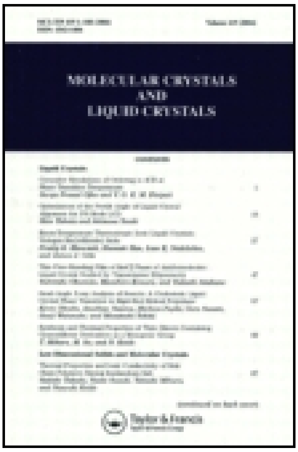

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: J. Shinar , A. V. Smith , P. A. Lane , K. Yoshino , Y. W. Ding & T. J. Barton (1994): UV-Excited Optically Detected Magnetic Resonance (UV-ODMR) Study of π-Conjugated Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 691-696

To link to this article: http://dx.doi.org/10.1080/10587259408039311

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 691–696
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UV-EXCITED OPTICALLY DETECTED MAGNETIC RESONANCE (UV-ODMR) STUDY OF π-CONJUGATED POLYMERS

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Abstract The photoluminescence (PL) and X-band ODMR of poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenyleneacetylene) (PPA), and polythiophene (PT) derivative films excited at $254 \leq \lambda_{ex} \leq 400$ nm is compared to those excited at 488 nm. In PPV and PT, but not in PPA, UV excitation yields a strong narrow PL-quenching ODMR in addition to the narrow PL-enhancing polaron resonance. In PPV and PT, the PL yield and the triplet exciton ODMR weaken at short λ_{ex}. The nature of the narrow resonance is discussed in relation to recombination of polarons, which may yield luminescent 1^1B_u singlet excitons but in any case eliminates them as nonradiative singlet and triplet exciton quenching centers. The UV-excited PL-quenching resonance is then discussed in relation to several scenarios, including geminate polaron recombination and spin-dependent decay of like-charged polarons into bipolarons. The behavior of PPA derivatives is suspected to result from structural defects which trap the charged excitations into polarons.

INTRODUCTION

Several optically detected magnetic resonance (ODMR) studies have yielded striking insight into the dynamics of photo- and electro-induced excitations in π-conjugated polymers and LEDs based on them.[1-10] The X-band PL-ODMR, excited at $\lambda_{ex} \geq 488$ nm, has invariably yielded three resonances. (i) A narrow ($12 \leq \Delta H_{1/2} \leq 20$ G) PL-enhancing resonance was attributed to magnetic resonance enhancement of singlet exciton generation by fusion of positive (p^+) and negative (p^-) polarons. (ii) Broad full- and (iii) half-field triplet powder patterns were attributed to similar generation of singlets from triplet-triplet exciton fusion. Other recent studies, however, are providing mounting evidence for the roles of bound p^+ - p^- pairs,[11,12] defect-stabilized polarons,[13,14] and the various antisymmetric 1^1B_u and 1^3B_u and symmetric m^1A_g and 1^3A_g singlet and triplet excitons, resp.[15] In particular, it appears that visible photoexcitation primarily generates the "rigid" 1^1B_u singlet exciton. In an effort to study higher-gap polymers and search for a distinct ODMR signature of other excitations, possibly including electron- and hole-like, we have measured the resonances of various polymers excited at bands around $\lambda_{ex} \sim 250$, 308, and 353 nm, and compared the spectra to those obtained at $\lambda_{ex} = 488$ nm. The polymer films included poly(*p*-phenylenevinylene) (PPV), the dialkoxy derivatives of PPV and poly(*p*-phenyleneacetylene) (PPA), and poly(3-hexylthiophene) (P3HT). The striking results are a strong UV-induced narrow PL-***quenching*** resonance in PPVs and P3HT, but not in PPAs, and the drastic weakening of the PL and the triplet exciton ODMR at short λ_{ex}. They strongly suggest that in the relatively ordered PPV and P3DT UV excitation leads to other excitations, probably including neutral states, charged geminate and nongeminate polaron pairs, and bipolarons. The PL-quenching resonance is then discussed in relation to several scenarios, including nonradiative quenching of excitons and polarons by bipolarons and geminate polaron recombination, to yield the PL-quenching resonance. The nature of the PL-enhancing polaron resonance is also reexamined, as p^+ - p^- recombination eliminates them as nonradiative singlet exciton quenching centers,[16,17] and they may also combine to form radiative singlet excitons. The weakness of the triplet exciton ODMR at short λ_{ex} suggests that the $1^1B_u \dashrightarrow 1^3A_g$ intersystem crossing is the major triplet exciton generation channel.

EXPERIMENTAL PROCEDURE

The syntheses of P3DT and the derivatives of PPV and PPA derivatives has been previously described.[10,18,19] Visible excitation of the ODMR was obtained from the 488 nm line of an Ar$^+$ laser, as described elsewhere.[1-4] The filtered output from an Oriel short-arc Hg lamp was reflected from mirrors blazed at 248, 308, and 353 nm to selectively excite the samples at these bands.

RESULTS

The PL spectra of PPV and P3HT films were measured at $\lambda_{ex} = 488$, ~353, ~308, and ~250 nm. The spectra are not shown, as the peak emission wavelengths and the widths of the emission were generally λ_{ex}-independent and similar to those published previously.[1,2] The PL yields, however, dramatically decreased with decreasing λ_{ex}, and at $\lambda_{ex} = 250$ nm they decreased to 4% and 10%, resp., of their values at $\lambda_{ex} = 488$ nm.

Figures 1 - 3 display the X-band narrow total PL-ODMR of DHOPPV, P3HT, and 2,5-dibutoxy PPA (DBOPPA) films, resp., excited at the noted wavelengths at 15 K. The solid lines are the sums of the Gaussians components shown as dotted lines. The PL-enhancing polaron resonance obtained by visible excitation has been extensively described and discussed.[1-4,7-10] The agreement between the observed lineshape and the sums of the Gaussian components is clearly excellent in all of these cases. The PL-quenching resonances at $\lambda_{ex} \approx 353$ and 308 nm in DHOPPV (Fig. 1), the presence of both enhancing and

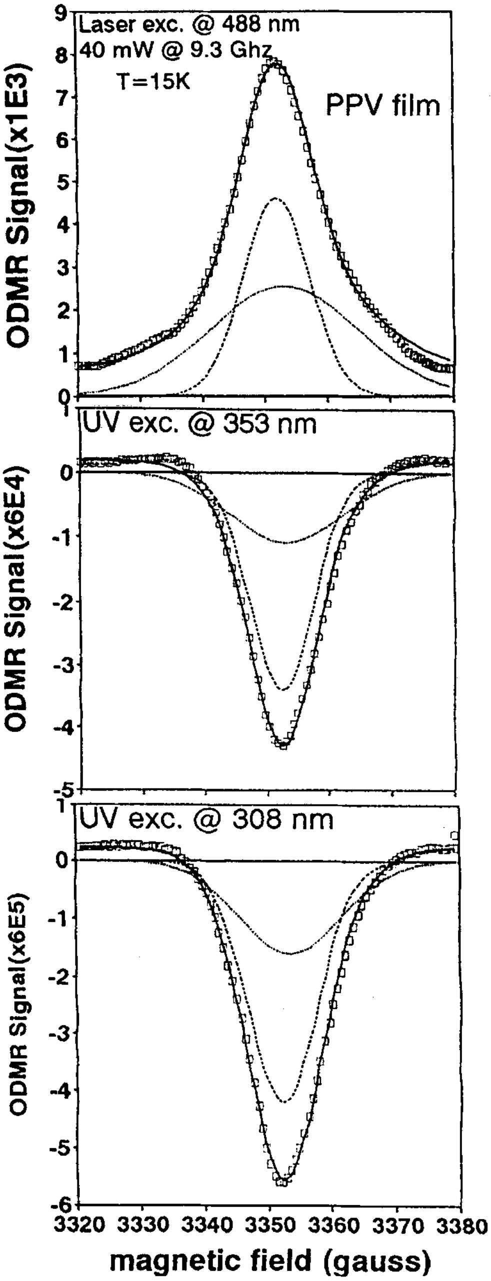

Figure 1. *X-band narrow total PL-ODMR of 2,5- dihexoxy PPV films excited at (a) 488 nm and at bands about (b) 353 and (c) 308 nm, at 15 K. The solid lines are the sums of the Gaussians components shown as dotted lines.*

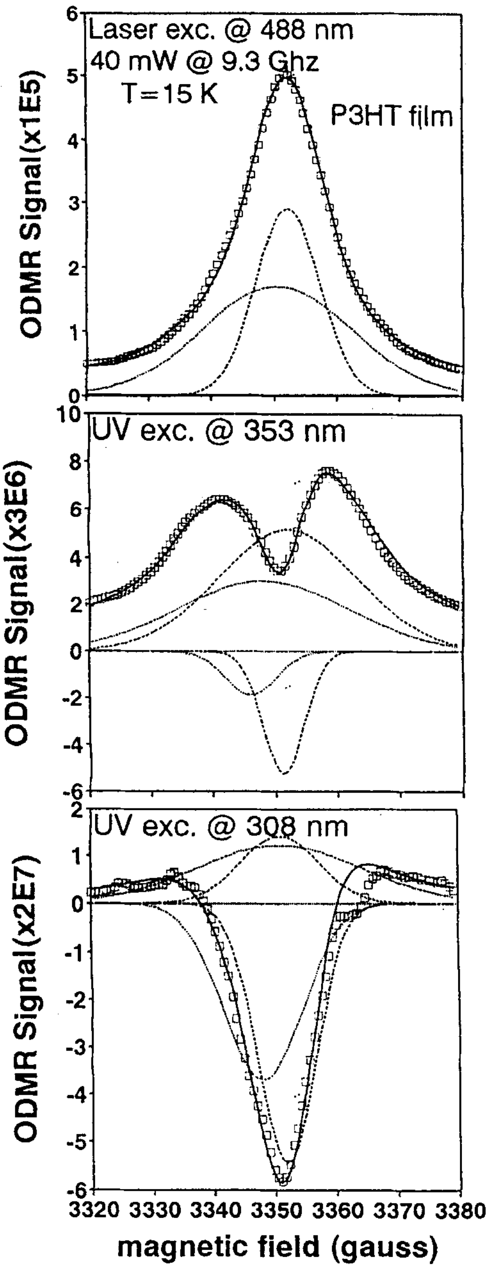

Figure 2. *X-band narrow total PL-ODMR of poly(3-hexylthiophene) films excited at (a) 488 nm and at bands about (b) 353 and (c) 308 nm, at 15 K. The solid lines are the sums of the Gaussian components shown as dotted lines. Excitation at 250 nm yielded a very weak PL and no detectable ODMR.*

quenching components in P3HT (Fig. 2), and the absence of a quenching resonance in PPA (Fig. 3) are obviously the most striking results.

Figures 4(a) - 4(e) display the full-field triplet exciton ODMR of P3HT films at $\lambda_{ex} \approx 308$ nm, PPV films at $\lambda_{ex} \approx 353$ nm, polyethylene blends of DHOPPV at $\lambda_{ex} \approx 353$ nm, and DHOPPV film at $\lambda_{ex} \approx 308$ and 250 nm, resp. Several observations are noteworthy: (i) The λ_{ex}-dependence of the intensities of the narrow PL-enhancing, the narrow PL-quenching, and the triplet exciton powder pattern ODMR are all different from each other. (ii) The triplet exciton pattern weakens with decreasing λ_{ex}. Thus, in P3HT it is very weak at $\lambda_{ex} \approx 353$ nm and undetectable at $\lambda_{ex} \leq 308$; in PPV it is still detectable, but barely, at $\lambda_{ex} \approx 250$ nm. (iii) The shapes of the triplet patterns in PPV at $\lambda_{ex} \approx 353$ nm (Fig. 4(b)) and in DHOPPV (Figs. 4(d) and 4(e)) indicate that the triplets are nearly axially symmetric (the zero field splitting parameter $E \approx 0$).

DISCUSSION AND CONCLUDING REMARKS

The narrow PL-enhancing resonance previously obtained and studied by visible excitation was attributed to magnetic resonance enhancement of singlet exciton generation by nongeminate p^+ - p^- fusion.[1-4, 7-10] However, the narrow PL-quenching resonance observed by UV excitation is clearly indicative of a different process. In searching for an alternative model, we consider several processes: Polarons and bipolarons are believed to be efficient singlet exciton quenching centers.[7,17] The PL-enhancing resonance results from spin-dependent nongeminate p^+ - p^- recombination, but it may enhance the PL by both generating 1^1B_u singlet excitons, and by removing the polarons as nonradiative singlet quenching centers. Several scenarios should be considered in discussing the PL-quenching resonance observed by UV excitation:

(i) The UV photogenerated excitations probably include high-energy neutral species as well as charged geminate polaron pairs and fully separated polarons. The high-energy singlets can rapidly decay into the 1^1B_u singlet exciton, providing the source of the geminate luminescence. Separated charges, however, may decay into long-lived spinless bipolarons.[7-10] The spin-dependent bipolaron formation would then reduce the rate of polaron fusion into the emitting 1^1B_u excitons and reduce the PL. Long-lived bipolarons would also quench other singlet excitons before they decay, probably nonradiatively, by capturing another polaron. This mechanism is believed to account for the electroluminescence (EL)-quenching EL-detected magnetic resonance exhibited by PPV- and PPA-based LEDs.[7-10] However, it fails to explain the absence of the PL-quenching resonance in PPA. This polymer is believed to contain a high density of structural defects in that system, which could rapidly relax and stabilize the various charged excitations into polaron states.

(ii) The enhanced generation of geminate polaron pairs rather than 1^1B_u excitons at short λ_{ex} could also explain the PL-quenching resonance: As these are spin-correlated but spin-uncoupled, magnetic resonance conditions decrease their spin correlation and reduce their fusion into the emitting 1^1B_u excitons.

(iii) The role of polarons and bipolarons as nonradiative singlet exciton quenching centers

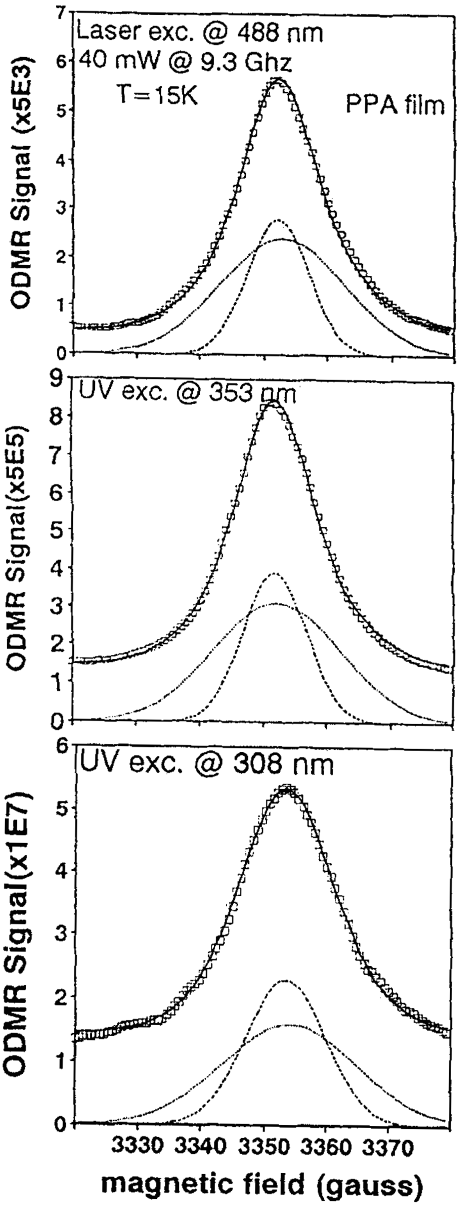

Figure 3. *X-band narrow total PL-ODMR of 2,5-dibutoxy PPA films excited at (a) 488 nm and at bands about (b) 353 and (c) 308 nm, at 15 K. The solid lines are the sums of the Gaussians components shown as dotted lines.*

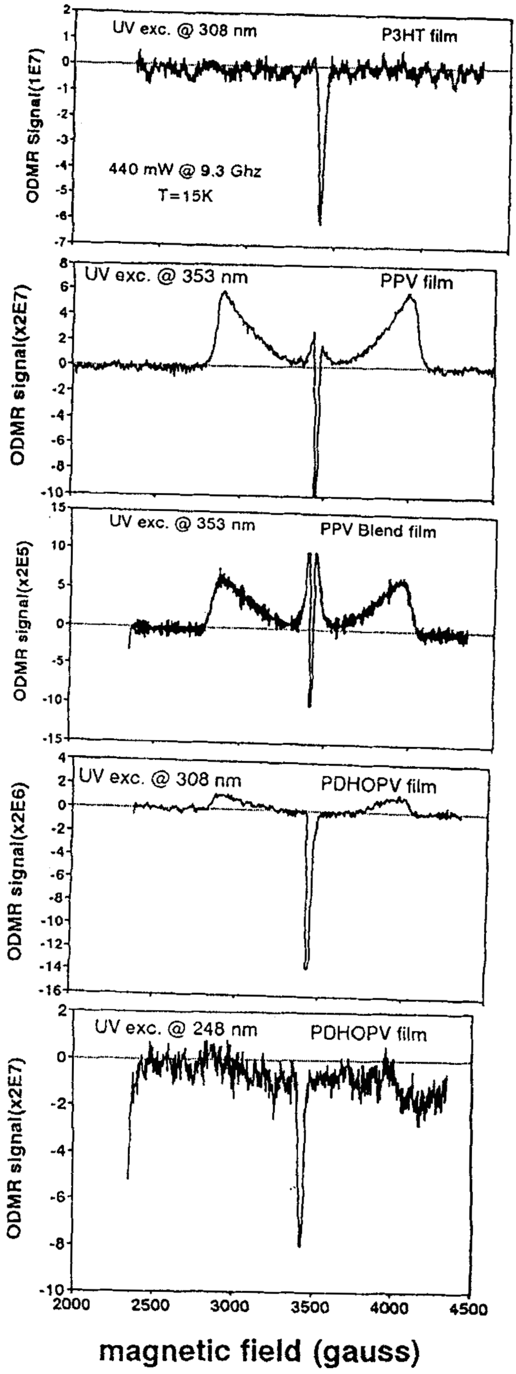

Figure 4. *Full-field X-band total PL-ODMR of (a) poly(3-hexylthiophene) films at $\lambda_{ex} \approx 308$ nm; (b) PPV films and (c) 2,5-dihexoxy PPV blends at $\lambda_{ex} \approx 353$ nm; 2,5-dihexoxy PPV film at λ_{ex} of (d) ~308 nm and (e) ~250 nm.*

also provides a simple explanation for the strong quenching of the PL by doping, which generates stable polaron and bipolaron states on the chains.

If the 1^1B_u --> 1^3B_u intersystem crossing is the major triplet exciton generation mechanism, the drastic reduction in the intensity of the triplet exciton resonance may be coupled to the strong reduction in the PL intensity. While visible photoexcitation directly produces geminate luminescent 1^1B_u excitons, UV excitation generates higher-energy states, which relax to the 1^1B_u state at a much lower rate.

Finally, the scenario in which defect-stabilized polarons and bipolarons are important nonradiative quenching centers of charge carriers in LEDs may provide striking insight into their performance and stability. If this picture is vindicated, then the possibility that the nonradiative recombination of the carriers with polarons and bipolarons generates defects in a mechanism similar to the Staebler-Wronski effect in hydrogenated amorphous Si should be considered.[20]

ACKNOWLEDGEMENTS

JS is grateful to Prof. Z. V. Vardeny for many valuable discussions. Ames Laboratory is operated by Iowa State University for the US Department of Energy under contract W-7405-Eng-82. This work was supported by NSF grant DMR-9202981.

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