Preparation and spectroelectrochemical behaviour of a new alternate copolymer of 3,3′-di-*n*-octyl-2,2′-bithiophene and fluoren-9-one

Renaud Demadrille,[a] Bernadette Divisia-Blohorn,[b] Malgorzata Zagorska,[c] Sophie Quillard,[d] Patrice Rannou,[a] Jean Pierre Travers[a] and Adam Pron*[a]

[a] *Laboratoire de Physique des Métaux Synthétiques (CEA-CNRS-Université Grenoble, UMR5819-SPrAM), DRFMC, CEA-Grenoble, 17 Rue des Martyrs, 38054, Grenoble cedex 9, France. E-mail: pron@cea.fr.; Fax: +33 (0)4 3878 5113; Tel: +33 (0)4 3878 4389*

[b] *Laboratoire d'Electrochimie Moléculaire et Structure des Interfaces (CEA-CNRS-Université Grenoble I UMR5819-SPrAM), DRFMC, CEA-Grenoble, 17 Rue des Martyrs, 38054, Grenoble cedex 9, France*

[c] *Faculty of Chemistry, Warsaw University of Technology, 00 664, Warszawa Noakowskiego 3, Poland*

[d] *Institut des Matériaux Jean Rouxel, 2 Rue de la Houssinière, B.P. 32229, 44322, Nantes cedex 3, France*

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The synthesis and spectroelectrochemical behaviour of a new solution processible conjugated polymer, namely poly[{5,5′-(3,3′-di-*n*-octyl-2,2′-bithiophene)}-*alt*-(2,7-fluoren-9-one)] (abbreviated as PDOBTF), are described. PDOBTF can be considered as the first member of a new family of conjugated copolymers—poly(oligothiophene-*alt*-fluoren-9-one)s—whose properties can be tuned by changing the length of the oligothiophene segments and their regiochemistry. PDOBTF can be obtained by oxidative polymerisation of 2,7-bis(4-octylthien-2-yl)-fluoren-9-one or by condensation polymerisation of 2,7-bis(5-bromo-4-octylthien-2-yl)-fluoren-9-one using a modification of Yamamoto coupling. Both preparation methods lead to a mixture of polymeric and oligomeric species and require post-polymerisation fractionating if high molecular fractions are to be obtained. Oxidative polymerisation gives product of a higher molecular weight ($M_n = 41.0$ kDa, $M_w/M_n = 1.81$ for the highest molecular weight fraction) as compared to the one prepared by Yamamoto condensation polymerisation ($M_n = 13.3$ kDa, $M_w/M_n = 1.45$ for the highest molecular weight fraction).

Electrochemical oxidation of PDOBTF in an nonaqueous electrolyte (0.1 M Bu_4NBF_4/acetonitrile) gives rise to an anodic peak at $E = 835$ mV, which can be ascribed to the p-type doping of the copolymer. The extension of the potential to $E = 1500$ mV results in the oxidative degradation of the copolymer and induces total loss of its electroactivity. UV-Vis-NIR and Raman spectroelectrochemical data are consistent with the oxidative doping. The latter technique enables the monitoring of the doping-induced changes in both structural sub-units of the copolymer: the bithiophene sub-unit and the fluoren-9-one one.

Introduction

Conjugated polymers constitute an extremely interesting class of macromolecular systems whose electronic, optical and electrochemical properties can be precisely tuned either by appropriate functionalisation of the polymer backbone with side groups influencing the electronic density of the conjugated backbone[1–6] or by preparing copolymers containing conjugated segments of different chemical nature.[7–12] In the copolymer approach two principal routes can be used. (i) Copolymerisation of two conjugated co-monomers. This method usually gives random conjugated copolymers although the use of special techniques may lead to alternate copolymers. (ii) Synthesis of specially designed "hybrid-type" monomers containing building blocks originating from both co-monomers. Homopolymerisation of such monomers leads to alternate conjugated copolymers. The latter approach seems especially interesting since it enables the preparation of copolymers with a highly regular chain microstructure that, by consequence, facilitates the formation of ordered supramolecular aggregations in the solid state.

In our recent research we have focused on the preparation of a new family of conjugated copolymers, namely alternate copolymers, in which fluoren-9-one units are linked together by oligoalkylthiophene units. These are extremely interesting macromolecular systems, which are solution processible due to the presence of alkyl substituents in the oligothiophene segments. Moreover, their electronic, photoluminescence, spectroscopic and electrochemical properties can be precisely tuned by changing the length of the oligothiophene spacer between the fluoren-9-one groups as well as by adjusting the regioregularity. Another interesting feature of these copolymers is the possibility of their post-polymerisation functionalisation *via* the carbonyl group of the fluoren-9-one unit, which allows the grafting of chemical species exhibiting specific electronic and electrochemical properties. For example, electroactive oligoaniline side groups can easily be branched to the polymer main chain using a $TiCl_4$ catalysed coupling reaction between the oligoaniline amine group and the carbonyl group of the fluoren-9-one unit.[13] Electrochemical, spectroscopic and spectroelectrochemical properties of polymers functionalised in such a manner can be tuned by changing the level of oligoaniline grafting.[14]

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In this paper we report on the preparation as well as on the electrochemical and Raman spectroelectrochemical properties of the first member of the above described family of copolymers, namely poly[{5,5′-(3,3′-di-*n*-octyl–2,2′-bithiophene)}-*alt*-(2,7-fluoren-9-one)], abbreviated as PDOBTF. Structural and photoluminescence properties of this copolymer will be the subject of a separate publication.

Experimental

Materials and methods

All reagents and chemicals were purchased from Aldrich and used as received with the exception of chloroform and nitromethane, which were dried over $CaCl_2$ and distilled in a vacuum line prior to the use.

Monomers for oxidative polymerisation and condensation polymerisation were characterised by ^1H NMR (Brucker AC 200 MHz or Varian 400 MHz), FTIR (Perkin Elmer Paragon500 spectrometer) and elemental analysis (Analytical Service of the CNRS, Vernaison, France).

Molecular weight determinations of the chloroform fractions of the polymers obtained by two polymerisation methods (oxidative polymerisation and condensation polymerisation) were measured using size exclusion chromatography (SEC) on a 1100HP Chemstation equipped with a 300*7.5 mm Plgel Mixed-D 5 μm/10^4 Å column. Detection was performed by a diode array UV-Vis detector and a refractive index detector. The column temperature and the flow rate were fixed to 313 K and 1 mL min^{-1}, respectively. The calibration curve was built using 10 polystyrene narrow standards (S-M-10* kit from Polymer Labs). Two runs of 20 μL injection of *ca.* 2 mg mL^{-1} polymer in HPLC grade THF solutions were typically analysed for each sample with a UV-Vis detection located at 355 nm.

For cyclic voltammetry investigations a thin layer of the chloroform fraction of the polymer was deposited on a platinum electrode by casting from solution. The experiments were carried out in a one-compartment electrochemical cell using a Pt counter electrode and an Ag/0.1 M $AgNO_3$ reference electrode. A 0.1 M solution of tetrabutylammonium tetrafluoroborate solution in acetonitrile was used as the electrolyte. The reference electrode was calibrated *vs.* the ferrocene couple measured in the same solution.

The same electrolyte as well as the reference and counter electrodes were used for the ultraviolet-visible-near infrared (UV-Vis-NIR) and Raman spectroelectrochemical studies. In the former case a thin polymer film was deposited on an ITO transparent working electrode whereas in the latter one a platinum electrode was used. The UV-Vis-NIR spectra where measured on a Lambda 2 Perkin Elmer spectrometer whereas the Raman spectra were obtained using an FT Raman Bruker RFS 100 spectrometer with the NIR excitation line (1064 nm).

Oxidative polymerisation

2,7-Bis(4-octylthien-2-yl)-fluoren-9-one (**1**), the monomer used for the preparation of PDOBTF by oxidative polymerisation, was prepared from 3-octylthiophene and 2,7-dibromofluoren-9-one, *via* Suzuki coupling, which involves the preparation of boronic derivative of the former.[11,15]

In a typical polymerisation procedure,[16] 530 mg of the oxidant (anhydrous $FeCl_3$, 4.18 mmol) was dissolved in a mixed solvent (5 mL of nitromethane and 30 mL of chloroform) and then added dropwise to a solution of **1** (450 mg, 0.79 mmol) in 30 mL of $CHCl_3$. The addition was carried out at 0 °C with constant stirring. At the end of the addition, the mixture was warmed to 10 °C and was maintained at this temperature for 60 min. The reaction mixture was then allowed to warm and as kept at room temperature (RT) for 12 h with constant stirring. In the next step it was concentrated by pumping under vacuum and finally the polymer was precipitated in 100 mL of methanol. The separated crude polymer was dissolved in 50 mL of chloroform and washed four times with a 0.1 M aqueous solution of ammonia (150 mL each time). Then it was stirred for 48 h with the same aqueous solution.

As synthesised thiophene-based polymers usually contain small amounts of dopants of unidentified chemical composition. Thus, their further purification requires dedoping. The dedoping process consisted in washing of the chloroform solution of the polymer with an EDTA aqueous solution (0.05 M, 200 mL). The polymer was then washed with water twice and then dried under vacuum to give 327 mg of a red-brown powder (yield 73%). As demonstrated by SEC, the polymer prepared according to the above procedure consists of a mixture of high molecular weight fractions and relatively short oligomers; thus, it requires further fractionating. This was achieved by sequential extraction of the crude polymer. The exact procedure can be briefly described as follows. The polymer was first extracted with ether in a Soxhlet apparatus until the filtrate was colourless. The remaining part, insoluble in ether, was then consecutively extracted with acetone, *n*-pentane, dichloromethane, tetrahydrofurane and chloroform in the same manner as in the case of the extraction with ether. For further electrochemical and spectroelectrochemical studies we used the highest molecular weight chloroform fraction, which showed $M_n = 41.0$ kDa equiv. PS with a polydispersity coefficient of 1.81. The characterisation of the polymer presented below refers to the chloroform fraction.

^1H-NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.91 (m, 2H), 7.69 (m, 2H), 7.49 (m, 2H), 7.29 (s, 2H), 2.60 (t, 4H, $J = 8$ Hz), 1.64 (m, 4H), 1.27 (m, 20H), 0.87 (m, 6H). ^{13}C-NMR ($CDCl_3$, 200 MHz, ppm) δ: 193.18 (C=O), 143.75 (2C), 142.60 (2C), 142.35 (2C), 135.07 (2C), 131.34 (2C), 128.76 (2C), 125.42 (2C), 125.12 (2C), 121.05 (2C), 120.66 (2C), 31.92 (2C), 30.72 (4C), 29.45 (4C), 29.24 (2C), 22.66 (2C), 14.08 (2C). IR (free standing film, cm^{-1}): 3042 (w), 2952 (s), 2926 (s), 2852 (s), 2727 (w), 2678 (w), 1718 (s), 1603 (m), 1585 (m), 1529 (m), 1473 (s), 1438 (s), 1376 (w), 1291 (m), 1253 (m), 1229 (w), 1204 (w), 1164 (m), 1127 (w), 1029 (w), 903 (w), 891 (w), 814 (s), 782 (s), 721 (w), 659 (w). Elem. anal.calcd for $C_{37}H_{44}OS_2$: C, 78.12% H, 7.80% S, 11.27%; found: C, 77.10% H, 7.70% S, 9.95%.

Condensation polymerisation

Direct bromination of monomer **1** using 2 equiv. of *N*-bromosuccinimide (NBS) affords monomer **2** in good yields. The latter can be polymerised to PDOBTF *via* Yamamoto coupling using a zero valent nickel reagent.[17,18]

Typical condensation polymerisation of **2** was performed in the following manner. $Ni(COD)_2$ (218 mg, 0.79 mmol), COD (72 mg, 0.66 mmol) and 2,2′-bipyridyl (124 mg, 0.79 mmol) were mixed together in 10 mL of dry DMF. The solution was then heated at 55 °C for 40 min and then slowly added (over 20 min) to a solution of **2** (480 mg, 0.66 mmol) in dry THF (10 mL) kept at the same temperature. The mixture was then kept at 55 °C with constant stirring for 48 h in the dark. It was then cooled to RT and the polymer was precipitated with 300 mL of methanol. The precipitate was filtered and dried under dynamic vacuum to provide 355 mg of a red powder (yield: 95%). Again, as shown by SEC the crude polymer was a mixture of oligomeric and polymeric species and had to be fractionated. The fractionation was carried out in exactly the same way as in the case of the polymer obtained by oxidative polymerisation (*vide supra*). For further investigations the highest molecular weight chloroform fraction was used: $M_n = 13.3$ kDa equiv. PS, polydispersity coefficient

1.45. Again the characterisation presented below refers to the chloroform fraction.

IR (free standing film, cm^{-1}): 3042 (w), 2952 (s), 2926 (s), 2852 (s), 2727 (w), 2678 (w), 1718 (s), 1603 (m), 1585 (m), 1529 (m), 1473 (s), 1438 (s), 1376 (w), 1291 (m), 1253 (m), 1229 (w), 1204 (w), 1164 (m), 1127 (w), 1029 (w), 903 (w), 891 (w), 814 (s), 782 (s), 721 (w), 659 (w). Elem. anal. calcd for $C_{37}H_{44}OS_2$: C, 78.12% H, 7.80% S, 11.27%; found: C, 76.41% H, 7.38% S, 10.74%.

Results and discussion

Synthesis

The polymerisation procedures used in this research are presented in Scheme 1. In general, the oxidative polymerisation methods yield conjugated polymers of higher molecular weight as compared to those prepared by condensation polymerisations.[8,19] This is also the case for PDOBTF since the highest molecular weight fraction of the polymer prepared from **1** shows a roughly three times higher M_n value than the corresponding fraction of the polymer prepared from **2** by Yamamoto-type condensation. It should, however, be noted that both M_n values reported here are overestimated. This overestimation arises from the fact that the exclusion phenomena in polyconjugated systems differ from those in polystyrene and, as a consequence, polystyrene standards are not well-suited for the determination of the molecular weight of conjugated polymers, as clearly demonstrated by the comparison of the SEC and MALDI-TOF data, in the case of regioregular poly(3-alkylthiophene-2,5-diyl).[19] For comparable molecular weights the overestimation factor in poly(3-alkylthiophene-2,5-diyl)s exceeds 2.

Cyclic voltammetry

Similarly as its corresponding homopolymers, poly[5,5′-(3,3′-di-*n*-octyl-2,2′-bithiophene)] and poly(2,7-fluoren-9-one), PDOBTF is electroactive and can be electrochemically n- or p-doped. In this paper we report only on the spectroscopic consequences of its p-type (oxidative) doping. In Fig. 1 a typical cyclic voltammogram (CV) of PDOBTF (obtained *via* oxidative polymerisation) is presented. The oxidation peak with a clear maximum at $E = 835$ mV can be ascribed to the p-type doping or in other words to the oxidation of the neutral polymer chains to polycations, accompanied by insertion of anions, originating from the electrolyte, to the polymer matrix. Upon reverse scanning a very broad cathodic peak is registered, corresponding to the reductive dedoping of the polymer. The doping/dedoping process is in large part irreversible, as seen from the time integration of the anodic and cathodic currents. This is even more clearly demonstrated in Fig. 2 in which three consecutive CV scans are compared. The first scan is limited to $E = 1000$ mV and shows similar features to that presented in Fig. 1. In the second scan the reverse potential is extended to $E = 1500$ mV. First we notice that the oxidative doping peak is of significantly lower intensity as compared to that recorded in the first scan, which unequivocally indicates significant irreversibility of the doping. At higher potentials a second oxidation peak appears with much higher intensity, which has no reduction counterpart. This peak can be attributed to an irreversible degradation of the polymer.[20] For this reason, upon the third scan, the polymer shows no electrochemical activity. In polythiophene-based systems the potential range of the doping process and that of the oxidative degradation frequently overlap[21] and this phenomenon is also the source of the irreversible component of the doping process in the polymer studied here.

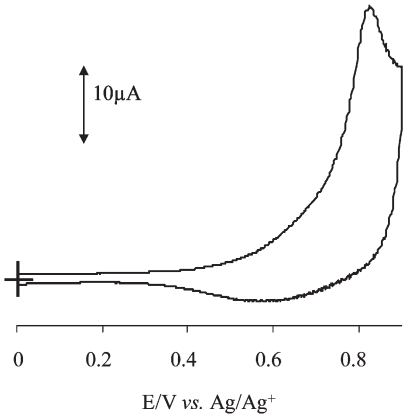
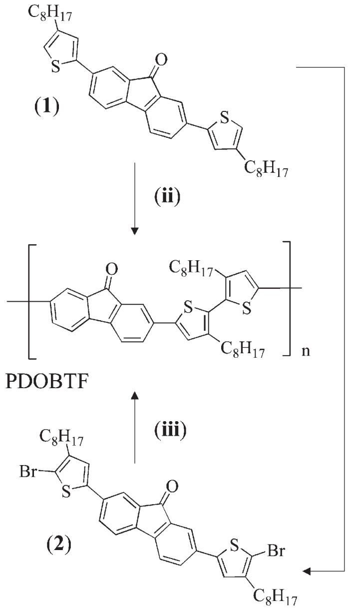


Fig. 1 Cyclic voltammogram of a thin film of poly[{5,5′-(3,3′-di-*n*-octyl-2,2′-bithiophene)}-*alt*-(2,7-fluoren-9-one)] (PDOBTF) registered in 0.1 M Bu_4NBF_4 solution in acetonitrile. Ag/Ag$^+$ reference electrode, scan rate: 50 mV s^{-1}.



Scheme 1 (i) 2.5 equiv. NBS, $CHCl_3$, RT, 12 h; (ii) $FeCl_3$, $CHCl_3$/CH_3NO_2, 0 °C to RT, 12 h; (iii) $Ni(COD)_2$, COD, Bpy, DMF/$CHCl_3$, 55 °C, 72 h.

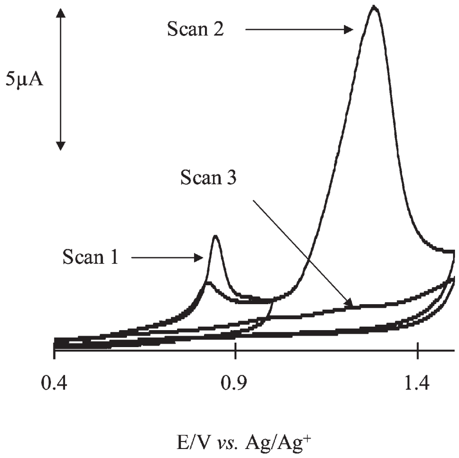


Fig. 2 Three consecutive cyclic voltammetry scans showing electrochemical oxidative degradation of a thin film of poly[{5,5′-(3,3′-di-*n*-octyl-2,2′-bithiophene)}-*alt*-(2,7-fluoren-9-one)] (PDOBTF). Electrolyte 0.1 M Bu_4NBF_4 solution in acetonitrile, Ag/Ag$^+$ reference electrode, scan rate: 50 mV s^{-1}.

UV-Vis-NIR spectroelectrochemistry

In the spectral zone characteristic of electronic transitions in the π-bonding system, two bands at 389 and at 485 nm can be distinguished in the spectrum of a thin solid film of PDOBTF (Fig. 3). The peaks recorded in the solid state spectrum are broadened and slightly red-shifted in comparison to the corresponding peaks in the solution (chloroform) spectrum. Following the interpretation related to the poly(2,7-fluoren-9-one) homopolymer, given in ref. 22, we attribute the band at 389 nm to the π-π* transition in the conjugated backbone of the copolymer and the band at 485 nm to the n-π* transition of the carbonyl group. A large red shift, of over 80 nm, of the peak corresponding to the n-π* transition in the carbonyl group is observed here for the polymer studied as compared to the analogous band in the fluoren-9-one molecule.[22] This can be interpreted as a spectroscopic manifestation of the conjugation of the carbonyl group π-bond with the delocalized π-bonding system of the polymer backbone.

The results of the UV-Vis-NIR spectroelectrochemical investigations are consistent with the above interpretation. The onset of the doping-induced spectral changes at $E = 700$ mV coincides with the onset of the anodic current in the CV of the polymer. In the majority of conjugated polymers oxidative electrochemical doping results in a gradual bleaching of the band corresponding to the π-π* transition in the polymer backbone with concomitant growth of three (or two) bands in the less energetic part of the spectrum, originating from transitions involving polarons (or bipolarons) created upon doping.[23] Indeed, the band at 389 nm decreases in intensity upon increasing the electrode potential. The first bipolaron band is clearly visible at *ca.* 655 nm whereas the onset of the second one appears in the form of a steadily increasing absorbance in the 850–1100 nm spectral range. The absorption band at 485 nm, which is ascribed to the n-π* transition in the carbonyl group, remains essentially unaffected by the doping. Its apparent increase in intensity is caused by the fact that it is superimposed on the higher energy side of the first bipolaron band, whose intensity grows with increasing electrode potential.

Raman spectroelectrochemistry

Raman spectroelectrochemistry is a very efficient tool for studying doping-induced changes in conjugated polymers since the doping process involves a redistribution of the π-electron charge density along the polymer chain and strongly influences the chain conformation. As a consequence shifts in the position of selected Raman bands are expected, especially these originating from deformations involving double bonds. Moreover, some bands may disappear and new ones appear because they may become symmetry-forbidden or symmetry-allowed as a result of doping-induced chain conformational changes. In Raman spectroelectrochemical investigations one should also consider resonant phenomena. Resonant enhancement of Raman bands takes place when the energy of the excitation line is close, or even better, coincides with the energy of a given electronic transition in the polymer studied. From the UV-Vis-NIR spectroelectrochemical behaviour of PDOBTF (see Fig. 3) it is clear that the blue excitation line ($\lambda_{exc} = 457.9$ nm) should enhance the bands originating from vibrations of the undoped segments of the polymer whereas the red ($\lambda_{exc} = 676$ 676 nm) and the infrared ($\lambda_{exc} = 1064$ nm) lines should enhance the bands associated with the vibration of the doped polymer segments since the doping process induces a significant increase of the absorbance in the red and in the NIR parts of the spectrum. For these reasons, in the studies of the electrochemical doping process, we have selected the NIR excitation line. In this case, being out of resonance for the neutral (undoped) polymer, we improved the resonant conditions with increasing doping level.

Raman spectra of neutral as well as doped PDOBTF are essentially independent of the preparation method. In the undoped (neutral) state, PDOBTF prepared by condensation polymerisation gives, however, a better resolved spectrum with slightly narrower lines, which may be indicative of a better structural order. For this reason, in the present communication we show only the spectra of the polymer prepared by Yamamoto coupling. The spectroelectrochemical behaviour of PDOBTF prepared by oxidative polymerisation is essentially the same.

The spectra of neutral and fully doped PDOBTF are compared in Fig. 4. For clarity the positions of the principal bands are indicated. To a first approximation the Raman spectrum of the neutral copolymer can be considered as a superimposition of the spectra of the corresponding homopolymers, poly[5,5′-(3,3′-di-*n*-octyl-2,2′-bithiophene)] and poly(2,7-fluoren-9-one). In the attribution of the bands we follow the literature data.[23–26] In particular, we attribute the band at 1496 cm^{-1} to C_α–C_β antisymmetric deformations in the thienylene ring whereas the bands at 1460 and 1439 cm^{-1} are ascribed to C_α–C_β symmetric deformations in the same ring. In regioregular head-to-tail (HT) coupled poly(3-alkylthiophene-2,5-diyl)s the C_α–C_β symmetric deformations give rise to only one line at *ca.* 1440 cm^{-1}.[23] However, the head-to-head (HH) coupling of the 3-alkyl (or alkoxy) 3-substituted 2,5-thienylene rings, as in our case, induces a splitting of the band corresponding to

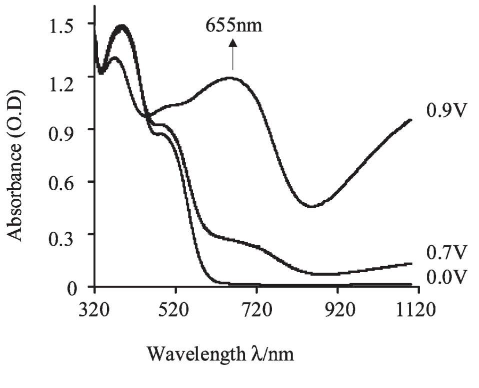


Fig. 3 UV-Vis-NIR spectra of a thin film of poly[{5,5′-(3,3′-di-*n*-octyl-2,2′-bithiophene)}-*alt*-(2,7-fluoren-9-one)] (PDOBTF) registered for increasing electrode potential *E vs.* Ag/Ag^+, electrolyte 0.1 M Bu_4NBF_4 solution in acetonitrile.

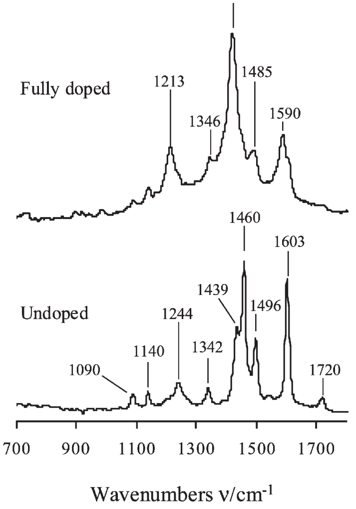


Fig. 4 FT Raman spectra ($\lambda_{exc} = 1064$ nm) of neutral and fully doped poly[{5,5′-(3,3′-di-*n*-octyl-2,2′-bithiophene)}-*alt*-(2,7-fluoren-9-one)] (PDOBTF).

the C_α–C_β symmetric stretching deformations. The C_β–C_β stretching deformations give rise to only one Raman band, independently of the type of coupling.[24,27] In the case of our copolymer this band is located at 1342 cm^{-1}. The band at 1244 cm^{-1} is, in turn, attributed to C_α–C_α, inter-ring stretching deformations. Two peaks of low intensity at 1140 and 1090 cm^{-1} correspond to the C_β–$C_{subst.}$ stretching deformations. The presence of the fluoren-9-one units is manifested, in the Raman spectrum, by two bands: a strong peak at 1603 cm^{-1}, which can be ascribed to C–C stretching deformations in the tri-substituted aromatic ring, and a second peak at 1720 cm^{-1} of much lower intensity, which is characteristic of the C=O stretching deformations in the carbonyl group.

The evolution of the spectra with increasing electrode potential is presented in Fig. 5. The top spectrum in this figure corresponds to the spectrum of the fully doped polymer in Fig. 4. The first signs of oxidative doping of PDOBTF appear in the Raman spectrum at $E = 650$ mV, that is at a potential lower by 50 mV as compared to that indicating the onset of the doping-induced spectroscopic changes in the UV-Vis-NIR spectra. This means that, in the case studied, Raman spectroscopy better probes a low level of doping than UV-Vis-NIR spectroscopy does. Below $E = 650$ mV the spectra are identical and characteristic of the polymer neutral state.

Before a detailed discussion of the doping-induced Raman spectral changes, it is instructive to describe general spectroscopic implications of the doping process. Oxidative doping of a conjugated polymer consists of electron removal from the π-bonding system, leading to the formation of radical cations (or spinless dications for higher doping levels). This simple approach implies an overall bond order lowering as a consequence of the doping. This bond order lowering is accompanied by a rearrangement of the bond sequence, which in the case of the polymer studied here results in the transformation of the aromatic-type bond sequence into the quinoid-type one. Thus, the doping should be manifested by a shift in the position of those Raman bands that are associated with the π-bonding system. However, different vibrations can be resonantly enhanced to different extents and this is the case for PDOBTF, for which doping-induced changes are much more pronounced in the band originating from the vibrations in the bithiophene sub-units. For clarity, the spectral changes in both structural sub-units will be discussed separately.

In regioregular poly(3-alkylthiophene-2,5-diyl)s, independent of the type of regioregularity (HT-HT or HH-TT), the oxidative doping is accompanied by a bathochromic shift of the band ascribed to C_α–C_β symmetric stretches by *ca.* 30–40 cm^{-1}.[23,24,27] This is also observed in PDOBTF where, in the potential range from $E = 650$ mV to $E = 800$ mV, two bands corresponding to the C_α–C_β symmetric stretches in the undoped bithiophene units (at 1460 cm^{-1}) and the doped ones (at 1420 cm^{-1}) coexist, with the latter growing quickly, with increase of the potential, at the expense of the former. The band at 1420 cm^{-1} already dominates the Raman spectrum at $E = 700$ mV, despite the fact that at the same potential the doping-induced changes in the UV-vis-NIR spectrum are hardly visible (compare Fig. 3 and Fig. 5). This is a clear manifestation of its resonant enhancement. At $E > 800$ mV only the band characteristic of the doped segments can be detected, showing that the oxidative doping of bithiophene units is completed, at least as probed by Raman spectroscopy. The bands due to C_α–C_β (at 1460 cm^{-1} in the neutral polymer) and C_β–C_β (at 1342 cm^{-1} in the neutral polymer) stretches, which are well-separated in the spectrum of undoped PDOBTF, strongly overlap in the spectra registered at higher potentials due to the doping-induced bathochromic shift of the former and hypsochromic shift of the latter. These changes are consistent with the aromatic to quinoid change in the π-bonding system occurring upon oxidative doping. The doping is also manifested by a bathochromic shift of two other peaks characteristic of the bithiophene sub-unit: the band due to C_α–C_β antisymmetric stretches (1496 cm^{-1} in the neutral segments) and the band ascribed to C_α–C_α inter-ring deformations (1244 cm^{-1} in the neutral segment). Again, in the potential range from $E = 650$ mV to $E = 800$ mV, bands corresponding to the undoped bithiophene units coexist with those characteristic of the doped units. At $E > 800$ mV only bands ascribed to the doped segments can be detected at 1485 and 1213 cm^{-1}, confirming that the doping of the bithiophene is completed.

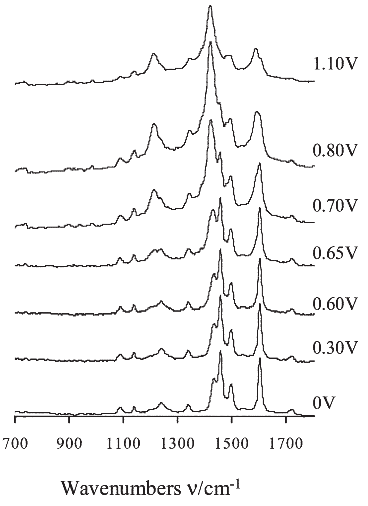


Fig. 5 FT Raman spectra ($\lambda_{exc} = 1064$ nm) of a thin film of poly[{5,5′-(3,3′-di-*n*-octyl-2,2′-bithiophene)}-*alt*-(2,7-fluoren-9-one)] (PDOBTF) registered for increasing electrode potential *E vs.* Ag/Ag^+, electrolyte 0.1 M Bu_4NBF_4 solution in acetonitrile.

The changes in the Raman bands characteristic of the fluoren-9-one sub-units are also consistent with the generally accepted mechanism of the oxidative doping of aromatic structures, which involves an overall bond order lowering accompanied by the formation of quinoid-type segments. In particular, the band ascribed to the C–C stretches in the aromatic ring first broadens, at $E = 650$ mV, and beginning from $E = 700$ mV starts to shift from a value of 1603 cm^{-1} in the neutral polymer to a value of 1590 cm^{-1} in the totally doped one, indicating more quinone-type character of the doped units.[26] It should be noted here that the doping-induced resonant enhancement is, in this case, much smaller than that observed for the C_α–C_β symmetric stretching band in the bithiophene sub-units. In the neutral state both bands are of approximately equal intensity whereas in the doped state the latter is *ca.* three times more intense.

A weak band at 1720 cm^{-1}, ascribed to the C=O stretch in the carbonyl group, is of little use in the spectroelectrochemical investigations. Upon increasing potential it broadens and then disappears.

For clarity, the doping-induced spectral changes in the bithiophene and fluoren-9-one sub-units were discussed separately. However, it must be pointed out that in PDOBTF both sub-units are in conjugation, so the removal of an electron from any sub-unit will change the π-electron density in the whole conjugated system.

Conclusions

To summarise, we have synthesised a new conjugated copolymer, namely poly [(5,5′-(3,3-′-di-*n*-octyl–2,2′-bithiophene))-*alt*-(2,7-fluoren-9-one)], which can be considered as the first member of a new family of solution processible conjugated copolymers—poly(oligothiophene-*alt*-fluoren-9-one)s. This new copolymer is electroactive and upon oxidative gives a very clear spectroelectrochemical response. The oxidation of both sub-units of the copolymer, the bithiophene sub-unit and the fluoren-9-one one, can be precisely monitored by Raman spectroscopy.

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