Optical Studies of Spin Coherence in Organic Semiconductors

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Abstract. Spin coherence in organic oligomer and polymer semiconductors is a crucial property in determining the performance of organic spin devices. Using the techniques of photo-induced absorption (PA) detected magnetic resonance (PADMR) and photoluminescence (PL) detected magnetic resonance (PLDMR), we have studied the influence of temperature, conjugation length, excitation energy, magnetic nano-particles mixing, and in-chain heavy metal atoms on the spin coherence in organic semiconductors. From the PADMR measurements in addition, we could infer the formation ratio of singlet/triplet excitons from electron-hole pairs in these materials, and found that the formation of singlet excitons is preferred in polymers. We also found that spin randomization induced by magnetic nanoparticles or heavy atoms lead to faster polaron recombination dynamics and lack of optically detected magnetic resonance signal.

INTRODUCTION

Organic semiconductors have emerged as the active materials in organic light emitting diodes, thin film transistors, photovoltaic cells and spin valve devices in the past decade [1-2]. By virtue of having large spin coherence, spin dynamics of charged carriers (polarons) have played an important role for the applications of these materials in spintronic devices [2]**.** The optically detected magnetic resonance (ODMR) technique has been extensively used in organic semiconductor thin films and devices for studying spin-dependent phenomena, such as excited states spin characterization, spin-dependent polaron recombination, triplet-triplet annihilation, and photoluminescence quenching processes [3-5]. Spin coherence in organic semiconductors has been always implied to be large, but has not been directly measured as yet.

In this work we propose to use the ODMR technique as a tool to study spin coherence of photogenerated charged polarons at different conditions that include variation of the temperature, excitation photon energy, and also by mixing the polymer chains with magnetic nanoparticles. We found that the processes of magnetic nanoparticles mixing, raising the temperature, and binding in-chain heavy atoms enhance the spin randomization rate. In our experiments the change of spin coherence has been monitored by PADMR and PLDMR measurements.

EXPERIMENT

The materials and suppliers used for this study were: regiorandom (RRa-) poly(3-hexylthiophene-2,5-diyl) (P3HT) from Sigma-Aldrich Co, and Fe_3O_4 nanoparticles from MACH II Inc. The samples were drop-cast films on glass substrates with peak optical density OD ≈ 2. The blends were mixed in a super-sonic bath for 30 minutes. The PL, PA and ODMR measurements were described elsewhere [4].

RESULTS AND DISCUSSION

The absorption, PL, PA, PADMR and PLDMR spectroscopies have been used to characterize the polymers, as shown in Figs. 1 and 2 for RRa-P3HT. PADMR, which measures the ratio δPA/PA, is obtained in the polymer film due to the following process: the photogenerated polaron pairs, with a characteristic PA band in the mid-ir spectral range (P_1 in Fig. 1), are spin polarized to some extent due to spin-dependent recombination rates, where pairs with parallel spins recombine slower compared to pairs with anti-parallel spins. Microwave absorption in resonance conditions with the Zeeman-splitted spin ½ polaron sublevels under the influence of an external magnetic field induces spin flips that redistribute the polaron spins causing a change in the steady state

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population and hence a change δPA is obtained. Same is also true for spin triplet sublevels of photogenerated triplet excitons (band T in Fig. 1) with half-field and full-field powder patterns (Fig. 2). Thus the PADMR signal depends on the steady state spin polarization process, which, in turn depends on spin coherence in the material. A faster spin decoherence process would decrease δPA. The PLDMR signal is directly related to the PADMR signal [3], but is easier to measure.

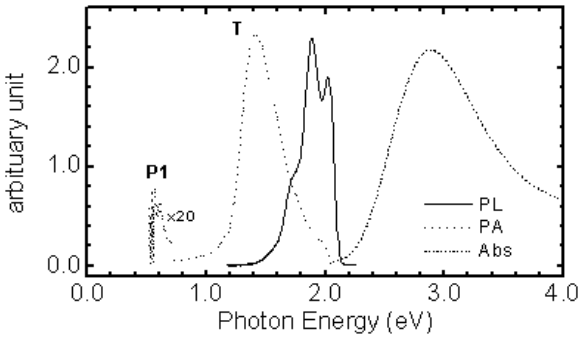

FIGURE 1. Absorption, PL, and PA spectra of RRa-P3HT film. The PA bands P_1 and T have been assigned to polarons and triplet excitons, respectively, by PADMR (Fig. 2).

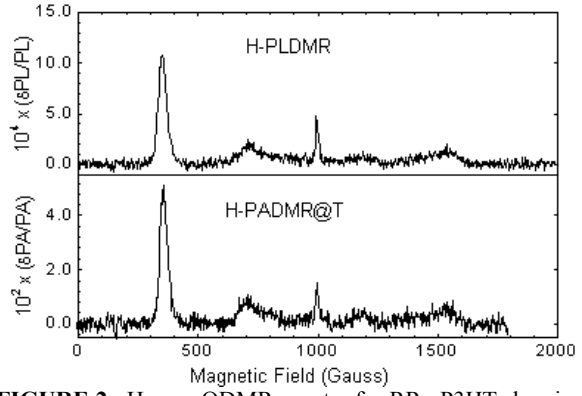

FIGURE 2. H-scan ODMR spectra for RRa-P3HT showing spin-1/2 polarons at ca. 1010 Gauss, and half-field and full-field powder patterns of triplet excitons at ca. 350 and 700 (1500) gauss, respectively.

In Fig. 3 we show the effect on ODMR of mixing the polymer chains with magnetic nanoparticles (Fe_3O_4). It is seen that adding nanoparticles actually kills the spin ½ ODMR signal. The reason for this ODMR decrease is the induced enhancement of spin 1/2 randomization rate. Lifetime measurement of the polarons verified that these randomization mechanisms indeed increase the recombination rate. In addition, raising temperature, adding charge transfer channels, increasing excitation energy and adding heavy atoms to the chain all result in smaller PADMR signal, indicating a decrease of spin ½ coherence in the sample [6].

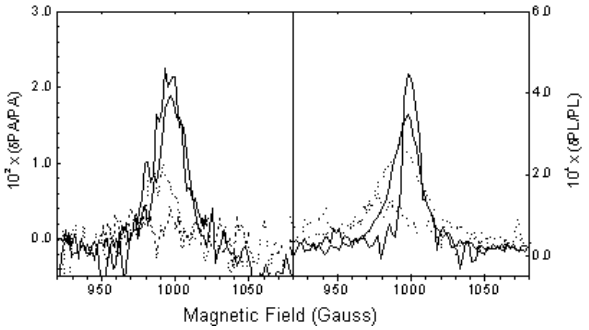

FIGURE 3. The dependence of the ODMR signal on the concentration of Fe_3O_4 magnetic nanoparticles in RRa-P3HT films. The thick line, black line, dotted line and dashed line correspond to nanoparticle molar concentration of 0%, 1%, 2% and 5%, respectively.

CONCLUSION

ODMR serves as a very useful tool not only for studying spin related recombination phenomena, but also for measuring spin coherence. Enhanced spin randomization rates by mixing the polymer chains with magnetic nanoparticles decrease the spin coherence that results in a decrease of the ODMR signal. The same effect was achieved by increasing temperature and adding heavy atoms to the chain.

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