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Photoexcitation spectroscopy of polythiophene

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Radiative recombination in polythiophene is studied by cw photoluminescence and photoinduced absorption spectroscopies and by photoluminescence-detected magnetic resonance. The fast-recombination centers are assigned to intrachain excitons in defect-free chains, while the slow recombination is due to intrachain excitons bound to spin-$\frac{1}{2}$ defects.

INTRODUCTION

Heterocyclic polymers such as polypyrrole and polythiophene with five-membered rings containing a N-H group or a sulfur atom, respectively, are of recent considerable interest. They represent a class of conjugated polymers with nondegenerate ground-state symmetry, leading thus to a finite confinement potential.[1] It was suggested that photoexcited electron-hole (e-h) pairs in such nondegenerate polymers quickly recombine because of the confinement potential which prevents their dissociation.[2] The first confirmation of this idea was observed in *cis*-$(\mathrm{CH})_x$:[2] Photocarrier recombination is very fast (less than 9 psec)[3] and no long-lived *cis*-related charge photoexcitations could be observed.[4] In other polymers with nondegenerate ground states which contain native defects, disorder, or amorphous character, or have a larger interchain coupling, there may exist other recombination channels which are quite different from those predicted by theory.[1,2,5] In particular, the recombination slows down under the following circumstances: (i) crossing to a triplet manifold, (ii) photogeneration of interchain excitons, and (iii) excitons bound to various native defects.

Neutral polythiophene (PT) which is stabilized in a single backbone geometry by the sulfur atom is an ideal candidate to study the recombination channels in a conjugated polymer with nondegenerate ground-state symmetry. Native spin-$\frac{1}{2}$ defects exist in PT and were measured by ESR[6] and by spin-echo modulation.[7] Also, long-lived ($\sim 10^{-2}$ sec) photocarriers were detected in neutral PT by the photoinduced absorption (PA) technique.[8] These results indicate that some of the above-mentioned mechanisms responsible for the slow recombination of the photoexcited e-h pairs are operative in PT.

In this Rapid Communication we report our study of the cw photoluminescence (PL) in PT. The PL spectrum and its excitation profile were measured and compared with the excitation profile for charge photocarriers measured by PA. We found that in addition to free intrachain excitons, there are also excitons bound to native defects. We have successfully studied, for what we believe to be the first time in conducting polymers, the PL optically detected magnetic resonance (ODMR) in PT. The PL-related defects could thus be identified as the same spin-$\frac{1}{2}$ defects which show up in ESR and in light-induced ESR measurements as well.[6] We also find it unlikely that triplet states are the cause for the slow PL recombination.

PHOTOLUMINESCENCE SPECTROSCOPY

The cw PL spectrum and its excitation profile were measured with a dye laser pumped by an Ar^+ laser. The emitted light was dispersed by a monochromator and detected by a Si detector and a lock-in amplifier. The PL spectra were corrected for the grating and detector responses but were not corrected for reabsorption in the sample. The PT samples were pressed KBr pellets[6] containing approximately 0.25 wt.% PT powder (obtained by condensation polymerization of 2, 5-di-iodothiophen). PL spectra for electrochemically prepared films were previously reported;[9,10] in our study, similar PL results were obtained for both types of samples.

Figure 1 shows the photoluminescence and optical absorption spectra of neutral PT. The absorption spectrum $\alpha(\omega)$ consists of a temperature-independent broadband which peaks at around 2.6 eV. The PL spectrum, on the other hand, is strongly temperature dependent and consists of several phonon sidebands superimposed on a much broader PL band (full width at half maximum of $\sim$0.3 eV). At 20 K, four well-defined equally spaced phonon sidebands at 1.95, 1.77, 1.59, and 1.41 are observed. At 300 K the overtones become less sharply defined and are shifted upward by about 30 meV. This energy shift rules out resonant Raman scattering (RRS) as the underlying mechanism for the phonon sidebands, which is the case in *cis*-$(\mathrm{CH})_x$.[2] The energy separation of the phonon sidebands in the PL spectrum is 0.18 eV, which is nearly equal to the strongest line observed in RRS.[11] This line has been identified as the carbon-carbon stretching mode and it is

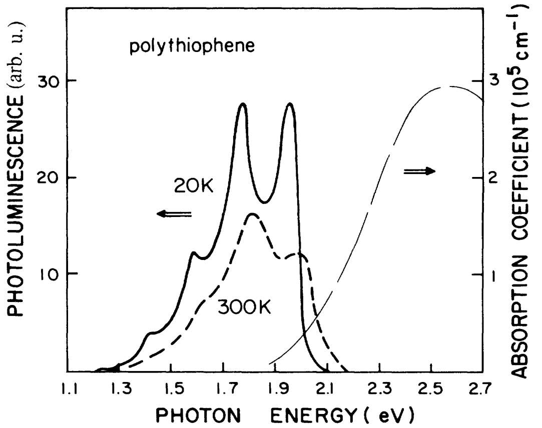

FIG. 1. Photoluminescence spectra at 20 and 300 K. The right-hand scale shows $\alpha(\omega)$ for comparison.

the mode with the strongest electron-phonon coupling in the PT backbone.

We note that the ultrafast PL spectrum measured in the picosecond regime by Wong *et al.*[10] shows only one broadband in contrast to the clear phonon sideband structure in the cw PL observed here. To further investigate the origin of the PL centers we have studied the PL excitation profile (denoted hereafter EXPL). The EXPL at 20 K measured for the PL emission at 1.83 eV is shown in Fig. 2. The EXPL abruptly increases at 1.95 eV, well below the one-dimensional (1D) gap at 2.2 eV (as deduced from the RRS analysis[11]) or the interband transition maximum at 2.6 eV, and remains constant thereafter. Vibrational overtones are not observed in the EXPL spectrum, indicating that the phonon sidebands seen in the PL spectrum (Fig. 1) are not due to internal vibrations of a point defect with a strong electron-phonon coupling. Moreover, the 1.95-eV onset *coincides* with the zeroth-order PL emission in Fig. 1, thus ruling out any Stokes shift.[9] We therefore identify the 1.95-eV energy as an exciton level. The difference between the 1D gap at 2.1–2.3 eV (Ref. 11) and the exciton level at 1.95 eV is interpreted as the binding energy of the exciton.

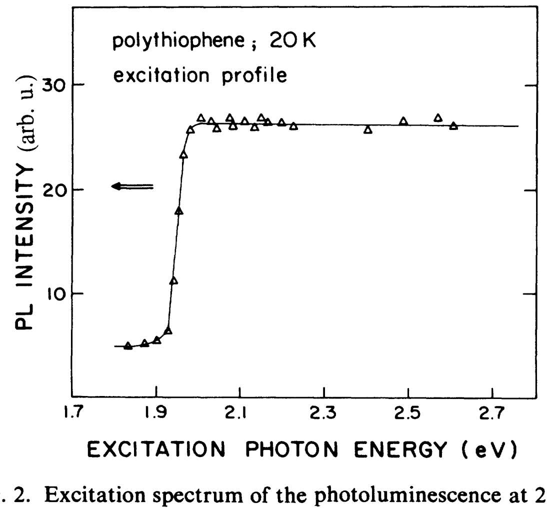

FIG. 2. Excitation spectrum of the photoluminescence at 20 K.

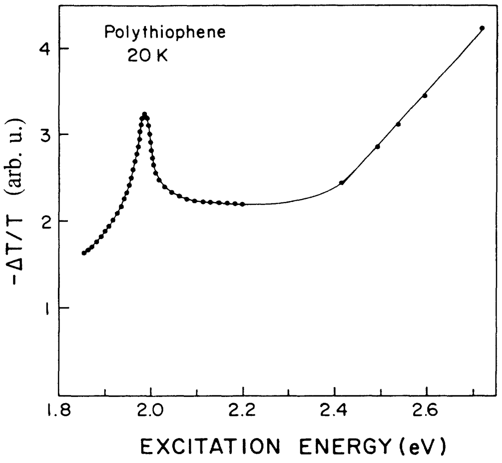

FIG. 3. Excitation profile of the long-lived photocarriers as measured by photoinduced absorption.

We have also studied the excitation profile of the photoinduced absorption of charge carriers (denoted hereafter EXPA) by measuring the excitation spectrum of the photoinduced ir-active vibrations which are the clearest signature of the charge defects.[5] In Fig. 3 we show the EXPA at 20 K; it consists of a relatively narrow peak at 1.95 eV followed by a steep rise at energies above 2.4 eV where 3D absorption plays an important role, thus indicating that free-carrier absorption is involved in the charge photogeneration. The photogenerated carriers above 2 eV are either directly photoexcited on neighboring chains by interchain absorption[8] or separated electron and hole polarons on the same chain. The 1.95-eV peak, in the EXPA spectrum, may therefore originate either from an *interchain* exciton or an *intrachain* exciton level. However, the EXPA extends well below the 1.95-eV level[8] where 3D transitions are negligibly small. Moreover, it is difficult to reconcile such a strong exciton coupling (Fig. 1) to the carbon-carbon stretching vibration (which is strictly intrachain) by an interchain exciton. We therefore suggest that the 1.95-eV peak be assigned to an *intrachain* exciton bound to defects. With this assignment, the large widths of the PL, EXPL, and EXPA spectra can be accounted for by an inhomogeneous broadening. Furthermore, a bound exciton represents the first step towards e-h separation, since the electron-defect (or hole-defect) coupling is strong. It is not surprising therefore that the quantum efficiency for charge photogeneration peaks at the bound intrachain exciton level (Fig. 3). The following ODMR results strengthen the proposed assignment for the 1.95-eV peak of the PL.

ODMR MEASUREMENTS

The ODMR was studied by measuring the changes induced in the PL intensity of a PT sample placed in an optically accessed X-band microwave cavity under resonance conditions in a magnetic field. The external magnetic field

(H) was modulated to allow for lock-in detection giving rise to derivativelike signals. In general, changes in the PL signal can be caused either via the radiative or the nonradiative recombination channels. As required by the optical selection rules, the rate at which a pair of photoexcited carriers recombines depends on its spin configuration. Thus, if under optical excitation carriers are created with an isotropic spin distribution, the population of the slow-decaying pairs becomes rapidly larger than the population of the fast-decaying pairs (provided that the spin-lattice relaxation time is not exceeded) and a spin correlation appears. Application of microwave power at resonance will therefore restore an isotropic spin distribution and, as has been shown,[12] will result either in an ODMR-enhancing signal when the radiative recombination channel is affected or in an ODMR-quenching signal when the nonradiative recombination channel is involved.

ODMR data for a PT sample immersed in liquid nitrogen at 77 K are shown in Fig. 4. The PL was excited with an Ar$^+$ laser (100 mW/cm^2) in a backscattering configuration. The emission was collected by lenses and focused onto a fast Si detector. The derivativelike ODMR signal obtained by sweeping the magnetic field through the resonance line is a PL-quenching signal; this was checked by comparing it with a low-defect *a*-Si:H sample.[12] We have carried out measurements in which H was swept up to 500 G around the resonant field but no other features were observed, indicating that triplet excitons are not responsible for the ODMR. The ODMR signal gradually decreases as the temperature increases. This decrease with temperature is accompanied by a parallel decrease in the spin-lattice relaxation time,[7] thus suggesting that unthermalized spins are giving rise to the ODMR process. We therefore conclude that the weakly correlated pair model[13] fits our data and that the ODMR-quenching signal of the PL is caused by a nonradiative spin-$\frac{1}{2}$ center acting as a shunt in a competing process to the main photoluminescence channel. When resonance ESR conditions are met, spin flip can occur at this center, thereby enhancing the spin-dependent nonradiative recombination channel. The ODMR results may thus be used to identify the nonradiative centers.

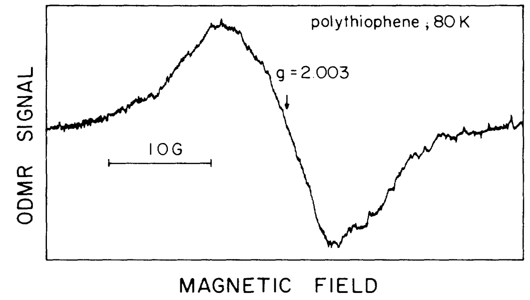

FIG. 4. ODMR of the photoluminescence shown in Fig. 1.

The symmetric quenching signal in Fig. 4 amounts to a relative change of about 10^{-3} of the PL intensity; it is centered at $g = 2.003$ and the derivative peak-to-peak linewidth is $\Delta H_{\mathrm{p.p.}} \sim 11$ G. The g shift is the same and the line is only slightly broader than that of the ESR signal in neutral PT[6,7] which is due to spin-$\frac{1}{2}$ intrachain native defects. We therefore conclude that the PL-related defects and the spin-$\frac{1}{2}$ defects in PT are the same. The quenching ODMR is thus related to e-h pairs excited on chains which contain such a defect; the exciton becomes bound via e-defect (or h-defect) interaction. This process may increase the PL lifetime due to the e-h separation and thus enable the ODMR signal to appear. Excitons on defect-free chains are less susceptible to spin-dependent nonradiative recombination since the electron and the hole are highly correlated and their recombination is too fast.[10]

In summary, the cw photoluminescence and photoinduced absorption spectra together with the ODMR results suggest that in addition to the fast radiative recombination centers in PT, slow radiative photoexcitations also exist. We identify these centers as intrachain excitons bound to the spin-$\frac{1}{2}$ intrachain native defects observed in ESR experiments. It should, however, be noted that this is only one of the various recombination channels that could be operative in a *real* polymer.

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[1] S. A. Brazovskii and N. N. Kirova, Zh. Eksp. Teor. Fiz. **33**, 6 (1981) [JETP Lett. **33**, 4 (1981)].

[2] L. Lauchlan, S. Etemad, T.-C. Chung, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B **24**, 3701 (1981).

[3] W. Hayes, C. N. Ironside, J. F. Ryan, R. P. Steele, and R. A. Taylor, J. Phys. C **16**, L729 (1983).

[4] Z. Vardeny, J. Orenstein, and G. L. Baker, Phys. Rev. Lett. **50**, 2032 (1983).

[5] P. L. Danienson and R. C. Ball, J. Phys. (Paris) **46**, 1611 (1985).

[6] M. Kobayashi, J. Chen, T.-C. Chung, F. Moraes, A. J. Heeger, and F. Wudl, Synth. Met. **9**, 77 (1984).

[7] D. Davidov, F. Moraes, A. J. Heeger, F. Wudl, H. Kim, and L. R. Dalton, Solid State Commun. **53**, 497 (1985).

[8] Z. Vardeny, E. Ehrenfreund, O. Brafman, M. Nowak, H. Schaffer, A. J. Heeger, and F. Wudl, Phys. Rev. Lett. **56**, 671 (1986).

[9] K. Kaneto, Y. Kohno, and K. Yoshino, Solid State Commun. **51**, 267 (1984).

[10] K. S. Wong, W. Hayes, T. Hattori, R. P. Taylor, J. F. Ryan, K. Kaneto, Y. Yoshino, and D. Bloor, J. Phys. C **18**, L843 (1985).

[11] Z. Vardeny, E. Ehrenfreund, O. Brafman, A. J. Heeger, and F. Wudl, Synth. Met. **18**, 199 (1986).

[12] R. A. Street, Phys. Rev. B **26**, 3588 (1982).

[13] S. P. Depinna, B. C. Cavanett, I. C. Austin, and T. M. Searl, Solid State Commun. **41**, 263 (1982).