

Raman Spectra of Electrosynthesized Polyfuran: A Combined Experimental and Theoretical Study

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Polyfuran (Pfu) films have been electrochemically deposited on slick platinum or gold electrodes via the direct oxidation of furan in a mixed electrolyte of boron trifluoride diethyl etherate and ethyl ether (1:1, by volume). The Raman spectra of the obtained films, both in the doped and dedoped states, were studied. Experimental results demonstrated that the Raman spectrum of Pfu in the doped state was different from that of neutral Pfu. Five bands related to the oxidized species were observed from the spectrum of doped Pfu and confirmed by in situ Raman spectroelectrochemical study, microconfocal Raman spectroscopy, and surface-enhanced Raman scattering techniques. The Raman spectra of Pfu in both doped and dedoped states also have been calculated with the Gaussian 98 program at the B3LYP/6-31G* level, and the results are in good agreement with the recorded Raman spectra. Based on these calculations, the bands associated with the oxidized species of Pfu were assigned.

Introduction

Extensive work has been devoted to conjugated heterocyclic polymers such as polypyrrole (Ppy),^{1,2} polythiophene (Pth),^{3,4} both theoretically and experimentally. The high conductivity and environmental stability of these materials provide applications in fabricating many types of microelectrical devices. Among them, polyfuran (Pfu), however, is an exception and remains as an ill-defined conjugated polymer, especially in its vibrational spectroscopy. This is possibly due to the drastic condition of synthesis and instability of the polymer.

Electrodeposition of Pfu was first achieved by Zotti et al. through the cathodic reduction of 2,5-dibromofuran in the presence of a Ni(bipy)²⁺ catalyst.⁵ The current efficiency of the system was fairly low and the polymer was powdery. To reduce the oxidation potential of furan, Glenis et al. used the trimer of furan (terfuran) as the starting monomer;⁶ however, the results indicated that the obtained polymer had more structural defects than those of the polymer synthesized from furan.⁷ On the other hand, boron trifluoride diethyl etherate (BFEE) was tested to be an effective medium for the low-potential oxidative polymerization of aromatic monomers such as thiophene and benzene.^{8–10} Free-standing Pfu films were also prepared by the electrochemical polymerization of furan in the mixed electrolyte of BFEE and ethyl ether, and the spectral results showed that the films had fewer defects.¹¹

The Raman spectra of Pfu were first reported by Hernandez et al.,^{12,13} and the bands related to neutral Pfu were assigned by theoretical calculation. However, the researchers found that the Raman spectral features of doped Pfu were similar to those of neutral Pfu, except for the difference in their signal-to-noise (S/N) ratios. Later studies of the same group demonstrated that the Fourier transform (FT)–Raman spectra of the doped Pfu contained some other strong scattering bands that did not exist in the Raman spectra that had been obtained previously. The

authors explained this phenomenon in terms of the existence of a second component in at least a bimodal distribution of conjugation lengths.^{14,15} Recently, we studied the Raman spectra of electrosynthesized Pfu in dedoped and doped states, respectively, and found that the spectral features of Pfu are strongly dependent on its doping level. Thus, the second component of Pfu was the oxidized species of the polymer. Through combination with theoretical calculation, the Raman bands associated with the oxidized species of doped Pfu were assigned.

Experimental Section

Chemical-pure-grade furan was purchased from Farco Chemical Supplies of Hong Kong (Hong Kong, China) and used after distillation under low pressure and with nitrogen protection. BFEE with a BF₃ concentration of 48.24 vol % and a water content of 0.25 vol % was purchased from Beijing Changyang Chemical Plant (Beijing, China) and used after distillation. Lithium perchlorate (analytical-grade purity, supplied by Special Chemical Development and Research Center of North China) was used after drying under vacuum.

Electrochemical syntheses and measurements were performed in a one-compartment cell, using a potentiostat–galvanostat (model 283, EG&G Princeton Applied Research) under computer control. The counter electrode was a slick platinum sheet, whereas the working electrode was slick platinum or a roughened gold electrode. The working and counter electrodes each had a surface area of 0.5 cm² and were placed 1 cm apart. All potentials were referenced to an Ag/AgCl electrode immersed directly in the solution. The potential of polymerization is 0.9 V. The typical electrolyte was BFEE mixed with ethyl ether in the volume ratio of 1:1 and contained 0.1 mol/L of furan. Dedoped polyfuran was prepared by electrochemically reducing the as-grown polyfuran film with a potential of −0.2 V (vs Ag/AgCl) for a long time (>5000 s). All solutions were deaerated by a dry nitrogen stream and maintained under a slight nitrogen overpressure during the experiments.

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Raman spectra were recorded with a microscopic confocal Raman spectrometer (model RM 2000, Renishaw PLC, England) that used a laser beam with an excitation wavelength of 514, 633, or 785 nm, and a charge-coupled device (CCD) detector with a resolution of 4 cm^{-1} . The power was always maintained very low ($\sim 0.1\text{ mW}$), to avoid destruction of the samples. Some complex Raman peaks were divided into component Lorentzian or Gaussian peaks with proper background subtraction using "automatic fitting" programs that were provided by the Raman spectrometer. The sample of Pfu film used for confocal spectra measurements was deposited on a slick platinum sheet and placed on an xyz automatic moveable platform. The confocal spectra were obtained by adjusting the platform in the vertical direction, to focus the laser beam on different transects of the sample. The Pfu that was deposited on the slick platinum sheet was also used for in situ Raman spectroelectrochemical studies. The sample was immersed directly in an acetonitrile solution that contained 0.1 mol/L lithium perchlorate, and Raman spectra were recorded simultaneously at different applied potentials. Surface-enhanced Raman scattering (SERS) was performed via the deposition of Pfu on a roughened gold substrate and the substrate was treated using published procedures.¹⁶ Ultraviolet–visible (UV–Vis) absorption spectra were recorded on a spectrometer (model Ultra-spec 4000, Bio-tech), and the near-infrared (NIR) fraction was recorded by another spectrometer (model Spectrum One NTS, Perkin–Elmer). The Pfu films that were deposited on the indium tin oxide (ITO)-coated electrodes were used for absorption spectroscopic examinations.

Computational Methods

The calculation of the vibration spectra of the neutral, radical cation, and dication species of oligofuran were conducted using the Gaussian 98 program.¹⁷ The neutral species, as well as the dication oligomers, were treated as a conventional closed-shell system, whereas the radical cation oligomers were regarded as an open-shell system. The effects of counterions were not included in the calculations of the radical cations and dications. The 6-31G* basis set and Becke's three-parameter exchange functional, in combination with the Lee–Yang–Parr correlation function (B3LYP), were used.¹⁸ The theoretical values of frequencies were scaled down uniformly by a factor of 0.96 for both the neutral and dedoped species, as reported by Scott and Radom.¹⁹

Results and Discussion

The Raman spectra of doped and dedoped Pfu films, using excitation wavelengths of 514, 633, and 785 nm, are shown in Figure 1. This figure shows that the 514-nm excited Raman spectrum of doped Pfu (spectrum A in Figure 1) resembles that of the dedoped sample (spectrum B in Figure 1). This result coincides with that reported by Hernandez et al.^{13,14} However, when the 785-nm laser is used the excitation source, the spectral features of the Raman spectra (spectra E and F in Figure 1) are different from those of spectra A and B in Figure 1, and similar to the FT–Raman spectra (excited at 1064 nm) reported previously.^{11,14,15} Furthermore, the Raman spectra of doped and dedoped Pfu are also almost the same (see spectra E and F in Figure 1), except for the intensity difference between the peaks at ca. 965 and ca. 945 cm^{-1} , and the appearance of a weak shoulder band centered at ca. 1310 cm^{-1} in spectrum F in Figure 1. A more distinct difference between the Raman spectrum of the dedoped Pfu and that of doped Pfu can be observed using a 633-nm laser beam as the excitation source (see spectra C

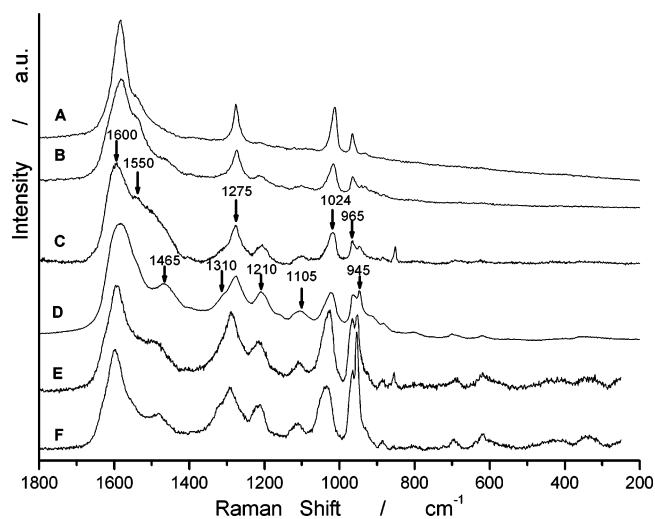


Figure 1. Raman spectra of a Pfu film in dedoped (spectra A, C, E) and doped (spectra B, D, F) states excited by a 514-nm (spectra A, B), 633-nm (spectra C, D), or 785-nm (spectra E, F) laser beam.

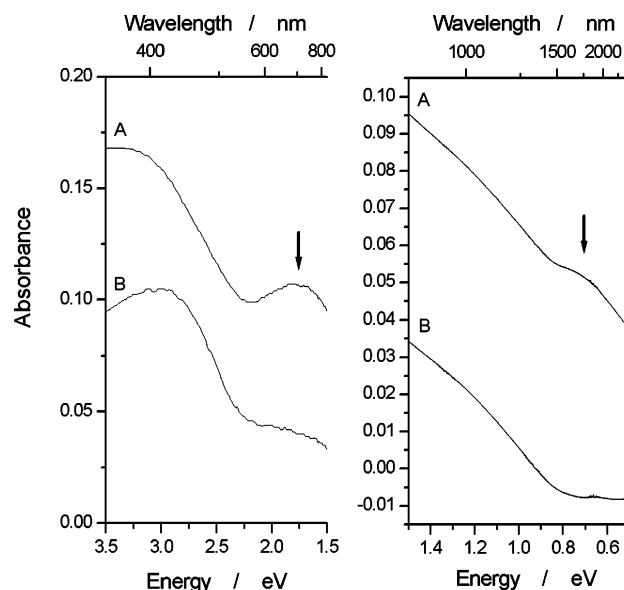


Figure 2. UV–Vis–NIR absorption spectra of a Pfu film in the (A) doped or (B) dedoped state.

and D in Figure 1). The UV–Vis (left) and NIR (right) absorption spectra of Pfu are illustrated in Figure 2. This figure shows that the dedoped Pfu exhibits a broad absorption that is centered at ca. 3.0 eV (420 nm) and tails off to $\sim 2.2\text{ eV}$ (560 nm); however, no absorption band is observed in the NIR region. On the other hand, the doped Pfu shows a new medium absorption at ca. 1.7 eV (727 nm) in the Vis region and a weak broad absorption at ca. 0.7 eV (1750 nm) in the NIR region. These two bands are associated with the oxidized species of Pfu, and the neutral species showed weak absorptions in these regions. Therefore, when excited at 514 nm, the resonance effect enhanced the Raman lines that were more specifically related to the neutral species. On the other hand, the new absorption band of the doped Pfu centered at 727 nm is similar to the wavelength of the 785-nm laser beam. Thus, the 785-nm excited Raman spectra are enhanced more specifically than the lines associated with the oxidized species. As a result, neither the 514-nm nor the 785-nm laser beam is the appropriate Raman excitation source for studying the differences between the Raman spectra of doped and dedoped Pfu, because of their structural selectivity. However, neither the neutral species nor

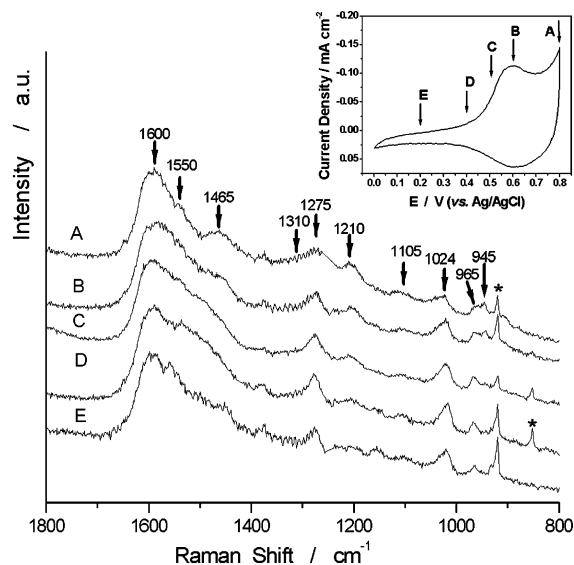


Figure 3. In-situ Raman spectra recorded at different applied potentials (asterisks indicate solvent): 800 mV (spectrum A), 600 mV (spectrum B), 500 mV (spectrum C), 400 mV (spectrum D), and 200 mV (spectrum E).

the oxidized species of Pfu show strong absorption at 633 nm. Therefore, the special enhancement of Raman bands, relative to the neutral or oxidized species, can be greatly avoided. Thus, the 633-nm laser beam is the best choice among the three laser beams for studying the doping level dependence of the Raman spectra, and the bands resulted from the oxidized species of doped Pfu film, because the 633-nm excited Raman spectrum can give structural information on neutral and oxidized species simultaneously. Furthermore, it should be addressed here that the doped Pfu showed two more absorption bands (marked with arrows in Figure 2) other than that of neutral Pfu from the Vis region to the IR region, corresponding to two other intragap transitions. This indicated that the main charge carriers of the polymer were positive polarons, according to the previous research.^{20–22} This point also is confirmed by the theoretical calculation described below.

The 633-nm excited Raman spectra of dedoped Pfu (see spectrum C in Figure 1) shows five main bands—at ca. 1600 (ν_1), 1550 (ν_2), 1275 (ν_3), 1024 (ν_4), and 965 cm^{-1} (ν_5)—and they are assigned to pristine Pfu.¹³ In this spectrum, several weak or shoulder bands also are present, at ~ 1465 (ν_1'), 1310 (ν_2'), 1210 (ν_3'), 1105 (ν_4'), and 945 cm^{-1} (ν_5'). In the 633-nm excited Raman spectrum of doped Pfu (see spectrum D in Figure 1), the relative intensities of these five bands are enhanced in comparison to those in spectrum C in Figure 1, whereas the bands associated with the neutral species of Pfu are still present. Therefore, it is reasonable to conclude that the ν_1' – ν_5' bands are attributed to the oxidized species of Pfu.

The in situ Raman spectroelectrochemical study confirmed the previously described conclusion. Figure 3 illustrates the 633-nm excited Raman spectra recorded from the Pfu-coated platinum electrode surface, which is immersed in a solution of acetonitrile and 0.1 mol/L LiClO_4 , and at different applied potentials. As shown in the stable cyclic voltammogram inserted in Figure 3, the oxidation potential of Pfu in acetonitrile was measured to be ca. 0.6 V (vs Ag/AgCl). Thus, at potentials of <0.6 V, the overall features of the Raman spectra are similar to those of dedoped Pfu. With the increase of applied potential, the Raman bands at 1465, 1310, 1210, 1105, and 945 cm^{-1} (ν_1' – ν_5' bands) are enhanced gradually. At 0.8 V, the entire spectrum is similar to that of a doped Pfu.

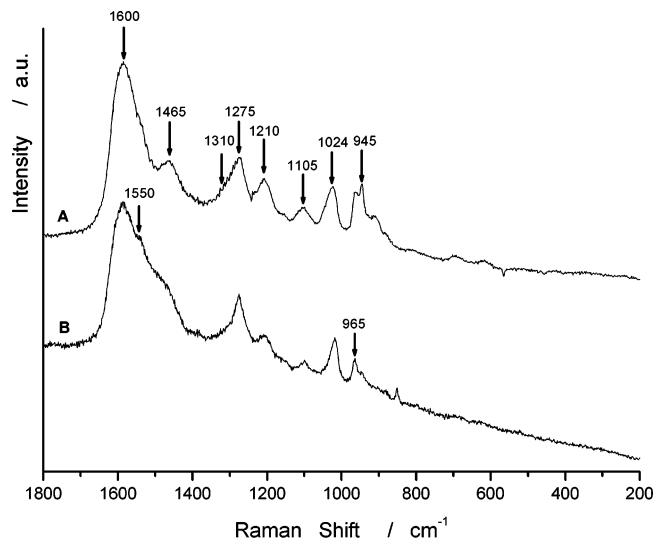


Figure 4. Raman spectra of a thin Pfu film electrochemically deposited on a roughened gold electrode surface (spectrum A) or on a smooth gold electrode surface (spectrum B).

The SERS technique is a powerful tool for studying the molecular structure and molecular orientation on a metallic surface.^{23,24} In addition, SERS has been determined to selectively enhance the Raman bands that are related to the oxidized species of the conducting polymers.^{25,26} Figure 4 demonstrates the Raman spectra of Pfu electrochemically deposited on a roughened gold substrate and on a smooth gold surface (for comparison). The Pfu film was thin (grown at 0.9 V for 1 s), and the Raman spectrum of Pfu on the smooth gold surface is similar to that of pristine Pfu, because of the low doping level of the film (see spectrum B in Figure 4). However, the SERS spectrum of a Pfu film with the same thickness selectively enhanced the bands at ca. 1465, 1310, 1210, 1105, and 945 cm^{-1} (see spectrum A in Figure 4). This result also confirms that the ν_1' – ν_5' bands are associated with the oxidized species of Pfu.

Recently, we found that the doping level of conducting polymer film increased during its electrochemical growth process, and the overall features of the Raman spectrum are strongly dependent on film thickness.^{27–29} The phenomenon was also observed in this system. Figure 5 is the 633-nm excited Raman spectra of an as-grown Pfu film recorded at different confocal depths, using the microscopic confocal technique. This figure shows that the overall features of Raman spectra change gradually with the increase of laser confocal depth. The Raman spectrum of a thick Pfu film, corresponding to the spectrum recorded at a low confocal depth, resembles that of doped Pfu, whereas the spectrum of a thin film resembles that of dedoped Pfu. Furthermore, the Raman bands centered at 1550 cm^{-1} , which are assigned to the C–C stretching of the dedoped Pfu ring, decrease,¹² whereas the relative intensities of the ν_1' – ν_5' bands increase gradually as the film thickness increases. Table 1 lists the intensity ratios of the Raman bands, in terms of confocal depth, according to Figure 5 (the overlapped bands were separated into their Lorentzian or Gaussian components). This table clearly shows the relative intensity changing tendencies of the ν_1' – ν_5' bands. The microscopic confocal Raman spectral results demonstrated that doping induced the five ν_1' – ν_5' bands, and the doping level of Pfu increased as the film thickness increased.

When an infinite Pfu chain is considered to be a one-dimensional (1D) lattice of furan units, all coplanar units are in

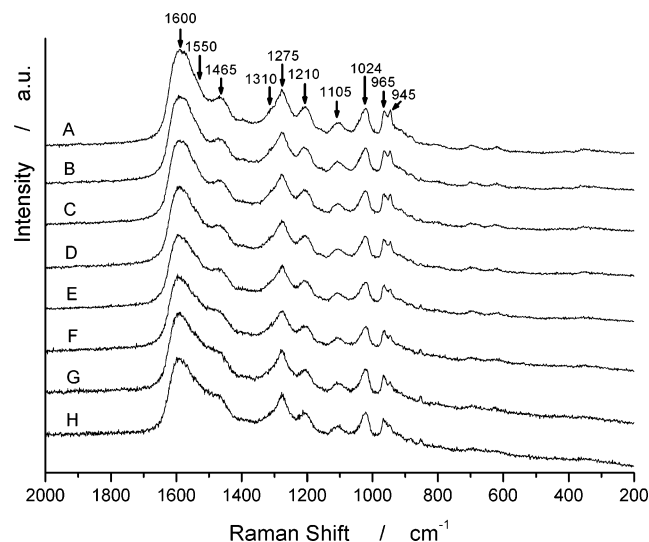


Figure 5. Raman spectra (wavelength of excitation was 633 nm) of a Pfu film recorded at different confocal depths: 0 μm (spectrum A), 3 μm (spectrum B), 6 μm (spectrum C), 9 μm (spectrum D), 12 μm (spectrum E), 15 μm (spectrum F), 18 μm (spectrum G), and 21 μm (spectrum H).

TABLE 1: Raman Band Ratios in Terms of Confocal Depth, According to Figure 5.

confocal depth (μm)	Raman Band Ratio				
	I_{1465}/I_{1550}	I_{1310}/I_{1275}	I_{1210}/I_{1275}	I_{1105}/I_{1275}	I_{946}/I_{965}
0	0.557	0.517	0.886	0.402	1.009
3	0.560	0.413	0.742	0.399	1.063
6	0.535	0.215	0.581	0.325	0.878
9	0.527	0.210	0.592	0.327	0.862
12	0.518	0.185	0.561	0.328	0.813
15	0.510	0.204	0.611	0.261	0.785
18	0.502	0.159	0.561	0.253	0.639
21	0.483	0.152	0.514	0.253	0.604

an “anti” conformation, and its repeat unit consists of two furan rings. The point group of such a 1D lattice is isomorphous with that of D_{2h} . Hernandez et al.^{12,13} calculated the Raman spectra of Pfu. The geometry and vibrational force fields were derived from semiempirical calculations that were performed on oligomers, and the parameters were also used for the polymer. The Raman spectrum of neutral Pfu consists of six lines assigned to A_g modes at the frequencies that are $<1700\text{ cm}^{-1}$. The calculated Raman spectrum of neutral sexifuran (Fu_6) at the B3LYP/6-31G* level is shown in Figure 6, which shows that the calculated spectrum is consistent with the recorded spectra of polyfuran.^{12,13} Therefore, Fu_6 can represent the most characteristics of Pfu.

To calculate the Raman spectrum of doped Pfu, the spatial extension of the defect (polaron and dipolaron) in doped Pfu must be estimated, because of a lack of oligomer model compounds. Usually, the defect length of the bipolaron is the same as that of the polaron. In doped poly(*para*-phenylene) (PPP), the defects without counterions extend over 3–5 monomer units, and those in doped polythiophene (Pth) are 6–10 monomer units.^{30–33} If one considers the counterions, the defect will show a shorter spatial extension.³⁴ On the other hand, the inter ring delocalization of Pfu is between those of PPP and Pth;¹² therefore, it is reasonable to deduce that the defect in Pfu extends over 6–8 monomer units. According to the absorption spectra of doped Pfu, the charge carriers in Pfu are mainly polarons. Hence, the Fu_6 or Fu_8 polaron can primarily represent the main characteristics of doped Pfu.

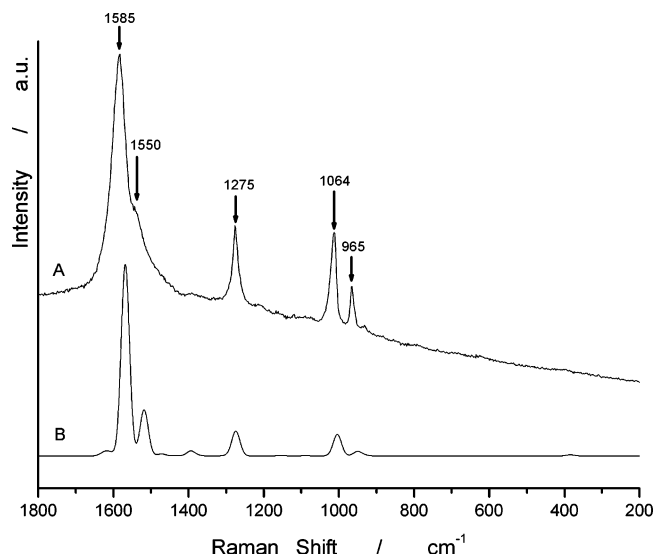


Figure 6. Observed Raman spectrum of neutral Pfu (spectrum A) and calculated Raman spectrum of neutral Fu_6 at the B3LYP/6-31G* level (spectrum B).

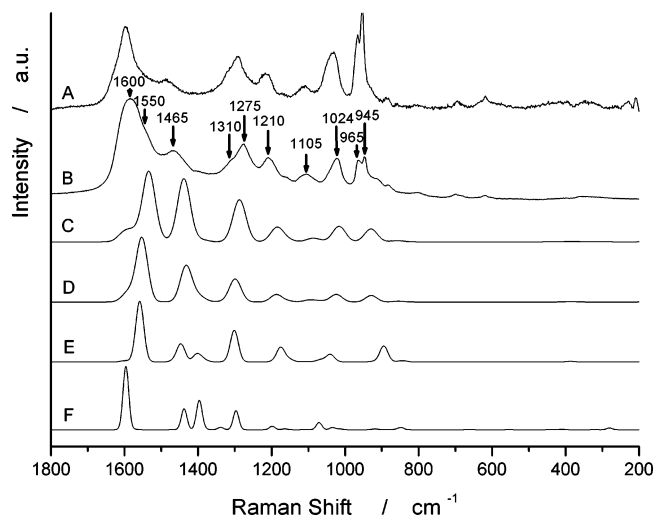


Figure 7. Calculated Raman spectra of the Fu_3 polaron (spectrum F), the Fu_6 bipolaron (spectrum E), the Fu_6 polaron (spectrum D), and the Fu_8 polaron (spectrum C) at the B3LYP/6-31G* level, and the observed Raman spectra of doped Pfu excited by a 785-nm laser beam (spectrum A) or a 633-nm laser beam (spectrum B).

The Raman spectra of doped oligofurans at the B3LYP/6-31G* level are shown in Figure 7, which shows that the calculated spectra change dramatically from the Fu_3 polaron to the Fu_6 polaron (see spectra F and D in Figure 7). However, there is almost no difference between the calculated spectra of the Fu_6 and Fu_8 polarons (see spectra D and C in Figure 7), which implies that the calculated Raman spectra are basically converged. The calculated Raman spectrum of the Fu_6 polaron has good agreement with the recorded Raman spectrum of doped Pfu (see spectrum A or B in Figure 7), in regard to both band frequency and band relative intensity. However, the calculated spectrum of the Fu_6 bipolaron (see Figure 7E) shows a distinct deviation from the observed spectrum of doped Pfu. Therefore, it can be concluded that the charge carriers (i.e., the defects in doped Pfu synthesized in this system) are mainly polarons. This result is consistent with that of the absorption spectrum shown in Figure 2. The Raman band assignments of doped Pfu are listed in Table 2.

TABLE 2: Raman Bands Assignment of Fu₆, Fu₈ Polarons and Doped Pfu.

Fu ₆ polaron		Fu ₈ polaron		Pfu (doped),	
cal.	scal.	cal.	scal.	Exp.	assignments
1615.0	1552	1595.5	1534	1600–1595	A _g , C=C stretching (ring–ring)
1491.3	1433	1497.1	1439	1465–1480	A _g , C–H wagging
1352.0	1299	1342.4	1291	1310–1325	A _g , C–C stretching
1235.0	1187	1232.6	1185	1205–1215	A _g , C–H wagging
1138.9	1094	1132.0	1088	1100–1112	A _g , C–H wagging
1066.0	1024	1058.3	1018	1013–1025	A _g , C–H wagging
968.3	930	968.4	931	945–955	A _g , ring deformation
964.2	926	965.9	929	945–955	A _g , ring deformation

Conclusions

Polyfuran (Pfu) films that have been electrochemically deposited from the mixed electrolyte of boron trifluoride dither etherate and ethyl ether have been studied by resonance Raman spectroscopy, in situ Raman spectroelectrochemical, microscopic confocal Raman, and surface-enhanced Raman scattering techniques. The bands of “the second component” shown in the spectra reported by Hernandez et al. changed as the doping level changed, and “the second component of the bimodal distribution of conjugation lengths” was determined to be the oxidized species of the polymer. Five Raman bands related to the oxidized species of Pfu were determined and confirmed experimentally. The Raman spectra of doped oligofurans have been calculated at the B3LYP/6-31G* level. The calculated spectrum shows satisfactory agreement with the recorded spectrum of doped Pfu.

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