Spin-dependent transitions of exciton precursor pairs in poly[2-methoxy-5-(20-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV)

S.-Y. Lee, S.-Y. Paik, D. R. McCamey and C. Boehme
Department of Physics and Astronomy, University of Utah, Salt Lake City, UT, 84112, USA

Observation of spin-beating of weakly coupled pairs

(a) B₀ field dependence of Fourier transformed spin Rabi nutation transients, FFT(N(t),B₀)
   (a) at B₀=0.55 mT, and 
   (b) at B₀=1.54 mT.

Solid and dashed curves are Rabi frequencies and Spin pair partners rotating together, causing beating, due to the strong B₀ field.

Ω = \sqrt{γ₁B₀} + (γ₂B₀ - 2g_{\text{iso}}) \Omega_{\text{b}} \Omega_{\text{bulk}} = \Omega_{\text{bulk}}

Strong agreement with the theoretical prediction for a weakly coupled [2] and disordered [3] spin ensemble is seen.

References


Conclusion

• The recombination model explains pODMR of MEH-PPV. Experiments indicate the system is comprised of weakly coupled, disordered pairs.
• Exciton precursor (polaron) pairs in MEH-PPV are weakly coupled via hyperfine coupling to surrounding hydrogen nuclei.
• Spin beating in MEH-PPV observed.
• The exciton precursor pairs can only be weakly exchange coupled since the beat frequency vanishes at low B₀ fields.

Introduction

Organic semiconductors are used for various optoelectronic devices including organic light emitting diodes, flat panel displays, solar cells and magnetic field sensors. Spin-dependent electronic transitions (especially recombination) are an important factor for the efficiency of these devices. In order to enhance our understanding of these processes we conducted pulsed Optically Detected Magnetic Resonance (pODMR) measurements on MEH-PPV.

Recombination in organic semiconductors

Recombination and dissociation processes occur via polaron pairs (excitonic precursor pairs). Weakly spin coupled singlet and triplet polaron pairs form due to Coulomb interaction. These pairs are two spin-½ systems which can dissociate spin-dependently (dᵣ, dₛ) into free charge carriers, and recombine (kᵣ,kₛ) into excitons. Spin-lattice relaxation (kₛ) between singlet and triplet pairs can therefore have an influence on conductivity and light emission. Magnetic resonance [1] allows us to change these processes experimentally and thus, to investigate their nature.

Apparatus for pODMR

Optically detected Rabi nutations

(a) ∆PL amplitude ∝ singlet to triplet change of the spin ensemble.
By integrating the transient for a fixed time following a microwave pulse of length τ, the Rabi nutation can be observed.
(b) Integrated PL changes as a function of B₀ and the excitation pulse length r.

Photoluminescence after resonant excitation

Change in Photoluminescence after a 128 μs pulse with B₀=0.55 mT
(a) Magnetic field (B₀) dependence of photoluminescence (PL) changes following a brief coherent microwave pulse – one can clearly observe a response at magnetic fields around B₀ = 345.5 mT.
(b) The B₀-dependence can be fit well with a double exponential function that is based on the pair model.
(c) The broad and narrow Gaussian peaks can be assigned to positive and negative polarons, respectively.