

Neutral excitons and metastable charged polarons in 5,5'-bis-(2-phenylethynyl)-2,2'-bithienyl

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We have carried out steady-state photoinduced infrared-absorption measurements on the newly synthesized organic molecule 5,5'-bis-(2-phenylethynyl)-2,2'-bithienyl (PhEtBT). We have found that the dominant elementary excitations in PhEtBT are Wannier-type neutral excitons formed between electrons and holes strongly localized in adjacent *intramolecular* or *intermolecular* C≡C sites. We observed that charge carriers which do not undergo direct radiative recombination are self-localized by forming metastable charged polarons. We have observed two different charge distributions on the polaron site; one is polaronlike for $T < 120$ K, and the other is bipolaronlike at $T > 120$ K. We suggest that the charge trap centers are provided by the large polarizability of the localized π' dimers in the C≡C site. [S0163-1829(98)04203-9]

I. INTRODUCTION

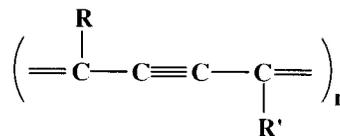
When charges are added to conducting polymers by chemical doping or by direct optical pumping above the energy gap, the excess charges are found to disrupt the perfect Peierls' bond-alternation pattern and form domain-wall-like self-localized charged nonlinear excitations, solitons in the case of a degenerate ground state, and polarons or bipolarons (confined soliton pairs) when the ground-state degeneracy has been lifted.¹ Therefore, when a pair of oppositely charged photogenerated solitons or polarons recombine, the recombination process is prone to be nonradiative because these charged excitations are intimately coupled to the lattice and, hence, multiphonon emission decay channels are readily available. To this end, *trans*-polyacetylene, which is a prototypical conducting polymer with a degenerate ground state, is a good example. However, it has been frequently observed that conducting polymers with a nondegenerate ground state tend to exhibit photoluminescence upon optical excitation,² suggesting that there exists a radiative decay channel for the photogenerated electrons and holes in the system.

The recent discoveries of electroluminescence in poly(*p*-phenylenevinylene), which is a nondegenerate ground-state conducting polymer,³ and its derivatives and oligomers⁴ have brought about research opportunities not only for the application of conducting polymers as a light source but also for understanding the origin of the photoluminescence in conducting polymers. It is clear that the electroluminescence is intimately related to the photoluminescence of the system, and that the light emission of conducting polymers has its origin in the recombination of Coulombically bound electron-hole singlet pairs generated either by photoexcitation or by the injection of electrons and holes via Ohmic contacts. However, what is not clear, and is even controversial, is the identification of the types of elementary excitations and the understanding of the detailed recombination mechanism which is responsible for the observed photoluminescence and electroluminescence. The physical origin of the photoluminescence may lie in the di-

rect transition between the two sublevels of neutral bipolarons (the bound state of a pair of oppositely charged polarons) which are also called polaron-excitons. In this picture, the zero-phonon peak energy in the photoluminescence corresponds to the confinement energy of the neutral bipolarons in the polymer chain.⁵ Then, the energy difference between the π - π^* gap and the zero-phonon emission peak measures the extent of lattice relaxation in the excited state, which is known as the Stokes shift which arises when the lattice distortion around the charges requires a nonadiabatic treatment.⁶ Hence, for a highly crystalline system, the photoluminescence is expected to carry information about the vibronic structure.

It is interesting to note that polydiacetylenes (PDA's), shown in Fig. 1(a), do not show electroluminescence despite the intense photoluminescence upon photoexcitation.⁷ These

(a) Polydiacetylenes (PDA's)



(b) 5,5'-Bis-(2-Phenylethynyl)-2,2'-Bithienyl (PhEtBT)

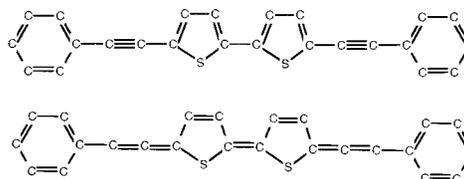


FIG. 1. (a) Repeat units of polydiacetylenes (PDA's). R and R' represent bulky side groups. For example, $R = \text{CH}_3$ and $R' = \text{CH}_2(\text{OH})$ for PDA-OH, $R = R' = (\text{CH}_2)_4\text{OCOCH}_2\text{C}_6\text{H}_5$ for PDA-9PA, and $R = R' = \text{CH}_2\text{SO}_3\text{C}_6\text{H}_4\text{CH}_3$ for PDA-TS. (b) Two energetically different chemical structures of 5,5'-bis-(2-phenylethynyl)-2,2'-bithienyl (PhEtBT). The upper configuration has the lower energy.

are the only known one-dimensional semiconducting polymers with a nondegenerate state which do not show electroluminescence, but photoluminescence, and can be grown into large single crystals. PDA's are especially well known for their chemically undopable nature, and for supporting neutral excitons like ordinary direct-gap semiconductors.⁸ Because the electroluminescence comes directly from the excess charges introduced into the polymer backbone through Ohmic contacts, studying the nature of nonlinear charged excitations and their dynamics through chemical doping of PDA's seems to be a natural step to take. However, because of the aforementioned chemically inert properties of PDA's, photoexcitation techniques may be used to generate band excitations in PDA's as an alternative to the chemical doping.

Initial efforts in the search for photoinduced charged bipolarons (and polarons) in crystalline PDA's using a standard photomodulation technique failed. It was discovered later by Kim *et al.* that the photocarriers in PDA's are indeed stored in the form of like-charged bipolarons after escaping from the radiative recombination process, and that these spinless bipolarons are in a metastable state at low temperatures.⁹ Such an unusually long lifetime of photoinduced bipolarons in crystalline PDA's made the observation via conventional photomodulation techniques virtually impossible, because the photomodulation techniques are designed to detect photoinduced signals on the order of 1 ms of lifetime.¹⁰ Kim *et al.* attributed the metastability of charged bipolarons in PDA's to the localization of charges at the carbon-carbon triple bond (C≡C) sites, resulting from the polarization of the π' dimer, and also to the unusually long interchain distances of PDA's due to long side chains.⁹ These long side chains of PDA's have also been used to explain the undopable nature, because they may keep the dopant ions from reaching the polymer backbones.¹¹

In order to address specific issues concerning charge localization and recombination dynamics of photocarriers in a system containing C≡C bonds, a newly synthesized organic system, 5,5'-bis-(2-phenylethynyl)-2,2'-bithienyl (PhEtBT) (Ref. 12) depicted in Fig. 1(b), was used in this study. PhEtBT has a nondegenerate ground state [see Fig. 1(b)]. Because this system does not contain the side-chain groups and has a three-dimensional close-packed crystal structure, one may identify the primary source of the charge localization in a system containing C≡C bonds, and understand subsequent recombination dynamics of photoexcited charges.

We found that PhEtBT also cannot be chemically doped as in the case of PDA's.¹³ In this work, we observed that PhEtBT has a three-dimensional energy gap of ~ 1.50 eV, and intense photoluminescence sharply peaked at ~ 2.30 eV with a shoulder at ~ 2.23 eV. Immediately after the photoexcitation, we found that principal excitations are primarily localized at the C≡C sites, and instead of existing as neutral bipolarons consist of Wannier-type neutral excitons formed between electrons and holes localized in adjacent *intramolecular* or *intermolecular* C≡C sites. We base this conclusion on observing the photoluminescence peaked at 2.30 eV with a shoulder at 2.23 eV without vibronic progression, which indicates no lattice coupling. In addition, the absence of the photoinduced infrared-active vibrational (IRAV) modes right after the photoexcitation further supports the

idea of Wannier-type exciton formation, because IRAV modes are induced by substantial structural relaxation in the vicinity of the self-localized charges.

However, we observed that IRAV modes develop at later times, suggesting that charges, which escaped from radiative or non-radiative decay, self-localize, forming charged polarons. In this work we found two major photoinduced IRAV modes that are associated with charges localized across the thiophene ring and C≡C sites. In particular, we observed that the C≡C sites involving charges are now substantially softened to form an allene-type structure ($=C=C=$).¹⁴ We believe that the initial strong charge localization at the C≡C sites is provided by the polarizability of the π' dimer of C≡C. It is surprising to find that the intermolecular distance plays virtually no role in the formation of metastable charged excitations. In other words, the previously suggested contributing role of the large *interchain* separation between the PDA polymer strands to the metastability is not of primary importance. Therefore, charges injected into PDA's or PhEtBT through Ohmic contacts are not expected to be mobile due to the charge localization centers at the C≡C sites, which, in turn, inhibits the formation of excitons for light emission.

We observed no photoinduced infrared activities associated with the phenyl rings of PhEtBT, suggesting that the phenyl rings remain unaffected by the charge localization and structural relaxations. We found that the principal elementary excitation in the PhEtBT molecule is intermolecular and intramolecular neutral Wannier-type excitons which are responsible for the intense photoluminescence, and that charged excitations are formed through the secondary processes. From the temperature dependence of the photoinduced IRAV modes, we suggest that the charge distribution around the self-localized charges in the PhEtBT molecules is polaronlike for temperatures below 120 K, and bipolaronlike for temperatures above 120 K. Therefore it appears that there exists a charge distribution tunneling barrier with 120-K (~ 0.01 -eV) height. Alternatively, bipolarons might be formed via intermolecular charge transfer for temperatures above 120 K, despite the cost of Coulomb energy incurred to store two like charges in a PhEtBT molecule. However, the amount of charge density associated with the charge-induced IRAV modes is constant for temperatures below and above 120 K. This sum-rule evidence is against the notion of actual bipolaron formation.

II. EXPERIMENT

PhEtBT molecules were synthesized using a 250-ml three-necked round-bottomed flask, equipped with a reflux condenser, magnetic stirrer, and nitrogen inlet, charged with 100-ml dry triethylamine, 42.8-mg copper (I) iodide, 6.48-g 5,5'-dibromo-2,2'-bithienyl, and 2.247-g phenylacetylene.¹² Nitrogen was then bubbled through for 20 min. To the stirred mixture, 71.6-mg tetrakis(triphenylphosphine)palladium(0) was added under a constant flow of nitrogen. The resulting mixture was heated with stirring at 95 °C for 24 h. The crude product was purified by column chromatography using 10% ethyl acetate/hexane as eluent and 5.49 g of pure PhEtBT was collected; mp 165 °C.

For the photoinduced absorption measurements, the

PhEtBT crystalline powder was mixed with KBr at a concentration of ~ 2 wt %. The homogeneous mixture was then compressed into semitransparent pellets with ~ 0.7 -mm thickness. The sample was mounted on a cold finger attached to a liquid-nitrogen-cooled cryostat. The sample temperature was controlled using a heater between 90 and 280 K. A BioRad FTS 6000 spectrometer was used to cover the frequency range between 400 and 5000 cm^{-1} , with a mercury cadmium telluride detector. The spectral resolution is set for 2 cm^{-1} . A silicon wafer was used to block the unnecessary He-Ne laser light, which was used to control the interferometer, entering into the sample chamber. A cw Ar⁺-ion laser (Spectra Physics) was used as an optical pump. The pump energy was 514 nm (2.41 eV) at ≈ 20 mW/cm². The vacuum shroud was designed to allow the laser beam to be coincident on the sample with an infrared beam. For the steady-state photoluminescence measurement, the PhEtBT crystalline powder sample was excited with the 514-nm (2.41 eV) line, and also with a 476.5-nm (2.6 eV) line for comparison. A SPEX grating monochromator was used for spectroscopic measurements at visible frequencies.

To our surprise, initial photoinduced absorption experiments using the standard photomodulation technique could not detect the photoinduced signal because of the unexpectedly long photogenerated carrier (photocarrier) lifetime, despite the fact that the PhEtBT crystals are close packed without side chains. Thus the standard steady-state photomodulation technique was modified to allow longer (and variable) sampling times in order to detect the photoinduced absorption, to time resolve the response, and to measure the carrier lifetime. Time resolution was varied from 10 to 30 s, depending on the sample temperature. A sequence of photoinduced absorption spectra were measured after exciting the sample using the 514-nm (2.41 eV) Ar⁺-ion laser line for 1 min. The photoinduced absorption spectrum was then obtained; after subtracting the dark reference spectrum.

III. RESULTS

The optical-absorption spectrum of PhEtBT crystals deposited on a sapphire substrate is shown in Fig. 2 along with the photoluminescence data. The optical absorption has an onset at ~ 1.5 eV, and rapidly increases as the photon energy increases. The optical transition shows a simple harmonic progression at ~ 2.80 , ~ 2.98 , ~ 3.17 , and ~ 3.35 eV arising from the coupling between the electronic state and molecular vibration(s). The vibronic splitting $\omega_0 \approx 0.18$ eV indicates that electronic band excitations couple to the symmetric C=C stretch mode among several Raman-active modes of PhEtBT. From the zero-phonon absorption peak at ~ 2.80 eV, we identified the π - π^* transition energy gap as 2.80 eV. The absorption below 2.80 eV is attributable to the three-dimensional energy gap arising from the intermolecular transfer interactions in the close-packed, highly crystalline structure of the PhEtBT sample. We estimate the three-dimensional energy gap to be ~ 1.5 eV from the absorption spectrum.

Upon photoexcitation of the PhEtBT sample with 476 nm (2.6 eV) photons at room temperature, an intense photoluminescence peaked at ≈ 2.30 eV, and a shoulder at ≈ 2.23 eV were observed. There also exists a shoulder at ~ 2.23 eV in

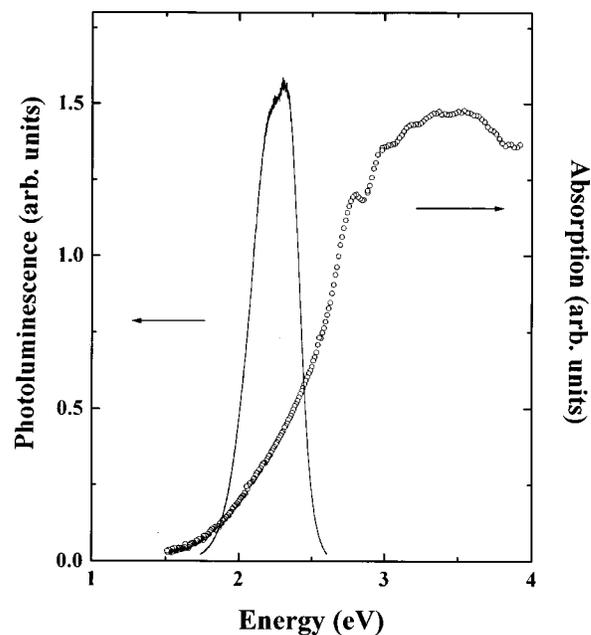


FIG. 2. Direct optical absorption of thin cast film of PhEtBT measured for photon energies between 1.5 and 3.9 eV and photoluminescence data of a single-crystalline powder sample of PhEtBT with 476-nm (2.6 eV) excitation. Both samples were measured at room temperature.

the photoluminescence. The absence of vibronic structure in the photoluminescence is rather surprising. The well-defined vibronic progression in the absorption spectrum would lead one to expect a mirror symmetry in the emission if neutral bipolarons are involved. This implies that the neutral excitons in PhEtBT are not coupled to the lattice vibrations. Moreover, the 0.5-eV energy difference between the zero-phonon absorption and the zero-phonon emission peaks is too large to be regarded as the Stokes shift involving neutral bipolarons in this highly ordered system.

The presence of the 2.23-eV shoulder in the photoluminescence peak deserves special attention. As shown in Fig. 3, the width of the photoluminescence spectrum obtained with 2.60-eV photons is broader than that obtained with 2.41-eV photons, because of the pronounced enhancement of the shoulder at 2.23 eV. The 0.07-eV energy difference between the observed 2.30-eV peak and the 2.23-eV shoulder is too small to be regarded as the vibronic structure. Had this system been a conducting polymer sample, it could have been due to a bimodal distribution in the conjugation length. However, because of the single-crystalline structure of PhEtBT molecules, this is not likely. It appears that the photoluminescence spectrum is a superposition of two well-defined Lorentzian peaks which are from two different types of excitons with two different binding energies; one is due to intermolecular, and the other due to intramolecular, excitons. The idea of Coulombically bound pairs of oppositely charged polarons on adjacent chains has been proposed.¹⁵ In this model, oppositely charged polarons are bound, forming molecular excimers. However, the lack of vibronic progression in the photoluminescence casts a doubt on molecular excimer formation. Therefore, we propose that two types of Wannier excitons are generated in PhEtBT crystals: one is the intermolecular exciton with a binding energy of 0.5 eV,

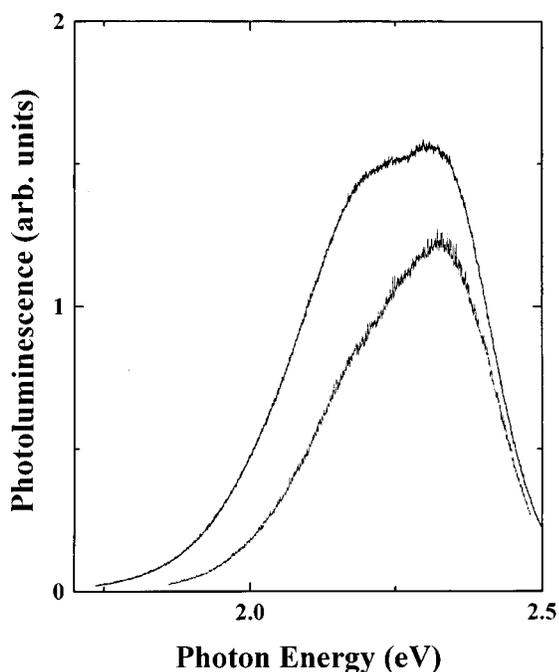


FIG. 3. Comparison of the photoluminescence spectra obtained with 476-nm excitation (upper curve) and with 512-nm excitation (lower curve).

populated primarily via the intermolecular charge transfer at photon energy below the $\pi-\pi^*$ energy gap, and the other is the intramolecular exciton with binding energy of 0.57 eV formed by optical pumping above (or near) the $\pi-\pi^*$ gap. Therefore, for the photoinduced absorption measurements of PhEtBT, we used the 2.41-eV (514 nm) laser line in order to enhance the intermolecular charge separation.

Direct infrared absorption and Fourier-transform (FT) Raman-scattering data of PhEtBT obtained at 300 K are shown in Fig. 4. There are a number of major infrared-active vibrational modes at 687, 755, 798, 1440, 1482, 1516, 1597, and 2194 cm^{-1} . There also exist a number of weak modes in the vicinity of 1000 and 1200 cm^{-1} corresponding to the Raman-active in-plane bending modes and C—C stretching modes, respectively. The absorption peaks at 1440 and

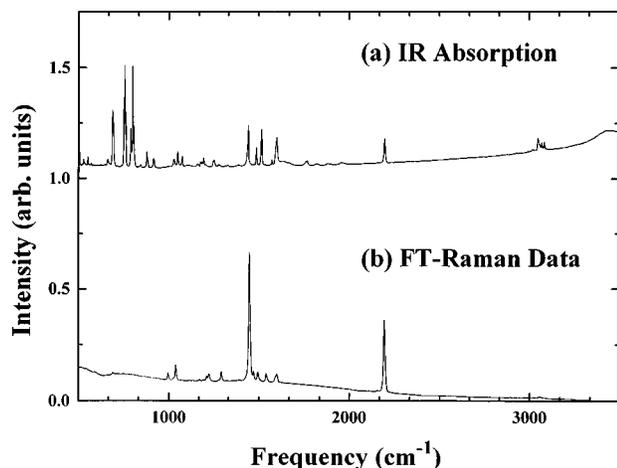


FIG. 4. Overall infrared absorption spectrum of 1 wt % PhEtBT dispersed in KBr and the FT Raman spectrum of a PhEtBT crystalline powder sample obtained at room temperature.

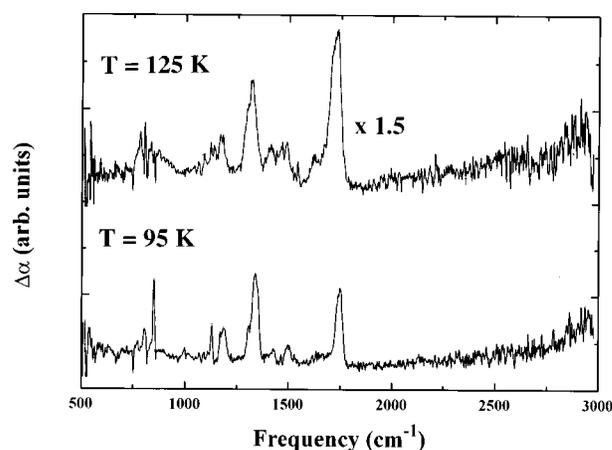


FIG. 5. Photoinduced absorption spectra of PhEtBT obtained after 1-min laser excitation at 95 and 125 K (see text). The sample is pumped with 20 mW/cm^2 at 2.41 eV (512 nm). Notice that the 125-K absorption spectrum has been multiplied by a factor of 1.5.

2194 cm^{-1} corresponding to the symmetric C=C and C≡C stretch modes, respectively. Detailed FT Raman results show intense modes at 1448 and 2193 cm^{-1} arising from the C=C and C≡C stretching modes. In addition, there exist weak Raman-active modes associated with the C—C stretch mode near $\sim 1200 \text{ cm}^{-1}$, and the C-H in-plane bending-type modes at 1038 cm^{-1} . Resonant Raman scattering measurement were not possible because of the intense photoluminescence of PhEtBT.

Photoinduced infrared-absorption spectra measured at 95 and 125 K are displayed in Fig. 5. At 95 K, we observed a number of photoinduced IRAV modes: a narrow mode peaked at $\approx 780 \text{ cm}^{-1}$; and two broad, strong modes at $\sim 1290 \text{ cm}^{-1}$ (ω_1) and $\sim 1720 \text{ cm}^{-1}$ (ω_2); as well as a series of weak modes located at ~ 1080 , ~ 1150 , ~ 1390 , and $\sim 1480 \text{ cm}^{-1}$. For temperatures above 120 K, there are noticeable changes in the photoinduced IRAV modes; the relative oscillator strength of the ω_1 mode to the ω_2 mode is reversed, and the oscillator strengths of the sharp modes at ~ 780 and $\sim 1150 \text{ cm}^{-1}$ have been decreased. This change is rather abrupt, as shown in Fig. 6 in a plot of the detailed

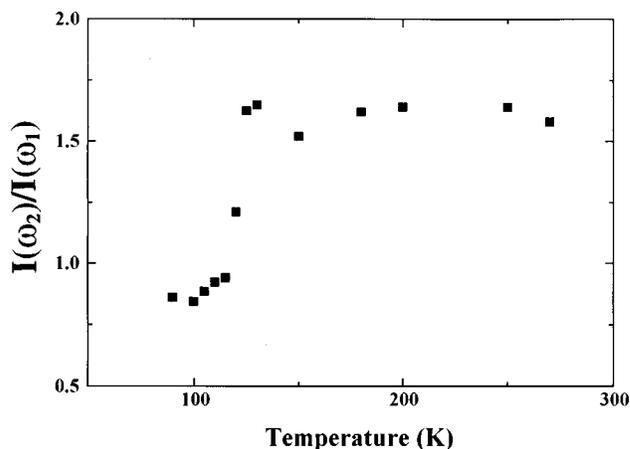


FIG. 6. Temperature dependence of the relative oscillator strength of two major photoinduced infrared-active vibrational modes $\omega_1 \approx 1290 \text{ cm}^{-1}$ and $\omega_2 \approx 1720 \text{ cm}^{-1}$.

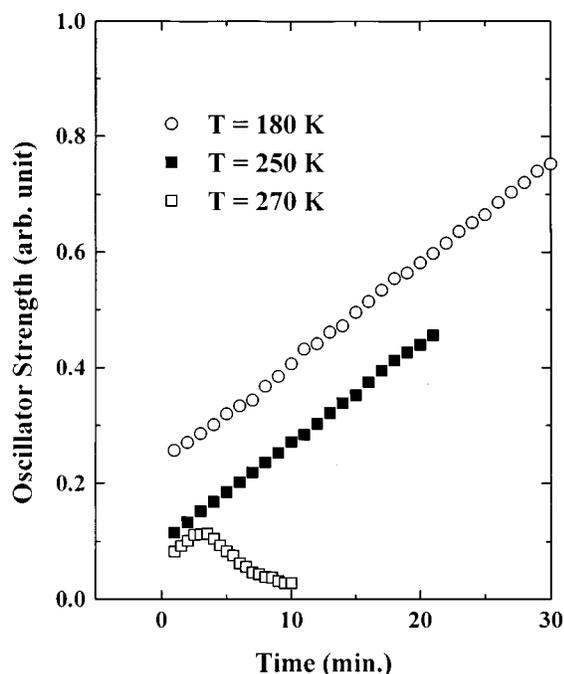


FIG. 7. Time dependence of the photoinduced ω_2 ($=1720\text{ cm}^{-1}$) mode measured at three different temperatures.

behavior of the oscillator strength ratio with temperature.

We found that this photoinduced activity persists for a time of over an hour at 90 K. Moreover, we observed that the oscillator strength of the photoinduced IRAV modes continuously increase with time. The time dependence of the oscillator strengths of the ω_2 mode (1720 cm^{-1}) at various temperatures is shown in Fig. 7. One can see from Fig. 7 that the magnitude of the oscillator strength (or intensity) at a given time decreases as the temperature increases. The photoinduced signal decays only when the temperature reaches 270 K (see Fig. 7). We observed that the rate of change at 90 K is ~ 5 times smaller than that at 180 K. We found no persistent photoinduced activity at ~ 290 K.

IV. DISCUSSION

It is now well established that the physical origin of the photoinduced IRAV modes in one-dimensional conducting polymers lies in the formation of self-localized charged state(s). When the excess charges in the polymer backbone self-localize, they break the local charge symmetry, and induce a net dipole moment which makes the Raman-active modes infrared active. The observed modes at 780, 1150, 1290, and 1720 cm^{-1} are the specific fingerprints of the formation of a self-localized charged state (polarons or bipolarons).

Amplitude mode formalism¹⁶ has been effectively applied to understand the one-to-one correspondence between the photoinduced (or doping-induced) IRAV modes and the Raman-active modes of conducting polymers. In this formalism, resonant Raman-active vibrational modes are described in terms of amplitude modes associated with oscillations of the lattice dimerization. The photoinduced and doping-induced IRAV modes are then identified by introducing a phenomenological pinning parameter to the phonon response function determined from the resonant Raman-scattering

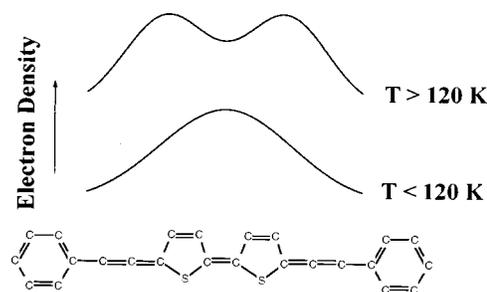


FIG. 8. A schematic diagram that represents charge distribution of self-localized charges in the PhEtBT molecule.

data of the system. An equivalent formalism has also been discussed from a molecular point of view by introducing the symmetry force constant relative to the out-of-phase vibration of C=C bond and C—C bond.¹⁷ Therefore, one anticipates that the photoinduced IRAV modes in a molecule have a direct one-to-one relationship with the Raman-active vibrational modes in the excited state. But a redshift in the frequency of a photoinduced IRAV mode is usually expected as the lattice softens at the self-localized sites.

By comparing the data shown in Fig. 5 with the photoinduced IRAV modes of polythiophenes, we identify the photoinduced IRAV modes at 780, 1150, and 1290 cm^{-1} with the characteristic charge-induced IRAV modes of the thiophene condition rings.¹⁸ The ω_2 mode at $\approx 1720\text{ cm}^{-1}$ then can be assigned to the characteristic vibrational mode of the allene-type structure,¹⁴ $=C=C-$, reflecting substantial softening of the C=C bond as polarons (or bipolarons) are formed. It is interesting to note that the photoinduced IRAV modes are site specific, despite the fact that PhEtBT is a fully π -electron conjugated system. In this study no photoinduced infrared activities associated with the phenyl rings were observed.

The abrupt change in the ratio of the oscillator strength of the ω_2 mode to that of the ω_1 mode is significant (see Fig. 6). The sum rule indicates that the ω_2 mode gains oscillator strength at the expense of the oscillator strength of the vibrational modes associated with the thiophene rings. This indicates that the total charge density involved in the photoinduced infrared activity remains constant throughout the change. Since the oscillator strength of the charge-induced IRAV modes is directly proportional to the strength of the dipole moment, which is equivalent to the amount of charge when the size of the lattice distortion is the same, the temperature dependence of the intensity ratio, $I(\omega_2)/I(\omega_1)$ suggests that the charge density redistribution abruptly takes place at ~ 120 K. Since no photoinduced IRAV modes associated with the phenyl rings were observed, we conclude that the redistribution of the charge density occurs mainly from the thiophene rings to the allene-type sites for $T > 120$ K, as depicted in Fig. 8. For temperatures below 120 K the excess charges are more localized on the thiophene ring sites, and exhibit a polaronlike character. For temperatures above 120 K the excess charges are more localized on the allene-type sites, which resembles a doubly charged bipolaronlike (a bound pair of like-charged polarons) charge distribution. Therefore, in PhEtBT, there seems to be a tunneling barrier between polaronlike and bipolaronlike charge distributions which is of the order of ~ 120 K (~ 0.01 eV).

The bipolaronlike charge distribution may have its origin in actual bipolaron formation for $T > 120$ K. To accommodate one more electron (or hole) to form a doubly charged bipolaron requires additional Coulomb energy, and this energy is expected to be large. Because the confinement energy of the bipolaron in PhEtBT is also large due to the short confinement length that extends over only two thiophene monomer units, bipolaron formation in PhEtBT may be possible. It has been reported that when thiophene tetramers are chemically doped, polarons are formed at low doping levels and bipolarons are generated at high doping levels.¹⁹ In the case of chemical doping, the Coulomb binding energy to the counter dopant-ion compensates for the Coulomb correlation energy, which allows doubly charged bipolaron formation.²⁰ Therefore, detailed balancing of energies for the photoinduced and doping-induced bipolarons needs to be studied through the measurements of the optical subgap transitions, which is not possible for PhEtBT because of its chemically inert nature. However, the integrated oscillator strength of the photoinduced IRAV modes above 120 K shown in Fig. 5 does not agree with the idea of bipolaron formation because the charge density involved in the IRAV modes remains unchanged across 120 K.

It is intriguing to observe that the oscillator strength of the photoinduced IRAV modes continuously increases with time at low temperature without further laser excitation after optically pumping the sample with the 512-nm laser (20 mW/cm²) for 1 min (see Fig. 7). This behavior implies that the number of self-localized charges increases with time, which indicates the presence of a steady charge source in PhEtBT. This is a very unusual behavior because we normally would anticipate a decay of the photoinduced signal immediately after the optical pump has been turned off. In order to increase the self-localized charge population without optically pumping the system, charges must come from already populated long-lived excitations that cannot induce IRAV modes, that is, charge neutral excitations, or trapped charges at deep trap centers. These neutral excitons or trapped charges must be immobile to prevent recombination.

It has been suggested that the large polarizability of the π' dimers in the C \equiv C bond is responsible for the metastable charged excitations in PDA's.⁹ In C \equiv C triple bonds, we have π' electrons with lobes in the molecular plane in addition to the delocalized $2p_z$ network. Although formally part of the σ framework, their identity is well preserved.²¹ The localized π' dimers in the PDA C \equiv C bonds provide a polarizable unit in intimate contact at sp centers. The π' excitation is polarized along the chain, and is well below σ -bond excited states. In PDA's, however, when the laser excitation is eliminated from the sample, the photoinduced signal is immediately followed by the expected decay.⁹ From the photoinduced signal decay curve of PDA's, the thermal activation energy of the trapped charges is estimated to be on the order of 150 K.

The continuously increasing photoinduced infrared activity in the PhEtBT system at low temperature is not fully understood at the present time, and demands further systematic studies of this new π -conjugate molecule system. In this paper we only speculate that neutral excitons localized at the adjacent C \equiv C sites are immobile. The highly crystalline close-packed structure of PhEtBT results in large intermolecular interaction, so that the charges which have escaped from direct radiative recombination remain trapped at the C \equiv C sites until they migrate to the neighboring thiophene or phenyl sites and become self-localized. In PhEtBT such charge separation and trapping were achieved far more efficiently than in PDA's due to the intermolecular hopping process. This picture is consistent with the behavior of the time-resolved photoinduced absorption data shown in Fig. 7.

V. SUMMARY AND CONCLUSION

We have found that the carbon-carbon triple bonds (C \equiv C) in PhEtBT are the principal source of charge localization as in polydiacetylenes, and the charge trapping provided by the π' bond of C \equiv C is the reason PDA's and PhEtBT are not promising light sources. In PhEtBT, the photocarriers which have escaped from the radiative recombination were stored in a metastable polaron state at low temperatures. We have observed that photocarriers are initially localized primarily at the C \equiv C sites, and then migrate to the neighboring thiophene sites via phonon-assisted processes, where they self-localize. This was deduced by monitoring the changes of the photoinduced IRAV modes arising from the thiophene rings, and the allene-type structure —C=C— , converted from the $\text{—C}\equiv\text{C—}$ bonds, as a fingerprint. The phenyl rings remain unaffected by the charge localization, as evidenced by the null photoinduced infrared activities associated with the vibrational modes of the phenyl rings. We propose that there exist two different charge distributions associated with the self-localized state in the PhEtBT molecule; one is polaronlike (below 120 K), and the other is bipolaronlike (above 120 K). This conversion from one distribution to the other is attributed to tunneling with an ~ 0.01 -eV barrier.

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