Low band gap EDOT–benzobis(thiadiazole) hybrid polymer characterized on near-IR transmissive single walled carbon nanotube electrodes†

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An electron donor/acceptor π-conjugated polymer composed of a bi-EDOT and benzobis(thiadiazole) repeat unit exhibits two reductions with a band gap ranging from ∼0.5 to 0.8 eV depending on the method of band gap determination.

Among the advantages of donor–acceptor conjugated polymers is their ability to access multiple redox states in a small potential window. Various combinations of donors and acceptors have been used to tailor the polymer properties for applications in photovoltaics,[1] OLEDs,[2] and electrochromics.[3] By combining strong donors with strong acceptors, it is possible to compress the band gap of the polymers.[4] The use of stronger acceptors with more positive reduction potentials, making them easier to reduce, will inevitably improve the stability of repetitive cycling in the reduced state. Here we have focused on the benzobis(thiadiazole) acceptor in order to enhance the reductive stability of the polymer due to easy access of its reduced state.

The combination of an electron rich donor such as 3,4-ethylenedioxythiophene (EDOT) in a donor–acceptor–donor architecture allows for ease of electrochemical polymerization due to its low oxidation potential.[5] However, one of the problems associated with low band gap donor–acceptor polymers is characterization of the band gap. Because the typically used transparent, conducting electrode ITO absorbs strongly beyond 1600 nm (Fig. 3), it becomes hard to determine the band gap optically. This problem is circumvented by switching to an electrode that has a high degree of transparency into the IR.[6] By using single walled carbon nanotubes (SWCNTs), which are transparent well into the IR, we are able to increase the accuracy of band gap determination. This can be corroborated by comparison to electrochemical band gap determination *via* cyclic voltammetry and differential pulse voltammetry.

Here we report the synthesis of 4,8-bis(2,3-dihydrothieno-[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2-*c*;4,5-*c*′]bis[1,2,5]thiadiazole (**4**, BEDOT-BBT). We utilize multiple techniques to accurately determine the band gap and offer a comparison of properties to the previously synthesized bisthienyl derivative of **4**.

As shown in Fig. 1, the synthesis of **4** started with the bromination of 2,1,3-benzothiadiazole[7] followed by nitration to give **1**.[8] Although the yield of the nitration is low, this step is early in the synthesis and is easily accomplished on a multi-gram scale. A Stille coupling between **1** and trimethyltinEDOT[9] gave **2**. Reduction of **2** with iron in acetic acid gave **3** in good yield. The final ring closing was done with *N*-thionylaniline in pyridine to yield **4**.[10] The final steps in the synthesis are high yielding.

Monomer **4** has a λ_{max} of 643 nm, which is significantly blue shifted compared to bisthienylBBT (BTh-BBT), which has a λ_{max} of 702 nm.[11] It was thought that using the stronger donor EDOT would lead to a red shifted absorbance, however this was not observed. This can be explained by examination of the crystal structure of **4** (Fig. 1) compared to that of the previously reported BTh-BBT monomer.‡ While the bisthienyl derivative has a dihedral angle of 0°, monomer **4** has a large twist with a dihedral angle of 53° due to steric interactions between the nitrogens of the benzobis(thiadiazole) acceptor and the oxygens of the EDOT. This twist does not allow for good overlap of the p-orbitals and thus limits the amount of intramolecular charge transfer (ICT).

Polymers were deposited from a 5 mM monomer, 0.1 M TBAP–ACN solution onto each of a platinum button, ITO coated glass, and thin transparent SWCNT film working electrodes *via*

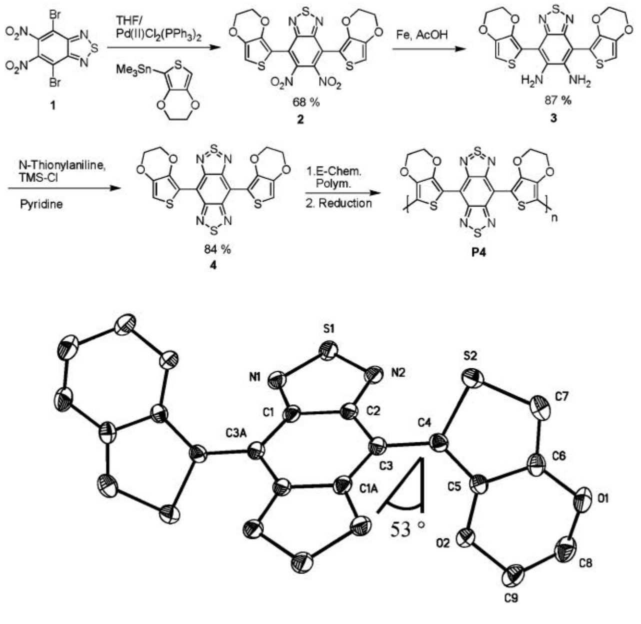

Fig. 1 Synthesis of monomer **4** and **P4** (top). Crystal structure of monomer **4** (bottom). Torsional angle between EDOT and benzobis(thiadiazole) is 53°. Selected bond lengths (Å): C1–C3A 1.405, C1–C2 1.447, C2–C3 1.412, C3–C4 1.463, C4–C5 1.372, C5–C6 1.420, C6–C7 1.356, S1–N2 1.603, N2–C2 1.365.

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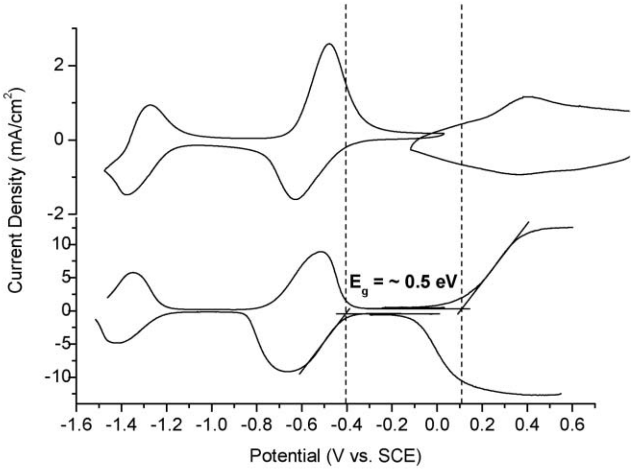

Fig. 2 Cyclic voltammetry (top) of **P4** on a platinum button working electrode in 0.1 M TBAP–ACN solution at 15 mV s^{-1}. Differential pulse voltammetry (bottom) of **P4** on a platinum button working electrode in 0.1 M TBAP–ACN with a step time of 0.1 s and a step size of 2 mV.

repeated scan cyclic voltammetry or potentiostatic methods. Monomer **4** has a peak oxidation potential of 1.02 V. Cyclic voltammetry of poly(bisEDOTbenzobis(thiadiazole)) **P4** shows an $E_{1/2}$ of 0.38 V for oxidation and two reductions with $E_{1/2}$ at -0.55 and -1.33 V, respectively (Fig. 2). To the best of our knowledge, this is the first report of a polymer containing the benzobis(thiadiazole) acceptor showing two reversible reductions. Having a polymer with access to four redox states in a small potential window should allow for more complex devices.

In order to improve the accuracy of measuring the electrochemical band gap, differential pulse voltammetry (DPV) was performed (Fig. 2). Due the increased sensitivity of DPV, the onsets of the redox processes are sharper and allow for a more accurate determination. The onsets of oxidation and reduction for **P4** are at $\sim$0.1 and ~-0.4 V, respectively. This leads to an estimated band gap of $\sim$0.5 eV.

Spectroelectrochemistry of **P4** (Fig. 3) shows a λ_{max} of 974 nm for the neutral polymer, which is olive green in color. Upon oxidation there is a slight decrease in the π–π* transition and the development of charge carrier bands farther out into the NIR around 1600 nm, giving a darker blue polymer. The optical band gap for neutral **P4** as measured on ITO appears to be $\sim$0.88 eV, which is higher than the electrochemical band gap of $\sim$0.5 eV. This can be attributed to the intense absorption of ITO beyond 1600 nm, which makes baseline absorption difficult to quantify. This can lead to inaccurate band gap determination. However, this problem was circumvented by using SWCNT films. **P4** was deposited potentiostatically onto a SWCNT film from 5 mM monomer **4** in 0.1 M TBAP–ACN solution. The film was then neutralized electrochemically by holding at -0.3 V *vs.* SCE for 90 s followed by a final chemical neutralization with a hydrazine–ACN solution. The film was then rinsed with ACN, dried, and a spectrum was taken under solvent-free conditions, necessary due to the strong absorptions associated with the solvent/electrolyte system used beyond 2100 nm (Fig. 4). This yields an optical band gap of $\sim$0.53–0.68 eV, depending on the determination of the onset of the π–π* transition.

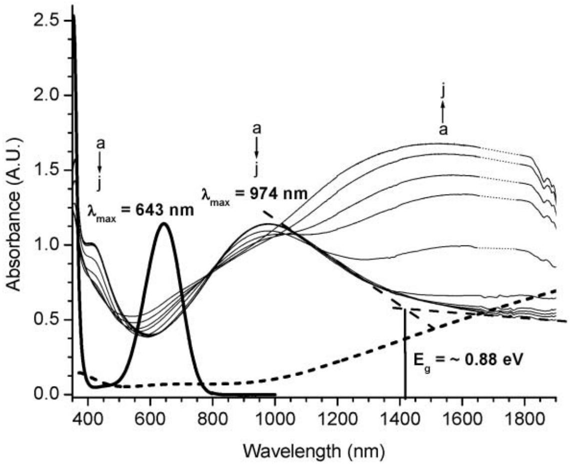

Fig. 3 Monomer **4** UV-VIS in $CHCl_3$ (bold); Absorption spectra of an ITO coated glass electrode relative to air (dashed); Spectroelectrochemistry of **P4** on an ITO coated glass working electrode in 0.1 M TBAP–ACN solution going from (a) -0.30 V, (b) -0.20 V, (c) -0.10 V, (d) 0.00 V, (e) 0.10 V, (f) 0.20 V, (g) 0.30 V, (h) 0.40 V, (i) 0.50 V, to (j) 0.60 V *vs.* SCE.

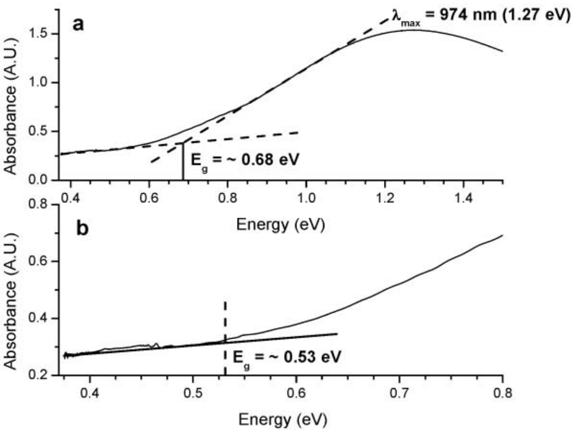

Fig. 4 Neutral spectrum of **P4** on the SWCNT electrode neutralized electrochemically at -0.30 V *vs.* SCE and then chemically neutralized in an ACN–hydrazine monohydrate (3–4 mL/3 drops) solution. (a) Full spectrum obtained, (b) low energy spectrum illustrating absorption onset from baseline.

In conclusion, we have shown that **P4** is a low band gap polymer with access to four charge states (oxidized, neutral, first reduced, and second reduced). It was thought that using a stronger donor such as EDOT with the benzobis(thiadiazole) acceptor might lower the band gap relative to the thienyl derivative. However, the crystal structure of **4** shows a large torsional angle preventing strong π overlap which limits the conjugation. This can be seen in the comparison of the dihedral angle and UV-Vis absorption of **4** relative to the planar BTh-BBT derivative. Thus the stronger donor effect is offset by the twist in the backbone. Characterization of the polymer on thin transparent SWCNT film working electrodes has been shown to be more effective for band gap determination compared to ITO. An optical band gap of 0.5–0.7 eV was determined for **P4** and is supported by the electrochemical results. Because ITO absorbs strongly beyond 1600 nm, this becomes a problem for all low band gap polymers whose absorption onset is beyond this value. As donors and acceptors become stronger in new polymer systems, ITO will become even less useful as the transparent electrode in optical determination of the band gap. SWCNT films provide a welcome alternative.

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Notes and references

‡ *Crystal data* for **4**: $C_{18}H_{10}N_4O_4S_4$, $M = 474.54$, triclinic, space group $P\bar{1}$, $a = 6.2143(7)$, $b = 10.8663(12)$, $c = 14.9797(16)$ Å, $\alpha = 69.407(2)$, $\beta = 81.976(2)$, $\gamma = 75.468(2)^\circ$, $Z = 2$, $V = 915.13(17)$ Å^3, $T = 173$ K, $\lambda = 0.71073$ Å, 3205 reflections ($I > 2\sigma(I)$), $R_1 = 0.0374$, $wR_2 = 0.0923$. CCDC 649009. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709672k

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