3DDT) and maleic anhydride (MA) in their blend in liquid solution of tetrahydrofuran was observed by the time-resolved electron spin resonance (TRESR) under UV flash photolysis at 308 nm. The observed spectra were identified as free-radical signals of positive polarons on polymer chains and MA anion radicals. Their emissive chemical induced dynamic electron polarization (CIDEP) originated mainly from excited triplet states (triplet mechanism of CIDEP). Analysis of radical spectra integral intensity distribution shows at the influence of radical pair mechanism (RPM) of CIDEP with the positive sign of the exchange interaction constant ( $J > 0$ ). The last is attributed to Coulombic interaction between geminately formed polarons and MA anion radicals. The spin relaxation times of radicals were determined by fitting the time evolution of the TRESR signal at near-resonance positions of the field using the Bloch equations and direct Fourier transform analysis.

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### 1. Introduction

The intermolecular photo-induced electron transfer (PET) process in conjugated polymer/electron acceptor blends continues to be of interest to organic charge separation systems for light energy conversion [1–3]. Although PET of conjugated polymers onto electron acceptors (mainly fullerenes and their derivatives [4]) is widely investigated by numerous time-resolved (TR) spectroscopic methods, the direct observation of radical ion pair formation in polymer/electron acceptor composites is more difficult in solids and liquid solutions. Moreover as expected here radical ion pairs (RIPs) should be generated in the system where one of the pair partners is the mobile polaron. The observation of this occurrence may open a new field of TRESR application, most likely dealing with the study of photovoltaic devices. This was well demonstrated in sexithiophene/fullerene derivatives composites [5] where the dipolar and spin exchange interaction parameters including electron–hole separation distance of spin correlated radical ion pairs were obtained. A short communication about TRESR registration of polarons in solid poly (paraphenylene vinylene) (PPV) films was published in [6]. However, from our knowledge, no data currently exists in literature about the RIP formation process in conjugated polymer blends with fullerenes and their derivatives in liquid solutions. Moreover, the formation of RIPs

represents on interest, to establish reason for the often positive sign in spin exchange interactions ( $J$ ), contrary to the negative one for most neutral radicals, as well as to study the role of Coulombic interaction (CI) in these inter-pair exchange processes [7]. Moreover this case is of particular interest because one of radical ion partners is a mobile polaron and an interaction on its 1D, 3D mobility is expected. MA was chosen for experiments since: a) the anion radical ( $MA^{\cdot-}$ ) has been thoroughly investigated by ESR under continuous photolysis (for example [8–12]) and by TRESR with flash photolysis [12,13], b)  $MA^{\cdot-}$  was investigated as an electron acceptor in RIPs formation studies and discussed in [7,14–16].

### 2. Experimental

Regioregular P3DDT and MA (99%) (Fig. 1a,b) were purchased from Aldrich. The solutions of both compounds were prepared ( $c_1 = 0.2$  M for MA and  $c_2 = 0.4$  g/l for P3DDT) and mixed before ESR experiments with different ratios ( $V_{c1}/V_{c2}$ ) of component solution volumes. The solutions were deoxygenated by blowing nitrogen gas through a flat quartz tube of  $40 \times 10 \times 0.35$  mm<sup>3</sup> at a rate of 0.2 ml/min. ESR experiments were carried out using a BRUKER X-band (~9.34 GHz) TRESR spectrometer ELEXSYS E500 with Bruker 4104 OR or 4102 ST cavities. No field modulation was used but direct detection was employed here. The transient traces of the ESR signal were digitized by a fast digital oscilloscope (LeCroy waverunner LT322) with a maximum acquisition rate of 200 MS/s synchronized with the laser pulse. Photolysis was

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