

Photogeneration of Confined Soliton Pairs (Bipolarons) in Polythiophene

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From photoinduced absorption and light-induced electron-spin resonance, we demonstrate that the dominant photocarriers generated in polythiophene with excitation above the energy gap (E_g) are charged bipolarons (spin 0). The observation of bipolarons ($B^{2\pm}$) rather than polarons (P^\pm) as the dominant photoexcitations demonstrates that the Coulomb contribution to the bipolaron energy (U_B) is sufficiently small that $P^\pm + P^\pm \rightarrow B^{2\pm}$. From the analysis of the spectra, we find $U_B/E_g \approx 0.12$.

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The possibility that the dominant charged excitations for a nondegenerate ground-state polymer are confined soliton pairs (bipolarons) with charge $\pm 2|e|$, rather than polarons, is a new idea¹⁻⁴ in the field of conducting polymers. The existence of stable bipolaron excitations would prove that when two like charges are injected onto a polymer chain, there is an indirect *attractive* interaction due to the presence of a self-consistently generated local structural distortion. Moreover, Brazovskii, Kirova, and Yakovenko have shown⁵ that such spinless bipolarons could exhibit Bose condensation to a novel charged superfluid state. Thus, the identification of the dominant charged excitations in conjugated polymers with a nondegenerate ground state is of special importance.

Most of the previous experiments⁶⁻¹⁰ on nondegenerate ground-state conducting polymers have used charge-transfer doping to study the charge-storage configuration. Although there is considerable evidence that upon doping charge is stored in bipolarons,⁶⁻⁹ the interaction of the electronic charges with the dopant ions could significantly change the energy. Moreover, in some cases the evidence from doping studies is controversial.^{6,10} Therefore, the question of whether bipolarons are intrinsically the lowest-energy charged configurations in such polymers remains open.

As a representative of the class of polymers with a nondegenerate ground state, polythiophene (PT) is an ideal candidate. It is highly crystalline¹¹ with a simple backbone geometry (Fig. 1) similar to that of *cis*-(CH)_x but stabilized in that structure by the sulfur. Since there is detailed evidence^{7,12,13} that the sulfur interacts only weakly with the π electrons of the backbone, PT may be thought of as a pseudopolyene.

Using steady-state photoinduced absorption spectroscopy^{14,15} and light-induced electron-spin reso-

nance,¹⁶ we show in this paper that charged bipolarons are photogenerated in neutral polythiophene. Although we find specific evidence of the repulsive Coulomb contribution (U_B) to the bipolaron energy, the existence of bipolarons (rather than polarons) as the dominant long-lived charged photoexcitations demonstrates that U_B is relatively small.

The photoinduced absorption spectrum of PT at 20 K is shown in Fig. 1. These data were obtained with a chopped laser ($\hbar\omega_L = 2.7$ eV) with $I_L = 10$ mW cm⁻² for the modulated pump beam and an incandescent light source dispersed by a monochromator as the probe beam. The PT samples were pressed KBr pellets

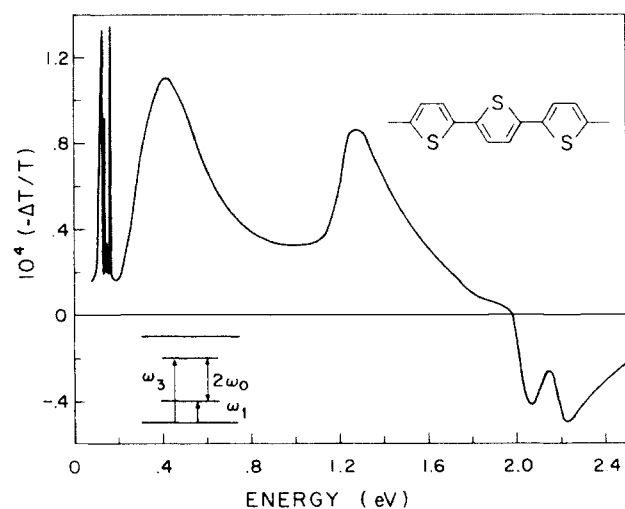


FIG. 1. Photoinduced absorption of PT at 20 K obtained with $I_L = 10$ mW cm⁻² at $\omega_L = 2.7$ eV. Insets: Upper, a chemical structure diagram of PT; lower, the energy levels and allowed transitions for B^{2+} .

containing approximately 0.25 wt. % PT powder (obtained by condensation polymerization¹⁷ of 2,5-diiodothiophene) with an optical density corresponding to an effective thickness of about 1000 Å. The transmission (T) and the photomodulation (ΔT) were measured with appropriate detectors and a lock-in amplifier. The system response was accounted for by our taking the ratio $\Delta T/T$ which is proportional to the change ($\Delta\alpha$) in the sample absorption coefficient. The photoinduced absorption spectrum consists of four main¹² infrared-active vibrational (IRAV) lines below 0.2 eV and two asymmetric electronic bands with $\Delta\alpha > 0$. The low-energy band peaks at 0.45 eV and the high-energy band peaks at 1.25 eV. The photoinduced absorption bands derive their strengths from states above 2 eV where $\Delta\alpha$ changes sign and turns into induced bleaching ($\Delta\alpha < 0$). The oscillations seen in the bleaching part of the spectrum are similar to those observed in the photoinduced spectrum¹⁸ of *trans*-(CH)_x and may be due to electroabsorption from the photocarriers or phonon overtones of a discrete defect level.

For the first time, the full photoinduced spectrum including IRAV lines, and the two electronic bands are observed together and compared *quantitatively* under the same experimental conditions. We verified that all of the features in Fig. 1 have a common origin by measuring their dependences on the excitation intensity I_L , temperature, and chopping frequency, and by measuring the individual excitation profiles. We found that all the spectral features show the same behavior. At low I_L , they all increase as $I_L^{1/2}$ followed by saturation at high I_L , similar to the photoinduced soliton absorption in *trans*-(CH)_x.^{15,19} They all monotonically decrease in intensity by an order of magnitude when temperature is changed from 20 to 300 K, and they all give signals which lag in phase by $\approx 40^\circ$ from the laser illumination chopped at 140 Hz (implying a photocarrier lifetime of ~ 5 ms).

The IRAV excitation profile is shown in Fig. 2. The absolute value of the number of photogenerated charges (N_{ch}) was estimated by comparison of the strength of the lower-energy electronic band with the corresponding band in samples of known doping concentration⁷; the two independent data sets were thus normalized to $N_{ch} = 2 \times 10^{-4}$ per thiophene ring at $\hbar\omega_L = 2.5$ eV. Consistent data (with minor quantitative deviations) were obtained with the modulation technique¹⁴ and with the Fourier-transform infrared spectroscopy method,¹⁵ by use of a dye laser as the pump beam in the former and high-intensity Xe lamp with a series of narrow-band-pass filters in the latter. The excitation profile consists of a relatively narrow peak at 1.95 eV followed by a steep increase for $\hbar\omega_L > 2.2$ eV. The two electronic bands show the same excitation profiles. The steep increase for $\hbar\omega_L$

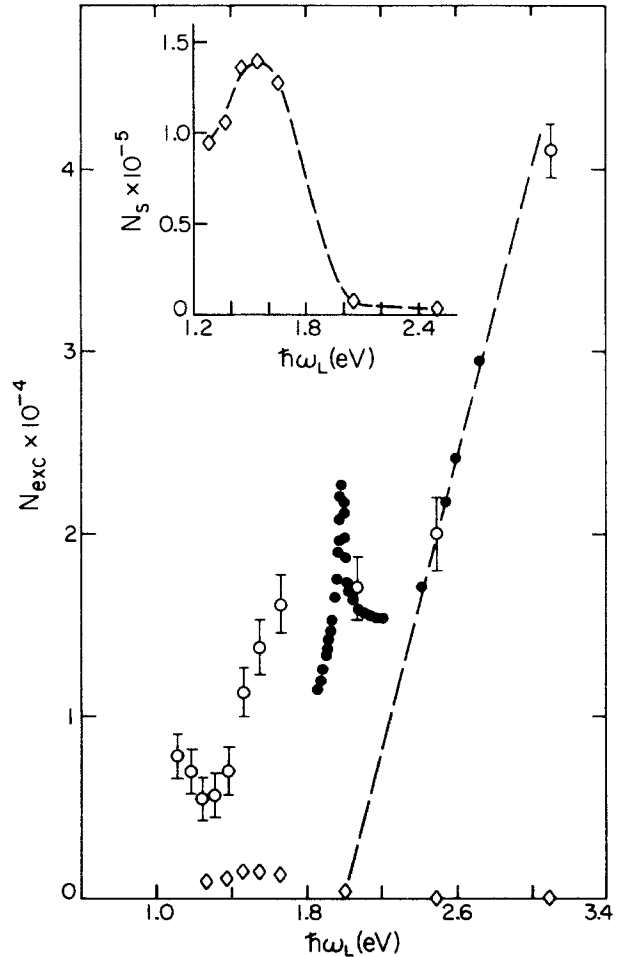


FIG. 2. Excitation profile of PT; N_{ch} (circles) and N_S (diamonds) plotted as functions of pump energy ($\hbar\omega_L$). The filled circles were obtained with the modulation technique (20 K), open circles with Fourier-transform infrared spectroscopy (~ 100 K). Both N_{ch} and N_S were normalized (by $I_L^{1/2}$) to an equivalent pump power of 10 mW cm^{-2} . The dashed line extrapolates to the observed energy gap (~ 2 eV). Inset: N_S vs $\hbar\omega_L$ on an expanded scale.

higher than the energy gap^{7,17} indicates that free-carrier absorption is involved as an intermediate step, similar¹⁹ to *trans*-(CH)_x. We identify the 1.95-eV peak as due to an exciton. Since a bound electron-hole ($e-h$) pair on a single polymer chain would rapidly recombine, the exciton is probably a bound state of an $e-h$ pair on neighboring chains. A specific defect level in the gap is ruled out, because the induced bleaching begins above 2 eV (Fig. 1). The proximity of the 1.95-eV peak to the peak in the luminescence spectrum⁹ may indicate that the luminescence is due to interchain exciton recombination.

Light-induced electron-spin resonance measurements were carried out¹⁸ at 20 and 100 K on similar samples (~ 1 wt. % PT powder in a KBr pellet); the

excitation profile for photogenerated spins (N_S) is shown in Fig. 2. The absolute value of N_S was estimated from the relative strengths of the photoinduced and dark signals (the latter is known^{13,17} to be about 260×10^{-6} per thiophene monomer). Although a photoinduced ESR signal was observed (indicative of photogeneration of polarons¹⁶), the excitation profile for photogenerated spins is completely different from the excitation profile for photogenerated charges. Moreover, after improvement of the structural order by annealing of the PT at elevated temperature,¹¹ the number of photogenerated spins drops below the detectable limit, whereas the photoinduced absorption signal remains. Thus, the dominant charged photoexcitations in PT are spinless. A relatively small number of spin- $\frac{1}{2}$ excitations are photogenerated in the lower-crystallinity (as-synthesized) samples as reported earlier.¹⁶ Since the spin- $\frac{1}{2}$ excitation profile peaks deep in the gap (~ 1.5 eV), and since the annealed samples show no photoinduced ESR, polaron excitation occurs via defect states deep in the gap which result from structural imperfection. The lifetime for the photogenerated spins is ~ 1 sec (much greater than that of the photogenerated charges) consistent with deep trapping on a defect.²⁰

We conclude that the photoinduced absorption spectrum shown in Fig. 1 defines a single charged photoexcitation with electronic levels self-consistently localized in the gap. We propose that it results from charged, spinless bipolarons, and we identify the 0.45- and 1.25-eV bands as transitions ω_1 and ω_3 , respectively, as shown in Fig. 1 (inset). The identification is based on the following: (a) The IRAV show that a structural distortion is involved and that the excitation is charged.²¹ (b) The 0.45- and 1.25-eV bands are asymmetric indicating that transitions from (to) continuum states are involved, in agreement with predictions⁴ for bipolaron transitions (Fig. 1, inset). (c) The photoinduced absorption spectrum is similar to the $\Delta\alpha$ spectra obtained for PT at dilute doping concentrations. These doping-induced spectral changes also show two asymmetric bands, at 0.65 and 1.45 eV, identified with bipolaron transitions.⁷ Moreover, the difference $\omega_3 - \omega_1 = 2\omega_0$ is the same (0.8 eV) for photoinduced and doping-induced⁷ $\Delta\alpha$ spectra. If bipolarons are produced in both cases, the splitting between the two gap states should be the same and not depend on the generation process, since $2\omega_0$ is due to confinement.⁴

Since the relation $\omega_1^0 + \omega_3^0 = E_g$ would hold in the absence of Coulomb repulsion, the transition energies are shifted,

$$\omega_1 + \omega_3 = E_g - 2U_B, \quad (1)$$

where U_B is the difference in Coulomb energy between initial state (double charge) and final state

(single charge) with fixed lattice coordinates. From Fig. 1, $\omega_1 + \omega_3 = 1.7$ eV, while $E_g \approx 2.1-2.2$ eV was inferred from the absorption spectrum.^{7,16} A more accurate value for E_g^{1d} has been obtained²² from analysis of the IRAV and resonance Raman data through use of the amplitude-modes formalism^{23,24}; $E_g^{1d} = 2.2$ eV. From Eq. (1), we find $U_B \approx 0.25$ eV or $U_B/E_g \approx 0.12$. This small value for U_B is consistent with the existence of bipolarons rather than polarons as the dominant charged excitation. Since the polaron is a bound state of a neutral and a charged soliton,⁴ whereas the bipolaron is a confined pair of charged solitons, a large U_B would favor polaron formation. For doping-induced bipolarons, the shift of each transition by U_B is compensated by the Coulomb binding to the dopant ion (E_B) so that $\omega_1 + \omega_3 = E_g - 2(U_B - E_B)$. Since U_B and E_B depend primarily on the spatial extent of the bipolaron, the two contributions approximately cancel.⁷ Since there is no splitting of either the 0.45- or the 1.25-eV band, charge-conjugation symmetry²⁵ holds for PT, and therefore Eq. (1) describes negative or positive bipolarons.

For such relatively strong confinement, the ratio of the intensities of the two absorption bands, $I(\omega_1)/I(\omega_3)$, is predicted⁴ to be about 12, whereas in Fig. 1, we find an experimental value of approximately 1.5 (compared to a factor of 2 in the analogous doping experiments⁷). Although this discrepancy is not understood in detail, it may be due to the oversimplified model since the transition oscillator strengths depend sensitively on the detailed form of the wave functions.

The finite *positive* value found for U_B demonstrates that the underlying mechanism for bipolaron formation in PT is quite different from the negative- U centers in 3d semiconductors introduced by Anderson²⁶ and carried over to defect pairs in the chalcogenide glasses²⁷ and to impurities and vacancies in silicon.²⁸ In PT (and presumably more generally in conducting polymers), the bipolarons result from the *confinement* of charged soliton pairs.

The existence of long-lived charged bipolarons requires pairs of like charges on PT chains. Although intrachain absorption processes are expected to dominate, the resulting electron-hole pairs evidently rapidly recombine (*neutral* bipolarons should be unstable with a short lifetime). Photoexcitation of electron-hole pairs on neighboring chains is expected to occur because of the finite interchain bandwidth. Such *interchain* pairs form polarons and/or weakly bound excitons, and they play a transient role in the formation of the charged bipolarons which are observed at long times. As these polarons diffuse, they will form bipolarons when two polarons with the *same* charge appear in a single chain. A similar mechanism was proposed²⁹ for the photoexcitation of charged solitons in *trans*-(CH)_x. The excitation profile (Fig. 2) suggests that

pumping of interchain excitons is a particularly efficient means of generating bipolarons in PT; the detailed mechanism by which this occurs is, however, not understood.

Our work does not exclude the importance of charge states different from bipolarons under different circumstances: Polarons were identified^{8,9} in electrochemically prepared samples at dilute doping concentrations (<1%). A small number of polarons are observed¹⁸ as photoexcitations at $\hbar\omega_L < E_g$ in as-synthesized PT, as described above.

In conclusion, we have shown that the dominant charge states in PT generated with $\hbar\omega_L > E_g$ are bipolarons. The observation of bipolarons, rather than polarons, as the long-lived charged excitations demonstrates that the Coulomb contribution to the bipolaron energy is relatively small; from analysis of the spectra, we find $U_B/E_g \approx 0.12$. Since $U_B > 0$, stable bipolarons result from the confinement of charged soliton pairs. The existence of bipolarons during photoexcitation or after doping thus implies an indirect attractive interaction between two like charges due to a self-consistently generated local structural distortion.

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