

Spin-dependent exciton formation rates in π -conjugated oligomers and polymers

M. Wohlgenannt^{a,*}, X.M. Jiang^b, Z.V. Vardeny^b

^aDepartment of Physics and Astronomy, University of Iowa, Iowa City, IA 52242-1479, USA

^bDepartment of Physics, University of Utah, 115 South 1400 East, Salt Lake City, UT 84112-0830, USA

Abstract

We have measured the ratio, $r = \sigma_S/\sigma_T$ of the formation cross section, of singlet (S) and triplet (T) excitons from polarons in π -conjugated oligomer and polymer films, using a spectroscopic/magnetic resonance technique. We show that exciton formation from separated polaron pairs in π -conjugated compounds is spin-dependent, specifically $r > 1$. Moreover, we discovered a universal relation between r and the conjugation length (CL): namely $r^{-1} \propto (\text{CL})^{-1}$.

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The efficiency of fluorescence-based organic light emitting diodes (OLED) is determined by the fraction of injected electrons (e) and holes (h) that recombine to form emissive spin-singlet excitons, rather than non-emissive triplet excitons. If the process by which these excitons form were spin-independent, then the maximum quantum efficiency, η_{\max} of OLEDs would be limited to 25% [1]. But recent reports have indicated that η_{\max} in OLEDs ranges between 22% and 63% [2–7]. We have previously showed that in OLEDs $\eta_{\max} = (1 + 3r^{-1})^{-1}$ [6]; thus the study of r in organic materials also provides information about η_{\max} in OLEDs.

Here, we discuss a spectroscopic/magnetic resonance technique based on photoinduced absorption (PA) and PA-detected magnetic resonance (PADMR) spectroscopies, which allows direct measurement of the ratio, $r = \sigma_S/\sigma_T$ of the formation cross section, σ of singlet (S) and triplet (T) excitons from oppositely charged polarons in films of π -conjugated materials, without the need to fabricate OLEDs. This allows us to study a large number of materials and examine the materials dependence of r . Once the material dependence of r is understood, this allows a priori selection of a π -conjugated material as the active layer for highly efficient OLEDs.

Our main result is the discovery of a universal material dependence of r , namely an approximately linear dependence of r^{-1} on the inverse conjugation length, CL^{-1} , irrespective of the chain backbone structure, side groups or film morphology.

*Corresponding author. Tel.: +1-319-353-1974; fax: +1-319-353-1115.

E-mail address: markus-wohlgenannt@uiowa.edu (M. Wohlgenannt).

Since r is directly related to the maximum possible electroluminescence quantum efficiency in OLEDs, our results indicate that polymers with long CL might be superior to small molecules for their use in OLEDs.

Our technique for measuring r uses both the PA and PADMR techniques. The PA technique has been widely used in π -conjugated materials for studying long-lived photoexcitations with PA bands at subgap energies [8,9]. Two light beams are used in PA; one excites the sample film and the other probes the modulated changes, ΔT in the optical transmission, T . For excitation we used an Ar^+ laser beam modulated with a chopper. An incandescent tungsten–halogen lamp and a variety of diffraction gratings, optical filters, and solid-state detectors were used to span the spectral range of probe photon energies between 0.3 and 3 eV. The PA spectrum, $\Delta\alpha$, was obtained by dividing $\Delta T/T$, where ΔT was measured by a phase sensitive technique, and $\Delta\alpha = -d^{-1}\Delta T/T$, where d is the film thickness.

The effect of spin-dependent recombination on the PA bands in the photomodulation spectrum was studied by the PADMR technique [10,11]. In this technique we measure the changes, δT , that are induced in ΔT by spin 1/2 magnetic resonance. δT is proportional to δN that is induced in the polaron density, N (see below). Two types of PADMR spectra are possible: the H-PADMR spectrum where δT is measured at a fixed probe wavelength, λ as the magnetic field H is scanned, and the λ -PADMR spectrum where δT is measured at a resonant H while λ is scanned. We note that the PADMR setup allows both PA and PADMR spectra to be measured under identical conditions, so that the fractional change $\delta T/\Delta T$ is obtained with high precision.

For illustration of our method we choose a soluble oligothiophene (12T, see Fig. 1(a), inset) and polymer material, namely methyl-substituted ladder-type poly-para-phenylene (mLPPP, see Fig. 2(a), inset). In Figs. 1(a) and 2(a) we show the PA spectra measured at 80 K. The assignment of the PA bands is by now well established: The PA bands labeled P_1 and P_2 are spectral signatures of polarons; both P^+ and P^- , T_1 is due to triplet exciton transitions.

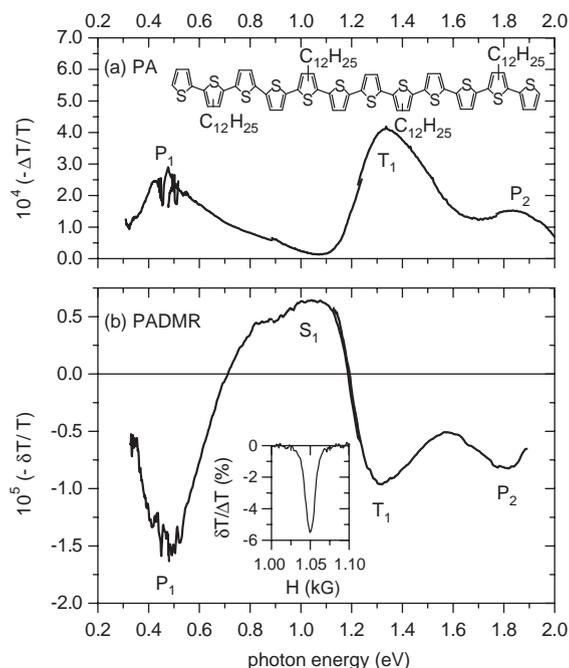


Fig. 1. (a) The PA spectrum of 12T (inset); (b) the PADMR spectrum at magnetic field $H = 1.05$ kG corresponding to $S = \frac{1}{2}$ resonance (see inset in (b)). Both spectra (a) and (b) show two bands (P_1 and P_2) due to polarons, T_1 due to triplet absorption. S_1 is assigned to singlets. The PA was measured at 80 K, excitation by the 488 nm Ar^+ laser line (500 mW); the PADMR spectrum was measured at 10 K.

In PA and PADMR charge transfer (CT) or recombination reactions occur between neighboring P^+ and P^- . The CT reaction rate R_P between spin-parallel pairs ($\uparrow\uparrow$, $\downarrow\downarrow$) is proportional to $2\sigma_T$, whereas the CT reaction rate R_{AP} between spin antiparallel pairs ($\uparrow\downarrow$, $\downarrow\uparrow$) is proportional to $(\sigma_S + \sigma_T)$, where the proportionality constant is the same in both cases [6]. Since (as will be shown below) $\sigma_S > \sigma_T$ in π -conjugated compounds, then $R_{AP} > R_P$, and spin-parallel pairs prevail at steady-state conditions. Under saturated magnetic resonance conditions the polaron densities with parallel and antiparallel spins become equal. Thus the PADMR measurements detect a reduction δN (which is proportional to δT) in the polaron density N (which is proportional to ΔT), since slowly recombining parallel pairs are converted to more efficiently recombining antiparallel pairs. At the same time the density of triplet excitons also

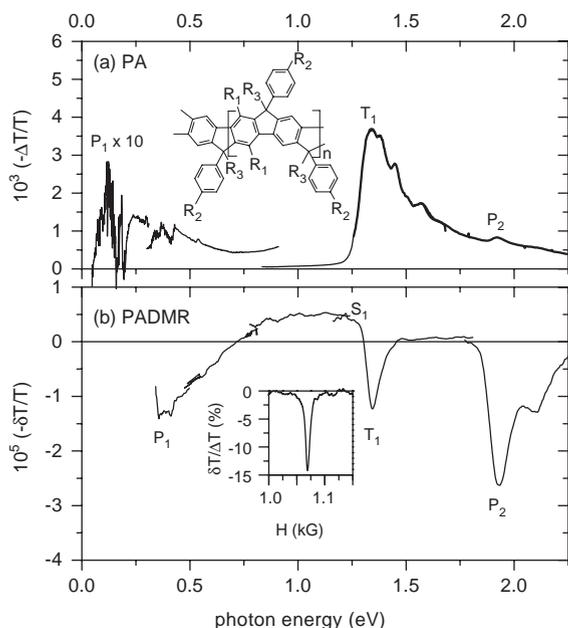


Fig. 2. (a) The PA spectrum of mLPPP (inset); (b) the PADMR spectrum at magnetic field $H = 1.06$ kG corresponding to $S = \frac{1}{2}$ resonance (see inset in (b)). Both spectra (a) and (b) show two bands (P_1 and P_2) due to polarons, T_1 due to triplet absorption. S_1 is assigned to singlets. The PA was measured at 80 K, excitation by the 457 nm Ar⁺ laser line (300 mW); the PADMR spectrum was measured at 10 K.

decreases as a result of the decrease in the density of parallel polaron pairs, whereas the singlet exciton density increases. For distant pair kinetics under saturation conditions we have [9] $\delta N/N = -(R_P - R_{AP})^2 / (R_P + R_{AP})^2$, which when using the proportionality relations above translates to [6]

$$r = \sigma_S / \sigma_T = \frac{1 + 3(\delta T / \Delta T)^{1/2}}{1 - (\delta T / \Delta T)^{1/2}}. \quad (1)$$

The spin $\frac{1}{2}$ PADMR spectra (Fig. 1(b) and 2(b)) clearly show the negative magnetic resonance response at P_1 , P_2 and T_1 , which are due to a reduction in the polaron and triplet density and confirm our assumption and directly prove $r > 1$. We assign the positive PA band in the λ -PADMR spectra (S_1) to excess singlet exciton absorption.

$\delta T / \Delta T$ was, respectively, determined for 12T (mLPPP) to be 5.5% (14%) at resonance (Fig. 1(b) and 2(b) inset); using Eq. (1) this translates to $r =$

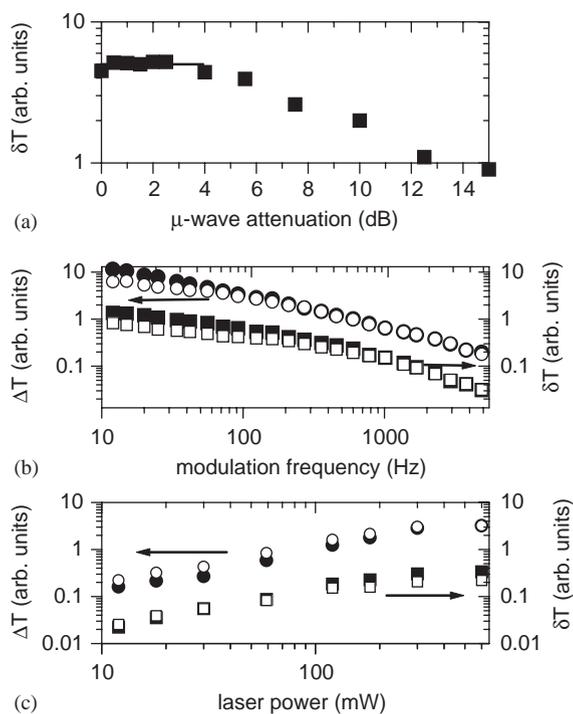


Fig. 3. (a) The dependence of δT in mLPPP on the μ -wave power shows that the magnetic resonance is saturated at the highest powers; (b) the modulation frequency and (c) laser intensity dependence of polaron PA (ΔT) and PADMR (δT) signals.

2.2 (3.5) indicating the material dependence of r . In Fig. 3 we report on several experimental checks performed on the mLPPP film. The condition of saturated magnetic resonance is fulfilled as is shown in Fig. 3(a), where the PADMR signal δT does not decrease initially upon reducing the μ -wave power. Also $\delta T / \Delta T$ does not depend on the parameters chosen for the experiment: Fig. 3(b) and (c) show that the ratio between δT and ΔT remains constant (within experimental error) over the range of modulation frequencies and laser powers achievable in our experiments. $\delta T / \Delta T$ is also independent of temperature, which we checked to a temperature up to 160 K.

We will now show our main result, namely the discovery that r increases with the CL, where $r \approx 1$ in small molecules. Oligomers have a well-defined CL equal to the chain-length; however polymers may have a very long chain-length. Nevertheless it is well established that the chemical conjugation

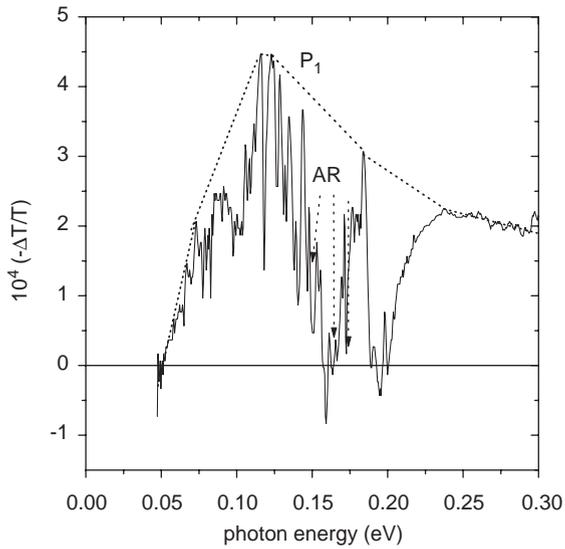


Fig. 4. The PA spectrum of mLPPP in the mid-IR range showing the P_1 band and antiresonances (AR).

and thus the extent of the π -electron wave functions are only defect-free over the much smaller CL [12]. We note that the P_1 band in the oligomer 12T (Fig. 1(a)) peaks at ≈ 0.47 eV, whereas the P_1 band in the polymer mLPPP (Fig. 2(a)) peaks at a much lower energy. Indeed it is necessary to use a Fourier transform infra-red (FTIR) spectrometer to completely cover the P_1 band. This spectrum is shown in Fig. 4, where several negative dips are superimposed on the P_1 PA spectrum, which have been identified as Fano-like antiresonances (AR) [13]. The inset to Fig. 5 shows the dependence of the lower absorption band P_1 of polarons vs. $1/CL$ for a variety of singly oxidized oligomers; the experimental values were taken from Ref. [14]. It is seen that the absorption band P_1 depends linearly on $1/CL$ irrespective of the π -conjugated backbone system. In fact, the dependence of P_1 on $1/CL$ is universal and therefore can be used to infer the average CL of many π -conjugated polymer films. We may therefore deduce the polymer CL in our studies from the P_1 peak energy in the PA spectrum.

In Fig. 5 we show our measurements of r in a large variety of π -conjugated materials vs. P_1 . Since P_1 is a linear function of $1/n$ we may actually

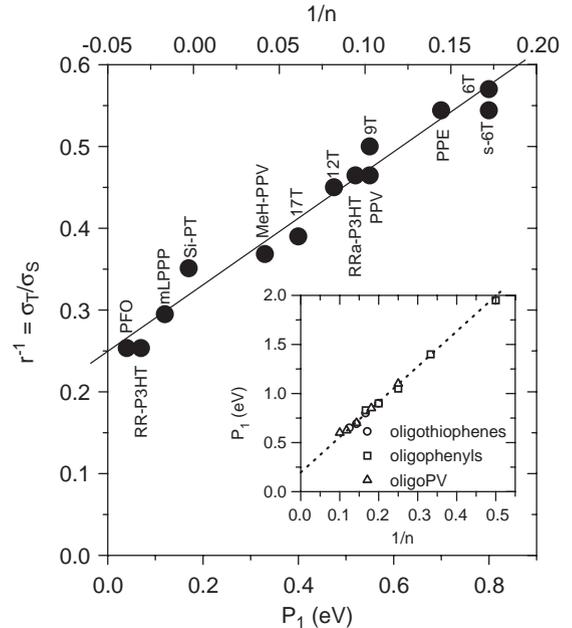


Fig. 5. The ratio $r^{-1} = \sigma_T/\sigma_S$ of spin-dependent exciton formation cross sections in various polymers and oligomers as a function of the peak photon energy of the P_1 transition (lower x -axis). r^{-1} is also shown as a function of the inverse conjugation length $1/n$ (upper x -axis), which was determined from P_1 by linear extrapolation (see inset). The line through the data points is a linear fit. The inset shows the peak photon energy of the low-energy polaron transition, P_1 in singly oxidized oligomers as a function of the inverse conjugation length (CL). The number n denotes a CL that corresponds to an oligothiophene with n rings. The experimental data was taken from Ref. [14]. The line through the data points is a linear fit.

plot r^{-1} vs $1/CL$ as is also shown in Fig. 5 (upper axis). Amazingly we discover a universal behavior of $r(CL)$, namely that r^{-1} depends linearly on $1/CL$ irrespective of the chain backbone structure, side groups or film morphology. We note that we encounter negative values for $1/CL$ for several polymers that have the lowest P_1 transitions (see Ref. [2] for a discussion).

In summary, we have measured the formation cross-section ratio, r of singlet and triplet excitons that are generated in π -conjugated materials from polaron pairs, using the PA and PADMR spectroscopies. We deduced r from the change in the spin-dependent recombination of polaron pairs in a wide variety of π -conjugated oligomer and

polymer films. Our main result is the discovery that r^{-1} is linearly proportional to the inverse CL in both polymers and oligomers.

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