

Optical studies of ordered and disordered α -sexithiophene films

P. A. Lane^a, M. Liess^b, Z. V. Vardeny^b, J. Partee^c, B. Uhlhorn^c, J. Shinar^c, M. Ibrahim^d, and A. J. Frank^d

^aDepartment of Physics, University of Sheffield, Sheffield S3 7RH, UK

^bDepartment of Physics, University of Utah, Salt Lake City, UT 84112

^cDepartment of Physics and Ames Laboratory, Iowa State University, Ames, IA 50011

^dNational Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401

ABSTRACT

We have studied α -sexithiophene (α -6T) films by photoinduced absorption (PA) and optically-detected magnetic resonance (ODMR). The PA of the disordered film is composed of two polaron PA bands and one bipolaron PA band, each with its own vibronic side bands. Measurements of an ordered film indicate that charge conjugation symmetry is broken and the polaron energy bands are shifted. The spin-1/2 ODMR of this film has a Gaussian lineshape with an 8 Gauss width. The PA of the ordered film shows no evidence for polarons. The bipolaron band is clearly split, indicating violation of charge conjugation symmetry. The ODMR of this film is significantly broader than that of the disordered film, which may be evidence for spin-spin interactions between paired charged excitations

Keywords: Optically detected magnetic resonance sexithiophene conjugated oligomer

1. INTRODUCTION

The novel optical and electronic properties of conjugated oligomers and polymers, together with the promise of device applications, have stimulated considerable studies of these materials. α -6T has drawn particular interest as organic thin-film transistors fabricated with α -6T as the active semiconductor have exhibited relatively high field-effect mobilities.¹ We have studied photoexcitation dynamics in α -6T by photoinduced absorption (PA) and optically detected magnetic resonance (ODMR). We observe quite dramatic effects of sample order on the optical properties of α -6T. Whereas the PA spectrum of a disordered α -6T film contains spectral features due to both singly- and doubly-charged excitations, only the latter are seen in ordered films. We also observed changes in photoexcitation dynamics as well as their magnetic resonance spectrum. Variations in the width of the ODMR spectra are indicative of exchange interactions between charged species.

PA spectroscopy uses standard phase-sensitive techniques with a modulated excitation source. The films were excited at 488 nm by an Ar⁺ laser and photoinduced changes in transmission of a probe beam are monitored by a photodiode. The normalized change in the transmission T is proportional to the photoexcitation density: $-\Delta T/T \propto n\sigma d$, where n is the photoexcitation density, σ the absorption cross-section, and d the sample thickness. The PA spectrum were corrected for sample photoluminescence (PL). In our ODMR measurements, the sample was mounted in a microwave cavity and excited at 488 nm by an Ar⁺ laser. Resonant absorption of microwaves modifies the excitation lifetime and leads to small changes δI in the PL intensity I (PLDMR) or δT in the transmission T (PADMR). The microwaves were amplitude modulated by a pin-switch diode and phase sensitive changes in I or T were detected by a silicon photodiode.

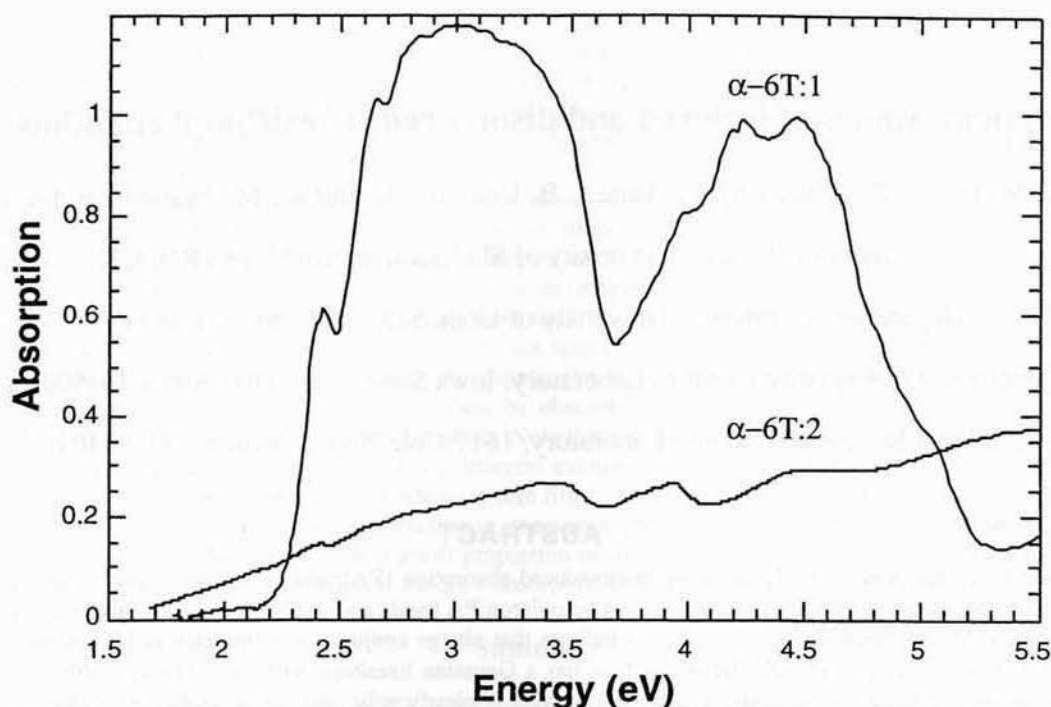


Figure 1. The absorption spectra of disordered (α -6T:1) and ordered (α -6T:2) films at 300K.

The absorption spectra of the two α -6T samples are shown in Figure 1. The first sample (α -6T:1) was deposited in vacuum onto a sapphire substrate cooled by liquid nitrogen (77 K); the absorption spectrum of this sample shows a clear vibronic structure, with local maxima at 2.42 and 2.65 eV, respectively, and maximum absorption at ≈ 3 eV. Higher energy absorption bands at 3.9 and 4.5 eV have been attributed to more localized transitions.² The low-energy vibronic structure is similar to that of isolated α -6T molecules,³ which suggests that α -6T:1 is disordered. The second sample (α -6T:2) was evaporated from CH_2Cl_2 solution onto a quartz substrate at approximately 310 K. This absorption spectrum of α -6T:2 exhibits virtually no vibronic structure and the dominant peak is blue-shifted to 3.4 eV. This spectrum was superimposed upon a broad background due to scattering. It has been shown that the absorption spectrum is quite sensitive to the deposition conditions. The use of heated substrates results in a more ordered sample with a similar effect on the absorption spectrum. The comparison of the absorption spectra lead us to conclude α -6T:2 is an ordered film.

2. STUDIES OF DISORDERED SEXITHIOPHENE

The PA spectrum of α -6T:1 measured with a modulation frequency of 200 Hz at temperatures between 10K and 300K is shown in Figure 2. The spectra were taken with the lockin amplifier set in phase with the laser modulation or in quadrature (90° out of phase). The spectrum taken at 10K contains three sharp bands at 0.80, 1.10, and 1.54 eV, each of which is accompanied by a high energy vibronic sideband. There are no changes in the PA spectrum as the temperature is raised from 10K to 80K, but the 1.10 eV band is absent above 100K. The in-phase spectra at 10K and 80K are bleached above 1.80 eV, whereas the 140K spectrum contains a feature which matches the vibronic structure of the PL spectrum. We attribute these features to changes in the PL intensity due to absorption of the probe beam. The PL intensity of the sample reached a maximum at about 120K. Above 120K, heating of the sample reduces the PL intensity and yields a positive offset to the PA spectrum. Below 120K, heating of the sample increases the PL intensity and yields a negative offset to the PA spectrum. This effect could be eliminated by carefully filtering the probe light. We also note that the relative intensity of the two polaron bands varies as the temperature varies. There is a curious negative PA (photobleaching) in the 300K spectrum which could not be attributed to effects on the PL. This may be due to a modulation of midgap defect states.

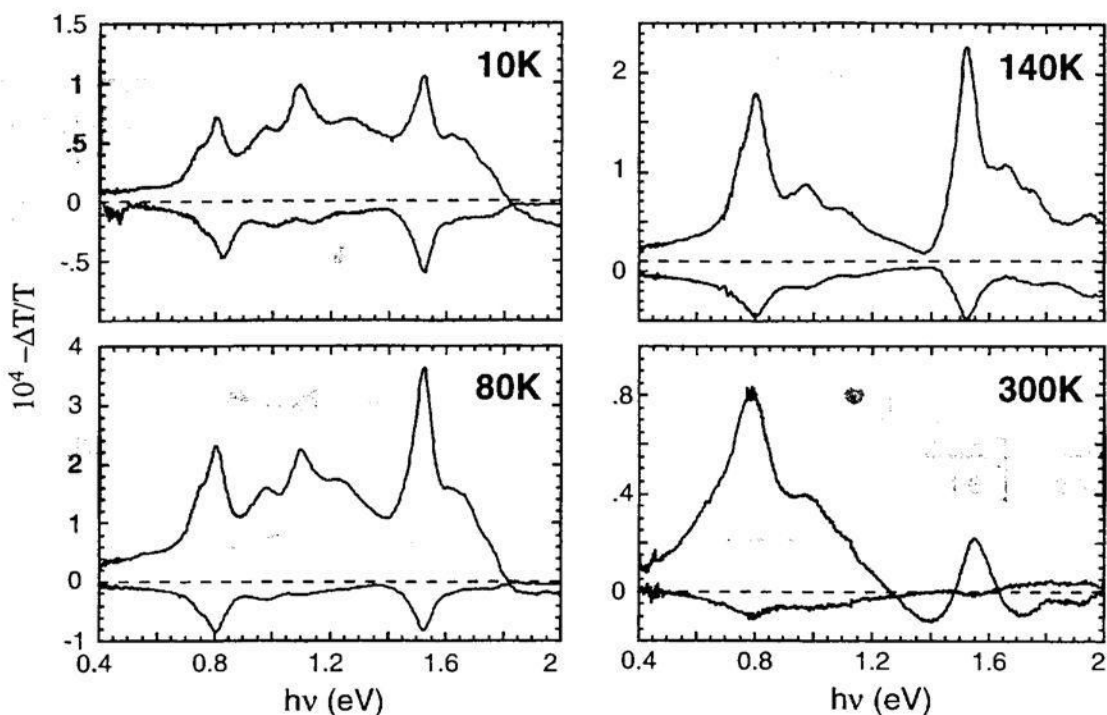


Figure 2. The PA spectrum of α -6T:1 at various temperatures. Both in-phase (top) and quadrature (bottom) spectra are shown.

Doping of α -6T in solution has shown that cation have doping induced absorption bands at 0.84 and 1.62 eV whereas dications have a single absorption band at 1.25 eV.⁴ Accounting for a shift in the absorption due to differences between film and solution, we assign the bands at 0.8 and 1.54 eV to cations and anions (polarons) and the band at 1.10 eV to dications and dianions (bipolarons). The polaron bands are labelled P_1 and P_2 and the bipolaron band is labelled BP_1 . The PA bands occur at slightly lower energies due to the differences between film and solution. Whereas the polaron bands can be easily seen in both the in-phase and quadrature PA spectra, the bipolaron band is much more prominent in the in-phase spectrum. These results are indicative of different excitation lifetimes for polarons and bipolarons. For square wave modulation and monomolecular recombination kinetics,⁵ the PA signals should have the following frequency dependence:

$$\text{In phase:} \quad \Delta T \propto 1 / \left[1 + (2\pi\nu_c\tau)^2 \right] \quad (1)$$

$$\text{Quadrature:} \quad \Delta T \propto 2\pi\nu_c\tau / \left[1 + (2\pi\nu_c\tau)^2 \right] \quad (2)$$

where τ is the photoexcitation lifetime and ν_c is the modulation frequency.

Figure 3 shows the dependence of the in-phase PA bands in α -6T:1, measured at the maxima of the various PA bands (0.80, 1.10, and 1.54 eV). The two polaron bands are correlated with one another, having virtually the same dynamics. In contrast, the bipolaron PA band at 1.1 eV is virtually flat from 10 Hz to 1000 Hz, indicating that polarons are longer lived than bipolarons in α -6T. Comparison of the polaron PA to this relationship shows that the polaron lifetimes have a broad distribution. In order to achieve the fit to the frequency dependence of the P_2 band, shown as a dashed line in Figure 2), lifetimes over a range of 20 μ s to 1 ms were required. In contrast, there is relatively little variation in bipolaron lifetimes. The fit to the BP_1 band required only lifetimes of 10 and 50 μ s. As polarons and bipolarons have been shown to be trapped by defects,⁶ these results suggest that polaron trap energies are much more broadly distributed than bipolaron trap energies. The slight decay of the BP_1 band as ν_c increases up to 1000 Hz may be due to contributions from the high-energy tail of the P_1 band.

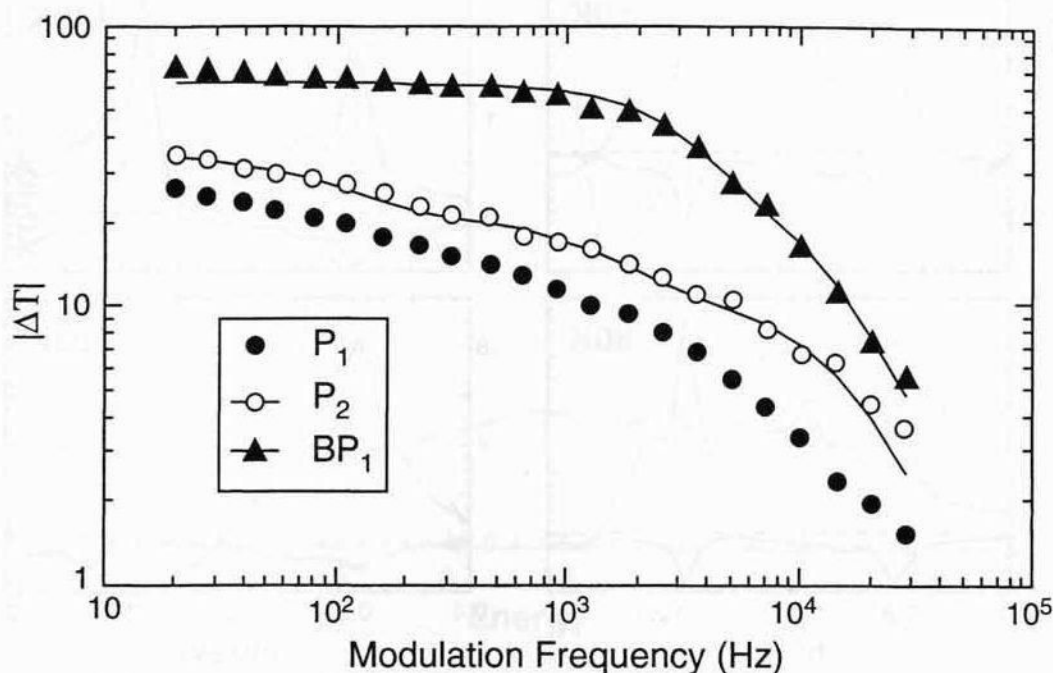


Figure 3. Modulation frequency of α -6T:1 PA, measured at the peaks of the polaron (P_1 and P_2) and bipolaron (BP_1) bands.

The H-PADMR spectrum of α -6T:1, shown in Figure 4(a), includes both a narrow resonance at $g \approx 2$ due to polarons with spin $S=1/2$ and a half-field ($\Delta m_s = 2$) resonance due to triplet excitons with spin $S=1$. By measuring the λ -PADMR spectra with H set to the maxima of the two bands, we were able to separately measure their PA spectra. The λ -PADMR of triplet excitons, shown in Fig. 4(b), consists of a single, broad band centered at 1.5 eV with a peaks at 1.4 and 1.55 eV. In contrast, the spin-1/2 λ -PADMR contains both PA-quenching and PA-enhancing features. The two sharp negative PADMR bands coincide in energy with the two polaron PA bands P_1 and P_2 . This is consistent with these two bands being due to spin-1/2 polarons and further indicates that magnetic resonance reduces the steady-state population of polarons. The presence of a broad, PA-enhancing PADMR between 1.0 and 1.45 eV suggests that magnetic resonance results in higher populations of bipolarons. In order to explain this result, we consider bipolaron generation and recombination processes:

Generation:



Recombination:



where S_0 is the ground state. As bipolarons are spinless, they can be formed only from like-charged polarons with antiparallel spins. Hence, this is a spin-dependent process which may be enhanced by magnetic resonance. While the recombination processes in Eqns. (4) and (5) are not spin-dependent, magnetic resonance reduces polaron populations which will in turn reduce the recombination rate of bipolarons. We conclude that microwave absorption due to magnetic resonance leads to increased steady-state bipolaron populations by either increasing their generation rate or reducing their recombination rate. The high-energy phonon sideband of P_1 is not seen in the λ -PADMR spectrum due to an opposite contribution from bipolarons.

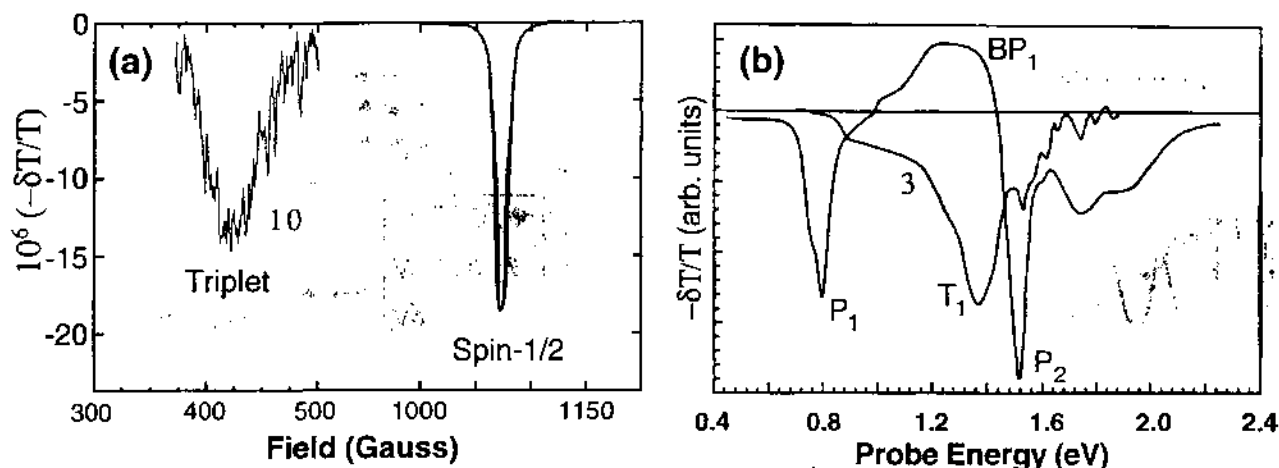


Figure 4. (a) H-PADMR spectrum of α -6T:1, measured at 10K with $\lambda=800$ nm. (b) λ -PADMR spectrum of α -6T:1, measured at 10K and 420 (dashed) and 1070 (solid) Gauss.

3. ORDERED SEXITHIOPHENE

Sample order has been shown to have dramatic effects on the absorption spectrum and carrier mobility in α -6T thin films. The PA spectrum is also sharply altered. Figure 5 shows the in-phase PA spectrum of α -6T:2, measured at 80K with a modulation frequency of 100 Hz. The PA spectrum is 20 times weaker than that of α -6T:1 and PA bands are evident at 0.70, 0.97, 1.07, and 1.20 eV. The features at 0.70 and 0.97 eV were observed in several different samples prepared by evaporation on a heated substrate, although their intensity relative to the bands at 1.07 and 1.20 eV varied. The PA spectrum above 1.4 eV closely resembles the PL spectrum (Figure 5, dashed line) and is assigned to modulation of the PL rather than PA. We measured the frequency-dependence of the PA to determine if the PA bands shown in Figure 5 are correlated. Fig. 6 shows the frequency dependence of the four PA bands in α -6T:2. The three bands at 0.92, 1.08, and 1.20 eV have the same frequency dependence and are hence correlated. All three bands are clearly due to bipolarons; the bipolaron PA band at 1.07 eV could be well fit by a single lifetime of $\tau=75$ μ s. Bipolaron lifetimes in ordered α -6T are thus roughly twice as long as in disordered α -6T.

The absence of any band corresponding to that at 0.97 eV in doped α -6T has led us to conclude⁴ that this band is related to charge conjugation symmetry breaking. This band is a consequence of slightly different transition energies for positive and negative bipolarons. The relation of this band to bipolarons also explains the varied structure of the PA spectra shown in Figure 1. At temperatures where bipolarons contribute to the PA spectrum (10 and 80K), the high energy vibronic sideband to the P_1 PA band and the low energy bipolaron band add together to produce an anomalously strong PA band at 0.97 eV. At 140 and 300K, where bipolarons are too short-lived to be observed by steady state PA, the band at 0.97 eV is roughly half as strong as the P_1 band. This matches the relative intensities of the P_2 band and its vibronic sideband. We note the presence of a shoulder on the low energy side of P_1 , which indicates that charge conjugation symmetry is also broken for polarons. The P_2 band has no low-energy sideband, indicating that the relative positions of the two midgap energy levels of a polaron are the same for both positive and negative polarons. The PA band at 0.70 eV in α -6T:2 has a frequency dependence fairly similar to that of polarons in α -6T:1. This band could be fit by adding together contributions of two lifetimes, $\tau_1=43$ μ s and $\tau_2=410$ μ s. Harrison *et al.*⁷ found that the P_1 band in an ordered α -6T film shifted to 0.71 eV and the P_2 band shifted to 1.70 eV. The PA spectrum shown in Figure 5 is in agreement with this assessment.

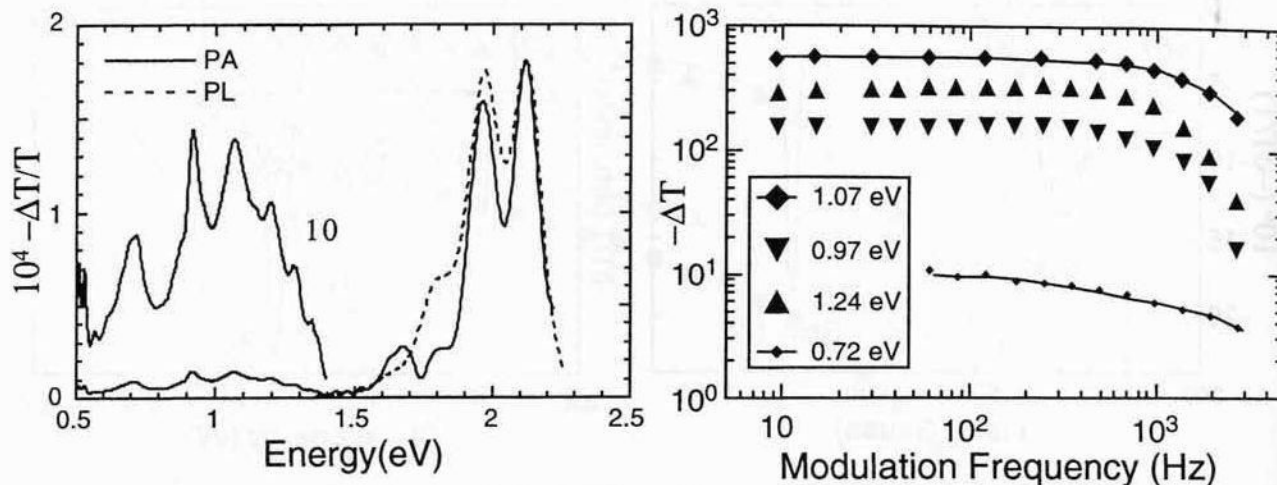


Figure 5. (a) The PA and PL spectra of α -6T:1 measured at 80K and with $\nu_c=200$ Hz. (b) Frequency dependence of PA in α -6T:2, measured at the peaks of the PA bands.

The S-Band and X-Band spin-1/2 PLDMR spectrum of α -6T:2 are shown in Figure 6(a). Allowing for a shift of the resonance due to the difference in the resonant frequencies, the two spectra are virtually the same. Surprisingly, the ordered film has a broader PLDMR spectrum than the disordered film, with a full-width at half maximum of 18 Gauss as opposed to 12 Gauss at the peak of the polaron H-PADMR band). We note that the width of the PADMR spectrum varied between 12 and 17 Gauss as the probe wavelength was varied. We consider several possible origins for the broadening of the ODMR spectrum in ordered α -6T. The width of the resonance is unaffected by the resonant field. If we were seeing the effects of a broader distribution of g -values, then the X-Band spectrum should be as much as three times broader than that measured at S-Band. Hyperfine interactions can like wise be disregarded as the samples were identical save for the deposition conditions. Both spin exchange and magnetic dipole interactions between spin-1/2 excitations can broaden the ODMR resonance.⁸ Hence, the resonance of paired photoexcitations such as bipolarons is significantly broader than the resonance of isolated excitations. We therefore suggest that the dominant long-lived photoexcitations in ordered α -6T films are paired.

The spin-1 PLDMR spectrum of α -6T:2 is shown in Figure 6(b). The spectrum is symmetric about the spin-1/2 resonance, with shoulders separated by 1160 Gauss and peaks separated by 532 Gauss. The full-field powder pattern of a triplet exciton has steps at $H = h\nu / g\beta \pm D$ and singularities at $H = h\nu / g\beta \pm (D - 3E) / 2$,⁹ where D and E are the zero-field splitting (ZFS) parameters. From the spectrum in Fig. 7(b), we calculate ZFS $D = 582$ Gauss and $E = 17$ Gauss. The ZFS are slightly larger than those of polythiophene ($D = 507$ Gauss and $E = 40$ Gauss); this difference is consistent with greater triplet delocalization in the polymer compared to the oligomer. Bennati *et al.*¹⁰ recently measured the ZFS of triplet states of a series of oligothiophenes and determined that the ZFS decrease as the reciprocal of the chain length ($D - D_\infty \propto 1/n$). As before, we measured the triplet PA spectrum by λ -PADMR spectroscopy. As the PA of α -6T:2 is quite weak, the higher energy portion of the λ -PADMR spectrum follows the PL spectrum (dashed line) due to PLDMR. After subtracting off the PL spectrum and dividing by the probe transmission, we find the triplet PA spectrum reaches its maximum intensity between 1.4 and 1.6 eV. The spin-1/2 λ -PADMR spectrum (not shown) above 1.7 eV also followed the PL spectrum, but the signal to noise ratio did not permit an unambiguous determination of the polaron PA spectrum.

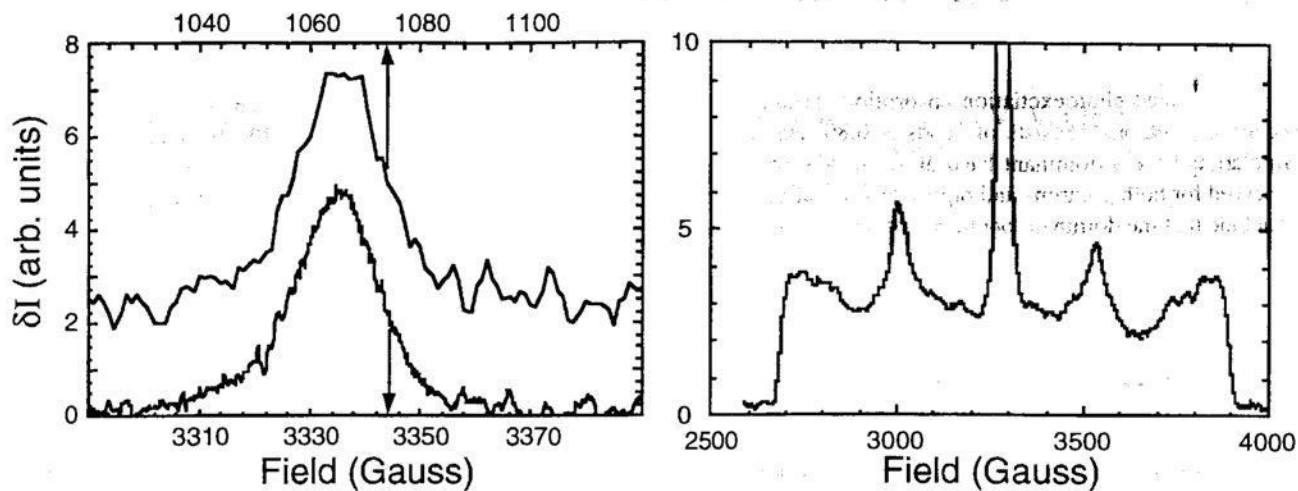


Figure 6. (a) Spin-1/2 PLDMR spectra of a-6T:2, measured at 2.99 and 9.35 GHz. (b) Spin-1 PLDMR spectrum of a-6T:2, measured at 9.35 GHz.

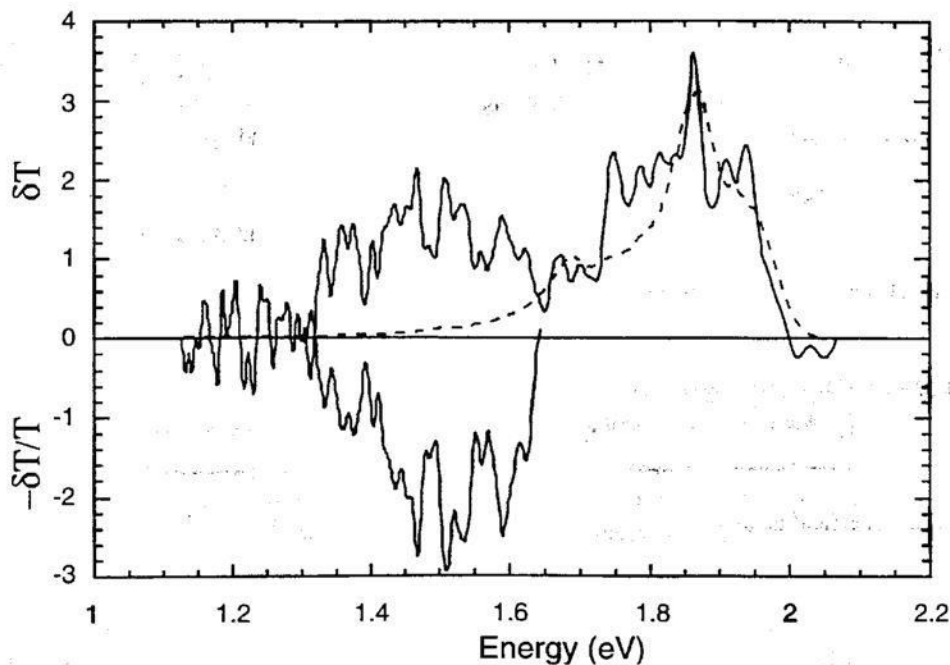


Figure 7. The PL (dashed line) and spin-1 λ -PADMR (solid line) spectra of α -6T:2, measured at $H=420$ Gauss. The normalized difference spectrum ($-\Delta T/T$) is shown in the bottom half of the figure.

CONCLUSIONS

We have studied photoexcitation absorption spectra and dynamics in ordered and disordered α -6T thin films. The absorption spectra of polarons consists of bands at 0.80 and 1.54 eV in disordered samples and 0.71 and 1.70 eV in ordered samples. Bipolarons have a dominant band at 1.10 eV in both kinds of samples. Charge conjugation symmetry violation has been observed for both polarons and bipolarons. Finally, spin pairing broadens the ODMR spectra. Based on this broadening, we conclude that the dominant photoexcitations in ordered α -6T thin films are paired species.

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Further author information -

P.A.L.: Email: p.a.lane@sheffield.ac.uk