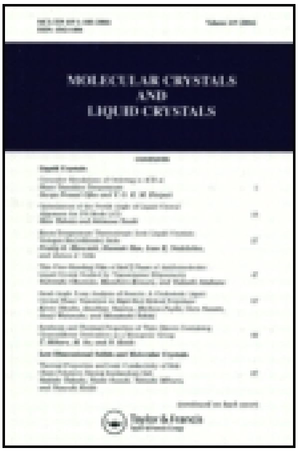

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Raman Studies of Doped Polythiophene and the Radical Cation and Dication of Quinquethiophene

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RAMAN STUDIES OF DOPED POLYTHIOPHENE AND THE RADICAL CATION AND DICATION OF QUINQUETHIOPHENE

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Abstract The near-infrared Raman and electronic absorption spectra of an as-polymerized BF_4^--doped polythiophene film have been measured and analyzed by referring to the data of the radical cation and dication of α-quinquethiophene, which are models of a positive polaron and a positive bipolaron, respectively. Similarities between the Raman spectrum of doped polythiophene and that of the radical cation suggest that the observed Raman bands of the doped polymer arise from positive polarons. It is shown that the two characteristic bands in the electronic absorption spectrum of the doped polymer are assignable to positive polarons.

INTRODUCTION

Polarons[1–3] and bipolarons[2–4] are proposed as charge carriers in polymers with nondegenerate ground states such as polythiophene (abbreviated as PT, depicted in Fig. 1a). Electronic absorption and electron spin resonance studies have shown that polarons and/or spinless bipolarons are generated by chemical doping.[5–7] The Pauli spin susceptibility indicative of a metallic density of states has been reported for doped PT.[6–8] However, the experimental results are sample dependent and in some cases controversial. For the purpose of understanding the electronic absorption spectra of doped PT in more detail, Fichou *et al.*[9] have studied the electronic absorption spectra of the radical cations of α-quaterthiophene (abbreviated as 4T), α-quinquethiophene (5T), and α-sexithiophene (6T) and the dication of 6T. Recently, Hill *et al.*[10] and

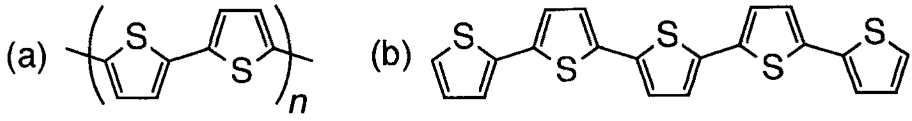


FIGURE 1 Structures of (a) polythiophene (PT) and (b) quinquethiophene (5T).

Segelbacher *et al.*[11] have proposed the spinless polaron-dimer model as an alternative to spinless bipolarons on the basis of the dimer formation of the radical cations of oligothiophenes.

Raman spectroscopy can provide detailed information on the structures of neutral and doped polymers. Although Raman measurements[12–16] and normal coordinate analyses[16–21] have been made for neutral PT, the Raman spectra of doped PT have not been fully studied yet. Two key features in Raman characterization of doped polymers are as follows.[22, 23] (1) Structural information on charged domains generated by doping can be obtained by using exciting laser lines in resonance with doping-induced electronic absorptions appearing in the region from visible to infrared. (2) The Raman spectra thus obtained can be analyzed by referring to those of the radical ions and divalent ions of oligomers, which are viewed, respectively, as polarons and bipolarons confined to limited sequences of repeating units (oligomer approach). Raman studies have shown that polarons and bipolarons coexist in Na- or K-doped poly(*p*-phenylenevinylene)[24, 25] and Na-doped poly(*p*-phenylene).[26, 27] In this paper we will present the electronic absorption and Raman studies of as-polymerized BF_4^--doped PT and the radical cation and the dication of 5T (shown in Fig. 1b) which are models of a positive polaron and a positive bipolaron, respectively.

EXPERIMENTAL

Samples

2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (α-quinquethiophene, 5T) was synthesized according to the previous method.[28] Oxidation of 5T was carried out in a way similar to that reported by Fichou *et al.*[9] Dried dichloromethane (CH_2Cl_2) solutions of anhydrous $FeCl_3$ were added to CH_2Cl_2 solutions of 5T in a sealed reaction apparatus connected to a cell for spectroscopic measurements. When the oxidation was performed by using about two equivalents of $FeCl_3$, the solution turned blue. When an excess amount of $FeCl_3$ was used, the solution became pale blue. Doped and dedoped (neutral) PT films were prepared electrochemically.[29] A PT film doped with BF_4^- was prepared on the surface of a Pt anode in a benzonitrile solution containing thiophene (0.4 mol dm^{-3}) and $LiBF_4$ (0.5 mol dm^{-3}). The voltage applied between this electrode and a Pt counter electrode was 12 V. After the as-polymerized doped film was washed with fresh benzonitrile, the solvent was removed under vacuum. The glass cell containing the doped PT film was sealed off under a reduced pressure. Such a film was used for Raman measurements. A doped PT film prepared on an In-Sn oxide (ITO) glass electrode was dedoped electrochemically and immersed in methanol. After the solvent was removed, this neutral PT film was sealed in a glass cell under vacuum and used for Raman measurements. A thin doped PT film prepared on an ITO electrode was used for absorption measurements.

Spectroscopic measurements

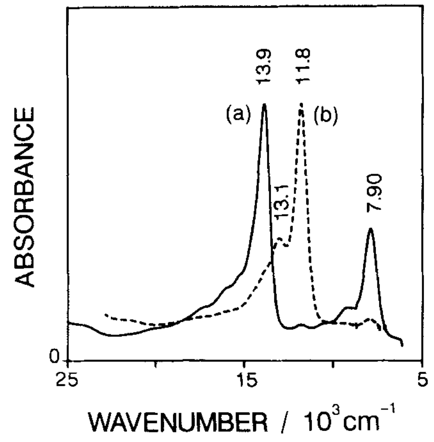
Raman spectra excited at 1064 nm were measured on a JEOL JIR-5500 Fourier transform spectrophotometer modified for Raman measurements.[22] The typical resolution was 2 cm^{-1}. Raman spectra excited at 514.5 and 753 nm were measured on a single polychromator (Spex 1870) equipped with a charge-coupled device (CCD) detector (Princeton Instruments LN/CCD-1024TKBS) operated at −120 °C. The CCD detector was controlled by an ST-135 controller (Princeton Instruments) linked with an NEC PC-9801FX computer through an IEEE-488 interface. Operational programs were coded by H. Ohtsuka. The typical resolution was 6 cm^{-1}. The Raman spectra were calibrated by the use of the Raman bands of indene. A long-wavelength-pass dielectric filter (Omega) and a holographic notch filter (Kaiser Optical Systems) were used to eliminate the elastic scattering for 753- and 514.5-nm excitations, respectively. The 514.5- and 753-nm laser lines were provided from an Ar ion laser (Coherent Radiation Innova 90-6) and a Ti:sapphire laser (Coherent Radiation 890) excited with the Ar ion laser, respectively. Electronic absorption spectra in the region between 200 and 2000 nm were measured on a Hitachi U-3500 spectrophotometer.

RESULTS AND DISCUSSION

Electronic absorption spectra of the radical cation and dication of quinquethiophene and doped polythiophene

The electronic absorption spectra of the oxidized species of 5T are shown in Fig. 2 and that of as-polymerized BF_4^--doped PT in Fig. 3. The first oxidized species of 5T gives rise to the two strong bands at 7900 (1268) and 13900 cm^{-1} (722 nm), which are called bands I and II, respectively. These bands are attributed to the radical cation of 5T ($5T^{\bullet +}$) by Fichou *et al.*[9] The second oxidized species giving rise to one strong band at 11800 cm^{-1} (848 nm), which is called band I', is assigned to the dication of 5T ($5T^{2+}$), by analogy with the assignments[9] of the first and second oxidized species of 6T to the radical cation and dication of 6T, respectively. The 13100-cm^{-1} (766 nm) side band of $5T^{2+}$ is assignable to a vibronic transition. The cation radicals of 4T, 5T, and 6T show two strong absorptions (bands I and II), whereas the dications of 5T and 6T show one strong absorption (band I').[9] The two-band and one-band patterns are consistent with those of the radical anions and dianions of *p*-oligophenyls.[26]

The as-polymerized BF_4^--doped PT film shows two broad absorptions at 5880 and 13500 cm^{-1} within the band gap (Fig. 3). Similar bands were observed at



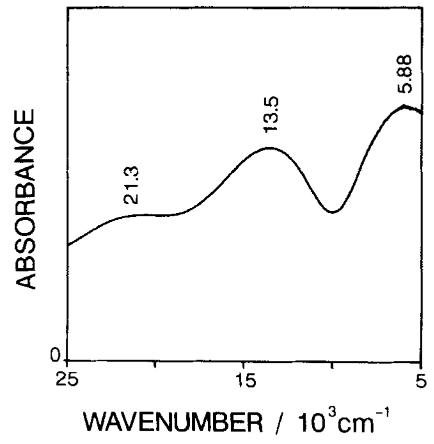


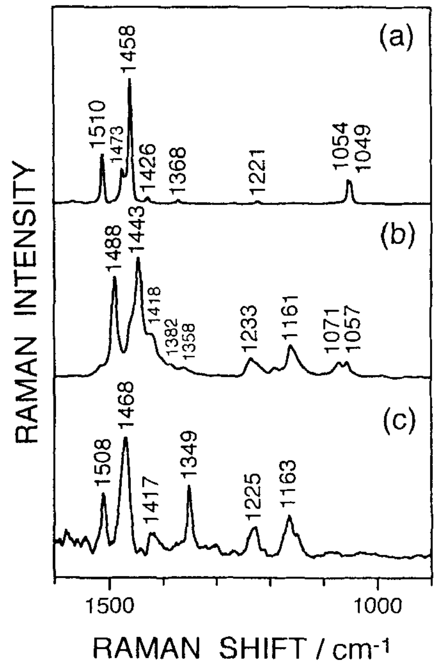
FIGURE 2 (left) Absorption spectra of (a) the radical cation and (b) the dication of quinquethiophene (5T) in CH_2Cl_2 solutions. The maximun intensities of both spectra are equalized.

FIGURE 3 (right) Absorption spectrum of an as-polymerized BF_4^--doped polythiophene film.

intermediate dopant concentrations by Chung *et al.*[5] and Kaneto *et al.*[7] The absorptions due to a polaron and a bipolaron (in polyacetylene) have been calculated by Fesser *et al.*[30] within a framework of a continuum model. According to their results, two localized electronic levels, bonding and antibonding, are formed within the band gap for both a polaron and a bipolaron: a positive polaron is expected to give rise to two strong bands (ω_1, bonding level ← valence band; ω_2, antibonding level ← bonding level) and a weak band (ω_3, antibonding level ← valence band), whereas a positive bipolaron is expected to give rise to a strong band (ω_1', bonding level ← valence band) and a weak band (ω_3', antibonding level ← valence band). The observed two absorptions of doped PT have been assigned to the ω_1' and ω_3' transitions,[5, 7] and have been regarded as the experimental evidence supporting the existence of bipolarons. However, an alternative explanation is possible on the basis of the electronic absorptions of the radical cations and dications of oligothiophenes. Since a radical cation and a dication correspond, respectively, to a positive polaron and a positive bipolaron, bands I and II of the radical cations can be correlated to the ω_1 and ω_2 transitions of polarons, respectively, and band I' of the dications to the ω_1' transition of bipolarons. The ω_3 and ω_3' transitions are symmetry forbidden for the radical cations and dications. Then, the observed two absorptions of doped PT can be assigned to the ω_1 and ω_2 transitions of polarons.

Raman spectra of quinquethiophene and neutral polythiophene

The Raman spectrum of 5T (Fig. 4a) will be discussed in relation to that of PT (Fig. 5a). If an infinite PT chain has the coplanar all-*anti* structure (Fig. 1a), its factor group is isomorphous with the point group D_{2h}. Raman active in-plane modes form the following irreducible representations: $7a_g + 7b_{1g}$. In the Raman spectra of oligothiophenes (2T, 3T, 4T, and 6T), two strong bands are observed in the 1556–1505 and 1463–1444 cm^{-1} regions.[13] According to our preliminary normal coordinate analyses, these bands are assigned to mixtures of the C=C and C_α–$C_{\alpha'}$ (inter-ring C–C) stretches. It has been shown that the higher frequency band shifts downward with increasing number of thiophene rings[13] (conjugation length); 1516 cm^{-1} for 4T, 1510 cm^{-1} for 5T, and 1505 cm^{-1} for 6T. In addition, the relative intensity ($I_{\text{high-freq.}}/I_{\text{low-freq.}}$) decreases as the number of thiophene rings increases. These spectral features



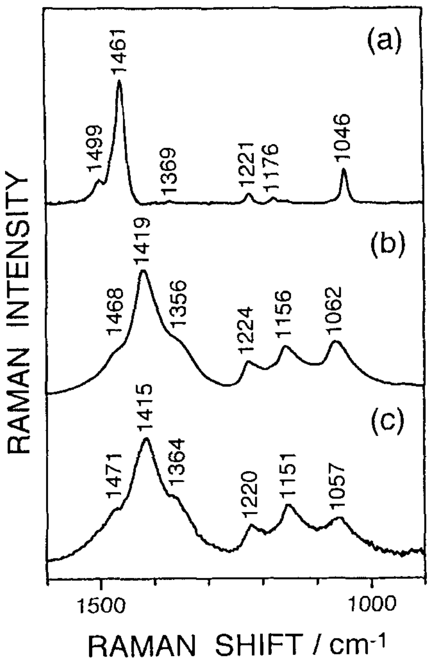


FIGURE 4 (left) Raman spectra of (a) neutral quinquethiophene (5T), (b) its radical cation, and (c) its dication. Excitation wavelengths are 1064, 753, and 753 nm for (a), (b), and (c), respectively. (a) in solid; (b) and (c) in CH_2Cl_2 solutions. Backgrounds are subtracted in (b) and (c).

FIGURE 5 (right) Raman spectra of (a) a neutral polythiophene film and (b and c) an as-polymerized BF_4^--doped polythiophene film. Excitation wavelengths are 514.5, 753, and 1064 nm for (a), (b), and (c), respectively. Backgrounds are subtracted in all spectra.

may be explained by assuming that contributions of the C=C antisymmetric and symmetric stretches increase for the higher and lower frequency bands, respectively, with increasing conjugation length. These bands correspond to the 1499 (b_{1g}) and 1461-cm^{-1} (a_g) bands of PT, respectively.[16] On the other hand, both of the two bands have been assigned to the a_g modes by Navarrete and Zerbi[19, 20] based on the effective conjugation coordinate theory. However, the presence of another band at 1369 cm^{-1} is disregarded in their assignments. Similar bands are observed for oligothiophenes: 1369 (2T), 1367 (3T), 1368 (4T), 1368 (5T), 1368 cm^{-1} (6T). These bands correspond to the 1369-cm^{-1} band of PT, which is assigned to a mode consisting of the C$_\beta$–C$_\beta$ and CS stretches in the a_g species.[16]

Raman spectra of the radical cation and dication of quinquethiophene

The resonance Raman spectra of 5T$^{\bullet+}$ and 5T^{2+} in CH_2Cl_2 solutions are shown in Figs. 4b and 4c, respectively. Spectral characteristics are as follows. (1) Two strong bands are observed in the region above 1440 cm^{-1}. The 1488- and 1443-cm^{-1} bands of 5T$^{\bullet+}$ and 1508- and 1468-cm^{-1} bands of 5T^{2+} are correlated to the 1510- and 1458-cm^{-1} bands of 5T, respectively. These two bands shift downward on going from 5T to 5T$^{\bullet+}$, whereas they shift upward on going from 5T$^{\bullet+}$ to 5T^{2+}. These downshifts and upshifts do not seem to be correlated to changes in the orders of the C=C and C$_\alpha$–C$_{\alpha'}$ bonds in a simple way, because these bands are assignable to mixtures of the C=C and C$_\alpha$–C$_{\alpha'}$ stretches. (2) A strong band at 1349 cm^{-1} is observed for 5T^{2+}, whereas a very weak band is observed at 1358 cm^{-1} for 5T$^{\bullet+}$. (3) The 1233-cm^{-1} band of 5T$^{\bullet+}$ and the 1225-cm^{-1} band of 5T^{2+} are correlated to the 1221-cm^{-1} band of 5T. (4) The 1161-cm^{-1} band of 5T$^{\bullet+}$ and the 1163-cm^{-1} band of 5T^{2+} are characteristic of the charged species. (5) The bands at 1071 and 1057 cm^{-1} of 5T$^{\bullet+}$ are correlated to those at 1054 and 1048 cm^{-1} of 5T. No corresponding band is observed for 5T^{2+}.

Raman spectra of doped polythiophene

The Raman spectra of as-polymerized BF_4^--doped PT excited at 753 and 1064 nm are shown in Figs. 5b and 5c, respectively. The excitation wavelength of 753 nm falls within the electronic absorption centered at 13500 cm^{-1} (741 nm) of doped PT (see Fig. 3). The Raman spectra of BF_4^--doped PT excited at 753 and 1064 nm are similar to each other and different from those of neutral PT, indicating that the observed spectra arise from charged domains generated by doping. The widths of the observed bands are broader than those of neutral PT. This is consistent with the broadness of doping-induced infrared absorptions.[12] Since 5T$^{\bullet+}$ and 5T^{2+} are viewed, respectively, as a positive polaron and a positive bipolaron confined in the sequence of five thiophene rings, they are expected to give information on the polarons and bipolarons in PT. (1)

The shoulder band at 1360 cm^{-1} of doped PT has a corresponding weak band at 1358 cm^{-1} in the spectrum of $5T^{\bullet+}$, whereas the 1349-cm^{-1} band of $5T^{2+}$ is strong in intensity. (2) Bands are observed at around 1060 cm^{-1} for both doped PT and $5T^{\bullet+}$, but no band is found in this region for $5T^{2+}$. These similarities between doped PT and $5T^{\bullet+}$ suggest that positive polarons exist in the as-polymerized BF_4^--doped PT.

Possibility of the existence of polarons or polaron dimers

The results obtained from the present studies of electronic absorption and Raman spectra cast doubt on the accepted view that spinless bipolarons are the self-localized excitations existing in the doped polymer. As mentioned earlier, there is a good possibility that the two characteristic bands in the electronic absorption spectrum of doped PT arise from polarons, although they have so far been assigned to bipolarons. The Raman spectra of doped PT are in favor of the existence of polarons rather than bipolarons. Recently, the polaron-dimer model has been proposed by Hill *et al.*[10] and Segelbacher *et al.*[11] to explain the observed diamagnetic property of charged species generated by doping. This model is based on experimental observations for the radical cations of oligothiophenes. A theoretical study[31] shows that the existence of chain ends and conjugation breaks can actually stabilize polarons. All the above findings and considerations by ourselves as well as by others seem to suggest that polarons or polaron dimers are created by chemical doping in a real polymer sample.

CONCLUSIONS

The Raman bands arising from charged domains in doped PT have been observed by near-infrared Raman spectroscopy. The possibility that the observed Raman bands are due to polarons rather than bipolarons has been suggested on the basis of comparisons with the Raman spectra of the radical cation and dication of α-quinquethiophene, which are models of a positive polaron and a positive bipolaron, respectively. It has also been shown that the two-band pattern in the electronic absorption spectrum is consistent with the existence of polarons.

ACKNOWLEDGMENTS

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