3,4-Alkylenedioxypyrrole-Based Conjugated Polymers with Finely Tuned Electronic and Optical Properties via a Flexible and Efficient *N*-Functionalization Method

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ABSTRACT: The poly(3,4-alkylenedioxypyrrole) family of conjugated polymers (the PXDOPs) shows potential for widespread applications due to their unique electronic and optical properties; however, progress has been limited due to synthetic limitations. We report an optimized synthetic route for a new compound, 3,4-propyledioxypyrrole-*N*-acetic acid (ProDOP-*N*-AcOH), which utilizes inexpensive reagents, high yielding steps that require little or no purification (and no chromatography), and which can be converted, using either one or two facile synthetic transformations, to a variety of ester, alcohol, and ether derivatives. The derivatives were electropolymerized onto Pt button working electrodes, and it was found that the polymers containing ester *N*-pendant groups exhibited a peak monomer oxidation potential 100 mV higher than that of the ethers, suggesting an inductive effect. Polymer $E_{1/2}$ values were measured to be between −0.24 and 0.01 V and were highly dependent on polymer pendant group structure and electrochemical media. HOMO values measured by DPV were found to be relatively independent of polymer structure. All monomers were electropolymerized onto transparent ITO/glass anodes for the purpose of generating electrochromic films. The predominant electrochromic processes occurred in the near-IR and UV regions, suggesting that they may be candidate materials for electrochromic applications outside the visible spectrum. The polymer containing a hydroxyl pendant group exhibited a brilliant red color upon both light and heavy doping and was transmissive upon dedoping. The strong absorbance in the visible region, the high band gap of 3.40 eV, and the passivating electrochemistry may be due to the formation of a tight polymer network, cross-linked through hydrogen-bonding interactions.

Introduction

Conjugated polymers provide properties which allow widespread application including electrochromic windows, mirrors and displays,[1,2] photovoltaic devices,[3] transparent conductors,[4] charge storage devices,[5] thin-film transistors,[6−10] light-emitting diodes,[11] antistatic coatings,[4] and biological applications.[12−14] It is clear from the wealth of scientific literature published over the past decade that the fundamental properties of conducting polymers are understood to the point that materials properties can be customized by controlled molecular and macromolecular structure. However, several challenges remain in order for this class of materials to become generally viable for production on a broad commercial scale. A major challenge is to design a material with tailored properties which allows a scaled-up synthesis at low cost. Some aspects of particular importance include safe and high yielding synthetic steps with minimal purification, the use of environmentally benign and inexpensive reagents, minimal synthetic transformations to obtain the final product, and minimal adaptation to established protocol to generate customized derivatives. To address this last item, it is desirable to synthesize materials from a common starting material, synthetically close to the end product, that could be efficiently mass-produced and subsequently converted to numerous derivatives with diverse and complex functionality.

The poly(3,4-alkylenedioxypyrrole) family of conjugated polymers, known as the PXDOPs, shows enormous potential for commercial applications due to their low oxidation potentials, a wide span of band gaps from 1.1 to 3.4 eV,[15−17] stable electrochromism, biocompatibility,[13] and ease of functionalization through the *N*-heteroatom. However, progress has been limited in the PXDOP chemistry due to a laborious monomer synthesis.[18]

Here we describe new 3,4-alkylenedioxypyrrole chemistry and have directed this work to consider the commercial scalability described above to the synthesis of XDOP monomeric subunits. We report an optimized synthetic route for a new compound, 3,4-propylenedioxypyrrole-*N*-acetic acid (ProDOP-*N*-AcOH, **5**). The synthesis of this compound is achieved in five high yielding steps utilizing common reagents, mild reaction conditions, and simple purification steps (importantly) without chromatography. It is clear that the ProDOP-*N*-AcOH synthon, due to its versatility toward further functionalization, is an excellent candidate for stimulating further development of 3,4-propylenedioxypyrroles and resultant polymers. We demonstrate the conversion of compound **5**, with either one or two facile synthetic transformations, to a variety of ester, alcohol, and ether derivatives. Their subsequent electropolymerization has been shown to lead to materials with diverse and unique electrochemical and optical properties that may prove to be useful in such applications as surface modified electrodes, charge storage, and electrochromic devices.

Results and Discussion

Synthesis. Our primary synthetic goal was to accomplish a large-scale synthesis of our target with high yielding steps and no chromatography. Scheme 1 illustrates the synthesis of the common starting material ProDOP-*N*-AcOH, compound **5**. This route has several advantages, including high yields, simple purification steps, and the minimal use of environmentally toxic reagents. (In this synthesis, the most potentially toxic substance used is 1,3-dibromopropane; however, this compound could be

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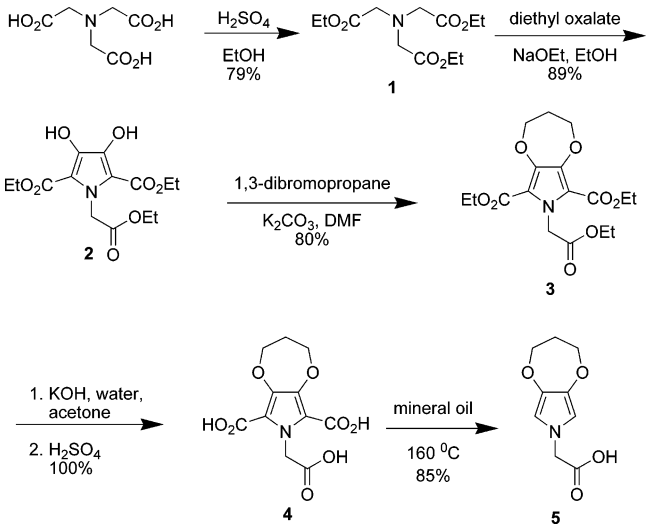
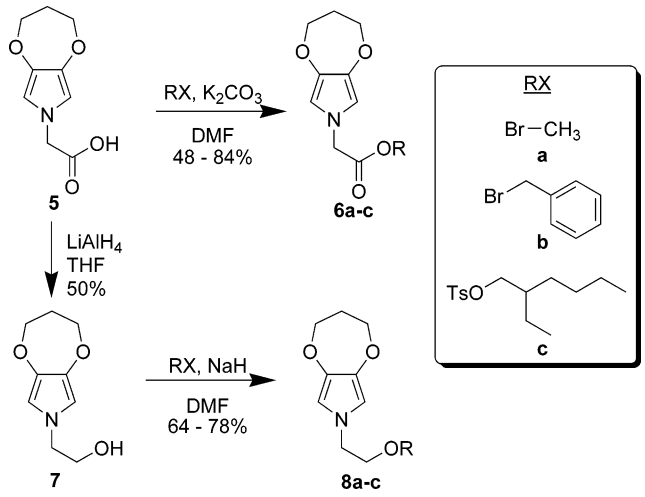
Scheme 1



Scheme 2



replaced with non-halogenated derivatives such as sulfonates.) The synthesis began with the reaction of the inexpensive, commercially available nitrilotriacetic acid in ethanol with sulfuric acid to yield triester **1**, which was purified by a simple short-path distillation. Compound **1** was mixed with diethyl oxalate and added to a solution of freshly prepared sodium ethoxide in ethanol, undergoing a Hinsberg condensation to yield, after acidic workup, the 3,4-dihydroxypyrrole triester **2**. Product of high purity was obtained by simple vacuum filtration and washing with water.

This high yielding reaction, compared to other literature examples of the dioxypyrroles,[19,20] can be explained in part by the 3-fold symmetry of compound **1**, as opposed to the 2-fold symmetry of the previously reported examples. First, the extra α-methylene provides an additional 1 equiv of reactive sites to form the initial linkage with diethyl oxalate. Second, the ring closure step is accelerated by the presence of two sites of attack instead of one. Additionally, the disodium salt obtained before workup forms a viscous gel (as opposed to precipitating out of solution) that does not interfere with the stirring mechanism. After acidic workup, high purity can be achieved by simple washing with water and drying.

Compound **2** was annulated with 1,3-dibromopropane to form compound **3** in good yield. This product was purified by precipitation of the reaction into water followed by filtration. Though recrystallization from methanol is reported in the

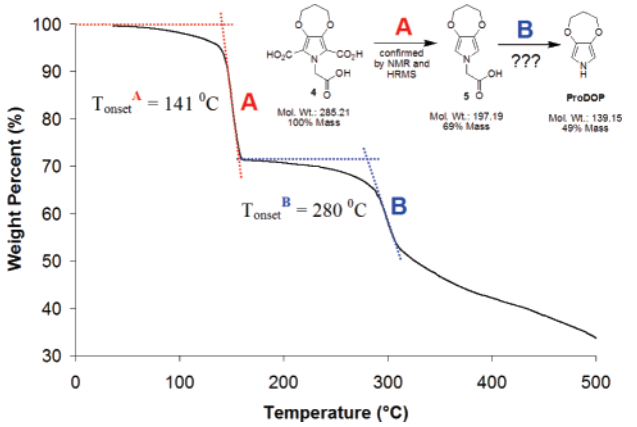
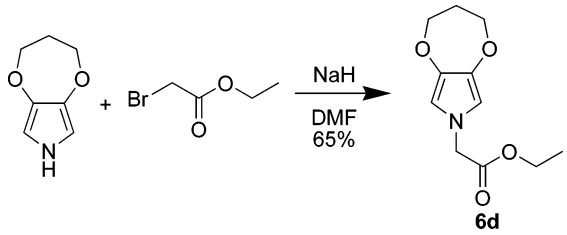


Figure 1. Thermogravimetric analysis of compound **4**. Measurements were performed under a nitrogen atmosphere at a temperature ramp of 10 °C/min. Horizontal dashed lines are drawn at the onset temperatures of the two transitions, and the slanted dashed lines are drawn tangent to the points of inflection.

Scheme 3



Experimental Section to provide **3** at high purity, it was found that this reagent, after filtration and washing with water, was of sufficient purity for the next step. This 3-fold saponification, which was achieved by the use of a water/acetone cosolvent system, was found to generate quantitative yield of compound **4** after acidic workup. This high yield was not achieved when the traditional water/alcohol cosolvent system used to saponify XDOP-2,5-diesters[15,19,20] was employed. It is believed the additional polar carboxylate functionality (with respect to other ProDOP derivatives) decreased the solubility of compound **4** in aqueous solution, and therefore acetone was used in place of alcohol to boost this solubility.

Compound **5** was subsequently prepared by the simple thermal decarboxylation of compound **4**. In procedures previously reported for the thermal decarboxylation of other N-functionalized ProDOP derivatives, triethanolamine or ethanolamine was used as the solvent followed by precipitation into water and extraction with dichloromethane.[15,19,20] However, compound **5** was found to be highly soluble in water, obviating the use of the triethanolamine/water precipitation procedure.

Several thermal decarboxylation methods for compound **4** were investigated, and we discovered that no solvent was necessary to effect the reaction. Figure 1 illustrates the thermogravimetric analysis of neat compound **4** under an inert atmosphere. It can be seen that a degradation onset was observed at 141 °C at a temperature ramp of 10 °C/min. A plateau is reached at ~71% mass remaining, which closely corresponds to a loss of two CO_2 units per molecule. It was confirmed by NMR and HRMS that this transition was indeed a double decarboxylation to yield compound **5**. Interestingly, a second degradation onset was observed at 280 °C and roughly corresponds to the loss of an acetyl group (possibly yielding ProDOP).

To synthesize compound **5** on a large scale, mineral oil was used as a heat transfer agent, and the thermal decarboxylation

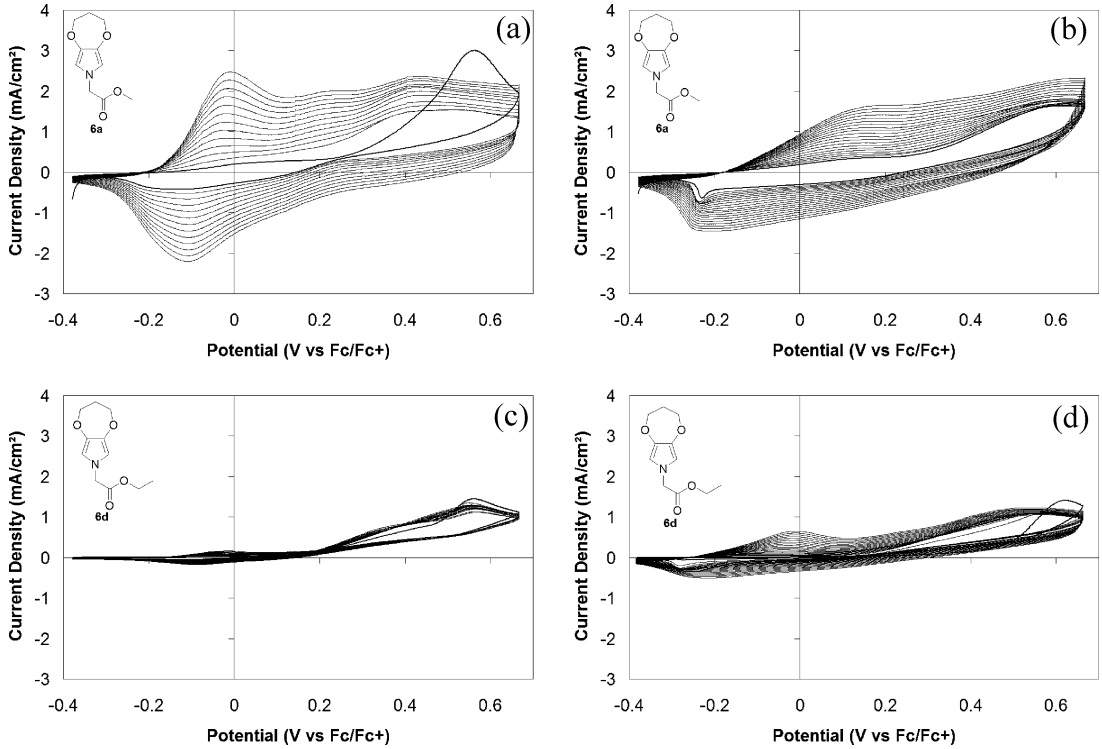


Figure 2. Electropolymerization of compounds **6a** and **6d** on a Pt button working electrode. All voltammograms represent stacked plots of 20 repeated scans at a scan rate of 50 mV/s. (a) **6a** in ACN; (b) **6a** in DCM; (c) **6d** in ACN; (d) **6d** in DCM.

shown in Scheme 1 was successful. A hexane wash was used to remove the mineral oil, and the product was purified by dissolving into methanol, filtration, and removal of solvent. It is presumed that the successful thermal decarboxylation in the TGA instrument was due to the nitrogen atmosphere being heated to the desired temperature. It is conceivable that large-scale decarboxylation could be achieved without the use of a heat transfer agent by flushing solid compound **4** with a hot inert gas such as nitrogen or argon.

Compound **5** is a convenient starting material for the synthesis of a number of N-functionalized ProDOP derivatives by transformation of the carboxylic acid functional group since the ProDOP ring system is tolerant to a variety of reaction conditions (except for strongly oxidative conditions). All of the previously established routes toward *N*-functionalized ProDOP derivatives use ProDOP as a common starting material.[17,20] The overall product yield from Scheme 1 is 48% for the five-step synthesis.

To illustrate the versatility of compound **5** in generating multiple *N*-functionalized ProDOP derivatives which can be considered for use as monomers to produce electroactive and conducting polymers, we have synthesized a family of ester and ether functionalized derivatives. As shown in Scheme 2, compound **5** was converted to ester derivatives **6a**−**c** by the reaction with the respective alkyl halide or tosylate in moderate to good yields. Compound **5** was also reduced to alcohol **7** by reaction with $LiAlH_4$ followed by Williamson etherification to yield ether derivatives **8a**−**c** in good yields.

For comparison purposes, and because of the commercial availability of the XDOP derivatives,[18] we were also interested in comparing our method with the synthesis of the ester derivatives directly from ProDOP. As shown in Scheme 3, ethyl bromoacetate was reacted with ProDOP under basic conditions in DMF to produce the ethyl ester **6d** in moderate yields. We feel that synthesis of the ester derivatives by the alkylation of ProDOP is deficient relative to the synthetic route outlined in Schemes 1 and 2 due to lower overall yields in cumbersome transformations for the synthesis of the benzyl-protected ProDOP diester, deprotection, and refunctionalization. Such a synthesis using the yield in Scheme 3 combined with the yields from literature preparations would be 14% overall compared to 40% overall using our new route, both starting with the simplest commercially available reagents.[15,19,20]

Monomer and Polymer Electrochemistry. The major motivation for development of this synthetic methodology was to generate monomers which could yield functional electroactive and conducting polymers. Compounds **6**−**8** with varied functionality were expected to yield polymers with varied electrochemical and optical properties. To demonstrate this, we chose the methyl, ethyl, benzyl, and 2-ethylhexyl substituents as *N*-pendant groups. It was expected that the methyl and ethyl groups would contribute minimally toward the overall polarity, steric hindrance to oxidative coupling, π-stacking interactions, and polymer solubility, while the benzyl group would add a degree of steric hindrance to the molecule, possibly providing an additional means of π-stacking. The racemic 2-ethylhexyl group was chosen as a hydrophobic moiety that would boost the monomer and polymer solubility and possibly disturb the polymer π-stacking interactions, allowing for more facile dopant ion penetration during redox doping.

To study these effects, we prepared monomer solutions of similar concentrations in various solvent/supporting electrolyte media. The solutions were then subjected to repeated scanning electropolymerization on a Pt button working electrode relative to a Fc/Fc^+ reference electrode, a common method for the synthesis of electroactive polymer thin films, and characterized electrochemically. The potential window for the experiments was chosen by setting the positive potential limit at a voltage ca. 20 mV positive of the peak monomer oxidation potential. The negative potential limit was chosen to include the entire polymer redox process. As shown in Figure 2, an irreversible oxidation process was observed at positive potentials and is

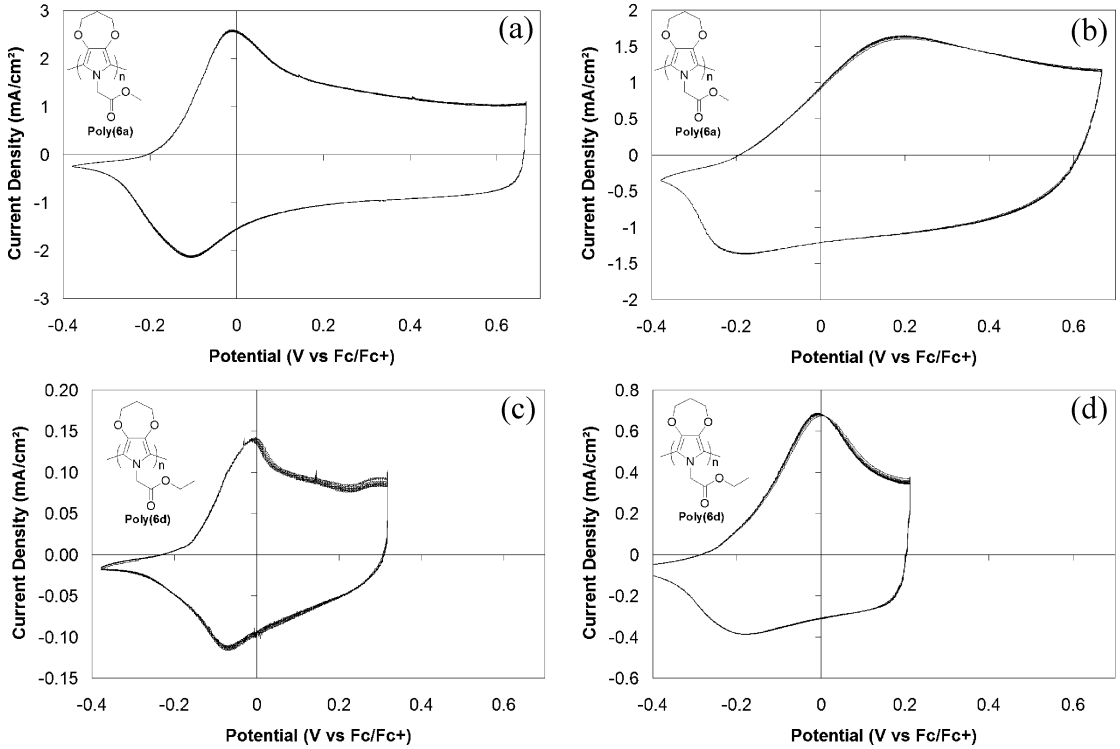


Figure 3. Repeated scan (20 scans, 50 mV/s) cyclic voltammograms in monomer free electrolyte solutions of (a) Poly**(6a)** and (b) Poly**(6d)** in acetonitrile and (c) Poly**(6a)** and (d) Poly**(6d)** in DCM. These CVs represent the same polymer films whose electrodepositions are illustrated in Figure 2.

attributed to the generation of monomer radical cations followed by coupling; this coupling effectively deposits a film of oxidized polymer onto the electrode surface. Upon reverse scanning, a reductive wave is observed at a lower potential and is attributed to the conversion of the oxidized (doped) polymer film to its charge neutral or undoped state. When the neutral polymer was then subsequently scanned from negative to positive potentials, an oxidation wave is observed at lower potentials than that of the monomer and is attributed to the conversion of the neutral polymer to its oxidized (doped) state. This process was repeated for a total of 20 potential scans for each monomer solution, and as evidenced by increasing polymer peak current density over 20 scans in Figure 2, with each progressive scan an additional layer of polymer was deposited onto the electrode surface.

There is a surprisingly strong effect of the monomer structure (methyl vs ethyl ester) and polymerization solvent on the shape of the CVs. After each monomer shows an initial scan oxidation peak at 0.5−0.6 V, the electrochemical depositions are strikingly different in that an extension of the ester substituent by a single CH_2 unit produces a fully reproducible and significant difference in the polymerization behavior. Because of the complexity of the electropolymerization process, it cannot be determined whether this difference occurs because of solubility differences, monomer or oligomer interactions with dopant ions or the electrode, or some other effect. The main conclusion of this effort is that the most effective electrochemical system for carrying out an electropolymerization is best found via experimental trial and error. In this specific comparison, it is evident that the methyl ester (**6a**) polymerized in ACN gave the most effective electropolymerization behavior (Figure 2a). At the same time, each experiment lead to an electroactive film, and Table 1 summarizes the electrochemical results obtained for all of the monomers and their respective polymers in various electrochemical media.

Table 1. Electrochemical Data of the Various ProDOP-*N*-R Derivatives

compd	solvent[a]	C^*_m[b]	$E_{p,m}$[c]	$E_{1/2,p}$[d]	ΔE_p[e]	HOMO[f]
5[g]	H_2O	11.8	0.48			
6a	DCM	11.2	0.63	0.01	0.38	
	ACN	12.1	0.57	−0.06	0.09	4.84
6b	ACN	10.3	0.61	−0.04	0.08	4.86
6c	ACN	10.8	0.67	−0.09	0.05	4.85
6d	DCM	10.3	0.63	−0.09	0.19	4.75
	ACN	10.3	0.58	−0.04	0.07	4.77
7	PC[h]	7.26	0.51	−0.01	0.09	
	DCM[i]	11.4	0.52			
8a	DCM	11.0	0.53	−0.21	0.02	4.76
	ACN	10.5	0.51	−0.07	0.07	4.84
8b	DCM	12.0	0.52	−0.24	0.03	4.73
	ACN	11.2	0.51	−0.14	0.03	4.86
8c	PC	11.6	0.54	−0.11	0.02	4.89
	ACN	10.3	0.51	−0.14	0.01	4.85

[a] The solvent for the subsequently reported data. Supporting electrolytes for the solvents: ACN, TBAP; DCM, $TBAPF_6$; PC, $LiClO_4$; H_2O, KCl. [b] Bulk monomer concentration (mM). [c] Monomer peak oxidation potential (mV vs Fc/Fc^+) at 50 mV/s. [d] Polymer half-wave potential (V vs Fc/Fc^+). [e] Separation of polymer peak oxidation and reduction potentials (V). [f] HOMO (eV) of the neutral polymer as determined by DPV. Values obtained by the assumption that the Fc/Fc^+ redox couple resides at 5.12 eV.[21] [g] Would not electropolymerize in any compatible solvents. [h] Polymerized galvanostatically at 50 μC to 0.51 V. [i] Large shifts in potentials were observed, producing nonquantifiable data.

All electrodeposited polymer films were removed from monomer solution and then gently rinsed with and immersed in their respective monomer-free electrolyte solutions. To characterize the films redox processes and to determine the stability of the polymer films toward repeated electrochemical switching, the films were subjected to several 20 potentiodynamic scans whose switching potentials were chosen as points outside the electrochemical diffusion tails, as shown in Figure 3.

In acetonitrile (ACN), the redox processes for Poly(**6a**) and Poly(**6d**) are well-defined, found at a low potential of −0.06

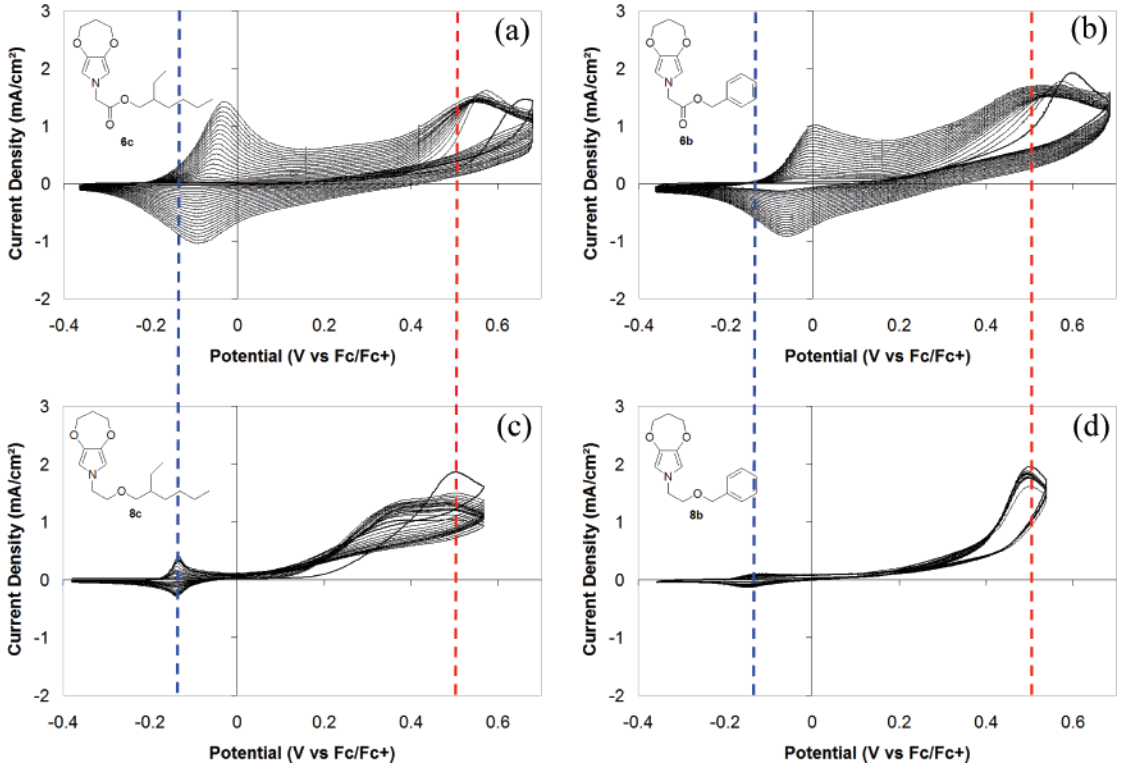


Figure 4. Comparative electropolymerization (20 scans at 50 mV/s) of the benzyl and ethylhexyl ethers and esters onto a Pt button electrode in acetonitrile of (a) **6c**, (b) **6b**, (c) **8c**, and (d) **8b**. Dashed lines are drawn to guide the eye. Red: positioned at the $E_{p,m}$ of the ether monomers; blue: positioned at $E_{1/2,p}$ of the ether polymers.

and −0.04 V, and the redox peak separation values (ΔE_p = 0.09 V and 0.07 mV, respectively) are quite low, indicating that facile electrochemical switching is taking place. The fact that the $E_{1/2}$ values are similar suggests that the two polymers are very close in electronic structure. At the same time, the current response for Poly(**6a**) is ca. 15 times larger than that of Poly(**6d**). This enhanced electropolymerization rate for Poly(**6a**) is likely due to a higher solubility of **6d** oligomers, which diffuse away from the electrode surface. The long capacitive tail shown in Figure 3a for Poly(**6a**) is indicative of a conducting polymer retaining its electroactivity over a broad potential range.

Poly(**6a**) and Poly(**6d**) exhibited different behavior in dichloromethane (DCM), which is less polar than acetonitrile, and it is presumed that the ester functionalized pendant groups would exhibit a decreased affinity for the solvent. Indeed, it can be seen that the redox process for the two ester polymers is broader in DCM, presumably due to a less solvated film with hindered ion transport, with redox peak separation values for Poly(**6a**) and Poly(**6d**) of ΔE_p = 0.38 and 0.19 V, respectively. These results are not surprising given the difference in polarity of the two monomers; silica gel TLC experiments in ethyl acetate show that the methyl ester (R_f = 0.24) is more polar than the ethyl ester (R_f = 0.78).

To observe the effect of monomer polarity on polymerization and switching, Figure 4 illustrates the electropolymerization of esters **6b** and **6c** compared to ethers **8b** and **8c.** In this instance, the monomers have exactly the same structures with the exception of an added carbonyl replacing a CH_2. It is evident that the ether derivatives did not polymerize as readily as the ester derivatives based on the polymer redox activity induced during the 20 scans. On close examination, one sees that the peak monomer oxidation potentials of the ether derivatives exhibited an ∼100 mV cathodic shift (easier to oxidize) with respect to the ester derivatives (indicated by the red vertical lines in Figure 4). We attribute this to the inductive effect of

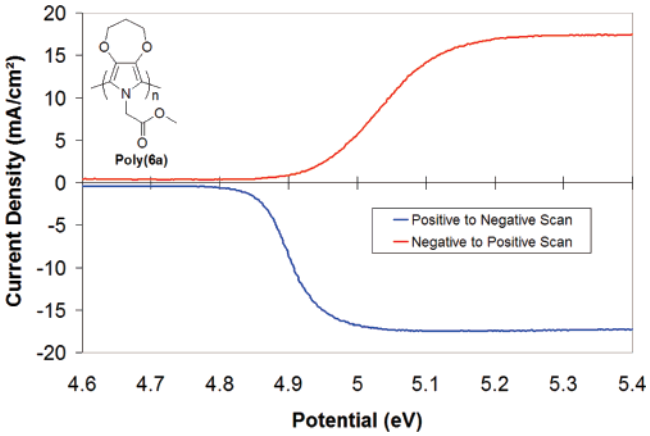


Figure 5. Differential pulse voltammogram of Poly**(6a)** in acetonitrile.

the carbonyl group which withdraws electron density from the π-system through the methylene group. Also observed is that the ether derivative polymer $E_{1/2}$ values also show an ∼100 mV cathodic shift with respect to the ester derivatives (illustrated by the blue vertical lines in Figure 4).

Since this cathodic shift carries over to the polymer $E_{1/2}$, it is expected that the HOMO levels of the ester derivatives would differ by ∼0.1 eV. HOMO values were determined by measuring the onset of oxidation in the differential pulse voltammogram (DPV) of the polymer in monomer-free electrolyte solution. This technique is preferred over CV for measuring polymer HOMO levels because the onset of polymer oxidation is more well-defined due to the elimination of double-layer capacitive currents. Figure 5 illustrates the DPV of Poly(**6a)** in acetonitrile and the HOMO was determined to be 4.84 eV (based on Fc/Fc^+ = 5.12 eV[21,22]). It can be seen in Table 1 that the HOMO values for all of the polymers (esters and ethers) measured in either ACN or DCM fall within the 4.82 ± 0.08 eV range. As

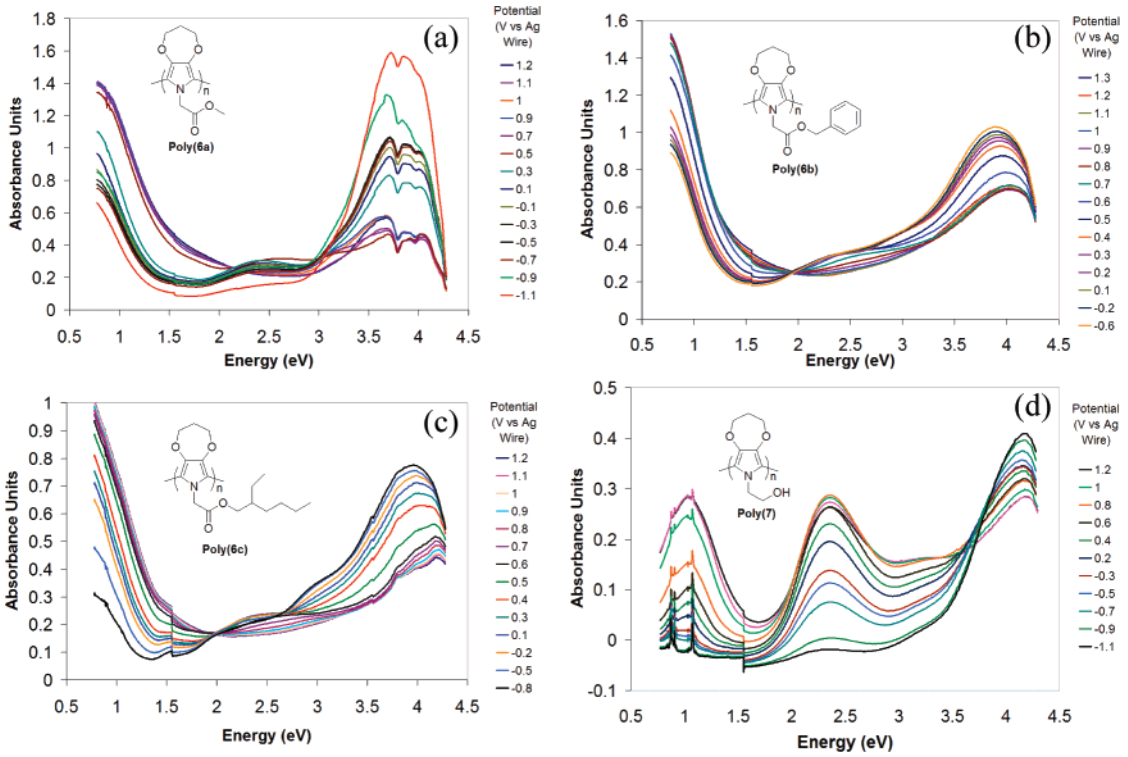


Figure 6. Spectroelectrochemistry on ITO/glass of (a) Poly**(6a)**, (b) Poly**(6b)**, (c) Poly**(6c)**, and (d) Poly**(7)**.

the HOMO level represents the easiest electron to remove from the system, and likely originates from polymer chains that attain the most planar states, it is evident that the nature of the pendant group contributes little to the polymer backbone electronic effects.

Polymer Optical Properties. In order to probe the polymer's coloration properties, all monomers were subjected to electropolymerization onto transparent ITO/glass anodes for the purpose of generating electrochromic films. All of the ester derivatives, **6a**−**d**, successfully formed electroactive polymer films, whereas the ether derivatives, **8a**−**c**, did not. In fact, for all solvents used, it was observed that the initial polymerization of the ether derivatives occurred at the ITO surface, but the films formed quickly delaminated, while the ester derivatives adhere presumably due to a favorable interaction between the ester groups and the ITO surface. The deposition method of choice was CV; however, potentiostatic polymerization (the preferred method for controlled film thickness) also successfully formed films. In addition to the successful film electrodeposition of the ester derivatives, the hydroxyl-functionalized derivative **7** was successfully polymerized onto ITO/glass.

As these dioxypyrrole polymers are *N*-substituted, steric interactions along the backbone take part in shifting the π,π^* transition (with respect to ProDOT) into the UV.[17,23] As shown in Figure 6, Poly**(6a)**, Poly**(6b)**, and Poly**(6c)**, upon electrochemical doping, exhibited a bleaching of the UV absorbance with increasing potential. This depletion was concomitant with the formation of doped states in the polymer: a low-intensity transient peak at ca. 2.5 eV, attributed to polaronic radical cations, and a steady increase in the IR, attributed to the formation of bipolaronic dications. It was observed that at heavy doping levels the films were bluish gray, became red or magenta at intermediate doping levels, and then upon dedoping became pale yellow; however, all colors were very faint to the eye. The predominant electrochromic processes occurred in the near-IR and UV regions, suggesting that they may be candidate materials for electrochromic applications outside the visible spectrum or as counter electrode materials in dual polymer electrochromic devices matched with strongly coloring polymers. This lack of color in the visible region (∼1.7−3.0 eV) in the doped state of Poly**(6a)**, Poly**(6b)**, and Poly**(6c)** originates from two phenomena: (1) a low absorbance with broad peaks results in a transmissive film with a low degree of color saturation; (2) the high degree of absorbance change in the IR (compared to that of the weak polaron peak at ca. 2.5 eV) indicates that bipolarons are easily formed in the polymer films and that a high degree of planarity of these chromophores results in an IR absorbance that does not tail into the visible.

An interesting divergence from the relatively similar ester polymers was the hydroxyl polymer Poly**(7)**. The film was a brilliant red color upon both light and heavy doping and transmissive upon dedoping. The high band gap of 3.40 eV (well into the UV), coupled with this strong absorbance in the visible region upon doping, may be due to entrapped polaron states with the formation of a tight polymer network, cross-linked thorough hydrogen-bonding interactions. This high degree of secondary interactions may impose a twist upon the conjugated backbone, thus shortening the effective conjugation length. The peak at 2.5 eV is most likely due to a strong presence of trapped polarons in the polymer film. A blue-shifted near-IR electrochromism (note peak at ∼1 eV) relative to the other polymers, coupled with the need for a very negative potential of −1.1 V vs Ag wire to affect a significant bleaching of the 2.5 eV peak, further suggests that the polymer film is densely cross-linked and is trapping charges.

Conclusions. A family of *N*-alkylated ProDOP based monomers was synthesized based on a common starting material, ProDOP-*N*-AcOH, via a facile, high-yielding route that requires no chromatography. This common starting material was found to be scalable and can be the synthon for many novel monomeric and polymeric materials. To illustrate the efficacy of this route, we have synthesized a family of ester, ether, and hydroxyl derivatives in either one or two simple synthetic steps. The monomers were then electropolymerized onto metal and trans-

parent electrodes. It was found that the ester derivatives possessed a greater affinity for the electrodes than the ether derivatives, due to the carbonyl interactions, and the redox processes of the films were highly dependent on the electrochemical environment, as evidenced by various electrochemical data. The ester and hydroxyl derivatives were polymerized onto ITO/glass anodes and were found to be electrochromic, with the properties dependent on the pendant group structure.

Experimental Section

Materials. All reagents were obtained either from Aldrich or Fisher Scientific, with the exception of ProDOP, which was obtained from Ciba Specialty Chemicals. All electrochemical solvents were distilled prior to use except for propylene carbonate, which was used as is. ITO-coated glass slides (7 × 50 × 0.6 mm, 20 Ω/□) were obtained from Delta Technologies and were cleaned by sonicating in acetone.

Instrumentation. NMR spectra were measured on a Gemini-300 FT-NMR, a VXR 300 FT-NMR, or a Mercury-300 FT-NMR. High-resolution mass spectrometry was performed on a Finnigan MAT 95Q Hybrid Sector or a Bruker APEX II FTICR. UV−vis−NIR spectra were recorded on a Varian Cary 5E UV−vis−NIR spectrophotometer. Elemental analysis was performed at Robertson Microlit, Madison NJ. TGA data were measured with a Perkin-Elmer TGA 7 thermogravimetric analyzer. Electrochemistry was performed on a Princeton Applied Research model 273A potentiostat/galvanostat. Electrochemical measurements were performed in a three-electrode cell configured with a Pt button (0.02 cm^2) working electrode, a Pt flag counter electrode, and a Ag/Ag^+ (10 mM in TBAP/ACN) reference electrode, which was calibrated to the Fc/Fc^+ redox couple. Electrochemistry on ITO/glass electrodes was performed in a three-electrode cell with ITO/glass as the working electrode, a Pt wire counter electrode, and a silver wire pseudoreference electrode. Contact to the ITO slides was made using conductive Cu tape (1131) purchased from 3M.

Synthesis. Triethyl Nitrilotriacetate (1). To a 1000 mL round-bottom (RB) flask containing a stir bar, an argon atmosphere, and outfitted with a reflux condenser was added nitrilotriacetic acid (50.00 g, 262 mmol), ethanol (200 proof, 500 mL), and sulfuric acid (concentrated, 15 mL). The mixture was refluxed for 3 h, cooled to room temperature, and concentrated in vacuo. The concentrate was immediately dissolved into DCM (300 mL) and washed with small portions of saturated sodium bicarbonate until the evolution of gas ceased. The solvent was removed, and the resulting concentrated liquid was distilled (bp 135 °C at 0.1 mmHg) to yield 56.61 g (79%) of a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.13 (q, 6H, J = 8.0 Hz), 3.62 (s, 6H), 1.23 (t, 9H, J = 8.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 60.8, 55.3, 14.3. HRMS (EI): Calcd for $C_{12}H_{21}NO_6$ ($[M]^+$), 275.1369, found *m/z*, 275.1364; Anal. Calcd for $C_{12}H_{21}NO_6$: C, 52.35; H, 7.69; N, 5.09%. Found: C, 52.11; H, 7.84; N, 5.37%.

Diethyl 1-(2-Ethoxy-2-oxoethyl)-3,4-dihydroxy-1*H*-pyrrole-2,5-dicarboxylate (2). To a 1000 mL RB flask containing a stir bar, an argon atmosphere, and outfitted with a reflux condenser was added ethanol (200 proof, 500 mL) and sodium metal (21.31 g, 927 mmol). When the sodium was completely dissolved, a mixture of compound **1** (56.20 g, 204 mmol) and diethyl oxalate (29.44 g, 204 mmol) was added. The mixture was refluxed overnight, whereupon it became a clear, gelatinous solution. After cooling to room temperature, the mixture was poured into 1200 mL of deionized (DI) water, chilled in an ice bath, and acidified with glacial acetic acid (200 mL). The resulting white precipitate was isolated via vacuum filtration and washed with several portions of DI water to yield 59.75 g (89%) of a white solid; mp 121.3−121.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (s, 2H), 5.32 (s, 2H), 4.39 (q, 4H, J = 7.7 Hz), 4.20 (q, 2H, J = 7.7 Hz), 1.38 (t, 6H, J = 7.7 Hz), 1.27 (t, 3H, J = 7.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 162.4, 139.6, 111.1, 61.6, 47.9, 14.5, 14.4. HRMS (EI): Calcd for $C_{14}H_{19}NO_8$ ($[M]^+$), 329.1111, found *m/z*, 329.1111. Anal. Calcd for $C_{14}H_{19}NO_8$: C, 51.06; H, 5.82; N, 4.25%. Found: C, 50.79; H, 5.83; N, 4.22%.

Diethyl 7-(2-Ethoxy-2-oxoethyl)-2,3,4,7-tetrahydro-1,4-dioxepino[2,3-*c*]pyrrole-6,8-dicarboxylate (3). To a 500 mL RB flask containing a stir bar and an argon atmosphere was added compound **2** (50.00 g, 152 mmol), 1,3-dibromopropane (30.69 g, 152 mmol), anhydrous potassium carbonate (52.46 g, 380 mmol), and anhydrous DMF (500 mL). The reaction was heated to 105 °C and became lime green after about 30 min. The reaction was stirred for 12 h, during which it became yellow, and was cooled to room temperature. The mixture was poured into DI water (500 mL); the solids were collected via vacuum filtration and washed with several portions of DI water. The solids were recrystallized from hot methanol to yield 44.90 g (80%) of a yellow solid; mp 139.7−139.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.43 (s, 2H), 4.30 (q, 4H, J = 7.7 Hz), 4.22 (q, 2H, J = 8.0 Hz), 4.20 (t, 6H, J = 6.3 Hz), 2.25 (p, 2H, J = 6.3 Hz), 1.34 (t, 6H, J = 7.7 Hz), 1.28 (t, 3H, J = 8.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 161.0, 142.7, 114.1, 71.7, 61.5, 60.9, 48.0, 33.4, 14.5, 14.4. HRMS (EI): Calcd for $C_{17}H_{23}NO_8$ ($[M]^+$), 369.1424. Found *m/z*, 369.1417. Anal. Calcd for $C_{17}H_{23}NO_8$: C, 55.28; H, 6.28; N, 3.79%. Found: C, 55.29; H, 6.37; N, 3.80%.

7-(Carboxymethyl)-2,3,4,7-tetrahydro-1,4-dioxepino[2,3-*c*]-pyrrole-6,8-dicarboxylic Acid (4). To a 100 mL RB flask was added compound **3** (17.56 g, 47.5 mmol), DI water (45 mL), acetone (25 mL), and potassium hydroxide (13.34 g, 238 mmol). The solution/suspension was bubbled with argon for 20 min, then refluxed for 2.5 h, resulting in a deep brown solution. The organic volatiles were removed in vacuo, and the resulting aqueous mixture was chilled in an ice bath. To the mixture was added concentrated sulfuric acid until a pH of 6 was reached, whereupon a white solid precipitated out of a red mother liquor. This precipitate was filtered and washed with several portions of DI water and after drying weighed 13.55 g (100%). The product was insoluble in all solvents tried, so NMR analysis was performed on the fully deprotonated version by dissolving into an $NaOD/D_2O$ solution. The product was used in the next reaction without further purification. ^{1}H NMR (300 MHz, D_2O/NaOD): δ 5.17 (s, 2H), 4.13−4.09 (m, 4H), 2.19 (p, 2H, J = 5.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.9, 171.0, 141.9, 120.3, 74.9, 51.9, 36.3.

2-(2,3-Dihydro-1,4-dioxepino[2,3-c]pyrrol-7(2H)-yl)acetic Acid (5). To a 250 mL RB flask containing a stir bar and an argon atmosphere was added heavy mineral oil (100 mL). The solution was heated to 80−100 °C, where it was deoxygenated with three vacuum/argon purges, after which it was heated to 160 °C. While maintaining a continuous argon blanket, compound **4** (13.55 g, 47.5 mmol) was added in small portions. The resulting slurry was stirred for an additional 10 min and then cooled to room temperature. Hexanes (250 mL) were added to the flask and decanted. The remaining solids were dissolved in methanol (250 mL), and the solution was filtered to remove trace solids. After removal of the solvent in vacuo, 7.94 g (85%) of a tan solid was isolated. ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.12 (s, 2H), 3.88 (s, 2H), 3.82 (dd, 4H), 1.97 (p, 2H, J = 5.7 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): δ 170.9, 137.4, 106.7, 71.8, 54.4, 35.1. HRMS (EI): Calcd for $C_9H_{11}NO_4$ ($[M]^+$),197.0688. Found *m/z*, 197.0687.

Methyl 2-(3,4-Dihydro-1,4-dioxepino[2,3-*c*]pyrrol-7(2*H*)-yl)-acetate (6a). To a 50 mL RB flask containing a stir bar and an argon atmosphere was added compound **5** (1.00 g, 5.07 mmol), anhydrous DMF (25 mL), methyl iodide (0.86 g, 6.08 mmol), and anhydrous K_2CO_3 (1.05 g, 7.61 mmol). The reaction was heated to 60 °C and stirred for 17 h, after which it was cooled to room temperature and poured into DI water (250 mL). The resulting mixture was extracted with 2 × 100 mL ethyl acetate, concentrated in vacuo, flashed through a pad of silica gel (ethyl acetate), and concentrated in vacuo to give 0.60 g (56%) of a white solid. TLC

$R_f = 0.24$ (silica gel, ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.20 (s, 2H), 4.39 (s, 2H), 4.01−3.98 (m, 4H), 3.75 (s, 3H), 2.17−2.10 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 139.7, 107.5, 72.6, 52.7, 51.5, 35.3. HRMS (ESI FTICR): Calcd for $C_{10}H_{14}NO_4$ ($[M + H]^+$), 212.0917, found *m/z*, 212.0918. Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.86; H, 6.20; N, 6.63%. Found: C, 56.13; H, 6.06; N, 6.38%.

Benzyl 2-(3,4-Dihydro-1,4-dioxepino[2,3-*c*]pyrrol-7(2*H*)-yl)-acetate (6b). To a 50 mL RB flask containing a stir bar and an argon atmosphere was added compound **5** (1.00 g, 5.07 mmol), anhydrous DMF (25 mL), benzyl bromide (0.91 g, 5.32 mmol), and anhydrous K_2CO_3 (1.05 g, 7.61 mmol). The reaction was heated to 60 °C and stirred for 17 h, after which it was cooled to room temperature and poured into DI water (250 mL). The resulting precipitate was isolated via vacuum filtration, washed with DI water, and air-dried to give 0.70 g (48%) of a white powder. TLC R_f = 0.81 (silica gel, 3:2 = hexanes:Et_2O); mp 71.8−72.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38−7.31 (m, 5H), 6.21 (s, 2H), 5.18 (s, 2H), 4.42 (s, 2H), 4.01−3.98 (m, 4H), 2.17−2.10 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9, 139.8, 135.3, 128.9, 128.8, 128.5, 107.5, 72.7, 67.4, 51.7, 35.3. HRMS (ESI FTICR): Calcd for $C_{16}H_{18}NO_4$ ($[M + H]^+$), 288.1230. Found *m/z*, 288.1229. Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.88%. Found: C, 66.87; H, 5.93; N, 4.53%.

2-Ethylhexyl 2-(3,4-Dihydro-1,4-dioxepino[2,3-c]pyrrol-7(2*H*)-yl)acetate (6c). To a 100 mL RB flask containing a stir bar and an argon atmosphere was added compound **5** (2.00 g, 10.1 mmol), anhydrous DMF (50 mL), 1-bromo-2-ethylhexane (2.06 g, 10.6 mmol), and anhydrous K_2CO_3 (2.10 g, 15.2 mmol). The reaction was heated to 60 °C and stirred for 15 h. After cooling to room temperature, the mixture was poured into DI water (250 mL) and extracted with 2 × 100 mL of Et_2O. The combined organic layers were washed with DI water (100 mL) and brine (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the concentrate was purified via flash chromatography on silica gel (deactivated with TEA, 7:4 = Et_2O:hexanes) to yield 2.65 g (84%) of a clear oil. TLC R_f = 0.23 (silica gel, 3:2 = Et_2O:hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.19 (s, 2H), 4.36 (s, 2H), 4.04 (dd, 2H, J = 6.0 Hz, J = 2.0 Hz), 3.99−3.96 (m, 4H), 2.15−2.09 (m, 2H), 1.55 (p, 1H, J = 6.3 Hz), 1.43−1.23 (m, 8H), 0.88 (t, 3H, J = 7.0 Hz), 0.86 (t, 3H, J = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 139.7, 107.5, 72.6, 68.0, 51.7, 38.8, 35.3, 30.4, 29.0, 23.9, 23.1, 14.2, 11.1. HRMS (ESI FTICR): Calcd for $C_{17}H_{28}NO_4$ ($[M + H]^+$), 310.2013. Found *m/z*, 310.2007. Anal. Calcd for $C_{17}H_{27}NO_4$: C, 65.99; H, 8.80; N, 4.53%. Found: C, 65.77; H, 8.72; N, 4.43%.

Ethyl 2-(3,4-Dihydro-1,4-dioxepino[2,3-*c*]pyrrol-7(2*H*)-yl)acetate (6d). Into a 250 mL RB flask equipped with a magnetic stir bar, a nitrogen inlet adapter, an additional funnel, and a rubber septum was added ProDOP (0.60 g, 4.31 mmol). Anhydrous DMF (40 mL) was then added to the flask, and the mixture was cooled to 0 °C. NaH (60% in mineral oil, 0.19 g, 4.74 mmol) was added to the solution. The pale yellow slurry was stirred for 2 h at room temperature, followed by addition of ethyl bromoacetate (0.56 mL, 4.74 mmol). The mixture was stirred overnight at room temperature, and then DI water (200 mL) was added. The crude compound was extracted with 3 × 100 mL of Et_2O, and the combined organic extracts were dried over Na_2SO_4. The solvent was removed in vacuo, giving a reddish oily residue. The compound was purified by column chromatography on silica gel (3:1 = hexanes:ethyl acetate) to yield 0.63 g (65%) of a colorless oil. TLC R_f = 0.78 (silica gel, ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.17 (s, 2H), 4.33 (s, 2H), 4.16 (q, 2H, J = 7.2 Hz,), 3.95 (m, 4H), 2.09 (m, 2H), 1.24 (t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7, 139.4, 107.2, 72.3, 61.4, 51.3, 35.0, 14.0. HRMS (ESI FTICR): Calcd for $C_{11}H_{16}NO_4$ ($[M + H]^+$), 226.1074. Found *m/z*, 226.1071. Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22%. Found: C, 58.44; H, 5.79; N, 6.90%.

2-(2,3-Dihydro-1,4-dioxepino[2,3-*c*]pyrrol-7(2*H*)-yl)ethanol (7). To a dry 250 mL RB flask containing a stir bar and an argon atmosphere was added compound **5** (1.50 g, 7.61 mmol) and dry THF (100 mL). The mixture was cooled in a CO_2/2-propanol bath, and $LiAlH_4$ powder (1.29 g, 34.0 mmol) was carefully added. When gas evolution stopped, the reaction was warmed to room temperature and stirred an additional 3 h. The reaction was quenched first with methanol and then ice, and then a minimal amount of H_2SO_4 was added to dissolve alumina aggregates. The mixture was extracted with 2 × 100 mL of Et_2O, and the combined organic layers were washed with saturated NH_4Cl and then brine. The solution was dried over Na_2SO_4 and concentrated in vacuo and filtered through a silica gel pad (deactivated with triethylamine) with ethyl acetate as the eluent. After removing the ethyl acetate in vacuo, the pure compound was isolated as 0.70 g (50%) of a pale yellow oil. TLC R_f = 0.67 (silica gel, ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.23 (s, 2H), 3.97 (dd, 4H), 3.78 (br s, 4H), 2.12 (p, 2H, J = 5.3 Hz), 1.84 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.1, 10.4, 72.6, 62.9, 52.8, 35.3. HRMS (EI): Calcd for $C_9H_{13}NO_3$ ($[M]^+$),-183.0895. Found *m/z*, 183.0892. Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65%. Found: C, 58.76; H, 7.45; N, 7.35%.

7-(2-Methoxyethyl)-2,3,4,7-tetrahydro-1,4-dioxepino[2,3-*c*]-pyrrole (8a). To a 50 mL RB flask containing a stir bar and an argon atmosphere was added compound **7** (0.50 g, 2.73 mmol), methyl iodide (0.47 g, 3.28 mmol), and anhydrous DMF (25 mL). The mixture was chilled in an ice bath, and then sodium hydride (60% dispersion in mineral oil, 0.22 g, 5.46 mmol) was added. The reaction was stirred for 15 h, during which the ice bath was allowed to warm to room temperature. The mixture was then poured into DI water (100 mL) and extracted with 2 × 50 mL of Et_2O. The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified via flash chromatography on silica gel (deactivated with TEA, 5:6 = hexanes:Et_2O) to yield 0.42 g (78%) of a clear oil. TLC R_f = 0.24 (silica gel, 1:1 = hexanes:Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.21 (s, 2H), 3.97−3.93 (m, 4H), 3.78 (t, 2H, J = 6.3 Hz), 3.55 (t, 2H, J = 6.0 Hz), 3.30 (s, 3H), 2.13−2.06 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.9, 106.5, 72.64, 72.58, 59.2, 50.2, 35.4. HRMS (ESI FTICR): Calcd for $C_{10}H_{16}NO_3$ ($[M + H]^+$), 198.1130. Found *m/z*, 198.1120. Anal. Calcd for $C_{10}H_{15}NO_3$: C, 60.90; H, 7.67; N, 7.10%. Found: C, 61.08; H, 7.64%; N, 7.10%.

7-(2-(Benzyloxy)ethyl)-2,3,4,7-tetrahydro-1,4-dioxepino[2,3-*c*]pyrrole (8c). To a 50 mL RB flask containing a stir bar and an argon atmosphere was added compound **7** (0.50 g, 2.73 mmol), benzyl bromide (0.56 g, 3.28 mmol), and anhydrous DMF (25 mL). The mixture was chilled in an ice bath, and then sodium hydride (60% dispersion in mineral oil, 0.22 g, 5.46 mmol) was added. The reaction was stirred for 15 h, during which the ice bath was allowed to warm to room temperature. The mixture was then poured into DI water (100 mL) and extracted with 2 × 50 mL of Et_2O. The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified via flash chromatography on silica gel (2:1 = hexanes:Et_2O) to yield 0.52 g (64%) of a clear oil. TLC R_f = 0.28 (silica gel, 1:1 = hexanes:Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36−7.25 (m, 4H), 6.25 (s, 2H), 4.47 (s, 2H), 4.00−3.97 (m, 4H), 3.84 (t, 2H, J = 6.0 Hz), 3.66 (t, 2H, J = 5.7 Hz), 2.16−2.10 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.9, 138.1, 128.6, 127.9, 127.8, 73.4, 72.7, 70.2, 50.4, 35.4. HRMS (ESI FTICR): Calcd for $C_{16}H_{20}NO_3$ ($[M + H]^+$), 274.1443. Found *m/z*, 274.1433. Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12%. Found: C, 69.61; H, 6.94; N, 5.00%.

7-(2-(2-Ethylhexyloxy)ethyl)-2,3,4,7-tetrahydro-1,4-dioxepino-[2,3-*c*]pyrrole (8c). To a 50 mL RB flask containing a stir bar and an argon atmosphere was added compound **7** (0.41 g, 2.24 mmol), 2-ethylhexyl tosylate (0.77 g, 2.69 mmol), and anhydrous DMF (25 mL). The mixture was chilled in an ice bath, and then sodium hydride (60% dispersion in mineral oil, 0.18 g, 4.48 mmol) was added. The reaction was stirred for 15 h, during which the ice bath was allowed to warm to room temperature. The mixture was then poured into DI water (100 mL) and extracted with 2 × 50 mL of Et_2O. The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified via flash chromatography on silica gel (deactivated with TEA, 5:1 = hexanes:Et_2O) to yield 0.42 g (64%) of a clear oil. TLC R_f =

0.46 (silica gel, 1:1 = hexanes:Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ 6.23 (s, 2H), 3.98−3.95 (m, 4H), 3.79 (t, 2H, J = 6.0 Hz), 3.58 (t, 2H, J = 6.0 Hz), 3.26 (d, 2H, 6.3 Hz), 2.15−2.08 (m, 2H), 1.47 (p, 1H, J = 6.7 Hz), 1.35−1.20 (m, 8H), 0.89 (t, 3H, J = 7.3 Hz), 0.84 (t, 3H, J = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.8, 106.5, 74.3, 72.6, 71.1, 50.4, 39.8, 35.4, 30.7, 29.3, 24.0, 23.2, 14.3, 11.3. HRMS (ESI FTICR): Calcd for $C_{17}H_{30}NO_3$ ($[M + H]^+$), 296.2225. Found *m/z*, 296.2216. Anal. Calcd for $C_{17}H_{29}NO_3$: C, 69.12; H, 9.89; N, 4.74%. Found: C, 68.85; H, 9.75; N, 4.75%.

2-Ethylhexyl Tosylate. To a 250 mL RB flask containing a stir bar and an argon atmosphere was added 2-ethylhexane-1-ol (5.69 g, 43.7 mmol) and pyridine (50 mL). The mixture was chilled in an ace bath, after which was added *p*-toluenesulfonyl chloride (10.00 g, 52.5 mmol). The reaction was stirred for 3 h, during which a white precipitate emerged. The reaction was poured into DI water (300 mL) and extracted with 2 × 125 mL of Et_2O. The combined organic layers were washed with DI water (100 mL), brine (50 mL), and dried over Na_2SO_4. After concentration in vacuo, the resulting liquid was purified via flash chromatography on silica gel (1:1 = hexanes:Et_2O) to yield 11.84 g (95%) of a clear oil. The product was used without further purification, but NMR data suggests that this product was of high purity. TLC R_f = 0.58 (silica gel, 1:1 = hexanes:Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, 2H, J = 9.0 Hz), 7.35 (d, 2H, J = 9.0 Hz), 3.92 (dd, 2H, J = 5.6 Hz, J = 1.7 Hz), 1.54 (p, 1H, J = 7.0 Hz), 1.37−1.09 (m, 8H), 0.84 (t, 3H, J = 7.7 Hz), 0.79 (t, 3H, J = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.8, 133.2, 129.9, 128.0, 72.6, 39.2, 29.9, 28.8, 23.3, 23.0, 21.7, 14.1, 10.9.

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