Spin-dependent exciton formation rates in $\pi$-conjugated oligomers and polymers

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

$^a$Department of Physics and Astronomy, University of Iowa, Iowa City, IA 52242-1479, USA
$^b$Department of Physics, University of Utah, 115 South 1400 East, Salt Lake City, UT 84112-0830, USA

Abstract

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

© 2003 Elsevier B.V. All rights reserved.

PACS: 78.55.Kz; 72.20.Jv; 78.66.Qn

Keywords: $\pi$-conjugated compounds; Spin-dependent exciton formation; Optically detected magnetic resonance

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, $\eta_{\text{max}}$ of OLEDs would be limited to 25% [1]. But recent reports have indicated that $\eta_{\text{max}}$ in OLEDs ranges between 22% and 63% [2–7]. We have previously showed that in OLEDs $\eta_{\text{max}} = (1 + 3r^{-1})^{-1}$ [6]; thus the study of $r$ in organic materials also provides information about $\eta_{\text{max}}$ 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, $r = \sigma_\text{S}/\sigma_\text{T}$ of the formation cross section, $\sigma$ of singlet (S) and triplet (T) excitons from oppositely charged polarons in films of $\pi$-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 $\pi$-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, $\text{CL}^{-1}$, 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).

0921-4526/$-$see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2003.08.012
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 $\pi$-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, $\Delta T$ 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, $\Delta z$, was obtained by dividing $\Delta T/T$, where $\Delta T$ was measured by a phase sensitive technique, and $\Delta z = -d^{-1}\Delta T/T$, 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, $\Delta z$, that are induced in $\Delta T$ by spin 1/2 magnetic resonance. $\delta T$ is proportional to $\delta N$ that is induced in the polaron density, $N$ (see below). Two types of PADMR spectra are possible: the H-PADMR spectrum where $\delta T$ is measured at a fixed probe wavelength, $\lambda$ as the magnetic field $H$ is scanned, and the $\lambda$-PADMR spectrum where $\delta T$ is measured at a resonant $H$ while $\lambda$ 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.

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 $2\Delta T$, 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 $\pi$-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 $\delta N$ (which is proportional to $\delta T$) in the polaron density $N$ (which is proportional to $\Delta T$), since slowly recombining parallel pairs are converted to more efficiently recombining antiparallel pairs. At the same time the density of triplet excitons also
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 \[ \delta N/N = -(R_P - R_{AP})^2/(R_P + R_{AP})^2, \] which when using the proportionality relations above translates to \[ r = \frac{\sigma_S}{\sigma_T} = \frac{1 + 3(\delta T/\Delta T)^{1/2}}{1 - (\delta T/\Delta T)^{1/2}}. \] (1)

The spin ½ 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 \( \lambda \)-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 \( r = 2.2 \) (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 \( \delta T \) does not decrease initially upon reducing the \( \mu \)-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 \( \delta T \) and \( \Delta T \) 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...
and thus the extent of the $\pi$-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 $\approx 0.47$ 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. $1/\text{CL}$ 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 $1/\text{CL}$ irrespective of the $\pi$-conjugated backbone system. In fact, the dependence of $P_1$ on $1/\text{CL}$ is universal and therefore can be used to infer the average CL of many $\pi$-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 $\pi$-conjugated materials vs. $P_1$. Since $P_1$ is a linear function of $1/n$ we may actually plot $r^{-1}$ vs $1/\text{CL}$ as is also shown in Fig. 5 (upper axis). Amazingly we discover a universal behavior of $r(\text{CL})$, namely that $r^{-1}$ depends linearly on $1/\text{CL}$ irrespective of the chain backbone structure, side groups or film morphology. We note that we encounter negative values for $1/\text{CL}$ 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 $\pi$-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 $\pi$-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.

Acknowledgements

We thank Dr. Mazumdar for useful discussions and Drs. Janssen for supplying the oligothiophenes, Scherf for the mLPPP polymer, Bradley for the PFO polymer and Barton for the Si-bridged PT and PPE polymers; DeLong and Chinn for preparing the DOO-PPV and PPV polymers. The work at Utah was partially supported by DOE ER-45490 and NSF DMR 02-02790.

References