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Tuning Hyperfine Fields in Conjugated Polymers for Coherent Organic Spintronics

Sang-Yun Lee,[†] Seo-Young Paik,[†] Dane R. McCamey,[†] Justin Yu,[‡] Paul L. Burn,[‡] John M. Lupton,[*,†] and Christoph Boehme[*,†]

[†]Department of Physics, University of Utah, Salt Lake City, Utah 84112, United States

[‡]Centre for Organic Photonics & Electronics, School of Chemistry & Molecular Biosciences, The University of Queensland, Queensland 4072, Australia

Supporting Information

ABSTRACT: An appealing avenue for organic spintronics lies in direct coherent control of the spin population by means of pulsed electron spin resonance techniques. Whereas previous work has focused on the electrical detection of coherent spin dynamics, we demonstrate here the equivalence of an all-optical approach, allowing us to explore the influence of materials chemistry on the spin dynamics. We show that deuteration of the conjugated polymer side groups weakens the local hyperfine fields experienced by electron−hole pairs, thereby lowering the threshold for the resonant radiation intensity at which coherent coupling and spin beating occur. The technique is exquisitively sensitive to previously obscured material properties and offers a route to quantifying and tuning hyperfine fields in organic semiconductors.

One of the most appealing promises of organic semiconductors is the ability to tune a particular property by synthetic means. While this approach has been explored widely, for example, in the context of color control for organic light-emitting diodes (OLEDs), there are some important material parameters relating to the spin degree of freedom which have received virtually no attention at all. Organic semiconductors typically consist of low atomic-order number atoms and are characterized by weak spin−orbit coupling, giving rise to exceptional spin lifetimes. In addition, exchange correlations and the high degree of localization of excitations give rise to a distinct splitting of excitations into the singlet and triplet manifold. This splitting controls crucial optoelectronic properties through spin-dependent dissociation and recombination of charge carriers.[1−4] Although the resulting spin-dependent transport phenomena have been studied for decades, it was recently realized that the electron spin can itself be used as the information carrier in an organic spintronics device.[5] Such devices promise new avenues toward information storage and processing as well as sensing and imaging, highlighting the need for a more systematic understanding and control of characteristics of the materials relating to spin.[6]

In the present contribution, we demonstrate direct control over the hyperfine field strength experienced by charge carriers in a conjugated polymer and explore the influence of deuteration on spin-dependent device characteristics. By comparing pulsed electrically and optically detected magnetic resonance (pE/ODMR), we are able to show the equivalence of spin-dependent observables under optical and electrical excitation. The hyperfine field strength controls the coupling between spins, leading to the pronounced effect of spin beating which is detected directly in the photoluminescence (PL) of the polymer.

Most investigations to date on spin-dependent processes in organic semiconductors have been carried out under static conditions, where it is not possible to coherently manipulate the spin orientations.[1,2] We recently reported applying pEDMR to OLEDs, which enables coherent manipulation of the spin polarization, leading to striking coherent features in macroscopic observables such as the device current.[7] We now use this sensitive technique to correlate materials chemistry with intrinsic spin dynamics. However, instead of measuring a current we detect spin-dependent recombination by a change in PL intensity under resonance. Figure 1 illustrates our experimental approach. We measure the dynamics of electron and hole spins in a film of MEH-PPV (poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene]). Optical excitation of the polymer leads to the formation of tightly bound excitons, which subsequently decay with the emission of a photon. However, a percentage of these excitons may dissociate to form electrostatically correlated weakly spin−spin coupled electron−hole pairs which typically reside on different chains in the bulk film. We can tune the local hyperfine field by varying the side groups of the polymer backbone (marked in green). Under electron spin resonance (ESR) conditions, a spin flip occurs within the carrier pair, shuttling it reversibly between the singlet and triplet spin manifold. For reasons of energy conservation and wave function symmetry, it is easier for a carrier pair in the singlet configuration to form a singlet exciton than for a triplet pair to relax to a triplet exciton:[1g] carrier recombination is spin-dependent and can be monitored by recording the singlet exciton PL yield.[1f]

The resonance condition can occur either for an individual charge or for both spins together, depending on the intrinsic ESR line width of each carrier. The hyperfine field, the random magnetic field originating primarily from the hydrogen nuclei in the polymer, constitutes the dominant ESR line broadening mechanism.[6a] As electron and hole wave functions need not have precisely the same shape on a polymer chain, it is unlikely that both carrier types will experience the same hyperfine field strength.[7b]

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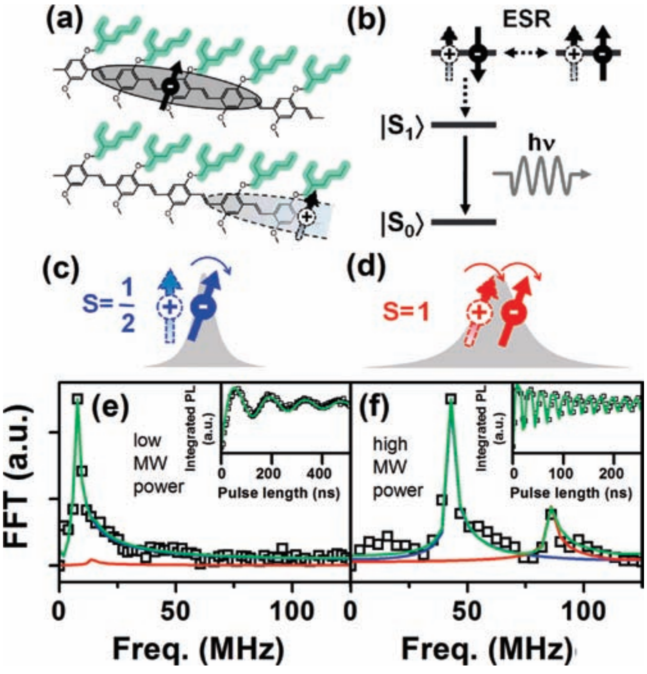

Figure 1. Coherent spin manipulation in organic semiconductors monitored by PL-detected spin resonance. (a) Charge carrier pairs are formed in MEH-PPV by optical excitation. (b) Under spin resonance conditions, a spin flip can occur, which is recorded by a change in singlet exciton emission intensity. (c) At low microwave intensities, only one spin precesses at a time, whereas both spins precess together at high intensities (d). (e) Inset: Rabi flopping in the polymer PL is dominated by a single frequency component at low intensities as shown by the Fourier transform in the main plot (X-band 9.8 GHz excitation). (f) At high intensities, spin beating occurs, leading to a harmonic appearing in the Fourier transform. The green lines in the time domain and frequency domain plots correspond to fits of the experimental raw data and its Fourier transform, respectively. Blue lines show the fundamental contribution in the oscillation; red lines indicate the beat signal. The data analysis procedure is outlined in the Supporting Information.

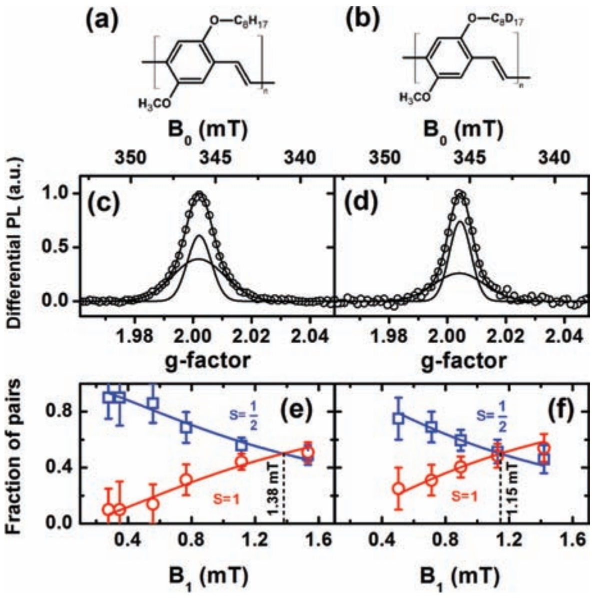

Figure 2. Effect of deuteration of the polymer side groups on the ODMR resonance spectrum and on spin beating [cf. Figure 1f]. (a, b) Structures of the polymers studied (C_8X_{17} = 2-ethylhexyl, where X = H or D). (c, d) The differential PL resonance spectrum is accurately described by a superposition of two Gaussians, representing electron and hole resonances. (e, f) Fourier analysis of the beating transients [see Figure 1e, f] allows the extraction of the spin-1 (red) and spin-$^{1}/_{2}$ (blue) contributions to the resonance. The crossing point of the two as a function of microwave field strength B_1 offers an estimate of the difference in local hyperfine fields experienced by a carrier pair.

The hyperfine broadening of the resonance must be seen in conjunction with the intensity of the microwave field, which itself contributes a time-varying magnetic field B_1. Once B_1 exceeds the difference in hyperfine field strengths acting on the two carriers, electron and hole resonances become indistinguishable and both carriers experience resonance. This situation is sketched in panels c, d: at low driving fields (microwave intensities), only one carrier spin precesses, leading to a spin-$^{1}/_{2}$ type resonance. As the B_1 amplitude is raised to exceed the difference in local hyperfine field of electron and hole, the two spins precess together. The nutation frequency between singlet and triplet configurations is doubled: spin beating occurs.

We recently described this effect in EDMR.[7b] Identical behavior is observable here using optical detection, as illustrated in panels e and f. Such ODMR is much simpler to perform than EDMR as it does not require the incorporation of conductive leads into the ESR resonator, which can potentially distort the local microwave field. A drop-cast sample mounted in a cryostat at 15 K was excited using a c.w. laser at 488 nm, and the PL was detected by a silicon photodiode. The inset of Figure 1e shows the dependence of the differential PL on the duration of the microwave pulse. As the pulse length is increased, the electron or hole spin precesses further, generating a triplet carrier pair from a singlet carrier pair, and vice versa. This precession leads to an oscillation in the singlet and triplet population density with pulse length, giving rise to Rabi flopping in the PL intensity. The curve can be accurately fitted by a single-frequency transient function.[8,9] The Fourier transformation (main panel of Figure 1e, black) of the time dependent data as well as a fit with two Fourier transformed transient functions (red, blue) and the respective sum of these (green) reveals only a single frequency component, as expected for a spin-$^{1}/_{2}$ resonance. At high microwave powers [panel f], the Rabi frequency increases (inset). In addition, now both the Fourier analysis of the data and the fit to both the time domain and frequency domain data reveal a distinct harmonic component to the resonance: spins precess either on their own or together.

The magnitude of the microwave field at which the beat oscillation signal dominates provides an estimate of the difference in hyperfine field experienced by electron and hole, $|\Delta B_{\mathrm{Hyp}}|$. This value can also be estimated by fitting to the resonance lines[7b] as long as hyperfine fields within the individual pairs are not correlated.[9] However, without a route to direct control of the hyperfine field, a model fit alone is not sufficient proof that the intrinsic spin properties really are dominated by nuclear fields: other broadening mechanisms such as spin−orbit coupling or dipolar interactions could also contribute. To conclusively probe for hyperfine effects, we compare conventional MEH-PPV to a deuterated compound in Figure 2. Here, only the polymer side groups are deuterated (panels a, b). The differential PL in panels c and d can be described by a superposition of two Gaussians, attributed to electron and hole carrier spin-$^{1}/_{2}$ resonances.[7b] As expected, the resonance is narrower for the deuterated compound with a smaller hyperfine coupling constant.[6a] From the line fits we extract $|\Delta B_{\mathrm{Hyp}}|$ = 1.36(1) mT [1.31(3) mT] for the hydrogenated [deuterated] sample. With such a small difference, it is difficult to confirm, based on line width change alone, that deuteration really influences $|\Delta B_{\mathrm{Hyp}}|$. However, the direct time-domain analysis of hyperfine-field-mediated spin beating, which is not prone to error by hyperfine field correlation between the two pair partners, provides clear support for the influence of deuteration.[9] Figure 2e, f plot the fractions of the numbers of spin pairs that produce beat oscillation signals (red) and pure spin-$^1/_2$ nutation signals (blue) for both materials, extracted from the Rabi-flopping curves [cf. Figure 1f]. The crossover point [1.38(10) mT hydrogenated; 1.15(8) mT deuterated; confidence level 95%] reveals a significant difference between the two materials. The fact that these values derived from the spin-beat measurements are systematically lower than those determined by the line shapes provides an indication of a correlation between the (hyperfine field-induced) distributions of Larmor precession frequencies of electron and hole.[9] This effect can be explained by the existence of a distinct subset of proton spins which influence the random hyperfine fields of both charge carriers within a given pair.

Deuteration of the polymer reduces the hyperfine field[6] so that electron and hole experience simultaneous resonance at lower microwave intensities. Thus, a sample in which line broadening is not dominated by hyperfine fields should display spin beating even at low microwave driving fields. As a next step, the entire backbone of the polymer should be deuterated, and the effect of symmetric versus asymmetric backbone substitution explored. Suffice to note that the present effect of deuteration (~20% change) is significantly weaker than expected for an isotropic system. A quantitative comparison of the hyperfine effects seen here and in the recent study by Nguyen et al.[6a] is not possible since exact charge carrier wave functions are not known in either one of the materials. In our study, the side groups were deuterated and not the backbone, whereas ref 6a reports deuteration of the backbone alone. The carriers appear to only weakly penetrate the side groups. Controlled deuteration thus offers a route to map the location and extent of the carrier wave function.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Discussion of the data analysis procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

lupton@physics.utah.edu; boehme@physics.utah.edu

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