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Communications to the Editor

Poly(thieno[3,4-*b*]furan). A New Low Band Gap Conjugated Polymer

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Conducting polymers have been termed the "fourth-generation polymeric materials" in part due to their wide range of applications in the fields of optical, electronic, and biological devices.[1] Low band gap conducting polymers are of particular interest for their electrochemical and optical properties.[2] Their relatively low absorption in the visible region, in their conductive state, makes them promising candidates for optically transparent electrodes[3] and hole injection layers for light-emitting diodes.[4] Low band gap conjugated polymers have also found use in photovoltaic devices,[5] electrochromic devices,[6] near-infrared applications,[7] and transistors.[8]

Low band gap polymers have been defined as being conjugated polymers with a band gap (E_g) below 1.5 eV.[9] The use of fused aromatics as monomers has proven to be one of the more effective ways to design these systems. Poly(isothianaphthene) (PITN) was the first low band gap polymer ($E_g = 1.0-1.2$ eV) making use of this strategy; however, lack of environmental stability has limited its use for practical application.[10,11] Many different derivatives of PITN have been prepared to achieve processable, relatively stable, and lower band gap conjugated polymers.[12,13]

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a commercially available conjugated polymer having an E_g ranging from 1.6 to 1.7 eV[14] due to electron-rich oxygen atoms in conjugation with the polythiophene backbone that raise the energy of the highest occupied molecular orbital. We first prepared conjugated polymers from thieno[3,4-*b*]thiophene (T34bT) and observed a band gap of 0.85 eV for electrochemically generated poly(thieno[3,4-*b*]thiophene) (PT34bT).[15] We have reported aqueous dispersion polymerizations of T34bT to produce dispersible PT34bT with band gaps ranging from 1.0 to 1.1 eV that are stable in water for over 12 months.[16] Furthermore, we have demonstrated that insoluble PT34bT prepared via oxidative chemical polymerization can be sulfonated to afford low band gap water processable polymer in which organized thin films can be assembled via layer-by-layer deposition.[17] We have reported that simultaneous electropolymerization[18] of T34bT and EDOT produce stable low band gap conjugated copolymers. Here we report the electrochemical polymerization, electro-optical properties, and some theoretical studies of a conjugated polymer comprised of thieno[3,4-*b*]furan (T34bF), a repeat unit bearing resemblance to both EDOT and T34bT.

T34bF was prepared in accordance with reported procedure[19] with modification. We observed 2-((prop-1-ynylthio)methyl)-furan and 2-((propa-1,2-dienylthio)methyl)furan in the ratio of 95:5 instead of the desired product 2-((prop-2-ynylthio)methyl)-furan when the reaction was carried out using conditions reported in the literature procedure for the first step of the synthesis. It was necessary to run this reaction at 0 °C in order to obtain the desired product 2-((prop-2-ynylthio)methyl)furan in a 61% purified yield. The product was purified by washing the crude product with aqueous potassium hydroxide solution (10% w/v). T34bF was characterized by infrared spectroscopy, nuclear magnetic resonance spectroscopy, and gas chromatography−mass spectroscopy. A 10 mM solution of T34bF in 0.1 M tetrabutylammonium perchlorate (TBAP)/acetonitrile (ACN) was prepared for carrying out electrochemical polymerization. The polymerization was carried out using a three-electrode cell containing a platinum flag counter electrode (1 cm^2), a platinum button working electrode (3.1 mm^2), and a Ag/Ag^+ nonaqueous reference electrode that was calibrated using a ferrocene−

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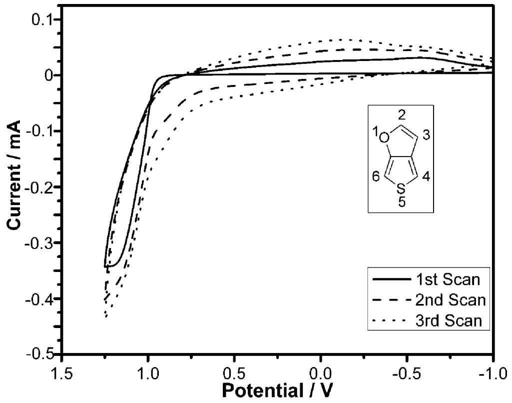

Figure 1. Electrochemical polymerization of 10 mM thieno[3,4-*b*]furan in 0.1 M TBAP/ACN at a scan rate of 100 mV/s. Potentials are reported vs Ag/Ag$^+$ nonaqueous reference electrode (0.44 V vs SHE). Inset shows thieno[3,4-*b*]furan with atom labeling.

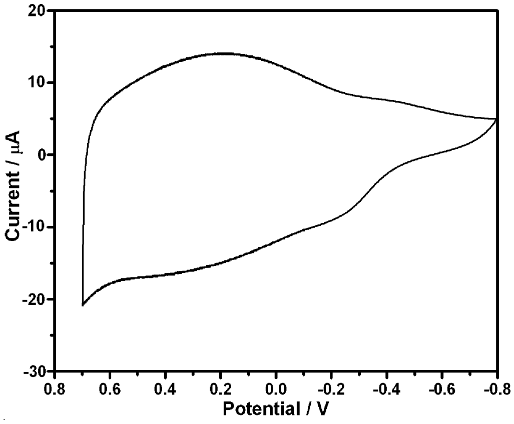

Figure 2. Cyclic voltammogram of poly(thieno[3,4-*b*]furan) film on Pt button electrode at 100 mV/s in 0.1 M TBAP/ACN. Potential reported vs Ag/Ag$^+$ nonaqueous reference electrode (0.44 V vs SHE).

ferrocenium solution to be 0.44 V vs the standard hydrogen electrode.

The electrochemical oxidative polymerization of thieno[3,4-*b*]furan (Figure 1) shows the onset for monomer oxidation at 0.92 V with a diffusion limited peak at 1.2 V. These values place the oxidative polymerization of T34bF at approximately the same potentials as EDOT[20] and T34bT.[15] The low monomer oxidation potential may help avoid overoxidation during electropolymerization. The current response at ~0 V is attributed to the neutral conjugated polymer to conductive polymer redox process, and its increase in intensity during subsequent scans indicates the deposition of conducting PT34bF onto the working electrode. During electrochemical polymerization, formation of an insoluble blue solid was observed on the working electrode. The PT34bF film was then rinsed with pure acetonitrile, and then cyclic voltammetry (Figure 2) was performed in 0.1 M TBAP/ACN. PT34bF exhibits a broad oxidation potential with an onset at ca. −0.4 V. Cyclic voltammetry at scan rates of 50, 75, 100, 125, and 150 mV/s indicates the current profile fits the modified Randles−Sevcik equation. PT34bF was found to be stable during electrochemical switching between neutral (−0.5 V) and oxidized state (+0.6 V) using 0.1 M lithium triflate/ACN solution, and a 9% decrease in charge was observed after 500 double-potential steps, without further optimization.

A 10 mM monomer/0.1 M TBAP/ACN solution was used to prepare a ca. 0.05 μm thick polymer film, as measured by profilometry, on ITO-coated glass at 1.15 V. The polymer film was reduced chemically by dipping it into a 0.2 vol % hydrazine solution. A Vis−NIR spectrum of the polymer in the neutral state is shown in Figure 3. The onset for the π-to-π^* occurs at 1.03 eV (1200 nm) with a peak at 1.72 eV (720 nm), and therefore this polymer meets the defined criterion for being a low band gap polymer.[9] PT34bF has a band gap 0.57 eV lower than that of PEDOT ($E_g = 1.6$ eV) and 0.18 eV higher than that of PT34bT ($E_g = 0.85$ eV). The fused furan ring helps stabilize the quinoidal form of PT34bF as does the fused benzene of isothianaphthene,[11] thereby leading to a polymer having a band gap lower than that of PEDOT. The slightly higher band gap of PT34bF as compared to PT34bT can be attributed to the difference in the stability of the quinoidal state by furan and thiophene ring, respectively. The polymer has pale blue color in the neutral form and is transmissive light blue in the oxidized state (p-doped). Polymer color was further confirmed by calculating [*L a b*] color coordinates of PT34bF using the spectral data from Figure 3. Calculations were performed by assuming blackbody illuminant and CIE 10 degree standard observer. [*L a b*] coordinates for PT34bF in reduced states were found to be [86.12, −3.56, −7.51] while the oxidized form showed [*L a b*] value of [91.23, −1.60, −0.37]. PT34bF was also reduced and oxidized electrochemically via chronocoulometry by applying −0.8 and +0.6 V (vs Ag/Ag$^+$ nonaqueous reference), respectively, and the polymer showed optical properties similar to the neutral and oxidized form obtained chemically.

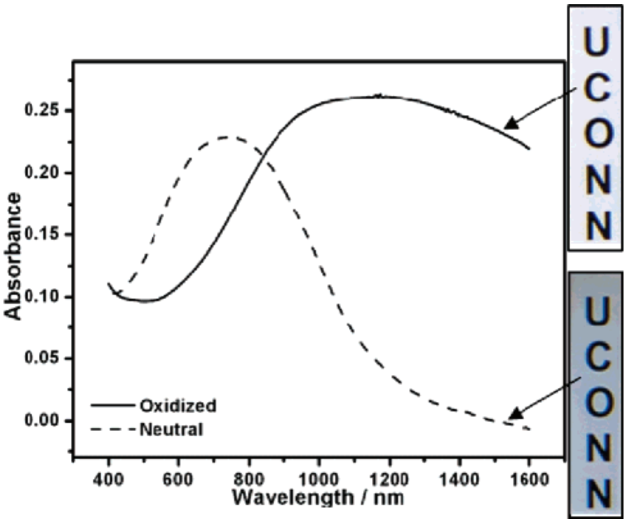

Figure 3. Vis−NIR spectrum of a 0.05 μm thick poly(thieno[3,4-*b*]furan) film on ITO glass. The film was chemically reduced using 0.2% v/v hydrazine solution in acetonitrile and oxidized using 0.2% v/v antimony(V) chloride solution in acetonitrile.

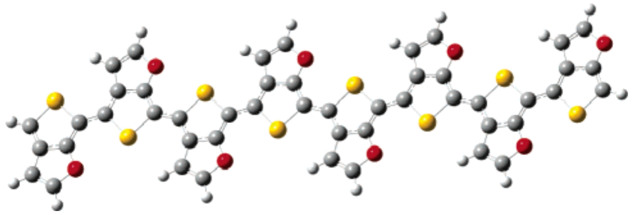

Figure 4. Optimized calculated structure of T34bF octamer. The band gap for this octamer was calculated to be 1.33 eV with a HOMO level of 4.43 eV and LUMO of 3.10 eV.

Calculations on poly(thieno[3,4-*b*]furan) were performed to calculate the band gap value on the assumption that repeat units are connected through positions 4 and 6. The ground-state geometry was optimized using the density functional theory (DFT) method treated with periodic boundary conditions at the

B3PW91 level of theory with the 6-31G(d,p) basis set.[21] The Gaussian 03 program package[22] was employed for this optimization. HOMO and LUMO energies for PT34bF were calculated to be −3.92 and −2.91 eV with a band gap of 1.01 eV, which is in good agreement with the observed value of 1.03 eV. The higher band gap value of PT34bF with respect to PT34bT[15] is due to a heteroatom effect arising from the presence of oxygen atom having lower electron affinity. The decrease in band gap value with increasing electron affinity has been shown theoretically by Hutchison et al.,[23] and our results are consistent with this trend. Dihedral angles of the optimized structure show that the structure can be assumed planar since extremely small deviations from planar structure take place.

DFT calculations were also performed for PT34bF where repeat units were connected through C2−C6 and C2−C4 using the above method. The band gap value for PT34bF with repeat units connected thru C2−C6 and C2−C4 were calculated to be 3.14 and 2.12 eV, respectively. PT34bF formed thru C4−C6 linkage showed a lower band gap as compared to that through C2−C6 and C2−C4 linkages, and the experimental band gap value is in close agreement with the theoretical band gap value of PT34bF formed via the C4−C6 linkage. These results further corroborate that polymerization of T34bF primarily occurs through the C4−C6 linkage to give mostly linear PT34bF, which was also predicted from the electron density contour of T34bF.

In conclusion, we have shown that the electropolymerization of thieno[3,4-*b*]furan affords conducting polymer with a low band gap value of 1.03 eV, which is lower than that of PEDOT and slightly higher than that of PT34bT. The polymer shows good stability and optical properties. In conjunction with the band gap, this material may serve well as a hole-injection layer for light-emitting diodes. Experimental results in correlation with DFT calculations predict the polymerization of T34bF through C4−C6 linkages, resulting in predominantly linear PT34bF. We project, on the basis of the stability of PT34bF and its similarity to PT34bT, that T34bF can be polymerized in the presence of poly(styrenesulfonic acid) to make water dispersion processable low band gap polymer. Moreover, the availability of C2 in PT34bF can also be utilized to substitute that position with numerous different functional groups to make them water- or organic-soluble.

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