

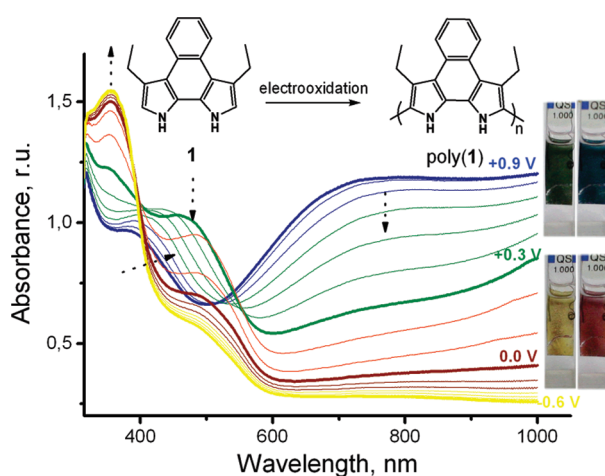
Naphthobipyrrole: Versatile Synthesis and Electropolymerization

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A facile synthetic route to a new polycyclic pyrrole derivative, 3,8-diethyl-1,10-dihydro-benzo[e]pyrrolo-[3,2-g]indole (**1**), is reported. This annulated bipyrrole acts as a monomer for electropolymerization and forms an electrochromic conducting polymer (poly**1**) when electrooxidized at low potentials (0.4 V vs Ag/Ag⁺) in acetonitrile. The presence of alkyl substituents at the 3 and 8 carbons (β -pyrrolic positions) induces regioselective 2,5'-coupling of the pyrrole repeat units and gives rise to the more uniform polymeric product, poly**1**. Poly**1** exhibits globular morphology, as judged from SEM pictures. Its spectroelectrochemical features can be attributed to the formation of four possible states: neutral, polaron, bipolaron, and transverse bipolaron. The relatively low switching potentials (−0.6 to +0.9 V vs Ag/Ag⁺ in MeCN) displayed by poly**1** leads us to suggest that **1** has a role to play as a polymerizable moiety for the development of multicolor electrochromic materials.

Introduction

Conjugated polymers obtained by polymerization of suitable redox active monomers are attracting considerable attention at present, in particular as electrochromic materials. Much of this interest reflects their potential utility in a variety of industrial and military applications that run the gamut from use in color-tuning windows, displays, smart windows, mirrors, and the like^{1,2} to the creation of specialty

security documents³ and chameleon and adaptive camouflage materials.^{4,5} This utility continues to drive new research in the area and is providing a specific incentive to create and test new electropolymerizable monomers.

It is now recognized that the defining features (and ultimate utility) of a given conjugated polymer material, including film-forming properties, color efficiency, response time, low-power operation, stability, etc., often depend critically

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on the structure and properties of the precursor (monomer) from whence it is derived. Desirable features for these precursors are, *inter alia*, ones that give rise to polymers with broader absorptions and decreased band gaps. This, in turn, has led to design criteria for monomers that include (1) increased planarity for better π - π^* overlap, (2) chemical rigidification to ensure structural integrity and uniformity following polymerization, and (3) properly chosen substituents to control intramolecular charge transfer interactions.⁶

To date, most common monomers for the preparation of electrochromic polymers have consisted of alternating or sandwich-structured donor and acceptor units, including arenes (benzene, alkyl- and alkoxybenzene, *N*-alkylcarbazole, 4,4'-biphenylene, and others) and electron-rich heterocycles (thiophene and pyrrole, and their derivatives with open α -positions for polymerization).^{7,8} Within the latter subset, most attention has focused on thiophene derivatives. Indeed, the literature on functionalized pyrroles as precursors for robust conjugated polymer materials is scarce; presumably, this reflects the low chemical stability of pyrrole toward overoxidation.⁹ For instance, a highly stable electrochromic polymer based on 3,4-ethylenedioxyppyrole was reported by Reynolds in 2000.¹⁰ In this case, the poly(3,4-ethylenedioxyppyrole) solutions obtained upon electrooxidation were found to pass from a bright red neutral state to a light blue transmissive form upon conversion to the corresponding oxidized state. Upon increasing the length of the alkyl bridge, i.e., on using the corresponding propylen- or butylen-analogues, another colored state is observed at low doping levels, thus producing materials characterized by multichromic changes.¹¹

A series of 1,4-bis(pyrrol-2-yl)phenylene monomers, as well as other bis(pyrrol-2-yl)arylene derivatives, were prepared by the groups of Reynolds and Katrizky in 1994 and 1996; this was done by exploiting further the basic concept of extending the conjugation in the monomer to reduce the oxidation potential.^{7,8} These monomers could be rapidly electropolymerized at ca. 0.15–0.4 V vs Ag/Ag⁺ to form highly electroactive polymers with electronic band gaps smaller than those for polypyrrole. This lowering of the band gap is attributed to an increased structural regularity arising from the use of a three-ring-containing monomer.

Generally, synthetic routes to regiochemically defined oligomers of a pyrrole-derived polymer involve polymerization of 2,5-disubstituted pyrrole monomers bearing a protective group on the nitrogen atom via the use of regioselective Stille or Ullman coupling strategies. An alternative approach to reducing unwanted 2,3'- and 2,4'-couplings is to employ a dimer, such as 2,2-bipyrrole, as the precursor in otherwise standard chemical polymerization protocols.⁹

Here, we report the synthesis of 3,8-diethyl-1,10-dihydrobenzo[*e*]pyrrolo[3,2-*g*]indole (**1**) (referred to as β,β' -diethyl-

naphthobipyrrole), as well as its electropolymerization and the characterization of the resulting polymeric material. This particular monomer offers several advantages, such as unequivocal reactivity at the pyrrole α -positions due to blocking of the β -positions by alkyl substituents, a higher level rigidity as compared to that of simple pyrrole or bipyrrole precursors, an expanded system of conjugated bonds, and a correspondingly low oxidation potential due to the annulated phenyl ring. It also benefits from a synthesis that appears cleaner and easier than those used to prepare various previously reported linked pyrrolic precursors. As a consequence, monomer **1** appears attractive for the development of multicolor electrochromic materials.

Several polycyclic benzodipyrroles were prepared by Berlin et al. in 1987 and studied as polymer precursors.¹² Unfortunately, chemical oxidative polymerization of these species resulted in the formation of black, insoluble powders that precipitated from the reaction medium. On the other hand, it has been reported that the use of a polycyclic aromatic core, such as that present in various poly(naphthodithiophene)s, serves to enforce planarity between the adjacent heterocycles in the monomeric precursor, resulting in a robust conjugated polymer.¹³

Evidence that this postulate extends to pyrroles (as opposed to thiophenes) comes from a report by Nadeau and Swager that appeared in 2004. These researchers proposed that the naphthobipyrrole intermediate **3** is formed via intramolecular oxidative cyclization during the electrochemical oxidation of a β -linked pyrrole monomer **2** (Scheme 1A).¹⁵ This putative naphthobipyrrole intermediate undergoes polymerization concurrent with its presumed formation. Therefore, it could not be isolated or characterized after its proposed electrosynthesis. Thus, the actual species involved in this particular polymerization remains indeterminate. Further complicating the chemistry is that fact that under the conditions of electro-oxidation, reaction at both the β - and α -pyrrolic positions could have occurred in either an intramolecular or intermolecular fashion (Scheme 1B).

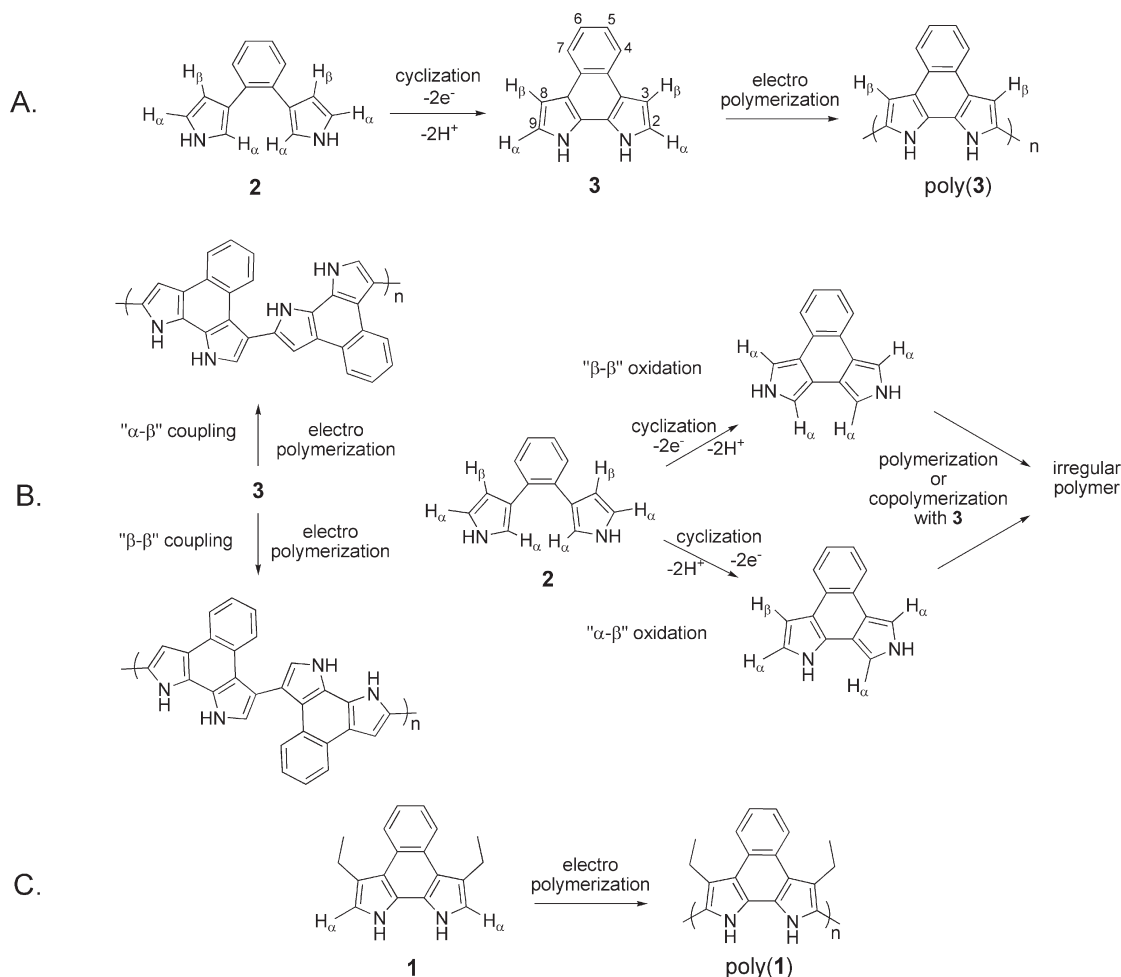
We thus sought to prepare a *bona fide* example of a naphthobipyrrole with no free β -pyrrolic substituents and to study its electropolymerization in accord with the conditions proposed by Nadeau and Swager.¹⁴ With this goal in mind, we have now prepared 3,8-diethyl-1,10-dihydrobenzo[*e*]pyrrolo[3,2-*g*]indole (**1**) (referred to as β,β' -diethylnaphthobipyrrole) and show that, after electropolymerization, it produces a stable multielectrochromic material. We ascribe the clean reaction that this monomer permits (Scheme 1C) to the presence of alkyl substituents on the β -pyrrolic positions.

Results and Discussion

Synthesis. Although unsubstituted naphthobipyrrole **3** is known,¹⁵ for the present study a viable synthesis of a β,β' -dialkylated derivative had to be developed. The route upon which we settled is shown in Scheme 2. It involves milder reaction conditions (tosic acid in ethanol rather

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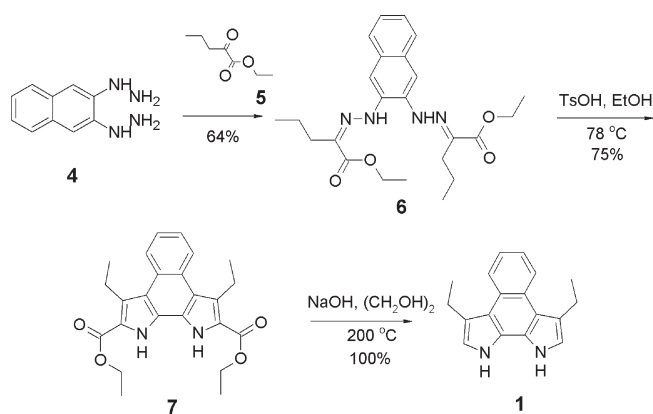
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SCHEME 1. Formation of Polynaphthobipyrroles^a


^a(A) Coupling reactions proposed by Nadeau and Swager.¹⁴ (B) Alternative structures that could arise from reaction of **2** or **3**. (C) Regiocontrolled electropolymerization as detailed in this report.

than neat polyphosphoric acid as reported earlier; see discussion below).¹⁶ It also imparts alkyl substituents in the β positions (carbons 3 and 8). As noted in the Introduction, this latter feature was considered important to prevent reaction at these carbons (e.g., indiscriminate coupling, overoxidation) and to direct the polymer chain growth toward the α -pyrrolic positions (carbons 2 and 9).

The synthesis of **1** starts with the naphthalene dihydrazine **4**, which is converted into the corresponding dihydrazone **6** via condensation with ethyl 2-oxopentanoate (**5**). A Fischer indole synthesis was then used to produce **7**. This key step, which introduces the two pyrrole rings adjacent to the naphthalene unit, proved somewhat problematic at first. While an ostensibly similar structure **3** is known in the literature, and its diethyl ester has been previously prepared via a Fischer indole synthesis using polyphosphoric acid as both the catalyst and the solvent,¹⁵ these latter conditions did not prove viable in the case of **5**. Therefore 10 equiv of tosic acid in ethanolic media was used instead.¹⁶ Saponification of **7** and subsequent decarboxylation were carried out as a single pot procedure as is typically done for bipyroles; this involved heating at reflux in

SCHEME 2. Synthesis of Monomer 1


ethylene glycol in the presence of an excess of NaOH (10 equiv) under an inert gas atmosphere.¹⁷

Previously, the unsubstituted naphthobipyrrole **3** was shown to react predominantly at carbons 3 and 8 (i.e., the β -pyrrolic carbons; cf. Scheme 1 for atom labeling). For instance, Vilsmeier

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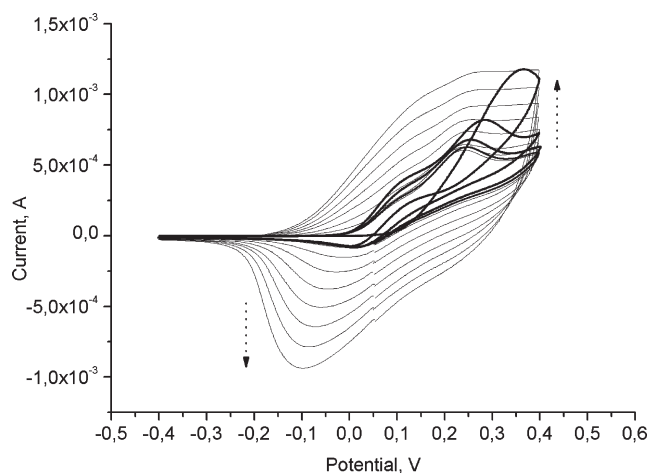


FIGURE 1. Cyclic voltammograms of **1** oxidation (first cycle) and polymer growth observed during repeated oxidation cycles (first–fourth cycles, thick line; after this, every fifth cycle up to the 40th cycle is shown) vs Ag/Ag⁺. The scan rate is 50 mV/s. Arrows denote the evolution of voltammograms as the cycle number increases.

formylation, aminomethylation, and reactions with aryldiazonium salts were found to result in electrophilic substitution at the β -pyrrolic positions.^{18,19} We thus considered it likely that under the conditions of electrochemical oxidation leading to polymerization, the putative bipyrrrolic intermediate produced by Nadeau and Swager¹⁴ undergoes reaction at the β -pyrrolic carbons in addition to, or instead of, coupling at the α -pyrrolic positions (cf. Scheme 1B and associated discussion above). Therefore, to enforce reaction at just the α -pyrrolic positions, monomer **1** was designed to incorporate ethyl groups at carbons 3 and 8. A further potential advantage of the present approach is that it entails a simpler synthesis than that used by Nadeau and Swager.¹⁴ In particular it avoids the need for metalation with butyl lithium and the use of a Suzuki coupling. Instead as noted above, it creates the key bipyrrrolic core under simple acid-promoted conditions.

Electrochemistry. The cyclic voltammograms recorded using an ITO electrode and an electrolyte solution of monomer **1** are shown in Figure 1. The first feature is an irreversible oxidation starting at a potential of ca. 0.15 V (this and other potentials are vs Ag/Ag⁺ unless otherwise noted). The same irreversible oxidation peak has been observed previously for a fused-pyrrole 1,4-dihydropyrrolo[3,2-*ss*]pyrrole²⁰ and for an α -linked bipyrrrolic that was studied at moderate scan rates (100 mV/s) and assigned to a one-electron process.²¹ By inference, a similar assignment is made here. This prior work also revealed that, in analogy to what is seen with pyrrole, repetitive cycling of the potential does not produce polymer unless water, typically 1%, is deliberately added. Water is thought to act as a proton scavenger, and in its presence normal nucleation and growth of polymer is observed.²¹

In the case of **1**, cycling several times over the potential range from -0.4 to 0.4 V gives rise to two redox peaks with

anodic potentials at 0.1 and 0.25 V, respectively (shown with a thick line in Figure 1). The currents of these peak decrease slightly with consecutive cycling. The solution of **1** after initial cycles quickly becomes red near the surface of the working electrode, and a more intense red coloration is observed after completing 40–60 cycles. The UV–vis spectrum of the red-colored product displays an absorption maximum at 320 nm, with a shoulder at 360 nm; a distinct spectral feature is also seen at 530 nm, which is ascribed to radical cation intermediates. In contrast to what is seen after electrochemical cycling, monomer **1** is characterized by a strong absorption in the UV region and a very weak absorption peak at 700 nm (for the UV spectra of **1** and the products produced upon subjecting it to electrooxidation, see Figure S1 in the Supporting Information). The red coloration observed after the solution-phase electrooxidation of **1** was retained without any visible changes being seen over the course of a couple of days at ambient conditions; subsequently, a black solid begins to precipitate out from solution.

Further potential cycling (cycles 10–40) revealed a continued growth in the anodic and cathodic currents and resulted in formation of a conducting polymer film, deposited on the ITO electrode. Two oxidation peaks observed during the course of the initial cycling are no longer seen distinctly; they are either combined or, more likely, become unresolved, presumably because of the resistance of the polymer film or ohmic contribution of the ITO electrode. It is interesting to note that a less reversible voltammetric response at a similar range of potentials was observed during the electropolymerization of the fused-pyrrole 1,4-dihydropyrrolo[3,2-*ss*]pyrrole;²⁰ this latter precursor also forms ultimately a black thin film on the electrode surface after being subjected to electropolymerization.

In analogy to what has been proposed in the case of α -linked bipyrrroles,^{21,22} we assume that the observation of two redox peaks during the course of the initial electrochemical cycling shown in Figure 1 is consistent with the fact that the short chain oligomers of **1** are oxidized further in MeCN to give in sequence the corresponding radical cation and dication. However, it is to be noted that no modification of voltammetric behavior was observed upon the repetitive redox cycling of a quaterpyrrole monomer in solution.²⁵ Further, the electropolymerization of pentapyrrole occurs only at more positive potentials than those of the first and second oxidation processes, i.e., only after generation of the cation radical and dication, respectively.²¹ Thus, we infer that higher order oligopyrrrolic species play a key role as intermediates in the electropolymerization of **1**.

Since the β -pyrrolic positions are blocked, oxidation-induced coupling is expected to take place exclusively at the α -positions. Reactions at the naphthalene ring are ruled out on the basis of the relatively low potentials used for electrooxidation. In general, polycyclic aromatic derivatives, such as acenaphthofluoranthene, undergo oxidative polymerization only at high potentials ($E_{pa} + 1.6$ vs SCE).²³ Although it is likely that the naphthalene subunit in **1** should have a lower oxidation potential than in the parent hydrocarbon, reactions at the naphthalene subunit are nevertheless considered unlikely to proceed at the applied potentials of between -0.4 to $+0.4$ V vs Ag/Ag⁺.

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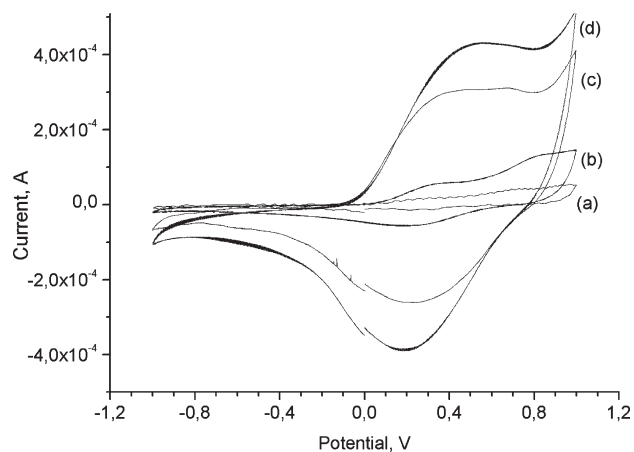


FIGURE 2. Typical cyclic voltammograms recorded for films of poly1 deposited on an ITO substrate (0.1 M LiClO₄, MeCN) vs Ag/Ag⁺ at (a) 5, (b) 20, (c) 50, and (d) 100 mV/s.

Cyclic voltammograms of poly1 in monomer-free electrolyte solution (Figure 2) are characterized by two redox waves with half-wave potentials at 0.215 and 0.675 V (at 5 mV/s), respectively. With scan rates higher than 20 mV/s, these waves become poorly resolved and the voltammograms are characterized by broad oxidation and reduction peaks at E_{pa} 0.4 and E_{pc} 0.23 V. Thus, monomer 1 oxidizes more readily than polypyrrole; however, the observed E_{pa} values are higher, at least in MeCN.²⁴

The dependence of current values on scan rate, as seen even for the first redox peak of poly1 (Figure 2), deviates from linearity at scan rates higher than 50 mV/s. A linear dependence would be consistent with an absence of any kinetic or diffusion limitations for the redox transformations of the species adsorbed at the electrode surface (i.e., polymer film). However, this is not true for poly1 or for polypyrrole. In fact, both the oxidation and reduction electrochemistry of polypyrrole is accompanied by doping and dedoping processes involving counteranions; we thus propose that the inferred barrier to reversibility seen for poly1 derives in part from a slow dopant exchange process. This could reflect the relatively thick nature of the film.

Morphology of the Polymer Film. The surface morphology of the poly1 film was investigated by scanning electron microscopy. The film prepared on an ITO electrode was cycled several times in background electrolyte between -0.7 and $+1.0$ V, before being left in its partially oxidized state (potential $+0.3$ V). The green film obtained in this way was dried at ambient conditions before imaging.

The SEM image presented in Figure 3a shows that the film is likely to be homogeneous and compact. The image taken with $2000\times$ magnification (Figure 3b) reveals finer small features of the poly1 film. It is particularly noteworthy that the surface consists of close-packed nodular grains of ca. $1\ \mu\text{m}$ diameter and spherical, almost uniform, globules of ca. $2\ \mu\text{m}$ diameter. A close-packed grain morphology, a so-called “cauliflower surface”, is typical for polypyrroles grown in acetonitrile and doped with perchlorate ions.²⁵ The presence of bigger spherical globules has, however, been reported for, e.g., polypyrrole grown from ionic liquids by electropolymerization.²⁵

It was found that a film suitable for use in spectroelectrochemical studies could be deposited via 15–20 rounds of potential cycling. Further cycling to 40 or 60 cycles results in the formation of very thick films, which easily detach from the electrode surface and which have a lot of cracks. However, it was found that the adhesion of the poly1 film to an ITO electrode could be improved by hydrophobization of the ITO surface by treating with alkylsilanes, e.g. (3-aminopropyl)trimethoxysilane, prior to carrying out the electropolymerization. On the other hand, the weak adhesion of the polymer to the electrode support seen in the absence of such a pretreatment is a feature that could prove useful in the preparation of free-standing films.

Spectroelectrochemistry. The poly1 film was cycled potentiodynamically at least 3–5 times between -0.7 and $+1.0$ V at 50 mV/s after deposition onto an ITO electrode so as to equilibrate the polymer before the spectroelectrochemical measurements. Changes in the absorption spectral features of poly1 as a function of the applied potential are presented in Figure 4. The evolution of the absorption spectra of poly1 with applied potential is similar to that of thin films of polypyrrole (less than ca. $0.5\ \mu\text{m}$) as observed in acetonitrile media.^{26,27} However, there are important differences in the spectral features of poly1 relative to those of polypyrrole.

Fully oxidized poly1 is blue in color (insert (d) in Figure 4). It exhibits a broad absorption band that extends into the near-IR region with a λ_{max} of ca. 750 nm (1.7 eV), as well as a band at 390 nm (3.2 eV) in the visible region. Fully oxidized polypyrrole highly doped with perchlorate ions is characterized by two bipolaron bands at 1240 nm and 450–475 nm, as well as a $\pi-\pi^*$ band,^{26,27} and is gray-black or brownish-black in color. Notably, the deep blue color observed for oxidized poly1 differs from the black color (broad band in the visible region) reported for oxidized poly(bipyrrolonaphthalene).¹⁴ We ascribe this difference to the presence of the β -alkylsubstituents and the cleaner nature of the polymerization expected in the case of 1 as compared to the system of Nadeau and Swager.

When the applied potential is decreased, the peak in the spectrum of poly1 at 390 nm shifts to 420 nm and the absorbance in the near-IR region decreases. At $+0.3$ V (insert (c) in Figure 4), a potential that corresponds to partially oxidized poly1, the absorption spectrum shows two peaks at 355 nm (4.5 eV) and 467 nm (2.6 eV) in the visible region, while the film itself is green. Further cathodic shifts in the applied potential result in a decrease in the absorption intensity at 470 nm with a slight bathochromic shift to 490 nm and an increase in the absorbance at 355 nm. At 0 applied voltage, the film appears red or red-brown (insert (b) in Figure 4). A corresponding partially oxidized form of polypyrrole, as reviewed by Murray in 1995,²⁷ showed three absorptions, at 1770, 885, and 590 nm. The band at 885 nm, was considered to be caused by the conditions of preparation and was not thought to be an intrinsic feature of polypyrrole.

Reduction of the poly1 to the neutral state causes the peak at 490 nm to diminish in intensity until, ultimately, it becomes a shoulder of the peak at 355 nm. When the potential reaches -0.6 V, the poly1 film becomes pale-yellow (insert

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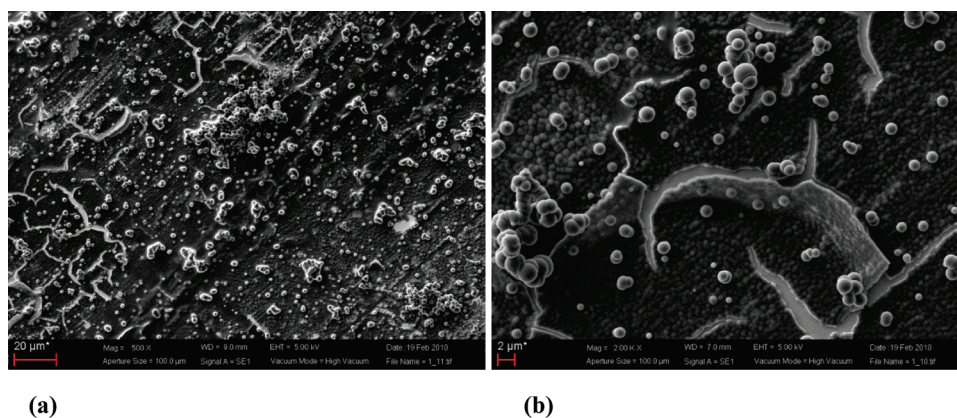


FIGURE 3. Scanning electron microscopy images of poly1 film deposited on an ITO electrode taken after equilibration of the film in a background electrolyte solution (0.1 M LiClO₄, MeCN). The enlargement is (a) 500× and (b) 2000×, respectively.

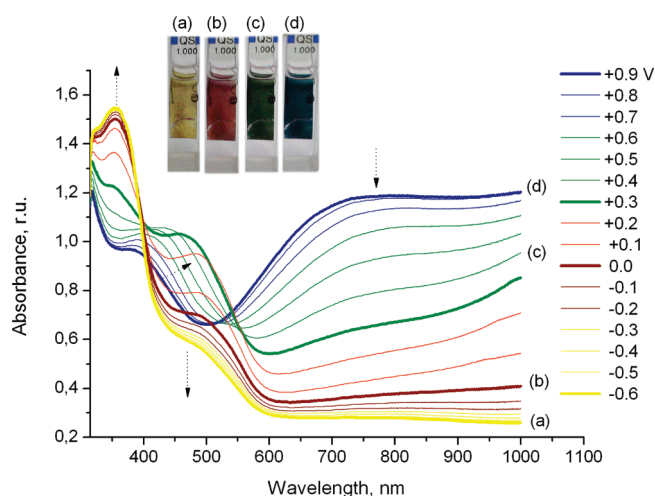


FIGURE 4. Results of spectroelectrochemical studies of poly1 film deposited on an ITO electrode. The measurements were conducted in MeCN, 0.1 M LiClO₄ with 100 mV steps between +0.9 and -0.6 V vs a Ag pseudo reference electrode (each step is 60 s long). Inserts show photographs of the polymer films as obtained at potentials of (a) -0.6, (b) 0.0, (c) +0.3, and (d) +0.9 V. Arrows denote changes in the spectra associated with a decrease in the applied potential.

(a) in Figure 4). The spectrum of the neutral form of poly1 gives a spectrum that is thought to originate in π - π^* transition, a feature that occurs at 344–390 nm in case of polypyrrole.^{26,27}

Poly1 undergoes two oxidations in the range of -1.0 to +1.0 V (Figure 2), which are accompanied by a reversible color change from pale-yellow (neutral form), red to green (partially oxidized and mixture of redox forms) and blue (fully oxidized). These chromatic changes are easily described in terms of the formation of four coexisting or dominating forms (states) of the polymer, namely the neutral form, as well as polaronic, bipolaronic, and so-called transverse bipolaronic states, with the latter state being caused by efficient interchain coupling of polarons on adjacent polymer chains.²⁷ The terms “polaron” and “bipolaron” were introduced to identify the charge carriers in polypyrrole, which are not unpaired electrons, and were used to explain its conductivity and optical features.²⁷

An overview of the optical absorption bands of polypyrrole was published by Potje-Kamloth in 2000,²⁶ who ascribed the absorption below 1.4 eV and the band at 1.8 eV to the sum of the polarons and transverse bipolarons, the band at 2.44–2.5 eV to the sum of polarons, bipolarons, and transverse bipolarons, and the band around 3.2–3.6 eV to the band gap transition of polypyrrole.

This ability to span multiple colors, including those needed for color mixing, does not appear to depend strongly on electropolymerization conditions or level of defects, as it does for regular polypyrrole. On the other hand, it is interesting to note that color changes similar to those seen for poly1 are reported for a hybrid polypyrrole material incorporating (octa-(thiophenphenyl)silsesquioxane) subunits within the polymer chains.²⁸ However, the properties of poly1 differ from those of polypyrrole and the previous system of Nadeau and Swager. These differences, noted in the discussion above, are specifically summarized in Table 1.

Figure 5 presents the results of chronovoltabsorptometry experiments, namely, subjecting the film to switching with an applied square wave potential between extreme electrochromic states (neutral and fully oxidized poly1). To estimate the switching time and the coloration efficiency, these cycling experiments were carried out while recording the optical absorption at a particular wavelength (700 nm) as a function of time.

Using the literature definition of the switching time (i.e., the time between 10% and 90% of steady state absorbance at the electrochromic extremes), we found a switching rate of 6–7 s.³⁰ This time is longer than typical switching times seen for thiophene derivatives but is comparable to the switching times seen for pyrrole derivatives, such as dipyrromethane (ca. 5 s).³¹

Coloration efficiency, defined as the ratio between the change in optical density units and the injected/ejected charge as a function of electrode area, was estimated from

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TABLE 1. uv–vis Spectral Features of Selected Polypyrrole Polymers

polymer/redox state		optical absorption bands	color	reference
poly 1				this report
neutral	355 nm	shoulder 490 nm	yellow	
partially oxidized		470–490 nm	red	
fully oxidized		shoulder 400 nm	blue	
poly(bipyrrolonaphthalene)				14
neutral	390 nm		yellow	
partially oxidized		540 nm		
fully oxidized	<i>a</i>	<i>a</i>	black	
polypyrrole				9, 26, 27, 29
neutral	344–390 nm		yellow	
partially oxidized		430, 490–508, 590 475 nm		
fully oxidized	387 nm		black (blue)	

^aA broad absorption is seen that covers the whole visible region. ^bThe existence of this band is still subject to discussion.

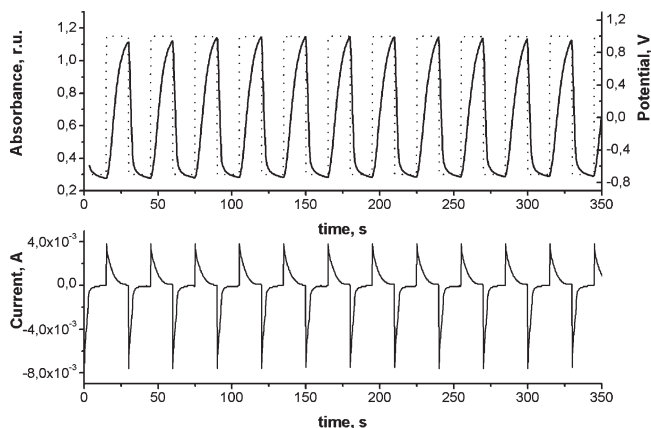


FIGURE 5. Current transients and changes in the absorbance features of a film of poly**1** supported on an ITO electrode (solid lines) at 700 nm observed upon repetitive switching of the applied potential between -0.7 and $+1.0$ V (dotted line) in 0.1 M LiClO_4 , MeCN.

the data shown in Figures 4 and 5 and was found to be $98 \text{ cm}^2/\text{C}$ at 700 nm and $74 \text{ cm}^2/\text{C}$ at 355 nm . These values are lower than what can be attained in the case of the widely used electrochromic material, poly(3,4-ethylenedioxythiophene) ($183 \text{ cm}^2/\text{C}$).³² On the other hand, the first maximal coloration efficiency approaches the $100 \text{ cm}^2/\text{C}$, a value considered acceptable for a working electrochromic device.³⁰

Conclusions

A new annulated bipyrrrole, **1**, was prepared, and its electrochemical properties were analyzed. It was found that **1**, a fully characterized monomeric species, can be electropolymerized under oxidizing conditions to form an electrochromic polymer, poly**1**. Poly**1** undergoes two redox transitions in the range of -0.6 to $+1$ V vs Ag/Ag^+ . These redox changes are accompanied by variations in color that range from pale-yellow, through red, to green, and then on to blue. The corresponding UV–vis spectra are characterized by considerable bathochromic shifts with an increase in the applied voltage. Compared to a previously reported polymer based on the in situ creation of **3**, poly**1** offers a number of advantages, including a structure that is necessarily better defined and a monomer that is easier to prepare. We thus

propose that poly**1** and its congeners could find use as electrochromic materials.

Experimental Section

Monomer Synthesis. 2,3-(Ethyl pentanoate-2)-naphthalene-hydrazine (6). A solution of **5** (6.70 g, 37.2 mmol, 80% mixture with diethyloxalate) in 2.5 mL of ethanol was added to a suspension of 2,3-naphthalene dihydrazine **4** (2.00 g, 10.64 mmol) in 25 mL of ethanol. The reaction mixture became a clear solution during the course of stirring for 3 h at rt. At this point, the solvent was removed under reduced pressure, and the crude product was purified via flash chromatography on silica gel with a mixture of hexane (10% to 0%)–dichloromethane being used as the eluent. The major yellowish band was collected, yielding **6** as an orange goo after removal of the solvent (2.99 g, 64%). ¹H NMR (400 MHz, CDCl_3): δ 9.34 (s, 2H), 7.65 (m, 4H), 7.42–7.05 (m, 2H), 4.33 (q, $J = 7.1$, 4H), 2.75–2.70 (m, 4H), 1.61 (m, 4H), 1.37 (t, $J = 7.1$, 6H), 0.99 (t, $J = 7.4$, 6H). ¹³C NMR (101 MHz, CDCl_3): δ 165.8, 138.9, 132.9, 131.0, 127.5, 125.6, 113.7, 62.1, 27.1, 19.7, 15.3, 14.9. ESI MS (+): 903 $[\text{2M} + \text{Na}]^+$. HiRes MS ESI(+): found 903.4740, calcd for $\text{C}_{48}\text{H}_{64}\text{N}_8\text{O}_8\text{Na}^+$ 903.4739.

3,8-Diethyl-1,10-dihydro-benzo[e]pyrrolo[3,2-g]indole-2,9-dicarboxylic Acid, 2,9-Diethyl Ester (7). Dihydrazone **6** (1.54 g, 3.51 mmol) and tosic acid hydrate (6.75 g, 35.53 mmol, 10 equiv) were heated at reflux in ethanol (150 mL) for 48 h. Then solvent was removed under reduced pressure, and the product was purified on silica gel using dichloromethane as the mobile phase; this yielded **7** as an off-white solid (1.07 g, 75%). Mp 267–270 °C. ¹H NMR (400 MHz, CDCl_3): δ 10.92 (s, 2H), 8.12 (br. s, 2H), 7.45 (br. s, 2H), 4.24 (br. d, $J = 6.9$, 4H), 3.02 (br. s, 4H), 1.23 (br. s, 6H), 1.11 (t, $J = 7.0$, 6H). ¹H NMR (500 MHz, $\text{DMSO}-d_6$): δ 11.68 (s, 2H), 8.41 (m, 2H), 7.50 (m, 2H), 4.42 (q, $J = 7.1$, 4H), 3.50 (q, $J = 7.4$, 4H), 1.42 (t, $J = 7.1$, 6H), 1.35 (t, $J = 7.4$, 6H). ¹³C NMR (101 MHz, CDCl_3): δ 164.6, 132.2, 128.5, 125.1, 124.8, 120.9, 120.9, 61.9, 20.2, 15.1, 14.7. MS ESI(+): 407 $[\text{M} + \text{H}]^+$. HiRes ESI MS (+): found 407.1967, calcd for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_4^+$ 407.1965. Note: most of the signals in the ¹H NMR spectrum of **7** were broadened at room temperature; however, the peaks narrowed upon heating the sample to 100 °C in $\text{DMSO}-d_6$.

3,8-Diethyl-1,10-dihydro-benzo[e]pyrrolo[3,2-g]indole (1). A mixture of **7** (220 mg, 0.54 mmol) and sodium hydroxide (216 mg, 5.4 mmol, 10 equiv) was heated at reflux in ethylene glycol (5 mL) under an argon atmosphere for 1.5 h. Then reaction was cooled to rt and diluted with cold water (70 mL). The resulting off-white precipitate was collected and redissolved in dichloromethane. The solution was dried over Na_2SO_4 and then filtered. The volatiles were removed using a rotary evaporator, and the sample was further dried under

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high vacuum at 50 °C. Yield 140 mg (100%). Mp 209–211 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.49 (dd, $J = 6.2, 3.4$, 2H), 7.48 (dd, $J = 6.3, 3.3$, 2H), 7.36 (s, 2H), 6.69 (s, 2H), 3.21 (q, $J = 7.3$, 4H), 1.49 (t, $J = 7.4$, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 127.6, 125.0, 124.0, 123.4, 122.8, 118.6, 117.7, 22.6, 15.2. ESI MS (+): 263 $[\text{M} + \text{H}]^+$. HiRes MS ESI(+): found 262.1467 $[\text{M}]^+$, calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2^+$ 262.1465. Elemental analysis calculated for $\text{C}_{18}\text{H}_{18}\text{N}_2$: C 82.41, H 6.92, N 10.68. Found: C 82.51, H 6.82, N 10.61.

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Supporting Information Available: Details of the chemicals and instruments used, as well as selected spectral characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.