Conjugation-Length Dependence of Spin-Dependent Exciton Formation Rates in Π-Conjugated Oligomers and Polymers

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We have measured the ratio, $r = \sigma_S/\sigma_T$ of the formation cross section, σ of singlet and triplet excitons from polarons in π-conjugated oligomer and polymer films, using a spectroscopic technique we developed recently. We discovered a universal relation between r and the conjugation length (CL): r^{-1} depends linearly on CL^{-1}, irrespective of the chain structure. Since r is directly related to the maximum possible electroluminescence quantum efficiency in organic light emitting diodes (OLED), our results indicate that polymers have an advantage over small molecules in OLED applications.

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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 nonemissive 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]. The reason for this 25% limit is that two spin-1/2 particles combine to give four possible total spin states, three of which have total spin 1, and only one is a singlet. But recent reports have indicated that η_{max} in OLEDs ranges between 22% to 63% [2–6], and the reason for this variation is under investigation. In particular, the dependence of η_{max} on the conjugation length (CL) was recently tested by measuring η_{max} in a monomer and related polymer, and the possibility that η_{max} increases with the CL was advanced [6].

In OLEDs the quantum efficiency, η_{EL} for electroluminescence (EL), is $\eta_{EL} = \eta_1 \eta_2 \eta_3$, where η_1 is the singlet emission quantum efficiency, η_2 is the fraction of the total number of excitons that are singlets, and η_3 is the probability that the injected carriers form e-h pairs [7]. Both $\eta_1 < 1$ and $\eta_3 < 1$; hence $\eta_{EL} < \eta_2 = \eta_{max}$. We have recently developed [5] a spectroscopic 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. We have previously showed that in OLEDs $\eta_{max} = (1 + 3r^{-1})^{-1}$ [5]; thus the study of r in organic materials also provides information about η_{max}. Using this spectroscopic technique we could infer r [5], and consequently also η_{max}, in a variety of π-conjugated materials

without the need to fabricate OLEDs from the particular materials. In the previous publication [5] we found that r depends on the material optical gap in a systematic but nonmonotonic way, and the reason for this was investigated.

In the present work, we measured the dependence of r on the CL in a large variety of π-conjugated oligomer and polymer films using the spectroscopic method developed previously [5]. We indeed found that r increases with the CL (here we denote with the number n a CL corresponding to the length of an oligothiophene with n "rings"), where $r \approx 1$ in small molecules. Moreover, we discovered a universal dependence of r on n, namely an approximately linear dependence of r^{-1} on n^{-1}, irrespective of the chain backbone structure or side groups. This discovery clarifies the previous results [2–7] and indicates that polymers with long CL may be superior materials for OLEDs.

We have employed the PA and PADMR spectroscopies to measure r. The PA technique has been widely used in π-conjugated materials for studying long-lived photoexcitations with PA bands at subgap energies [8–10]. Two light beams are used in PA, one to excite the sample film and the other to probe 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 (silicon, germanium, and indium-antimonide) was used to span the probe photon energy, $\hbar\omega$ between 0.3 and 3 eV. The PA spectrum $(\Delta\alpha(\omega))$ 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 [11,12]. In this technique we measure the changes δT that are induced in ΔT by μ-wave absorption in magnetic field, H in resonance with the Zeeman split spin-1/2 sublevels of polarons. δT is proportional to δN that is induced in the polaron density, N due to changes in the polaron pair recombination rates. 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 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 [12 T; see Fig. 1(a), inset]. In Fig. 1(a) we show the PA spectrum of a 12 T film measured at 80 K. The PA bands labeled P_1 and P_2 are spectral signatures of polarons, both P^+ and P^-. The PA band marked T_1 is due to triplet exciton transitions [13]. In pristine 12 T film the polaron bands appear only as small shoulders to T_1. For the present measurements on oligomer films, where the po-

laron dynamics is essential we thus substantially enhanced the polaron bands in the PA spectrum by a photo-oxidation process known to increase the photogeneration yield with no effect on the P^+P^- recombination kinetics [14]. We thus expect that the obtained r will not be changed by the photo-oxidation process.

In PA under steady state excitation conditions charge-transfer (CT) 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 [5]. Since $\sigma_S > \sigma_T$ in π-conjugated compounds, then $R_{AP} > R_P$, and spin polarization of the recombining polaron pairs is built up over time, such that spin parallel pairs prevail at steady state conditions. Under saturated magnetic resonance conditions the Zeeman split sublevels become equally populated, so that the polaron pair densities with parallel and antiparallel spins are 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 decreases as a result of the decrease in the density of parallel polaron pairs. For distant pair kinetics under saturation conditions we have [10] $\delta N/N = -(R_P - R_{AP})^2/(R_P + R_{AP})^2$, which when using the proportionality relations above between R_P, R_{AP}, and σ_S and σ_T translates to [5]

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

Thus the combination of PA and spin-1/2 PADMR spectroscopies gives a direct measure of r.

The spin 1/2 PADMR spectrum of 12 T [Fig. 1(b)] clearly shows the negative magnetic resonance response at the PA bands P_1 and P_2, which are due to a reduction in the polaron density. In addition, we also see a negative response at the triplet band T_1, which confirms our assumption that $r > 1$. The resonant reduction of triplets should be compensated by an increase in the singlet exciton population, and thus an increase in the photoluminescence under magnetic resonance condition was measured [15]. Also we tentatively assign the positive PA band in the λ-PADMR spectrum around 1 eV to a singlet exciton absorption band caused by singlet excitons that result from the excess spin antiparallel polaron pairs created upon the μ-wave absorption. However, more work, especially in the ps time domain, has to be completed to confirm this assignment.

$\delta T/\Delta T$ was determined for 12 T to be 5.5% at resonance [Fig. 1(b), inset]; using Eq. (1) this translates to $r = 2.2$. Similar measurements were also completed for three other oligothiophenes, where r was also determined.
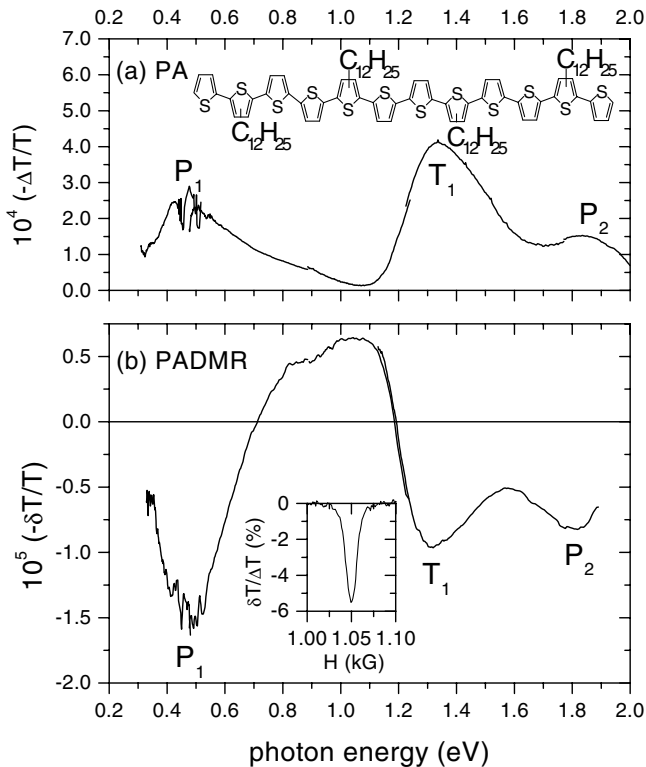

FIG. 1.   (a) The photoinduced absorption (PA) spectrum of 12 T, the molecular structure of which is shown in the inset; (b) the PA-detected magnetic resonance (PADMR) spectrum at magnetic field $H = 1.05$ kG corresponding to $S = 1/2$ resonance [see inset of (b)]. Both spectra (a) and (b) show two bands (P_1 and P_2) due to polarons, and one band (T_1) due to triplet absorption. 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.
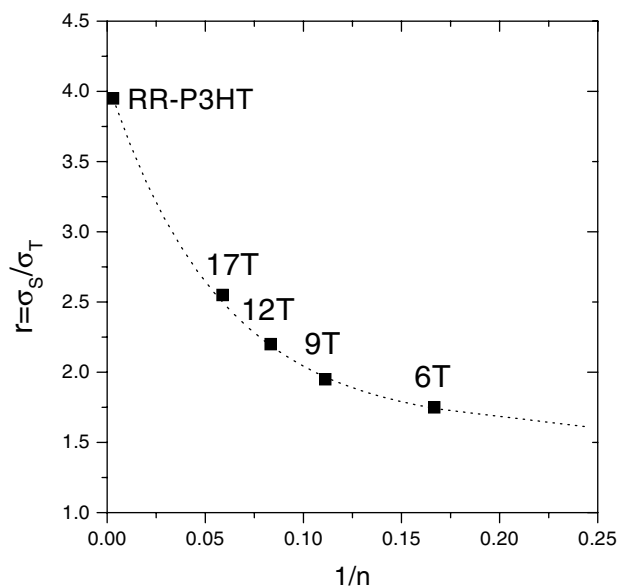
FIG. 2.   The ratio $r = \sigma_S/\sigma_T$ of spin-dependent exciton formation cross sections for four oligothiophenes and RR-P3HT as a function of $1/n$, where n is the number of rings in the oligomer; we assumed $1/n = 0$ for RR-P3HT (see text). The line through the data points is a guide to the eye.

The results are summarized in Fig. 2, where r for the oligothiophenes and regio-regular poly(3-hexylthiophene) [RR-P3HT] is plotted vs $1/n$, where n is the number of the five-member rings in the oligomer; we assumed $1/n = 0$ for RR-P3HT due to the lamellar morphology of this film [16,17]. From Fig. 2 it is seen that r decreases for short oligomers in a monotonous way, which by extrapolation reaches $r \approx 1$ for the monomers. However, we show below that our results are more general, where r decreases with the CL largely independent of the polymer backbone structure.

   For this purpose we first demonstrate a direct spectroscopic method that we found to obtain the CL of π-conjugated compounds. 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 π-electron wave functions are only defect-free over the much smaller CL [18]. We may therefore deduce the polymer CL by inspecting the optical transitions of intrachain electronic excitations that are constrained by the CL. The inset of Fig. 3 shows the dependence of the lower absorption band P_1 of polarons vs $1/n$ for a variety of singly oxidized oligomers; the experimental values were taken from the literature [19]. We emphasize that the inset of Fig. 3 contains data for many oligomers of different lengths as well as for three different π-conjugated systems, namely oligothiophenes, oligophenyls, and oligophenylene-vinylenes. It is seen that the absorption band P_1 depends linearly on $1/n$ irrespective of the π-conjugated backbone system. In fact, the dependence of P_1 on $1/n$ is universal and therefore can be used to infer the average CL of many π-conjugated
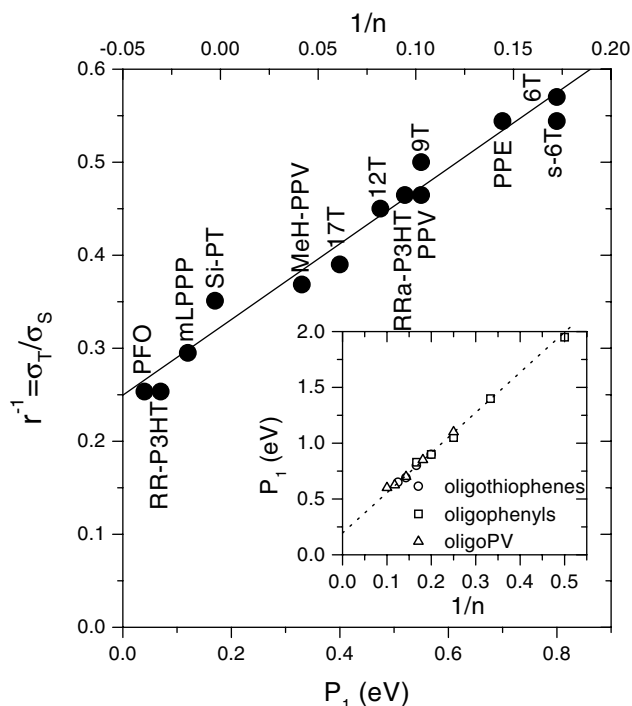

FIG. 3.   The ratio $r^{-1} = \sigma_T/\sigma_S$ of spin-dependent exciton formation cross sections in various polymers and oligomers as a function of the peak photon energy of the P_1 transition (lower x axis). r^{-1} is also shown as a function of the inverse conjugation length $1/n$ (upper x axis), 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 were taken from [19]. The line through the data points is a linear fit.

polymer films. We may therefore deduce the polymer CL in our studies from the P_1 peak energy in the PA spectrum.

   In order to show the universality of the function $r(n)$ in π-conjugated materials we replotted in Fig. 3 our results of r vs the optical gap [5], in the form of r^{-1} vs P_1; for completeness we have also included in this plot our present results in oligothiophenes. Since P_1 is a linear function of $1/n$ we may actually plot r^{-1} vs $1/n$ as is also shown in Fig. 3 (upper axis). Amazingly, we discover a universal behavior of $r(n)$, namely that r^{-1} depends linearly on $1/n$ irrespective of the chain backbone structure [20]. We note that, as is apparent from Fig. 3, we encounter negative values for $1/n$ for several polymers that have the lowest P_1 transitions (see [21] for a discussion).

   By linearly extrapolating the universal dependence of r^{-1} on n^{-1} we get $r \approx 1$ for $n \approx 2$ (≈ 7 Å [22]). We conclude therefore that exciton formation should become spin independent for oligomers of length ≈ 7 Å or less. This shows that $\sigma_S \approx \sigma_T$ for small molecules, in agreement with the previous results in AlQ$_3$ [2] and a monomer [6], which were deduced more directly from η_{EL} of OLEDs. Since η_{EL} is related to r, our results show that if all

other factors are equal, then the quantum yield of polymer OLEDs is larger than that of OLEDs based on small molecules.

We now advance a speculative explanation for the universal $r(n)$ dependence. First we note that the wavefunction extent of singlet excitons was measured to be as large as the CL [18]. On the contrary, triplet excitons are always very confined: An average separation of electron and hole in the triplet state of PPV was measured to be ≈ 3.2 Å [23]. Therefore the difference between the singlet and triplet exciton wave functions significantly decreases with $1/n$ [24], and this may explain the reason that r decreases with $1/n$. Moreover, we note that the measured r values are apparently film morphology independent. This indicates that the recombination processes to form singlet and triplet, respectively, depend on morphology in a similar way and that this dependence cancels out in measurements of the ratio r.

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 upon magnetic resonance of polaron pairs in a wide variety of π-conjugated oligomer and polymer films. In oligothiophenes we found that r increases with the chain length. Based on a universal relationship between the low-energy polaron absorption and the chain length in oligomers, we discover that r^{-1} is linearly proportional to the inverse CL in both polymers and oligomers.

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[20] We note that the measured r values for the photo-oxidized oligothiophene films follow the universal dependence on $1/n$ together with the pristine films. This indicates that the photo-oxidation process does not influence r.
[21] In the present scheme these polymers would therefore be assigned a conjugation-length "larger than infinity." This situation was actually also encountered previously [17] in RR-P3HT, which was shown to form two-dimensional lamellae [16,17]. It was indeed shown [17] that exceptionally low photon energy for the P_1 band results from a delocalization of polarons not only along the conjugated polymer backbone, but also in the two-dimensional lamellae. This suggests an interpretation of the "larger than infinite" CL as a situation where excitations extend not only along the backbone, but also along the perpendicular directions. It is, however, not entirely clear whether the linear extrapolation of the data presented in Fig. 3 inset to $1/n = 0$ is exactly valid. In any case polymers with low P_1 band correspond to highly conjugated systems.
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