Defunctionalization of Ester-Substituted Electrochromic Dioxythiophene Polymers

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ABSTRACT: This work demonstrates a simple process to form insoluble poly(3,4-propylenedioxythiophene) (**Poly[ProDOT]**) films by defunctionalization of a soluble form, which is useful in the fabrication of multilayer polymer devices. Three new ester disubstituted **Poly[ProDOTs]**, soluble in common organic solvents, including chloroform, methylene chloride, toluene, tetrahydrofuran, and ethyl acetate, have been synthesized by oxidative polymerization using iron(III) chloride. These **Poly[ProDOT-diesters]** have the expected repeat unit stuctures along with GPC determined number-average molecular weights ranging from 9000 to 12 000 g mol^{-1}. Dilute polymer solutions in toluene exhibited red fluorescence with quantum efficiencies from 0.24 to 0.32. Homogeneous thin films were formed by spray casting polymer solutions onto ITO coated glass slides and compared to films prepared by electropolymerization. These **Poly[ProDOT-diesters]** are electroactive, switching from a dark blue-purple to a transmissive sky blue when potentials are applied between −0.9 and +0.3 V vs Fc/Fc.$^+$ A thin film saponification method was developed and rendered the spray-cast films insoluble by submersion into 0.1 M KOH in hot methanol for 1 h to remove the solubilizing ester group. In the case of a bis(heptanoate) **Poly-[ProDOT-diester]** (**1**), spectroelectrochemistry showed minimal change in its electronic spectra after methanolysis and the resulting alcohol-substituted polymer (**Poly[ProDOT-diol]** (**4**)) could be repeatably switched between neutral and oxidized states in subsecond times. In contrast, when a more highly functionalized **Poly[ProDOT-tetraester]** (**3**) was used, a small change in the electronic spectrum which is associated with a distinct color change from burgundy to blue was observed upon methanolysis to **Poly[ProDOT-tetraol]** (**6**). The insoluble alcohol-substituted polymer films were found to be efficient hole transport layers in polymer light-emitting diodes.

Introduction

Conjugated electroactive polymers have promising electronic and optical properties for a broad spectrum of applications including electrochromic devices,[1] hole transport layers in field effect transistors,[2] and light-emitting diodes,[3] along with chemo- and biosensors.[4] The synthetic flexibility of the conjugated backbone structure allows for side-chain derivatization to improve solubility and processability, as well as specific functionalization to tailor redox and optoelectronic properties.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is an electron-rich conducting polymer that exhibits excellent switching stability and is widely known for its high conductivity and fast electrochromism.[5] Our group has taken advantage of the ease in modification of the monomer structure and designed and synthesized a family of dioxythiophene polymers with a broad range of physical and electronic properties.[6] Within this family of polymers, a series of disubstituted poly(3,4-propylenedioxythiophenes) (**Poly[ProDOT(R)$_2$]**) of significant molecular weight (M_n ~40 000 g/mol) were reported that are soluble in organic solvents and can be spray cast from solution to form homogeneous films on electrode surfaces.[7] The resulting films redox switch in subsecond times between a dark purple neutral state and a transparent sky blue oxidized state with high coloration efficiencies (1000 cm^2/C). Absorptive/transmissive and absorptive/reflective electrochromic devices have been fabricated by spray casting these polymer films from solution, a promising step toward possible commercial application.[8]

The processability of hole transport layers (HTLs) in light-emitting diodes poses a challenging problem, since the solubility of the layer must be incompatible with the light-emitting material when depositing by multiple film spin-casting.[9] One of the most commonly used HTLs is the commercially available PEDOT-PSS, which is an aqueous dispersion of PEDOT with poly(styrenesulfonate) that can be spin-cast to render insoluble films with moderate conductivities (300 S/cm).[10] Although PEDOT-PSS is an effective hole transport material, the long-term stability of the device is limited due to the acidic nature of the polymer electrolyte, which leads to etching of the electrode.[11]

Conjugated polymers substituted with esters[12−15] and protected alcohols[16] have been developed, which offer the utility of easy conversion to the alcohol or carboxylic acid after polymerization. This method has been used efficiently to process films of conducting polymers from solution, which after treatment, are incorporated into multilayer devices such as photovoltaics.[13]

Here, the synthesis of a new series of **Poly[ProDOTs]** which are disubstituted with long chain esters is reported. The ester functionality enhances solubility in polar solvents such as ethyl acetate, leading to more environmentally friendly processing to form thin films. Spray cast films were treated with base in hot methanol to saponify these ester groups, leaving insoluble alcohol-substituted **Poly[ProDOT]** films, as shown in Scheme 1. The electrochromic properties of both ester- and alcohol-substituted polymer films were characterized in order to develop an understanding of the effects of the defunctionalization of the ester groups on the **Poly[ProDOTs]** redox and spectral properties. The insoluble alcohol-substituted polymer films were

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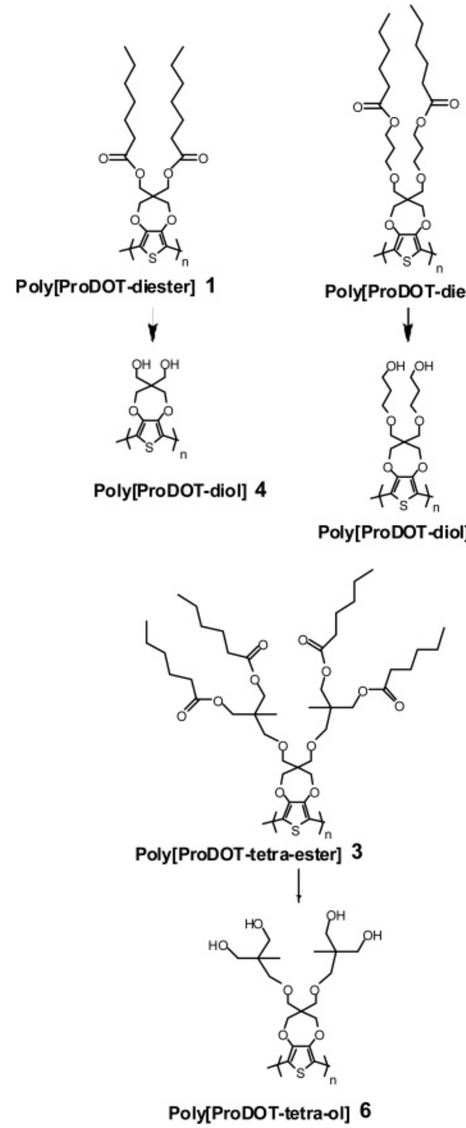
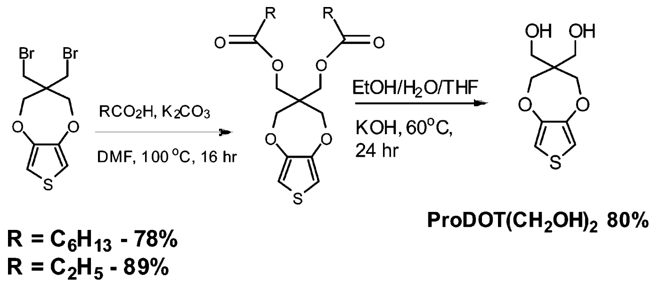
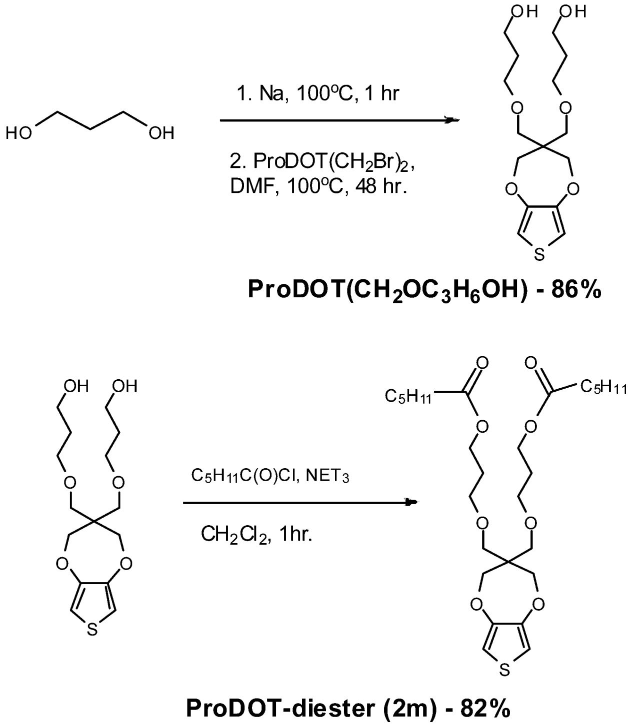
Scheme 1



Scheme 2



Scheme 3



also studied as electrochromic materials and hole transport layers in polymer LEDs to demonstrate the utility of the process.

Results and Discussion

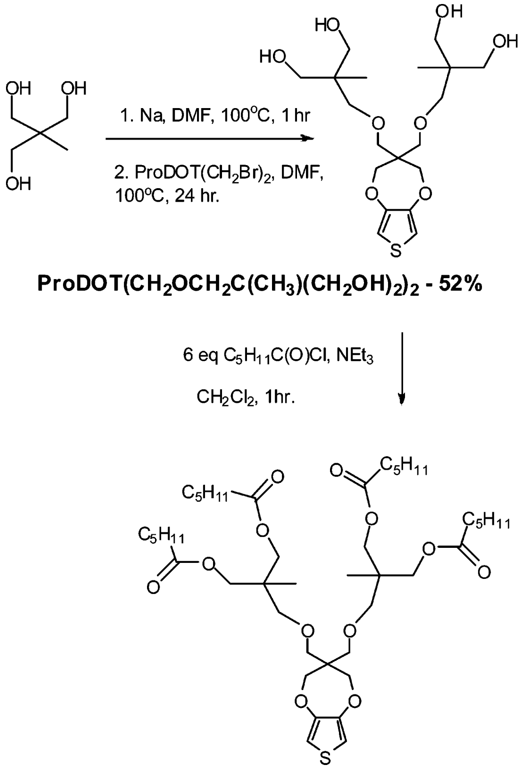
Monomer Synthesis. Ester-derivatized ProDOTs were synthesized in one of two ways. In a first method, substitution of previously synthesized **ProDOT(CH_2Br)$_2$**[7] with carboxylic acids was carried out using K_2CO_3 as shown in Scheme 2. This reaction produces esters that can be hydrolyzed to afford **ProDOT(CH_2OH)$_2$** in good yield as a versatile building block toward new ProDOT structures and may improve overall yields of compounds relative to those prepared by the Williamson etherification of **ProDOT(CH_2Br)$_2$**.[7]

The second method used to synthesize ester-substituted ProDOTs starts with the synthesis of alcohols from **ProDOT(CH_2Br)$_2$** followed by acylation. **ProDOT($CH_2OC_3H_6OH$)$_2$** was synthesized by first making a 10 equiv alkoxy solution of 1,3-propanediol to which was added a 1.5 M **ProDOT(CH_2Br)$_2$** solution in DMF (DMF required for dissolution of the dihalide) as illustrated in Scheme 3. This minimum amount of DMF is required for the reaction as early attempts without it failed. The 10 equiv excess of 1,3-propanediol alkoxide ensured the formation of the diol over cyclization to the eight-membered ring. The addition of 0.25 equiv of sodium was used with respect to the diol to ensure the formation of the monoalkoxide and limit the formation of the dialkoxide. *n*-Hexanoyl chloride (4 equiv) was added to a **ProDOT($CH_2OC_3H_6OH$)** solution in methylene chloride and triethylamine to yield a yellow oil which was purified by column chromatography to afford **ProDOT-diester** (**2m**) (where the **m** denotes the monomer needed to form the polymer in Scheme 1) as a clear oil. When this methodology was repeated, **ProDOT($CH_2OCH_2C(CH_3)(CH_2OH)_2$)** could be synthesized as shown in Scheme 4. The compound was purified by column chromatography to afford a clear oil and subjected to 6 equiv of *n*-hexanoyl chloride to form the ester derivative **ProDOT-tetraester** (**3m**).

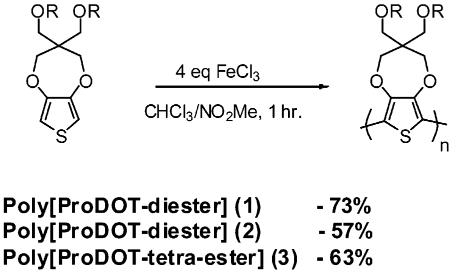
Polymer Synthesis. Ester-substituted **Poly[ProDOTs]** were synthesized by oxidative polymerization using $FeCl_3$[14] as outlined by Scheme 5. The reaction was performed by adding an $FeCl_3/NO_2Me$ solution to a monomer/$CHCl_3$ solution turning the color from clear to green to black during addition. The reaction was run at room temperature and for only 1 h as a precaution to minimize hydrolysis of the esters (none was observed) in the acidic environment. Hydrazine reduced the polymer, immediately turning the color from black to bright fluorescent red, comparable to other alkyl- and alkoxy-substituted **Poly[ProDOTs]** prepared by Grignard metathesis polymerization.[7]

Chloroform was then added and the red solution was washed with 1 M HCl to remove the oxidizing agent and other byproducts. The solvent was removed and the resulting purple solid was redissolved in chloroform and precipitated in metha-

Scheme 4



Scheme 5



nol. Filtration afforded the pure polymer, which was soluble in common solvents including chloroform, methylene chloride, toluene, tetrahydrofuran, and ethyl acetate.

Proton NMR Spectroscopy. The proton NMR spectra of **ProDOT-diester** (**2m**) and **Poly[ProDOT-diester]** (**2**) are shown in Figure 1. The major difference between their spectra is the absence of the thienyl proton signal (a) and the broadening of the peaks in the polymer spectrum. The protons on the **ProDOT** bridge (b) are deshielded in the polymer compared to the monomer by 0.15 ppm as highlighted by the dashed line, and the signal overlaps with the methylene protons attached to the ester oxygen (f). The alkoxy methylene protons (c and d) at 3.50 ppm overlap with one another in both the polymer and monomer and a shoulder exists in the polymer spectrum at 3.6 ppm, indicative of a downfield shift of the methylene protons next to the propylene ring (c). The methylene protons at 2.3, 1.9, 1.6, 1.3, and 0.9 ppm (g, e, h, i, and j, respectively) give splitting patterns as expected in the monomer spectrum, which fall at the same frequency for the polymer, but do not resolve. The upfield shift is most apparent for protons closest to the polymer backbone. A peak corresponding to water from dueterated chloroform falls at 1.5 ppm, close to the multiplet from the methylene protons (h). These spectra are illustrative of the series of ester-substituted monomers and polymers.

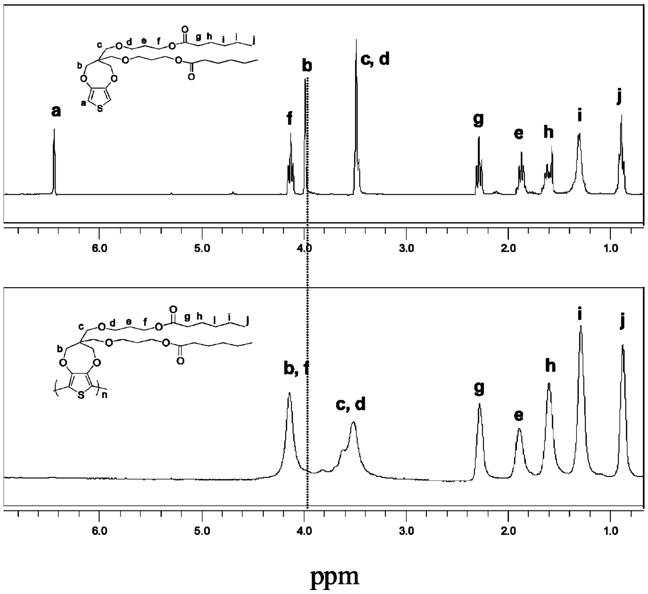


Figure 1. ^1H NMR (300 MHz, $CDCl_3$) of (top) **ProDOT-diester** (**2m**) and (bottom) **Poly[ProDOT-diester]**(**2**).

Table 1. Molecular Weight Estimation Results by GPC

	M_n	M_w	X_n	PDI
1	9000	13 000	20	1.5
2	12 000	19 000	24	1.6
3	11 000	17 000	13	1.5

Molecular Weight Estimation. Molecular weights of all polymers synthesized were estimated by GPC vs polystyrene standards and are listed in Table 1. Theses values are lower than those obtained when using Grignard metathesis polymerization,[7] with the number-average degree of polymerization (X_n) falling between 13 and 24 rings. While the low molecular weight may be due to the relatively short polymerization times employed to limit ester hydrolysis, the polymers are comparable in appearance to those synthesized by Grignard metathesis, providing magenta solutions and reflective purple solids suggesting that the chains are sufficiently long in terms of both their degrees of conjugation and film forming abilities. The polydispersities were all lower than 2 after purification by precipitation.

TGA and DSC. Thermogravimetric analysis of all polymers was performed scanning from 50 to 800 °C at 20 °C/min. No evidence of degradation was observed below 150 °C in all cases. An onset of weight loss exists between 290 and 320 °C. The ester substituents did not thermally cleave as seen in other cases where dimethyl-substituted alkyl functional groups were specifically designed to facilitate elimination to an alkene,[13] but rather the polymer degraded continuously. DSC scans from -150 to $+100$ °C at 10 °C/min were absent of transitions for all polymers.

Fluorescence Spectroscopy. Solution absorbance and fluorescence spectroscopy was performed on the polymers in toluene solutions. The ester-substituted **Poly[ProDOTs]** show one peak in the absorbance spectrum and two peaks in the photoluminescence spectrum, as seen for **Poly[ProDOT-diester]** (**1**) in Figure 2. The spectral maxima for each polymer as well as the quantum efficiencies are listed in Table 2.

The fine structure in the photoluminescence spectrum is due to vibronic coupling, where the peaks are separated by 1350 cm^{-1} corresponding to thiophene ring stretching or ring breathing modes. The quantum efficiencies were 25–30% which are lower in comparison to the polymers synthesized by Grignard

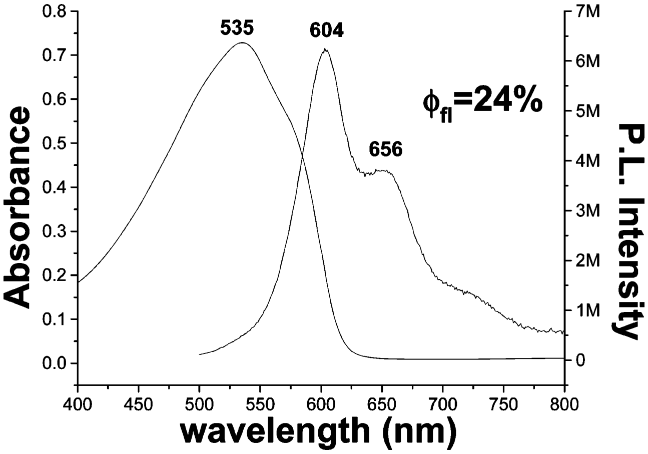


Figure 2. UV−vis absorbance spectrum (left) superimposed upon the fluorescence emission spectrum (right) of a toluene solution of **Poly[ProDOT-diester]** (**1**).

Table 2. Absorption and Fluorescence Spectroscopy Results with Quantum Efficiencies

	$\lambda_{(\text{absorbance})}{}^{a}$	$\lambda_{(\text{fluorescence})}{}^{a}$	$\phi_{\text{fl}}{}^{b}$
1	535	604, 656	0.24
2	538	602, 652	0.30
3	531	595, 645	0.32

[a] Peaks (nm) from the absorbance and fluorescence spectra of polymer solutions in toluene. [b] Fluorescence quantum efficiency in toluene solution.

metathesis (30−50%), possibly due to different solubilities in toluene or fluorescence quenching by iron impurities. **Poly[ProDOT-diester]** (**1**) exhibited a quantum efficiency of 0.24 while the bulkier **Poly[ProDOT-diester]** (**2**) and **Poly[ProDOT-tetraester]** (**3**) exhibited higher quantum efficiencies of 0.30 and 0.32 respectively, likely due to less aggregation of the polymer chain. Although the molecular weight of the polymers were lower in comparison to the alkoxy-substituted **Poly[ProDOTs]**, the $\lambda_{\max}$ values are similar for **1** and **2**, exhibiting a bright red fluorescent color. An exception is the solution of **3**, which exhibits a red-orange color, with a 5−10 nm blue shift of the $\lambda_{\max}$ in comparison to the other disubstituted **Poly[ProDOTs]**.[7] This blue shift is attributed to steric interactions of the branched side chains, which disrupt the planarity of the polymer backbone.

Post-Polymerization Reactions: Alcohol-Substituted Poly[ProDOTs]. Ester-substituted **Poly[ProDOTs]** were spray cast onto ITO coated glass slides from toluene solutions, dried under vacuum, and then submersed in a 0.1 M KOH methanol solution and heated at 60 °C for 1 h to saponify the ester groups. The solution turns light pink after half an hour of heating in the case of **Poly[ProDOT-diester]** (**2**) and **Poly[ProDOT-tetraester]** (**3**), indicating slight solubility of the hydrolyzed polymer, while **Poly[ProDOT-diester]** (**1**) did not discolor the solution. The treated films of all polymers were insoluble in nonpolar solvents, ethyl acetate, and water. In the cases of **1** and **2**, the as-cast ester functionalized polymer films are blue-purple which stay the same perceivable color after methanolysis of the esters, with a band gap of 1.8 eV. In contrast, solutions of **3** spray cast to form films that are burgundy in color and have a higher band gap than the other polymers at 2.0 eV, along with a $\lambda_{\max}$ of 541 nm. Figure 3 shows the electronic spectra and photographs of the spray cast **3** film before and after methanolysis to form **Poly[ProDOT-tetraol]** (**6**). After methanolysis, the film changes color to a blue-purple with a slightly lower band gap of 1.95 eV and exhibits two peaks at 595 and 556 nm, a considerable red shift in comparison to the ester-substituted polymer spectrum. The film is then cooled, washed with methanol, and vacuum-dried at 50 °C. The color change suggests that the esters decrease the effective conjugation length of the polymer due to the steric bulk. This is relieved upon cleavage of the ester, resulting in a smaller band gap (1.95 eV), a red shift of the electronic spectrum, and a different perceived color.

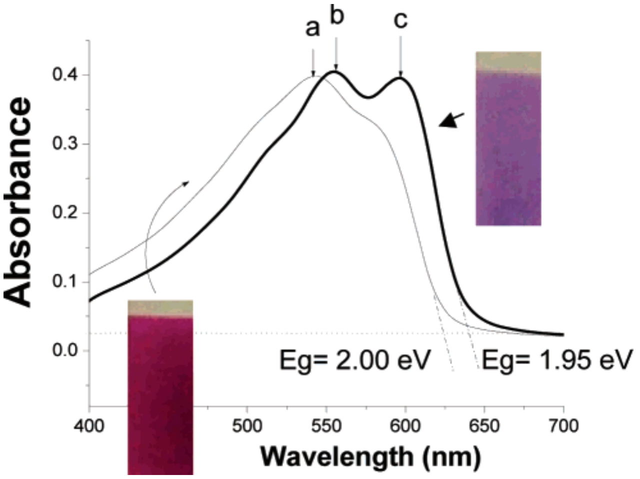


Figure 3. UV−vis spectra of a spray cast film of **Poly[ProDOT-tetraester]** (**3**) (thin line, $a = \lambda_{\max} = 541$ nm) and a film treated with 0.1 M KOH at 60 °C for 1 h followed by cooling, washing in methanol, and vacuum drying at 50 °C for 4 h to form **Poly[ProDOT-tetraol]** (**6**) (thick line, $b = 556$ nm, $c = 597$ nm). Photographs of the films are shown next to the spectra.

The insoluble alcohol-substituted polymers were characterized by IR spectroscopy. Figure 4 compares the IR spectra of ester- and alcohol-substituted **ProDOTs** along with the polymers. The esters, both monomeric and polymeric, exhibit a strong absorbance at 1740 cm,$^{-1}$ corresponding to the carbonylstretch. This peak disappears upon saponification while an OH stretch at 3350 cm^{-1} appears, indicating that both the monomeric and polymeric esters are fully converted to alcohols in the solid state. Little changes in the IR spectra are observed between the ester- and alcohol-substituted polymer and monomer with the exception of the disappearance of a peak at 3110 cm^{-1} in the polymers, corresponding to the C−H stretch of the thiophene ring. This is further evidence of a substantial molecular weight.

Electrochemistry and Electrochromism. Poly[ProDOT-diester] (**1**), **Poly[ProDOT-diol]** (**4**), and **Poly[ProDOT-tetraester]** (**3**) could be reversibly switched between the oxidized and neutral state and therefore the electrochemistry and electrochromism of these polymers were studied. The oxidized state of **Poly[ProDOT-diester]** (**2**), **Poly[ProDOT-diol]** (**5**), and **Poly[ProDOT-tetraol]** (**6**) dissolve in water, PC, and acetonitrile, and they therefore are not included in this section. The solubility of the oxidized form of the ester- and alcohol-substituted polymers, coupled with their insolubility in nonpolar solvents, may be advantageous for the processing of hole transport layers in the fabrication of multilayer polymer electronic devices such as polymer light-emitting diodes and photovoltaic devices and will be explored and reported in the future.

Poly[ProDOT-diester] (**1**) films were formed by either potentiostatic electrodeposition at 1.2 V or by spray casting from toluene solution. The $E_{1/2}$ was found to be approximately 0.0 V by cyclic voltammetry, switching the color from blue-purple to transmissive. The films were then treated by submersion in

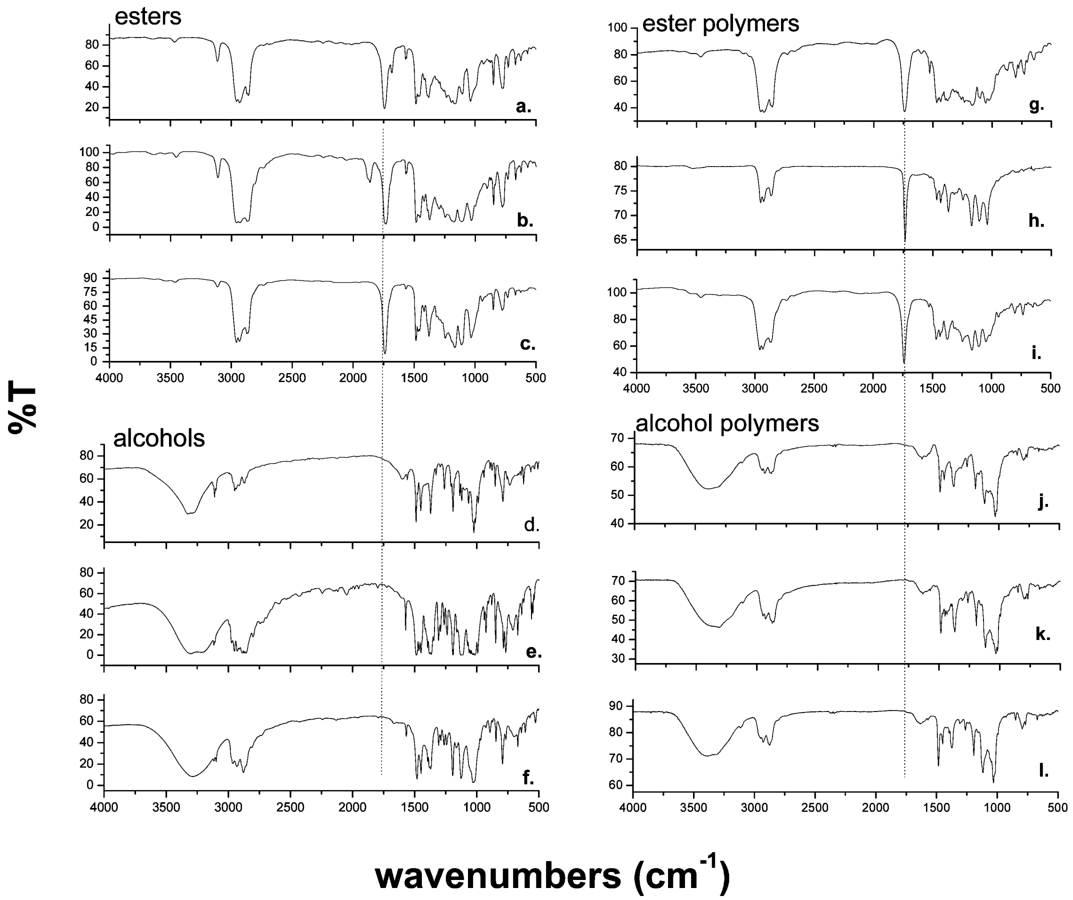


Figure 4. IR spectroscopy of films on KBr plates (esters) or pressed pellets (alcohols): (a) **ProDOT-diester** (**1m**); (b) **ProDOT-diester** (**2m**); (c) **ProDOT-tetraester** (**3m**); (d) **ProDOT(CH_2OH)$_2$**; (e) **ProDOT($CH_2OC_3H_6OH$)$_2$**; (f) **ProDOT($CH_2OCH_2C(CH_3)(CH_2OH)_2$)$_2$**; (g) **Poly[ProDOT-diester]** (**1**); (h) **Poly[ProDOT-diester]** (**2**); (i) **Poly[ProDOT-tetraester]** (**3**); (j) **Poly[ProDOT-diol]** (**4**); (k) **Poly[ProDOT-diol]** (**5**); (l) **Poly-[ProDOT-tetraol]** (**6**).

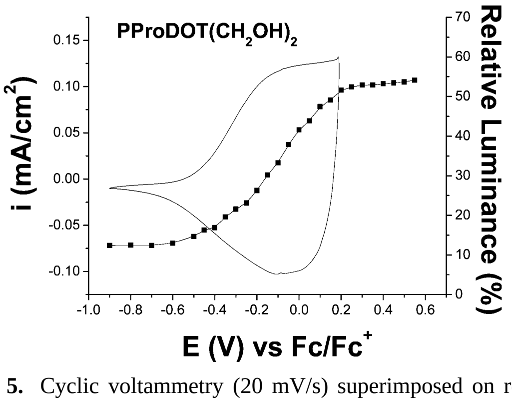


Figure 5. Cyclic voltammetry (20 mV/s) superimposed on relative luminance for a film of **Poly[ProDOT-diol]** (**4**) in 0.1 M (TBA) PF_6/PC.

0.1 M KOH in methanol and heated at 55 °C for 1 h. After cooling, washing the films in methanol, and drying over a stream of argon, the films were examined by cyclic voltammetry, as seen in Figure 5, and the relative luminance is superimposed on the current response to compare the relationship between the color change and the current response. The **Poly[ProDOT-diol]** (**4**) film switches between a colored dark blue neutral state to a transmissive oxidized state with a change in relative luminance of ($\Delta\%$ Y) of 42%.[17] The onset of color change occurs at an unusually low potential of −0.6 V, much lower than the analogous ester polymer or other **Poly[ProDOTs]**. This is an indication of the large range of chemical environments and effective conjugation lengths influenced by the diol substituents. The redox process is broad, making the $E_{1/2}$ assignment difficult, but is seen to be centered around −0.1 to 0.0 V.

Spectroelectrochemistry was performed, as seen in Figure 6, on a spray cast film of **1** as well as a film of **4** to study how the saponification process affects the optical properties of the resulting polymer. Little change is observed between the two polymers. The neutral polymers both have band-gaps of 1.8 eV with a λ_{max} of 567 nm and similar fine structure. Upon oxidation, the alcohol-substituted polymer begins to change color at potentials 300 mV lower than the ester-substituted polymer. This was consistent with the luminance and CV studies performed and seen in Figure 5, where the onset of current response and color change occurs at remarkably low potentials.

Switching studies were performed on ester- and alcohol-substituted **Poly[ProDOT]** films at the λ_{max} of the polymer and measurements are listed in Table 3. Switching times were measured as the time required for 95% of the full electrochromic contrast to be attained when switching from the colored neutral state to the transparent oxidized. Contrast ratios of **1** and **4** were approximately 60% and switching times were under a second. The composite coloration efficiency (CCE)[18] of the ester polymer was substantially higher than the alcohol polymer, which is consistent with previous work, which determined that increasing the size of the substituent groups on **Poly[ProDOTs]** increases the CCE by two to three times.[7] **Poly-[ProDOT-tetraester]** (**3**) also has a high CCE even though the switching time is much slower. The slow switching time is likely due to the large bulky substituent groups that interfere with ion transport. The contrast ratio is lower, typically seen when the

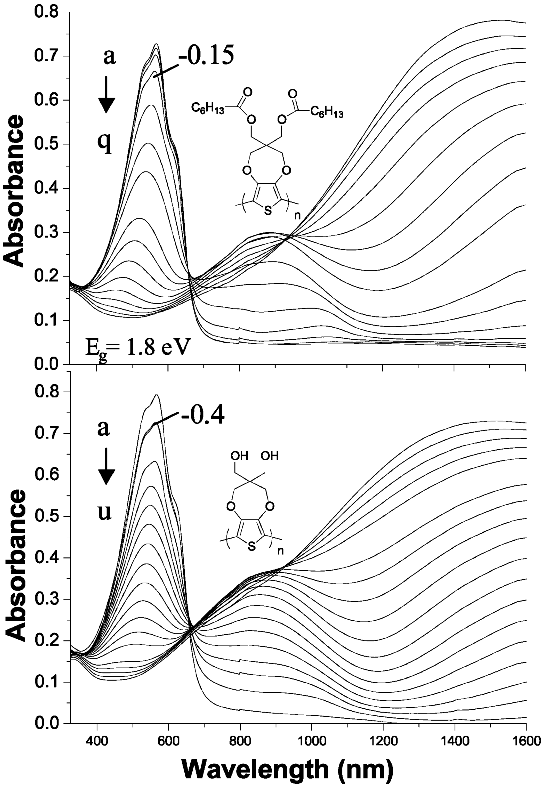


Figure 6. Top: Spectroelectrochemistry of a spray cast film of **Poly[ProDOT-diester]** (**1**) at potentials of (a) −0.6, (b) −0.25, (c) −0.2, (d) −0.15, (e) −0.1, (f) −0.05, (g) 0.0, (h) 0.05, (i) 0.10, (j) 0.15, (k) 0.20, (l) 0.25, (m) 0.30, (n) 0.35, (o) 0.40, (p) 0.45, and (q) 0.5 V vs Fc/Fc$^+$. Bottom: Spectroelecctrochemisry of **Poly[ProDOT-diol]** (**4**) at potentials of (a) −0.9, (b) −0.4, (c) −0.35, (d) −0.30, (e) −0.25, (f) −0.20, (g) −0.15, (h) −0.10, (i) −0.05, (j) 0.0, (k) 0.05, (l, m) 0.10, (n) 0.15, (o) 0.20, (p) 0.25, (q) 0.30, (r) 0.35, (s) 0.40, (t) 0.45, and (u) 0.5 V vs Fc/Fc$^+$.

Table 3. Electrochromic Properties of Ester- and Alcohol-Substituted PProDOTs

	% Δ*T*	CE[a]	*t* (s)[b]
1	63	660	0.8
4	57	396	0.9
3	48	703	3.6

[a] Composite coloration efficiency (cm^2/C). [b] Time required for 95% of Δ*T* to be attained when switching from the colored neutral state to the oxidized transparent state.

π−π* transition is broad. All films could be switched over 20 times without substantial loss of electroactivity and contrast between states.

Hole Transport Layers in LEDs. The alcohol-substituted **Poly[ProDOTs]** were studied as hole transport layers in light-emitting diodes with MEH−PPV as the emitting polymer. First, the ester-substituted **Poly[ProDOTs]**were spin-cast onto ITO coated glass slides followed by defunctionalization with KOH in methanol, washed with methanol, and vacuum-dried for 2 h at 55 °C. The emitting polymer, MEH−PPV, was spin-cast on top of the insoluble alcohol-substituted **Poly[ProDOTs]** film, and the devices were characterized, as shown in Figure 7. An external quantum efficiency of 0.05% was achieved when using thin films of **6** as the HTL at 6 V where the current flow is 180 mA/cm^2. The luminance was found to increase as the applied voltage was increased and reached a maximum value of 650 cd/m^2 at 10 V. These initial results show that the insoluble **6** nicely allows organic soluble light-emitting polymer to be processed on top and are potentially useful HTL materials.

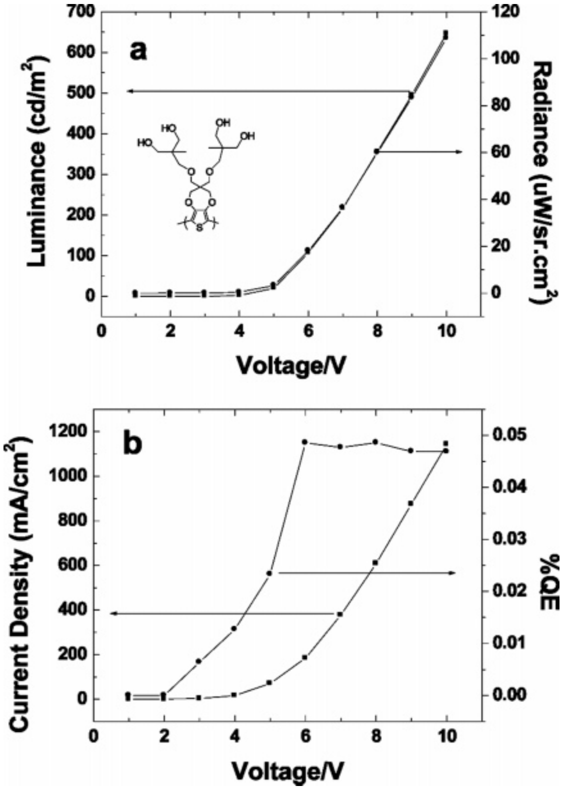


Figure 7. (a) Luminance and (b) current density and percent quantum efficiency as a function of applied voltage for a ITO/**Poly[ProDOT-tetraol]** (**6**)/MEH−PPV/Ca/Al device.

All three alcohol-substituted PProDOTs were tested in this manner and gave PLED characteristics that were similar to devices made using PEDOT-PSS as a HTL. All devices gave similar luminance results reaching maximum values of 30−40 cd/m^2 and external quantum efficiencies of up to 0.3%.

Summary and Perspective

Ester-substituted PProDOTs were synthesized by oxidative polymerization to yield polymers that were all soluble in ethyl acetate as well as other common organic solvents such as toluene and chloroform. Toluene solutions were spray cast to form thin films, which were electrochemically and electrochromically characterized. **Poly[ProDOTdiester]** (**1**) exhibited promising electrochromic properties, switching in under a second with a contrast ratio of 63% and a composite CE value of 660 cm^2/C. **Poly[ProDOTtetraester]** (**3**) also gave a high CE value at 703 cm^2/C, but with slower switching speeds and lower contrast ratios. **Poly[ProDOT-diester]** (**2**) dissolved upon switching due to the solubility of the oxidized form in propylene carbonate.

Ester **PProDOTs** were saponified with KOH in methanol, resulting in insoluble films. Spray cast films of **3** exhibited a burgundy color, which changed to a blue color upon conversion to the alcohol. The other esters exhibited the same optical properties as the resulting alcohols after treatment. **Poly[ProDOT-tetraol]** (**6**) and **Poly[ProDOT-diol]** (**5**) films were insoluble in the neutral form, but dissolved when electrochemically switched to the oxidized form while **Poly[ProDOT-diol]** (**4**) was insoluble in both electrochromic states, switching between a blue-purple color to transmissive in under a second with a contrast ratio of 58% and a composite CE value of 396 cm^2/C, comparable to other **Poly[ProDOTs]** with small substituents. The onset of color change occurs at much lower potentials, approximately −0.6 V, in comparison to other alkylenedioxythiophene polymers.

This work presents the synthesis of a family of dioxythiophene polymers that are soluble in polar solvents such as ethyl acetate, allowing for more environmentally friendly film processing by replacing chlorinated and aromatic solvents normally used with conjugated polymers. The oxidized polymers show solubility in a wide range of polar solvents such as water, acetonitrile, and propylene carbonate, and film processing techniques for these forms are being developed more thoroughly. The ability to spray cast the ester-substituted **Poly[ProDOTs]**, followed by a thin film saponification to the polymeric alcohol, allows the formation of neutral insoluble **Poly[ProDOT]** films. These insoluble films retain the electroactivity and electrochromic switching properties of the parent organic soluble polymers. This property will prove important to the utilization of these polymers in electrochromic displays where interaction of the polymer with solvent or gel electrolyte will decrease switching lifetimes. Further, these insoluble alcohol-substituted PProDOTs can be used as the hole transport layer in PLEDs, thus allowing organic soluble polymers to be directly applied to the HTL via spin-coating.

Experimental Section

Instrumentation. GPC was performed on two 300 × 7.5 mm Polymer Laboratories PLGel 5 μM mixed-C columns with Waters Associates liquid chromatography 757 UV absorbance detector at 585 nm or a 2996 photodiode array detector. Polymer solutions were prepared in THF. A constant flow rate of 1 mL/min was used. Molecular weights were obtained relative to polystyrene standards. NMR spectra were recorded on a Gemini 300 FT-NMR, Mercury 300 FT-NMR, or a VXR 300 FT-NMR. High-resolution mass spectrometry was carried out on a Finnigan MAT 95Q mass spectrometer. IR spectroscopy was carried out on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Samples were prepared by casting a film from 1 mg/mL methylene chloride solutions onto KBr slides. In the case of insoluble alcohol-substituted polymers and compounds, a KBr pellet was made using a hydraulic press. Electrochemical studies were carried out using an EG&G PAR model 273A potentiostat/ galvanostat in a three-electrode cell configuration consisting of a Ag^0 wire pseudo reference electrode calibrated with a Fc/Fc^+ couple, a glassy carbon button, platinum button, or ITO-coated glass slide (7 × 50 × 0.6 mm, 20 Ω/□) as the working electrode, and a Pt flag as the counter electrode in a 0.1 M tetrabutylammonium hexafluorophospate propylene carbonate solution. All absorption spectra and switching studies were carried out on a Varian Cary 500 scan UV−vis−NIR spectrophotometer. Colorimetry was carried out using a Minolta CS-100 Chroma Meter and CIE recommended normal/normal (0/0) illuminating/viewing geometry for transmittance measurements. The sample was illuminated from behind with a D50 (5000 K) light source. Fluorescence data was collected with a Spex F-112 photon counting fluorimeter at room temperature. Emission quantum yields were measured relative to Rhodamine 6G in methanol where $\phi_f = 1.00$, and optical density of solutions was kept below $A = 0.1$. The difference in refractive index between toluene and methanol were taken into account in the calculations.

HTL Studies. Electroluminescent devices were prepared by first masking ITO coated glass slides (Delta Technologies, $R_s = 8-12$/square) followed by etching by exposing the unmasked area to aqua regia vapor (3:1 v:v $HCl:HNO_3$).The etched ITO slides were then cleaned by sonication in sodium dodecyl sulfate, Milli-Q water, acetone, and isopropyl alcohol. The hole transport layer was formed by spin-coating 300 uL of either PEDOT/PSS or 2 mg/mL ester-substituted polymer in toluene at 4000 rpm. For the case of PEDOT/PSS, the films were dried in a vacuum oven at 150 °C for 2 h to remove residual water. The cast ester-substituted polymers were submersed into 0.1 M KOH/methanol for 1 h at 55−60 °C, then cooled, washed with methanol, and vacuum-dried at 55 ºC for 2 h. Then a 5 mg/mL electroluminescent layer MEH−PPV/dichloromethane was spin-coated at 1000 rpm on top of the hole transport layer. Ca and Al electrodes were subsequently deposited by thermal evaporation at 10^{-6} Torr. The thickness of the Ca and Al layers were 50 and 2000 Å, respectively. After the deposition, devices were encapsulated by epoxy to minimize the exposure to air. Electroluminescence spectra were recorded on an ISA-SPEX Triax 180 spectrograph fitted with a liquid N_2 cooled CCD detector.

Materials. All reagents were purchased from Acros or Aldrich. The DMF was 98% anhydrous packaged in a sure seal bottle under nitrogen. Chloroform and nitromethane were dried under $MgSO_4$ before use and all other reagents were used as received. **ProDOT-(CH$_2$Br)$_2$** was synthesized using a reported procedure.[7]

Synthesis. General Procedure for the Esterification of ProDOT-(CH$_2$Br)$_2$. Into a 100 mL round-bottom flask equipped with a water condenser and argon inlet were added 2.92 mmol (1 g) of **ProDOT(CH$_2$Br)$_2$**, 8.76 mmol of carboxylic acid (3 equiv), and 11.68 mmol (1.46 g) of K_2CO_3 (4 equiv) into 20 mL of DMF, and the mixture was heated to 100 °C. The reaction was followed by TLC (1:1 CH_2Cl_2/Hexanes) and shown to be completed in 16 h. The brown liquid was cooled, and 50 mL of water was added. The mixture was extracted 3 times with CH_2Cl_2 and the organic fraction was washed once with water and then dried with $MgSO_4$, and the solvent was removed by rotary evaporation. The yellow oil was purified by column chromatography using CH_2Cl_2 to afford a clear oil.

Propionic Acid 3-Propionyloxymethyl-3,4-dihydro-*2H*-thieno-[3,4-*b*][1,4]dioxepin-3-yl Methyl Ester [ProDOT(CH$_2$OC(O)-Et)$_2$]. We obtained 0.37 g of a clear oil (78%).^{1}H NMR (300 MHz, $CDCl_3$): δ 6.49 (s, 2H), 4.21 (s, 4H), 4.10 (s, 4H), 2.37 (q, 4H, $J = 7.5$ Hz), 1.16 (t, 6H, $J = 7.5$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.8, 149.9, 105.7, 72.6, 62.7, 46.3, 27.6, 9.25. HRMS: calcd for $C_{15}H_{20}O_6S$, 328.0981; found, 328.0971.

Heptanoic Acid 3-Heptanoyloxymethyl-3,4-dihydro-*2H*-thieno-[3,4-*b*][1,4]dioxepin-3-yl Methyl Ester [ProDOT-diester (1m)]. We obtained 1.13 g of a clear oil (89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.47 (s, 2H), 4.18 (s, 4H), 4.04 (s, 4H), 2.32 (q, 4H, $J = 7.5$ Hz), 1.61 (m, 4H), 1.30 (m, 12H), 0.89 (t, 6H, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 149.0, 105.5, 72.4, 62.4, 46.0, 34.1, 31.4, 28.9, 24.8, 22.4, 14.0. HRMS: calcd for $[C_{23}H_{36}O_6S + H]^+$, 441.2310; found, 441.2309. Anal. Calcd for $C_{23}H_{36}O_6S$: C, 62.70; H, 8.24. Found: C, 62.38; H, 8.43.

(3-Hydroxymethyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-3-yl)methanol [ProDOT(CH$_2$OH)$_2$]. Into a 50 mL round-bottom flask equipped with a condenser was added 2 mL of a 0.272 M solution of ProDOT(CH$_2$OC(O)Et)$_2$ in THF followed by 2 mL of 3 M KOH in 1:1 H_2O/EtOH, and the solution was heated to 60 °C. The reaction was monitored by TLC (EtOAc) and was complete in 24 h. The clear solution was cooled and neutralized with concentrated HCl followed by extraction 5 × with CH_2Cl_2, drying with $MgSO_4$, and rotary evaporation to remove solvent. The white powder was purified by column chromatography (EtOAc) to afford 0.096 g of a white solid (80%): mp 159−161 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 2H), 4.03 (s, 4H), 3.81 (s, 4H). ^{13}C NMR (75 MHz, CD_3OD): δ 174.8, 150.5, 105.3, 73.4, 61.2, 48.5. HRMS: calcd for $C_9H_{12}O_4S$, 216.0456; found, 216.0462.

3-[3-(3-Hydroxypropoxymethyl)-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-3-ylmethoxy]propan-1-ol [ProDOT(CH$_2$OC$_3$H$_6$OH)$_2$]. Into a 50 mL round-bottom flask equipped with a reflux condenser and an argon inlet was added 5 mL of 1,3-propanediol (62.4 mmol) followed by 0.35 g of Na (15.2 mmol), and the mixture was heated at 100 °C for 1 h, at which time the metal dissolved into the solution. Then 1 mL of a 1.46 M solution of **ProDOT-(CH$_2$Br)$_2$** in DMF was added, and the reaction continued to proceed for 48 h followed by TLC (EtOAc). The yellow solution was cooled and 10 mL of water was added, extracted 3× with CH_2Cl_2, and dried with $MgSO_4$. The solvent was removed with rotary evaporation and the resulting yellow oil was purified by column chromatography using EtOAc to obtain 0.42 g of a white solid (86%): mp 40−42 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.41 (s, 2H), 3.99 (s, 4H), 3.76 (t, 4H, $J = 5.3$ Hz), 3.64 (t, 4H, $J = 5.3$ Hz), 3.49 (s, 4H), 3.08 (bs, 2H), 1.83 (m, 4H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 149.0, 104.9, 72.7, 70.1, 69.7, 61.0, 47.5, 31.7. HRMS: calcd for $C_{15}H_{24}O_6S$, 355.1186; found, 355.1200. Anal. Calcd for $C_{15}H_{24}O_6S$: C, 54.20; H, 7.28. Found: C, 53.79; H, 7.35.

2-[3-(3-Hydroxy-2-hydroxymethyl-2-methylpropoxymethyl)-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-3-ylmethoxymethyl]-2-methylpropane-1,3-diol [ProDOT($CH_2OCH_2C(CH_3)(CH_2OH)_2)_2$]]. Into a 50 mL round-bottom flask equipped with a water condenser and an argon inlet were added 7 g of 2-hydroxymethyl-2-methylpropane-1,3-diol (58.26 mmol) and 5 mL of DMF followed by 0.35 g Na (15.2 mmol) and heated to 100 °C for 1 h at which time the metal is dissolved. Then 2 mL of a 1.46 M solution of **ProDOT($CH_2Br)_2$** (2.92 mmol) was added dropwise via syringe, and heating of the solution continued was for 24 h followed by TLC (EtOAc). Then the resulting yellow solution was cooled, and 10 mL of water was added followed by extraction 5× with CH_2Cl_2, drying with MgSO$_4$, and rotary evaporation to remove the solvent. The yellow solid was purified by column chromatography using 10:1 EtOAc/MeOH to obtain 0.63 g of a white solid (52%): mp 144−146 °C. ^{1}H NMR (300 MHz, CD$_3$OD): δ 6.51 (s, 2H), 4.00 (s, 4H), 3.50 (s, 4H), 3.46 (s, 8H), 3.32 (s, 4H, overlap with CD$_3$OD signal). ^{13}C NMR (75 MHz, (CD$_3$)$_2$SO): δ 154.8, 111.2, 79.3, 78.5, 75.1, 69.4, 53.1, 47.0, 22.1. HRMS: calcd for $[C_{19}H_{32}O_8S + Cl]^-$, 455.1501; found, 455.1489. Anal. Calcd for $C_{19}H_{32}O_8S$: C, 54.27; H, 7.67. Found: C, 54.00; H, 7.77.

Hexanoic Acid 3-[3-(3-Hexanoyloxypropoxymethyl)-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-3-ylmethoxy]propyl Ester [PProDOT-diester (2m)]. Into a 50 mL 3-neck round-bottom flask equipped with an argon inlet, a septum, and a stopcock were added 0.5 g of **ProDOT($CH_2OC_3H_6OH)_2$** (1.50 mmol), 0.42 mL of triethylamine (3.01 mmol, 2 equiv), and 5 mL of CH_2Cl_2. Then 0.84 mL of hexanoic acid acyl chloride (6.02 mmol, 4 equiv) was added dropwise via syringe. The reaction was complete in 1 h as determined by TLC (EtOAc). Then 5 mL of water was added and the mixture was extracted 5× with CH_2Cl_2 and dried with MgSO$_4$, and the solvent was removed by rotary evaporation. The resulting yellow oil was purified by column chromatography using 10:1 CH_2Cl_2/EtOAc to obtain 0.65 g of a clear oil (82%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.44 (s, 2H), 4.13 (t, 4H, J = 6.5 Hz), 3.99 (s, 4H), 3.49 (m, 8H), 2.27 (t, 4H, J = 7.5 Hz), 1.87 (m, 4H), 1.62 (m, 4H), 1.31 (m, 8H), 0.90 (t, 6H, J = 6.5 Hz). ^{13}C NMR (75 MHz, CDCl$_3$): δ 173.8, 149.6, 105.2, 73.5, 69.7, 68.0, 61.6, 47.7, 34.3, 31.3, 28.1, 24.7, 22.3, 13.9. HRMS: calcd for $[C_{27}H_{44}O_8S]^+$, 528.2757; found, 528.2769. Anal. Calcd for $C_{27}H_{44}O_8S$: C, 61.34; H, 8.39. Found: C, 61.59; H, 8.63.

Hexanoic Acid 3-[3-(3-hexanoyloxy-2-hexanoyloxymethyl-2-methylpropoxymethyl)-3,4-dihydro-2*H*-thieno[3,4-*b*]dioxeoin-3-ylmethoxy]-2-hexanoyloxymethyl-2-methylpropyl Ester [ProDOT-diester (3m)]. Into a 50 mL 3-neck round-bottom flask equipped with an argon inlet, a septum, and a stopcock were added 0.3 g of **ProDOT($CH_2OCH_2C(CH_3)(CH_2OH)_2)_2$** (0.72 mmol), 0.4 mL of triethylamine (2.88 mmol, 4 equiv), and 5 mL of CH_2Cl_2. Then 0.6 mL of hexanoic acid acyl chloride (4.32 mmol, 6 equiv) was added dropwise via syringe. The reaction was complete in 1 h as determined by TLC (EtOAc). Then 5 mL of water was added and the mixture was extracted 3 × with CH_2Cl_2, dried with MgSO$_4$, and the solvent was removed by rotary evaporation. The resulting yellow oil was purified by column chromatography using 30:1 CH_2Cl_2/EtOAc to afford 0.5 g of a clear oil (85%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.44 (s, 2H), 3.97 and 3.95 overlap (12H), 3.47 (s, 4H), 3.30 (s, 4H), 2.30 (t, 8H, J = 7.5 Hz), 1.64 (m, 8H), 1.30 (m, 16H), 0.97 (s, 6H), 0.89 (t, 12H, J = 6.4 Hz). ^{13}C NMR (75 MHz, CDCl$_3$): δ 173.6, 149.5, 105.3, 73.8, 73.4, 70.5, 66.0, 48.0, 39.3, 34.2, 31.3, 24.7, 22.3, 17.2, 13.9. HRMS: calcd for $C_{43}H_{72}O_{12}S$ + Na, 835.4637; found, 835.4607. Anal. Calcd for $C_{43}H_{72}O_{12}S$: C, 63.52; H, 8.93. Found: C, 63.71; H, 9.27.

General Procedure for the Synthesis of Ester-Derivatized PProDOTs. Into a 50 mL 3-neck round-bottom flask equipped with an argon inlet, a septum, and a stopcock was added a 1 M solution of FeCl$_3$ (4 equiv) in NO$_2$Me dropwise via syringe over 10 min to a 0.1 M ester-derivatized ProDOT solution in CHCl$_3$, and the resulting black solution was stirred for 1 h. Then 1 mL of hydrazine was then added and the resulting mixture stirred for 30 min at which time the solution gradually turned bright red. The solution was washed twice with 1 M HCl and dried with MgSO$_4$, and the solvent was removed by rotary evaporation. The purple solid was dissolved in CH_2Cl_2 and precipitated in MeOH. Filtration afforded a dark purple solid.

Poly(heptanoic acid (3-heptanoyloxymethyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-3-yl methyl ester)-2*H*-thieno[3,4-*b*]-[1,4]dioxepin-3-yl)methanol [Poly[ProDOT-diester (1)]. A 220 mg yield of a purple solid was obtained (73%).^{1}H NMR (300 MHz, CDCl$_3$): δ 4.25(bs, 4H), 4.05 (bs, 4H), 2.23 (bs, 4H), 1.60 (bs, 4H), 1.40 (bs, 12H), 1.61 (m, 4H), 1.30 (m, 12H), 0.90 (bs, 6H). ^{13}C NMR (75 MHz, benzene-d_6): 173.3, 145.7, 114.9, 73.9, 63.3, 47.1, 34.8, 32.4, 29.8, 25.8, 23.5, 14.8. IR spectroscopy: 1733 cm^{-1} (C═O stretch). Anal. Calcd for $(C_{23}H_{34}O_6S)_n$: C, 62.98; H, 7.82. Found: C, 63.36; H, 7.70.

Poly(Hexanoic acid 3-[3-(3-hexanoyloxy-propoxymethyl)-3,4-dihydro-2*H*-thieno[3,4-*b*] [1,4]dioxepin-3-ylmethoxy]propyl ester) [Poly[ProDOT-diester (2)]. A 0.33 g yield of a purple solid was obtained (57%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.15 (bs, 8H), 3.53 (m, 8H), 2.28 (bs, 4H), 1.90 (bs, 4H), 1.60 (bs, 4H), 1.29 (bs, 8H), 0.88 (bs, 6H). ^{13}C NMR (75 MHz): 174.1, 145.4, 114.3, 74.6, 70.4, 68.5, 61.7, 48.4, 34.6, 31.6, 29.3, 25.0, 22.6, 14.2. Anal. Calcd for $(C_{27}H_{42}O_8S)_n$: C, 61.57; H, 8.05. Found: C, 59.84; H, 7.88.

Poly(Hexanoic acid 3-[3-(3-hexanoyloxy-2-hexanoyloxymethyl-2-methyl-propoxymethyl)-3,4-dihydro-2*H*-thieno[3,4-*b*]-dioxeoin-3-ylmethoxy]-2-hexanoyloxymethyl-2-methyl-propyl ester) [Poly[ProDOT-tetraester (3)]. A 0.25 g yield of purple solid was obtained (62.5%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.10 (bs, 4H), 4.00 (s, 8H), 3.61 (bs, 4H), 3.33 (bs, 4H), 2.28 (t, 8H, J = 6.9 Hz), 1.58 (m, 8H), 1.27 (m, 16H), 1.00 (bs, 6H), 0.86 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 173.5, 145.3, 113.8, 74.4, 74.0, 71.0, 66.0, 48.3, 39.6, 34.3, 31.6, 24.8, 22.5, 17.5, 14.1. Anal. Calcd for $(C_{43}H_{70}O_{12}S)_n$: C, 63.67; H, 8.72. Found: C, 63.31; H, 8.97.

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