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Rational design of an electrochromic polymer with high contrast in the visible region: dibenzyl substituted poly(3,4-propylenedioxythiophene)†

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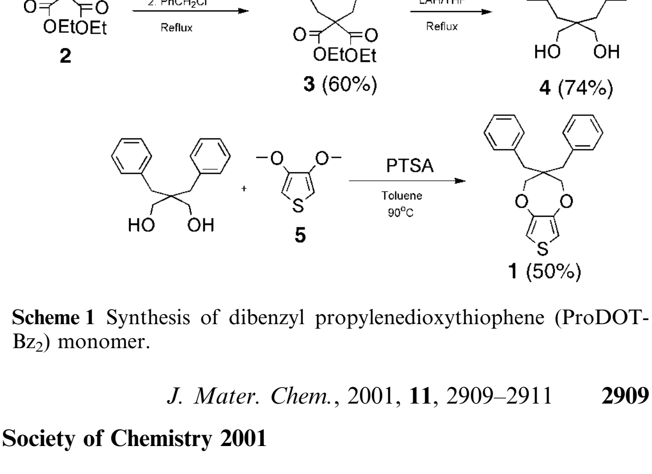
A dibenzyl substituted poly(3,4-propylenedioxythiophene) was designed and synthesized, and exhibited a contrast of 89% at 632 nm with switching speeds of 400 ms and coloration efficiency of 575 cm^2 C^{-1}.

Conjugated polymers[1] belong to an important class of polymers due to their widespread use in industrial applications like sensors, electrochromic materials, light emitting diodes (LEDs), actuators, and batteries *etc.* Electrochromics (ECs) are materials where the color exhibited is a function of applied potential.[2–4] Both inorganic and organic materials have been used as EC materials but there is still a lot of scope for further improvement in terms of switching speeds, stability, contrast and ease of synthesis and processing. Conducting or conjugated polymers have been found to be more promising as EC materials because of their better stability, faster switching speeds and easy processing compared to the inorganic EC materials.[2] EC materials where the color changes from a highly opaque colored state to highly transmissive bleached state are highly desirable as they are potential candidates for applications in display devices. In these systems, the change in percentage transmittance ($\Delta\%T$) between the two states is called the contrast and the higher the contrast, the better the material is for display applications. Conjugated polymers based on 3,4-alkylenedioxythiophene have attracted a lot of attention, both in academic as well as in industrial labs, as potential candidates for display applications because of their high contrast, low oxidation potential, better stability to air exposure at ambient and at elevated temperature conditions, and faster switching speeds.[5] Recently, Reynolds and co-workers have extensively studied the effect of ring size and also of ring substitution on the electrochromic properties of polymers based on 3,4-alkylenedioxythiophene.[5] They observed that the electrochromic contrast improves on increasing the ring size and also on increasing the interchain separation by the incorporation of a rigid/bulky side chain.[6] A tetradecyl substituted polyethylenedioxythiophene derivative was found to exhibit a $\Delta\%T$ of 64%. However, the highest contrast ($\Delta\%T$ of 78%) reported to date was observed in the case of a dimethyl substituted polypropylenedioxythiophene (PProDOT-Me$_2$).[7] Therefore, if one has to design a polymer with even better contrast than PProDOT-Me$_2$ one has to use more rigid/bulky substituents instead of methyl groups. Based on these facts, we designed and synthesized a dibenzyl propylenedioxythiophene (ProDOT-Bz$_2$) monomer (**1**). Incorporation of benzyl groups as the substituents, we think, will increase the interchain separation due to its rigid and bulky nature and hence the contrast. PProDot-Bz$_2$ exhibits an extremely high contrast of 89% at $\lambda_{\max}$ (632 nm) with coloration efficiencies of the order of 575 cm^2 C^{-1}; in fact, these are the best reported values to date. In this communication, we report its synthesis, electrochemical and optical properties.

The monomer **1** was synthesized by the standard transetherification reaction between 3,4-dimethoxythiophene and 2,2-dibenzylpropane-1,3-diol as shown in Scheme 1 and was recrystallised from acetone.[8] 2,2-Dibenzylpropane-1,3-diol was synthesized starting from diethyl malonate. Monomer **1** was characterized by ^{1}H NMR, GC–MS and elemental analysis, and the crystal structure was solved using X-ray crystallography.[9] The crystal structure of **1** (Fig. 1) showed that the benzyl substituents are orthogonal to the thiophene ring confirming our design strategy. Interestingly, the two benzyl groups are on opposite sides of the thiophene plane and hence will be very effective for interchain separation.

For optoelectrochemical studies, monomer **1** was electropolymerized on indium tin oxide (ITO) coated glass slides from a 30 mM solution of the monomer in 0.1 M tetrabutylammonium tetrafluoroborate (TBAFB) in acetonitrile (ACN) at a constant potential of 1.2 V *vs.* Ag/Ag$^+$. This quickly results in the formation of nice and homogeneous films on the ITO electrode. The films were then washed with monomer-free electrolyte solution and were vacuum dried before measuring the thickness as a function of charge density using a profilometer. A linear relationship was observed for change in film thickness *versus* charge density (mQ cm^{-2}). The change in film thickness as a function of charge density was then calculated from the slope and was found to be 54.2 nm. This value is almost double that reported for tetradecyl substituted



Scheme 1 Synthesis of dibenzyl propylenedioxythiophene (ProDOT-Bz$_2$) monomer.

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†Electronic supplementary information (ESI) available: cyclic voltammograms of polymer films in 0.1 M tetrabutylammonium tetrafluoroborate–acetonitrile. See http://www.rsc.org/suppdata/jm/b1/b108654e/

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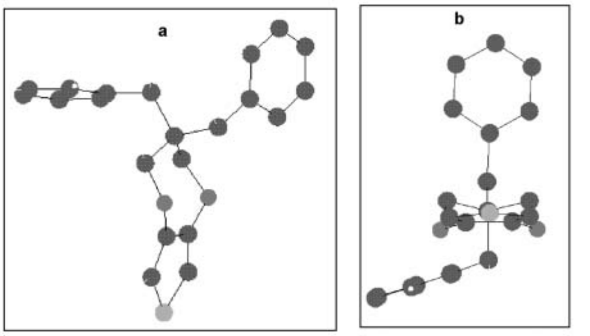

Fig. 1 X-Ray crystal structure of ProDOT-Bz_2; hydrogen atoms are not shown for clarity. a) View showing that the benzyl groups are nearly orthogonal to the thiophene ring and b) view showing that the two benzyl groups are on opposite sides of the plane of the thiophene ring.

PEDOT (28.7 nm) which indicates a more expanded morphology because of the rigid dibenzyl side chains which hold the polymer chains apart.[6] In order to do the spectroelectrochemical studies, films were washed with monomer free electrolyte solution and a series of UV–vis spectra of the film were obtained as a function of applied potential (Fig. 2). The neutral form of the polymer shows a distinctive π to π^* interband transition which is split into two sharp peaks at 578 nm and 632 nm. This splitting is attributed to vibronic coupling which suggests a high degree of regularity along the polymer backbone.[6]

Stepwise oxidation of the polymer shows a reduction in absorbance throughout the visible region as the color changes from the dark blue absorbing state (fully reduced form) to a highly transmissive state (oxidized form). The interesting feature to note in Fig. 2 is the growth of the peak at 850 nm. The intensity of this peak increases during the initial oxidation of the polymer but subsequently decreases in intensity upon further oxidation of the polymer. This decrease in intensity increases the transmissivity throughout the visible region as the near-infrared tail is eliminated. This results in higher contrast electrochromic material and gives a more color neutral appearance to thin films of the polymer.

For optical switching studies, polymer films were synthesized on ITO coated glass slides in the same manner as described above. Polymerization charge was varied in order to vary the film thickness and each polymeric film was stepped between its reduced (−1.0 V) and oxidized (+1.0 V) state. While the films were switched, the percentage transmittance at λ_{max}(632 nm) was monitored as a function of time. The contrast is given as the difference between $\%T$ in the reduced and oxidized states and reported as $\Delta\%T$. Switching data for films with the thickness that produced maximum $\Delta\%T$ are given in Fig. 3.

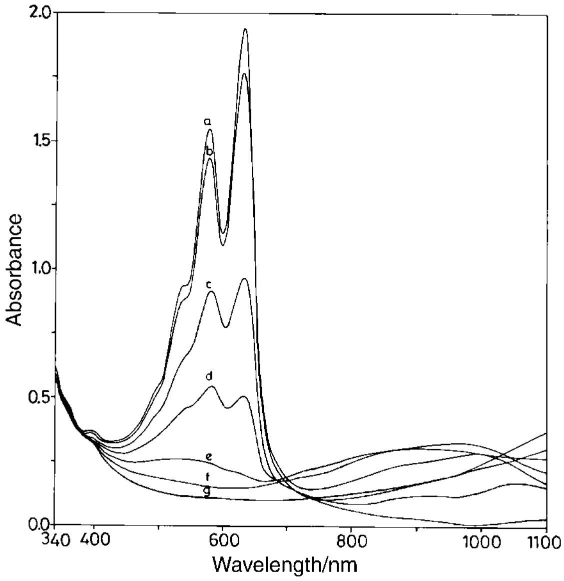

Fig. 2 Optoelectrochemical spectra of the PProDOT-Bz_2 (charge density 22.5 mC cm^{-2}) as a function of applied potential in 0.1 M TBAFB–ACN. a) −1, b)−0.4, c) −0.2, d) 0.1, e) 0.3, f) 0.5, and g)1.0 V.

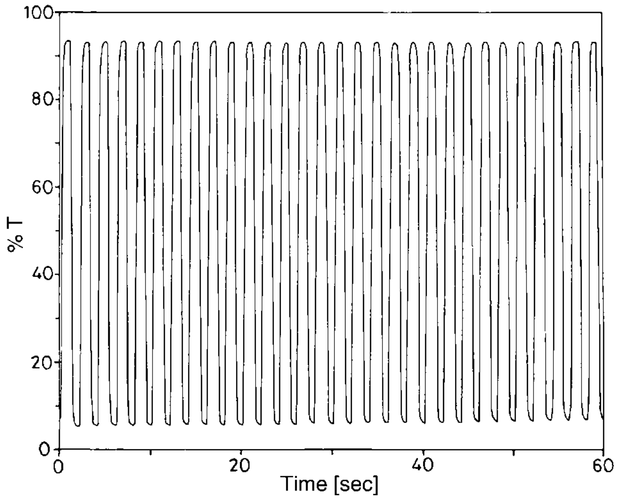

Fig. 3 Optical switching studies for PProDOT-Bz_2 film (charge density 15.2 mC cm^{-2}) monitored at 632 nm, when it was stepped between its reduced (−1.0 V) and oxidized (+1.0 V) state.

As expected from the spectroelectrochemistry, a $\Delta\%T$ of close to 89% was observed in PProDOT-Bz_2, which is significantly higher than the best reported $\Delta\%T$ of 78% for PProDOT-Me_2 to date. The measured switching times, at 95% of full contrast for varying film thickness, range from 0.4 s to 0.6 s. Stability studies were also carried out by measuring the contrast as a function of time when the films on ITO were continuously switched in solution from +1.0 V and −1.0 V under a normal lab environment. No significant change in the contrast was observed even after 5000 cycles indicating that PProDOT-Bz_2 films are highly stable. Apart from the contrast, coloration efficiencies (CEs) have also been used for the comparison of different EC materials.[7] The CE values were calculated at varying film thicknesses for PProDOT-Bz_2 on ITO in solution and were found to vary from 550 to 600 $cm^2\,C^{-1}$. These values are much higher than that of PProDOT-Me_2 (200 $cm^2\,C^{-1}$) and are characteristic of high quality EC material.

In conclusion, a new dibenzyl substituted PProDOT-Bz_2 derivative was designed and synthesized which exhibited much higher contrast, switching speeds and coloring efficiency than any other system reported to date. These results further support the hypothesis that the effective interchain separation leads to higher contrast and faster switching in alkylenedioxythiophene based systems.[6,7]

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Notes and references

1 T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynolds, *Handbook of Conducting Polymers*, Marcel Dekker, Inc., New York, 1998.
2 P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism: Fundamentals and Applications*, VCH: Weinheim, 1995.
3 R. J. Mortimer, *Electrochim. Acta*, 1999, **44**, 2971.
4 D. R. Rosseinsky and R. J. Mortimer, *Adv. Mater.*, 2001, **13**, 783.
5 L. B. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J. R. Reynolds, *Adv. Mater.*, 2000, **12**, 481.

6 A. Kumar, D. M. Welsh, M. C. Morvant, F. Piroux, K. A. Abboud and J. R. Reynolds, *Chem. Mater.*, 1998, **10**, 896.

7 D. M. Welsh, A. Kumar, E. W. Meijer and J. R. Reynolds, *Adv. Mater.*, 1999, **11**, 1379.

8 Diethyl 2,2′-dibenzylmalonate (**3**) was synthesized by the reaction of diethyl malonate with benzyl chloride under NaOEt–EtOH conditions in 60% yield. Diethyl 2,2′-dibenzylmalonate (**3**) was converted to 2,2′-dibenzylpropane-1,3-diol (**4**) by lithium aluminium hydride reduction in THF under reflux conditions in 74% yield (mp 85 °C). The diol (**4**) was then coupled with 3,4-dimethoxythiophene under standard transetherification conditions in refluxing toluene with toluene-*p*-sulfonic acid as a catalyst for 24 h to get dibenzyl propylenedioxythiophene (**1**) in 50% yield. The product was purified by flash column chromatography [silica gel as the stationary phase and petroleum ether–ethyl acetate (98 : 2) as the mobile phase] followed by recrystallization from a mixture of $CHCl_3$–acetone to give a white crystalline solid with melting point 177–178 °C. ^1H NMR ($CDCl_3$): 2.8 (s, 4H), 3.8 (s, 4H), 6.5 (s, 2H), 7.2 (m, 10H). Elemental analysis: Calculated for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99; S, 9.53. Found: C, 74.30; H, 5.74; S, 8.04%.

9 Crystal data for ProDOT-Bz_2: orthorhombic crystal system with $Pn2_1a$ (No. 33) space group. Cell volume is 1754.76(23) $Å^3$ and Pearson code is $oP0$. Unit cell dimensions in Å are $a = 8.0540(8)$; $b = 9.4720(5)$; and $c = 23.0020(15)$.