Conformational locking for band gap control in 3,4-propylenedioxythiophene based electrochromic polymers†

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We report a tethered poly(3,4-propylenedioxythiophene) derivative with a built-in polymer conformation restriction which locks the conjugated chain at a specific dihedral angle, thus providing a handle in which to tune the optical and electronic properties of the material.

In recent years, extensive research has been devoted to new variable gap conjugated polymers.[1–5] Often, band gap control is attained by modifying conformational or aggregate behavior through functional group modifications.[6–8] Properties such as color, conductivity, ion selectivity, *etc.* are tuned by changing a pendant group. Perhaps the most important principle behind these types of materials property studies is that the modifications made to the systems are accomplished without making fundamental changes to the chemical identity of the conjugated polymer backbone. This elimination of variability in repeat unit composition allows for the systematic study of a family of materials whose properties are governed by a single parameter. One such systematic modification consists of polymer repeat units connected by a functional group that serves to restrict the rotational angle between them. Ground-breaking work by Benincori *et al.* has shown that conformation locking of polythiophene derivatives allows for a variable-length tether to control the electronic and optical properties of the polymer.[9–14] The groups of Swager and Roncali have used PEO-tethered polythiophene and PEDOT derivatives for applications in sensors.[15–19]

Here, we use tethered macrocyclic dimers of 3,4-propylenedioxythiophenes (ProDOT), as schematically illustrated in Fig. 1 with alkylene bridged PProDOT, to restrict polymer backbone rotation and decrease the pi overlap as a means to elevate the electronic band gap. This new class of materials is the first known example of using the conformational restriction motif to form macromolecules with well-defined repeat unit structures composed of electron-rich subunits. We demonstrate that the convenient low polymer oxidation potential similar to the untethered parent system is maintained while the band gap of the material is elevated. Furthermore, these materials are seen to maintain their electroactivity, displaying a brilliant colored to transmissive electrochromism upon electrochemical switching.

As outlined in Scheme 1, synthesis began with compound **1**, which was prepared from 3,4-dimethoxythiophene *via* transetherification with 1,1,1-tris(hydroxymethylethane),[20,21] and was reacted

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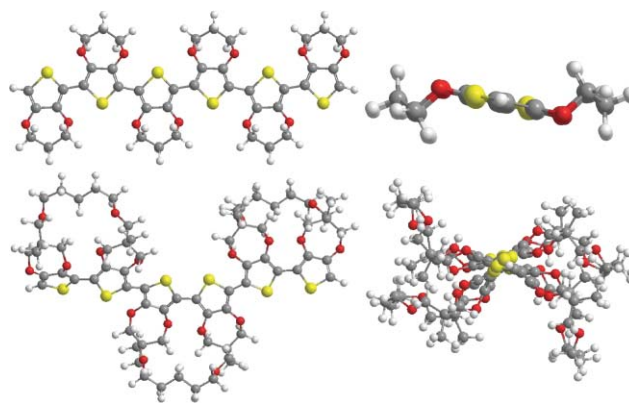

Fig. 1 Front view (left) and side view (right) 3D representations (not to scale) of top: PProDOT, and bottom: a conformationally locked analogue. Atom colors: yellow, S; red, O; gray, C; white, H.

with the ditosylate of 1,5-pentanediol in DMF with sodium hydride to yield monomer **2** in good yield. Macrocycle **3** was formed in moderate yields by reacting compound **2** with two equivalents of *n*-butyllithium, followed by oxidative coupling with Fe(acac)$_3$. Monomer **4** was synthesized from compound **1** and
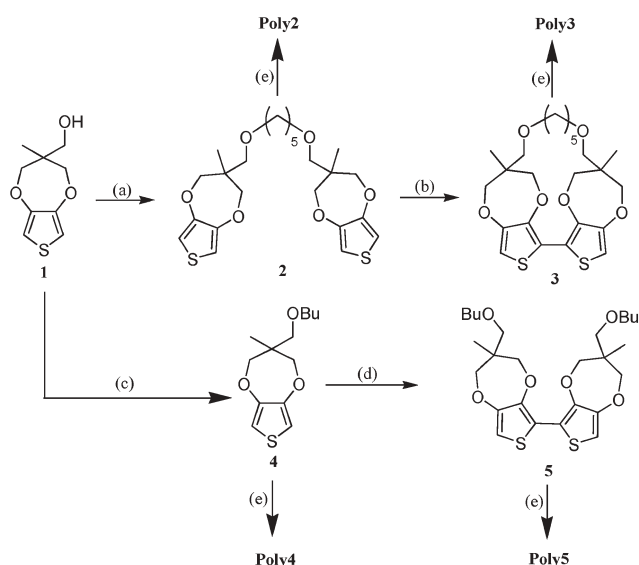
Scheme 1 a) TsO(CH$_2$)$_5$OTs, DMF (71%); (b) (1) 2.1 equiv of *n*-BuLi, THF, −78 °C → RT; (2) THF, 2.5 equiv of Fe(acac)$_3$, reflux (15%); (c) TsO(CH$_2$)$_3$CH$_3$, NaH, DMF (63%); (d) (1) 1.2 equiv of *n*-BuLi, THF, −78 °C → RT; (2) Fe(acac)$_3$, reflux (15%); (e) anodic oxidation.
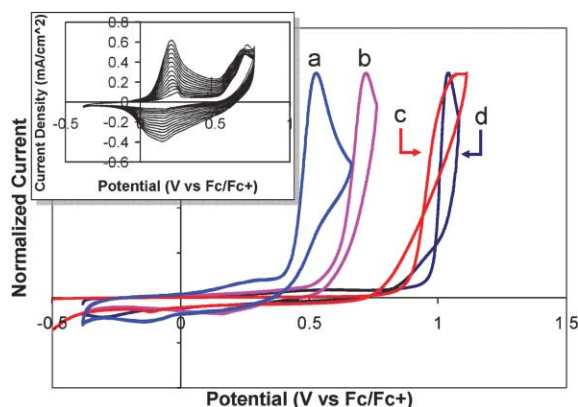
Fig. 2 Overlaid first scan CVs of monomers (a) **5**; (b) **3**; (c) **4**; (d) **2**. Concentrations were approx. 20 mM monomer in a solution of 0.2 M TBAP in PC. Current was normalized to facilitate visualization. Inset: potentiodynamic deposition of **Poly3**.

n-butyl tosylate, and dimer **5** was synthesized in moderate yields from compound **4** *via* oxidative coupling.

Shown in Fig. 2, single-ring monomers **4** and **2** exhibited peak oxidation potentials of 1.08 V and 1.05 V, respectively as is common for many electropolymerizable dioxythiophenes. Due to extended conjugation, dimer **5** showed an oxidation peak at 0.54 V and macrocycle **3** at 0.73 V. Polymer films were electrodeposited on platinum button electrodes *via* repeated potential scanning as shown for **Poly3** in the inset to Fig. 2. The electropolymerization was well-behaved, as evidenced by the low potential redox process that evolves with multiple scans, and even after 15 scans the resulting polymer redox peaks remained sharp, and of constant potential. It was believed that due to its tetrafunctionality, polymerization of **2** would form a cross-linked network of **Poly2** on the electrode surface, thus limiting the effective conjugation length. Indeed, it was observed that during the electropolymerization of **Poly2**, anodic shifts of both the polymer and monomer redox processes occurred, passivating the electrode and strongly suggesting cross-linking. In contrast, the electropolymerization of control polymers **Poly4** and **Poly5** exhibited broad oxidation processes and a lower polymer oxidation potential with respect to **Poly3**. It was also found that the $E_{1/2}$ values of **Poly3**, when Li^+, Na^+, K^+, and Ba^{2+} were used as supporting electrolytes, were approximately 225 $\pm$ 30 mV. However, when Cs^+ was used, the $E_{1/2}$ of **Poly3** was found to be 506 mV. Future studies will address this potential ion sensitivity in greater detail.

As seen in Fig. 3, the X-ray crystal structure[22] of macrocycle **3** showed an approximately 30.1° torsion angle between thiophene
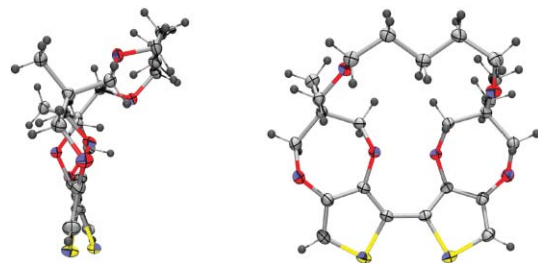

Fig. 3 X-ray crystal structure for **3**. Left: Side view. Right: Front view. Torsion angle between thiophene rings: 30.14(5)°. Thermal ellipsoids are at the 50% probability level.
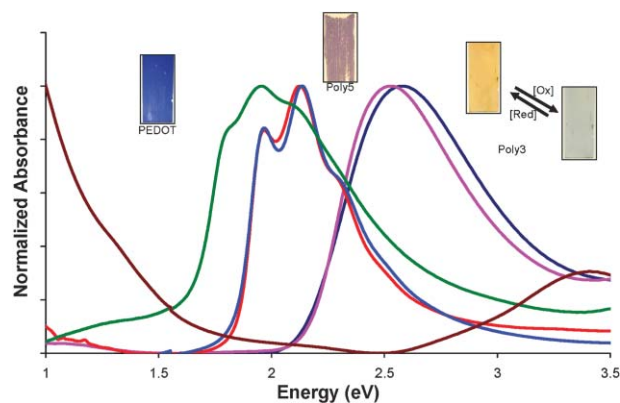

Fig. 4 UV/vis/NIR spectra of neutral polymer films of (pink) **Poly3**; (green) **PEDOT**; (blue) **Poly5**; (red) **Poly4**; (dark blue) **Poly2**; and of (brown) oxidized **Poly3**. To aid the eye, the baselines were zeroed, and the absorbances were normalized to λ_{max}. Photographs: the neutral forms of **PEDOT**, **Poly5**, and the switching of **Poly3**.

rings, and the macrocyclic bridge adopted *syn*-connectivity. This angle is in stark contrast to previously reported dimeric ProDOT and EDOT derivatives, which usually have[23,24] torsion angles close to 180°. It can be seen that the macrocyclic cavity resembles a crown ether.

Fig. 4 shows UV/vis/NIR spectra for all four polymers potentiostatically deposited onto ITO/glass anodes with the spectrum for PEDOT as a comparison. The spectrum for the oxidized form of **Poly3**, which was nearly transparent (with a bluish hue), is also shown. It is evident that the band gap of **Poly3** is elevated in comparison to the polymers formed from the simple monomeric and untethered dimeric dioxythiophenes. As such, where PEDOT is blue, and **Poly4** and **Poly5** are blue-purple, the conformationally locked **Poly3** is translucent orange. The extreme color shift seen in the tethered **Poly3** is unprecedented in a structurally comparable family of polymers, and can be attributed to the alkylene tether restricting the extent of π-overlap along the polymer backbone. This is evident in the spectra where **Poly4** and **Poly5** had band gaps (measured as the π, π* absorption onset) equal to 1.75 eV and **PEDOT** of 1.61 eV. Fine structure observed in **PEDOT, Poly4** and **Poly5**, normally attributed to vibronic coupling,[25] suggests inter-chain π-stacking interactions. In contrast, **Poly2** and **Poly3** have elevated band gaps equal to 2.13 eV (0.38 higher than the control) and no fine structure was observed. This lack of fine structure may originate from inefficient π-stacking of the twisted backbone and may also explain the sharp, well-defined polymer redox process. While the optical properties of a thin film of **Poly2** are essentially identical to those of **Poly3**, it is much less electroactive, precluding its use as an effective electrochrome, and this demonstrates that the macrocyclic monomer is critical in producing a material with desirable electrooptical properties.

In conclusion, conformational locking of a tethered PProDOT derivative has provided an electrochromic polymer with an elevated band gap and a well-characterized repeat unit structure due to the monomer's bifunctionality. The X-ray crystal structure of the macrocycle indicates that the locked torsion angle reduces the extent of π-overlap relative to the control polymers. This is the first known example of a dioxythiophene-based orange neutral polymer that becomes highly transmissive when oxidized. The

tethered repeat unit structure shows potential in finely tuning optical properties by changing the composition of the tether. This is being explored in further studies.

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22 $C_{23}H_{30}O_6S_2$, M_r = 466.59, Monoclinic, $P2_1/n$, a = 12.8140(7) Å, b = 11.3396(6) Å, c = 15.5221(8) Å, β = 92.432(1)°, V = 2253.4(2) Å^3, Z = 4, $D_{calc.}$ = 1.375 g cm^{-3}, Mo Kα (l = 0.71073 Å), T = 173 K. 282 parameters were refined in the final cycle of refinement using 3856 (out of 5124 unique reflections and a total of 14603; $R_{int.}$ = 5.3%) reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.47 and 8.7, respectively. Refinement was done using F^2. CCDC 293188. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517819c.
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