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# A neutral state green polymer with a superior transmissive light blue oxidized state†

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**This report highlights the synthesis of only the second green polymer in the literature, which possesses superior properties over the first: a highly transmissive light blue color in the oxidized state with high optical contrast and excellent switching properties.**

In the literature there is a vast amount of conducting polymer based electrochromic materials that possess red or blue colors in their neutral state. However, up to date there is only a single work that reports the synthesis of a true green polymer in the neutral state. This report highlights the synthesis of a second green polymer which possesses superior properties: a highly transmissive light blue color in its oxidized state. In addition, the polymer reveals a high optical contrast in the visible region and excellent switching properties, which make the polymer an outstanding candidate for polymer electrochromic device applications.

A reversible optical change observed in a material due to an applied external voltage is generally defined as electrochromism. Although many inorganic materials, especially tungsten oxide, have received enormous attention over the past 30 years,[1] the use of conjugated polymers as active layers in electrochromic devices has become popular because of their fast switching times,[2,3] high optical contrasts,[4] processability[5] and fine-tuning of the band gap by structure modification.[6]

Research on electrochromic polymers in the past 30 years has resulted in materials reflecting mainly blue and red colors in their neutral states. The main reason for these results is the one dominant wavelength revealed by these materials. To obtain a green color there should be at least two simultaneous absorption bands in the red and blue regions of the visible spectrum. Furthermore, the difficulty in controlling both absorption bands with the same applied potential must be overcome. These phenomena have been fulfilled with ground-breaking work of Sonmez *et al.*[7]

One of the main approaches to achieve the requirements could be the "donor–acceptor" theory. The main idea behind this approach is to narrow the band gap by constructing a conjugated chain of alternating donor and acceptor units, which would show broadening of its valence and conduction bands.[8] In the literature there are examples[9] of this approach where the resultant polymer revealed two distinct π–π* transitions: (1) between the valence band (whose major contribution is from the thiophene units) and its antibonding orbital, and (2) between the valence band and the narrow conduction band (localized mainly on the donor substituents).[10]

A donor–acceptor type material 4,7-di(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (BDT) was synthesized according to a previously reported method.[11] It is interesting that even the material has been synthesized and its electrochemical properties were studied; it was published as a short communication where the electrochromic properties were not investigated[12] (Scheme 1).

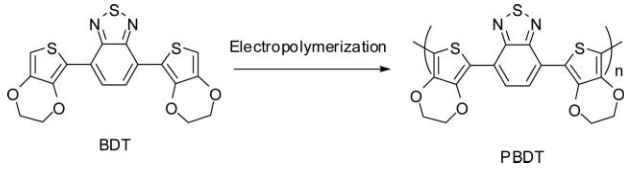
The donor–acceptor nature (keeping in mind that the first green polymer was also a donor–acceptor type) and narrow band gap of the polymer encouraged us to synthesize and re-investigate PBDT as a potential electrochromic material.

The homopolymer of BDT, PBDT, was synthesized on platinum or indium tin oxide (ITO) coated glass slides by oxidative electropolymerization from a dichloromethane (DCM) solution containing $10^{-2}$ M BDT and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$).‡ Some other electrolytes such as tetrabutylammonium tetrafluoroborate and tetrabutylammonium perchlorate are not as good as this one in terms of polymer film formation on electrodes. The monomer oxidation occurs at 0.95 V *vs.* $Ag/Ag^+$ ( 0.01 M $AgPF_6$ in MeCN) which is consistent with the previously reported data.[12] A reversible redox process evolved at significantly lower potentials as electroactive PBDT was deposited on ITO (Fig. 1).

The resultant polymer revealed both p and n doping properties where the p doping was indicated by the peak at −0.06 V and −0.26 V due to doping and dedoping. The coated PBDT film is green in its neutral state, and in the oxidized state the color changes to a highly transparent light blue.

This rare property, n-doping, for conjugated polymer systems was clearly observed by CV studies for PBDT with a definite reversible redox couple with an $E_{pa}$ of −1.13 V and $E_{pc}$ of −1.4 V *vs.* the same reference electrode.

As seen in Fig. 2 the scan rate dependence of the polymer film was investigated by CV and a true linear relation was observed



**Scheme 1** Electropolymerization of BDT.

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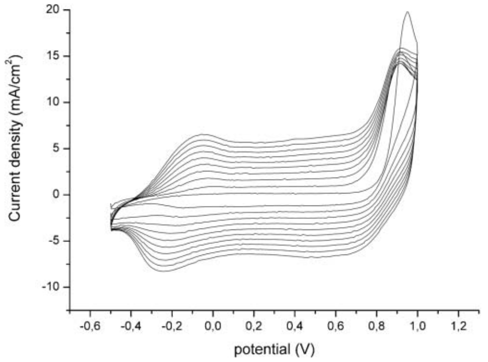

**Fig. 1** Repeated potential scan electropolymerization of BDT at 75 mV s$^{-1}$ in 0.1 M TBAPF$_6$–DCM on an ITO electrode.

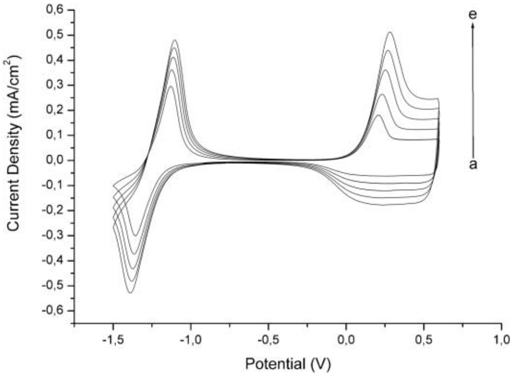

**Fig. 2** Scan rate dependence of PBDT film in TBAPF$_6$–MeCN (a) 100, (b) 150, (c) 200, (d) 250, (e) 300 mV s$^{-1}$.

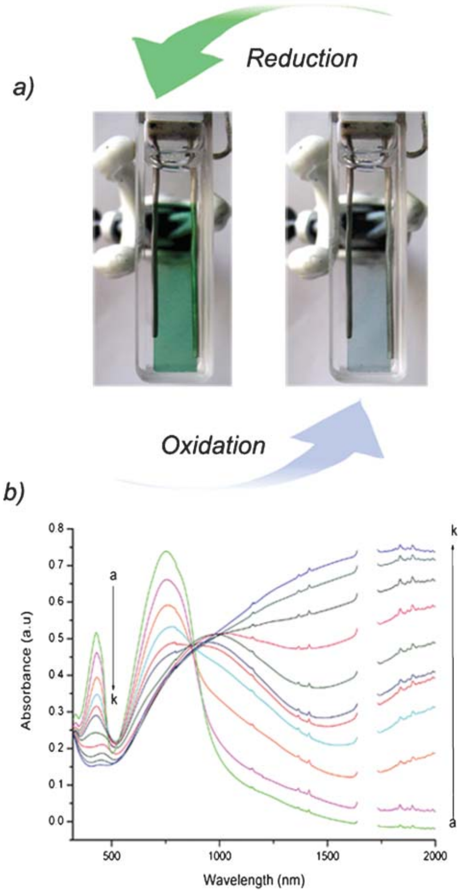

**Fig. 3** **a**. Colors of PBDT film on an ITO coated glass slide in the neutral and oxidized states. **b**. Spectroelectrochemistry of PBDT film on an ITO coated glass slide in monomer-free, 0.1 M TBAPF$_6$–MeCN electrolyte–solvent couple at applied potentials; (a) −0.8, (b) −0.5, (c) −0.2, (d) −0.15, (e) 0.0, (f) 0.1 (g) 0.3, (h) 0.5, (i) 0.7, (j) 0.9, (k) 1.1 V.

between the peak current and the scan rate, which indicates the presence of a well adhered electroactive film with a non-diffusion limited redox process.[13]

Stability is one of the most significant properties for commercial polymer electrochromic device applications. To investigate this property, PBDT films coated on a Pt wire were cycled between their fully neutral state (−0.8 V) and fully oxidized state (0.7 V) 5000 times in PC–LiClO$_4$ solvent–electrolyte (PC = propylene carbonate). Once the polymer electrochemical equilibrium has been reached (400 cycles), PBDT showed tremendous stability without any considerable charge loss (less than 2%) after 5000 cycles. Since the charge under the curves remains intact after 5000 cycles we did not proceed with further cycling.

Fig. 3 illustrates the optoelectrochemistry of the PBDT films. In neutral state the polymer revealed two well separated absorption maxima at 428 nm and 755 nm which is essential for a true green color to be observed. The band gap of the polymer was calculated as 2.33 and 1.19 eV according to the onset of the two π–π* transitions. Polymers with donor–acceptor units exhibit band gaps between 0.9 eV to 1.3 eV in general.[7,9] A minimum absorption was observed at around 500 nm and the 38% and 51% transmittance values were calculated with respect to this point.

Upon oxidation of the PBDT film, the intensity of both of the absorption bands decreases and a new absorption band in the NIR region arises due to the formation of charge carriers. This decrease in absorption in the visible region makes the polymer film nearly transparent with a residual tail starting from 600 nm. Fortunately, the human eye is not that sensitive. The higher absorption region of the tail begins at 750 nm where human eye is completely insensitive. As Sonmez *et al.* indicated, the residual pale brown color in the oxidized form of PDDTP (2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-*b*]pyrazine), the only example of a true green polymeric material in the literature, was the major problem that hindered possible applications and had to be improved.[14] This enhancement was achieved in our group with PBDT where the polymer not only displays a green color (*Y*: 376 *x*: 0.277 *y*: 0.415) in the neutral state but also a transmissive light blue (*Y*: 439 *x*: 0.268 *y*: 0.323) in the oxidized state. Hence, as previously predicted this superior polymer could be utilized as the green polymer for RGB applications since poly(3-methylthiophene) (red in the neutral state) and poly(3,4-ethylenedioxythiophene) (blue in the neutral state) already reveal a light blue color in their oxidized state. The spectra of the blue and red polymers in their oxidized states are almost identical. Since the oxidized state of the green polymer also has a similar spectrum, a suitable color filter could be used to bring all the RGB colors to the "white point".

Electrochromic switching studies were performed to monitor the transmittance changes with time during repeated potential stepping between the neutral and oxidized states to differentiate the changes in optical contrast. As illustrated in Fig. 4, PBDT was switched by

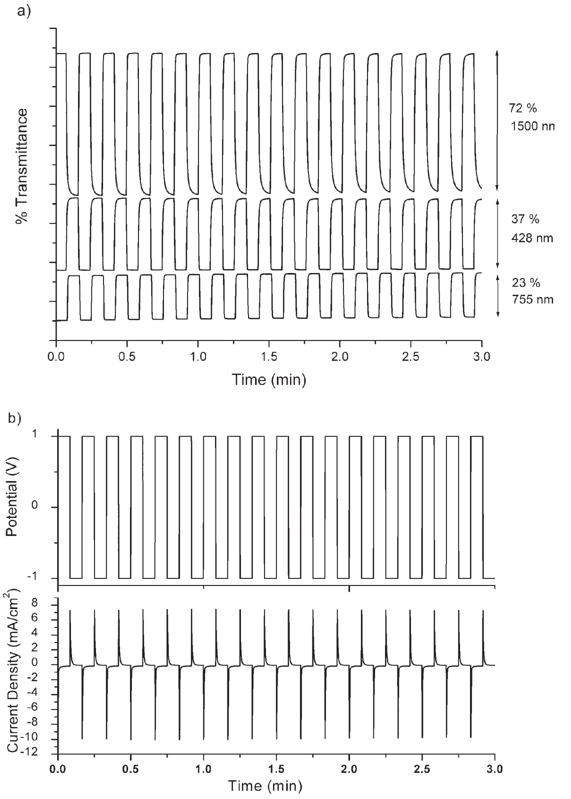

**Fig. 4** **a**. Electrochromic switching; optical absorbance change monitored at 428 and 755 nm and 1500 nm for PBDT in 0.1 M TBAPF$_6$–MeCN. **b**. Potentials and current densities during switching studies.

stepping the potential between −1.0 and +1.0 V with a switching interval of 5 s in a 0.1 M TBAPF$_6$–MeCN electrolyte–solvent system while measuring the transmittance at 428 nm, 755 nm and 1500 nm.

The PBDT films showed 80% transmittance at the oxidized and a 43% transmittance at the neutral state with a remarkable optical contrast of 37% in the visible region which is 14% percent higher than the first green polymer PDDTP.[7] The polymer switches very rapidly and achieves 95% of its optical contrast in less than 1 s at 428 nm. At 755 nm, which corresponds to the second $\pi$–$\pi^*$ transition, the optical contrast was calculated as 23% with a very fast switching time of 0.4 s. At 1500 nm PBDT films show an outstanding optical contrast of 72% with a fast switching time of approximately 1 s.

Coloration efficiency (CE), which provides information about the contrast ratio acquired for a certain amount of charge introduced in the material, is a significant electrochromic material characteristic. It is the relation between the injected/ejected charge per unit area of the electrode and the change in optical density at a specific dominant wavelength.[15] The coloration efficiency of the PBDT film was found to be 130 cm$^2$ C$^{-1}$ which is almost identical with that of PEDOT (at 100% of full switch, at 428 nm).

In conclusion, PBDT is the first green electrochromic material which has a highly transmissive sky blue oxidized state. It reveals nearly 40% optical contrast in the visible and 70% in the NIR region with exceptional switching properties and remarkable stability. Hence, PBDT is the paramount choice for the ECD applications. Ongoing studies are pursued both to tune the "green" color *via* techniques like lamination and copolymerization which enable the construction of ECDs for possible application areas like displays.

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## Notes and references

‡ All chemicals were purchased from Aldrich Chemical. Acetonitrile was dried and distilled over calcium hydride under nitrogen.

All electrochemical studies were accomplished with a Voltalab 50 potentiostat. Electropolymerization was performed in a three-electrode cell consisting of platinum button or indium tin oxide (ITO) coated glass as the working electrode, platinum wire as the counter electrode, and Ag/Ag$^+$ as the reference electrode. The electrolyte used was 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in DCM. Electrodeposition was performed from a 0.1 M solution of TBAPF$_6$ at a scan rate of 75 mV s$^{-1}$ for 40 cycles.

Cyclic voltammograms of the polymers were obtained using the same electrode setup using monomer-free solution. TBAPF$_6$ was used as the electrolyte in MeCN.

UV-Vis-NIR spectra were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm min$^{-1}$. A three-electrode cell was utilized consisting of a silver wire reference electrode, a Pt wire counter electrode, and an ITO coated glass working electrode. The potentials were controlled using Solartron 1285 potentiostat/galvanostat. Colorimetric measurements were achieved by a Minolta CS-100A Chroma Meter with a 0/0 (normal/normal) viewing geometry as recommended by CIE.

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