# Conducting Polymers Containing *peri*-Xanthenoxanthenes via Oxidative Cyclization of Binaphthols

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ABSTRACT: We report an electrochemical transformation of binaphthols to give *peri*-xanthenoxanthene (PXX) groups in small molecules and within polymer backbones. The monomer 7,7′-bis(2,2′-bithiophen-5-yl)-1,1′-bi-2,2′-naphthol (**2**) was subjected to electropolymerization, resulting in the segmented conducting polymer that is stable at low potentials. However, high-potential electrochemical oxidation promoted cyclization of binaphthol units gives PXX, which transforms the moderately conducting segmented polymer into a highly conducting fully conjugated polymer. This oxidative cyclization is a highly effective means by which to incorporate a planar polycyclic heteroaromatic structure (i.e., PXX) into thiophene-based conducting polymers. A model compound study conclusively proved the proposed oxidative cyclization scheme.

## Introduction

Polycyclic aromatic and heteroaromatic compounds are highly desirable elements for the construction of organic electronic or optoelectronic materials due to their photo- and electrochemical properties arising from their π-electrons.[1–6] These materials range from small molecules, such as pentacene and its derivatives, to ladder-type polymers.[7] Carbon nanotubes[8] and graphenes[9] can also be considered as essentially infinitely extended polycyclic aromatics with one- and two-dimensional structures, respectively.

Designing new types of polycyclic aromatic and heteroaromatic structures is desirable but often hampered by poor solubility associated with an extended planar structure and a lack of efficient synthetic methods. These hurdles have limited access to easily processable polymeric materials. One approach to overcome this limitation is to first prepare soluble precursor polymers with a molecular structure that is easily cyclized to a desired polycyclic target. Toward this end, we have previously reported directed electrophilic cyclizations to give phenanthrene moieties[10–12] and tandem cyclization–polymerization methods to produce polymers having highly stable naphthodithiophene moieties.[13,14]

Herein, we report a facile route to produce new electron-rich polycyclic heteroaromatic units via a postpolymerization oxidation treatment. Specifically, we demonstrate that main-chain binaphthols are fused into *peri*-xanthenoxanthenes (PXX) by electrochemical oxidative cyclization (Scheme 1). PXX has been known for decades but only recently found use in conductive charge-transfer complexes.[15,16] The postpolymerization cyclization method reported herein greatly facilitates the incorporation of PXX in conjugated polymeric materials and should be applicable to a variety of other polycyclic heteroaromatic compounds.

## Results and Discussion

The target monomers are described in Scheme 2. The precursor 2,2′-binaphthol can be functionalized with electroactive oligothiophenes for the purpose of electropolymerization. It should be noted that electropolymerization results in a segmented conjugated polymer,[17,18] which is not fully conjugated as a result of the binaphthyl "hinge" structure. In contrast

**Scheme 1. Oxidative Cyclization of Binaphthol to *peri*-Xanthenoxanthene**
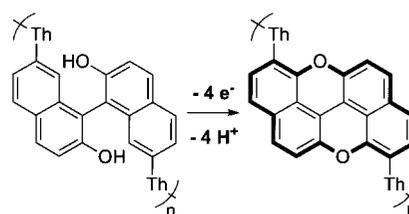


**Scheme 2. Synthesis of Electropolymerizable Binaphthol Monomer 2**
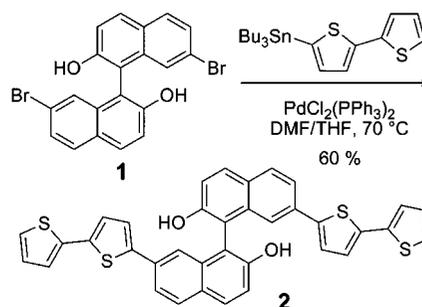


to the conventional 6,6′-disubstituted binaphthols,[19] 7,7′-disubstitued binaphthols are less common and only recently were utilized in catalyst development.[20,21] The 7,7′-dibromobinaphthol **1** was synthesized as described in the literature via oxidative dimerization of the respective naphthol with a copper–amine catalyst.[21] The desired monomer **2** was then synthesized by a Stille coupling reaction in a moderate yield.

The electropolymerization of **2** was performed with swept potential conditions in $CH_2Cl_2$ with 0.1 M TBAPF$_6$ as a supporting electrolyte (Figure 1). The 7,7′-susbstituted monomer **2** has electron-donating hydroxyl groups at the nonconjugated position relative to the oligothiophenes; hence when compared to the more common 6,6′-substituted analogue,[22] it displays a higher oxidation potential (Supporting Information).

Cyclic voltammetry and in situ conductivity measurements[23–25] of a film of poly(**2**) revealed interesting properties that are dependent on the scanned potential range. When we limited the potential cycles to ∼0.65 V vs Fc/Fc⁺, the cyclic

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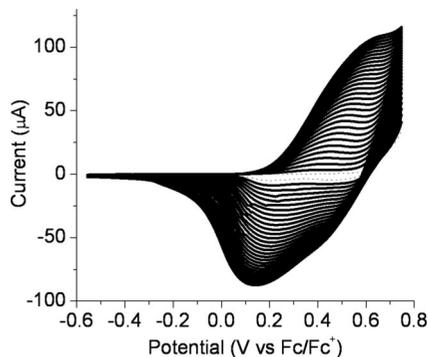
**Figure 1.** Electropolymerization of **2** on a Pt button electrode in $CH_2Cl_2$ with 0.1 M $TBAPF_6$ as a supporting electrolyte under ambient atmosphere.
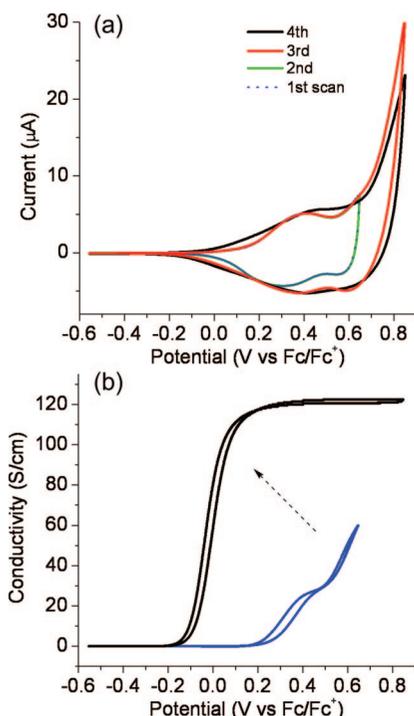


**Figure 2.** (a) Cyclic voltammograms of poly(**2**) on a Pt button electrode in $CH_2Cl_2$ with 0.1 M $TBAPF_6$ as a supporting electrolyte under air. The first two scans (blue and green lines) were limited up to 0.65 V (vs Fc/Fc[+]) and almost identical. The last two scans (red and black lines) were cycled to ~0.9 V. (b) In situ conductivity profiles of poly(**2**) on an interdigitated microelectrode (5 $\mu$m gap) measured in the similar conditions. The blue line represents the profile when the potential cycle was limited up to 0.65 V, and the black line is the profile after the extended potential cycle (to ~0.9 V).

voltammograms (CVs) displayed a stable reproducible pattern (Figure 2a, first and second scans). Over this range we see a clear correlation between the conductivity maxima (Figure 2b, blue line) and the redox peaks. Such a correlation is a characteristic of self-exchange redox processes arising from hopping localized redox units.[17,18] However, if the potential was scanned higher than the second redox wave (~0.9 V vs Fc/Fc[+]), an irreversible chemical reaction occurs (Figure 2a, third and fourth scans).

From the data in Figure 2, we conclude that subjecting poly(**2**) to higher potentials produced a more conductive and delocalized polymer structure. The spike of the oxidative current in Figure 2a suggests that the oxidation results in irreversible chemical transformations, presumably the formation of new bonds. In the CVs, the onset of oxidation is shifted to the lower potentials and the net electroactivity (integration of the total current) is
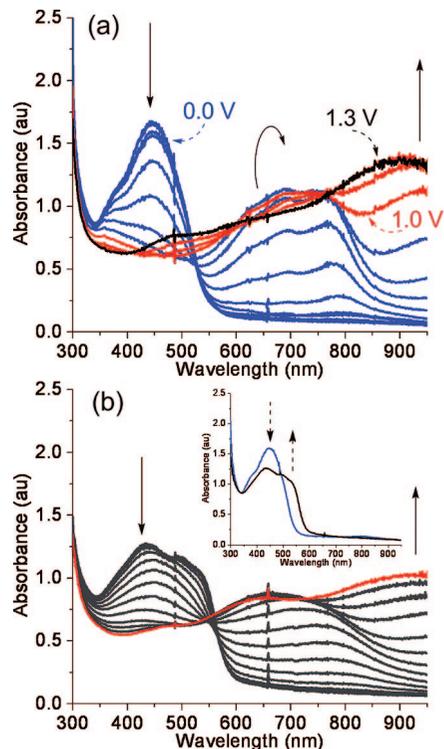


**Figure 3.** (a) UV−vis absorption spectra of poly(**2**) initially deposited at *V* < 0.9 V vs Ag/Ag^{+} (0.01 M) on an ITO-coated glass electrode in $CH_2Cl_2$ with 0.1 M $TBAPF_6$ as a supporting electrolyte under air, as a function of oxidation potential from 0.0 to 1.3 V vs Ag/Ag^{+} (0.01 M). The polymer underwent an irreversible chemical transformation at the potentials above 1.0 V. (b) UV−vis absorption spectra of the same poly(**2**), but after high-potential oxidation, as a function of oxidation potential from 0.0 to 1.3 V vs Ag/Ag^{+} (0.01 M). Inset: comparison of absorption spectra of poly(**2**) (neutral, unoxidized state) before and after high-potential oxidation.

maintained after the oxidation at the higher potential, both of which suggest a more delocalized structure is being produced. The conductivity profiles (Figure 2b) display a dramatic change after the high-potential oxidation. Specifically, the conductivity onset was shifted to a lower potential and the maximum conductivity almost doubled. The conductivity also displayed a featureless plateau, which is usually found in fully conjugated polymers.[25]

The spectroelectrochemical measurements provide additional evidence that the conjugation is increased after high-potential oxidation. When poly(**2**) was oxidized over the low-potential region (Figure 3a), new optical transitions developed in the sub-bandgap region as is typical of polaron-like absorptions (radical cations).[25−27] The fine structure and relatively narrow absorptions suggest that the radical cations are localized to the finite segments.

After the high-potential oxidation (Figure 3a, from 1.0 to 1.3 V vs Ag/Ag^{+}), we find that the bandgap, determined by the onset of the optical absorption, decreased significantly (Figure 3b, inset). When the polymer was reoxidized, the subgap transitions become featureless (Figure 3b), which is similar to fully conjugated polythiophenes.[25] On the basis of the above results, it is highly likely that the chemical transformation at the high potentials, which leads to the increase in conjugation, is an oxidative cyclization of 2,2′-binaphthol to PXX, as shown in Scheme 3.

Considering the structure, we postulate that 8- and 8′-positions are prone to nucleophilic attacks because of the electron-withdrawing nature of charged oligothiophenes at the 7- and 7′-positions (Scheme 3). The phenolic oxygens, which do not actively participate in the stabilization of the generated

**Scheme 3. Proposed Mechanism for Oxidative Cyclization of Binaphthol to PXX**
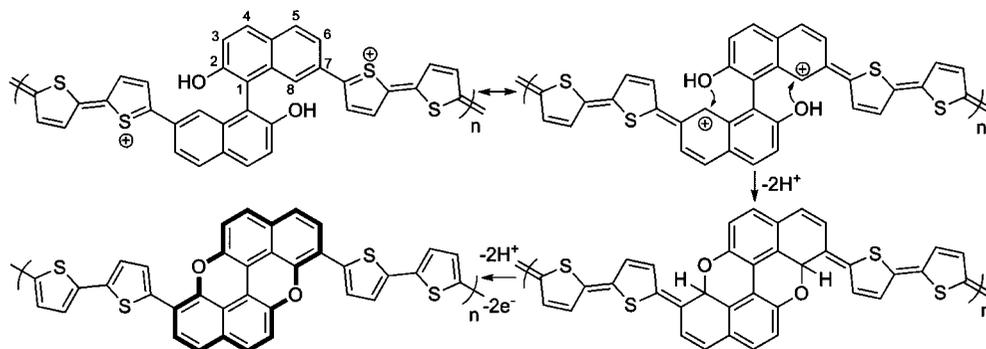


charges,[17,25] attack those positions to form the extended aromatic structure, PXX.

Interestingly, this transformation does not occur with isomeric poly(**3**), 6,6′-connected version (Figure 4). Scanning to the higher potentials resulted in only slight overoxidation[28] of the polymer (Supporting Information). In poly(**3**), the phenolic oxygens at the 2,2′-positions are in conjugation with the thiophenes and thereby take part in the charge stabilization similar to what has been observed in the other *p*-phenolic oxygen containing conducting polymers.[17,25] Furthermore, 8- and 8′-positions are less prone to nucleophilic attack when compared to the case of poly(**2**) because they are cross-conjugated to oligothiophenes.

The O-alkylated polymers provide further evidence that oxidative cyclization with phenolic oxygens is responsible for
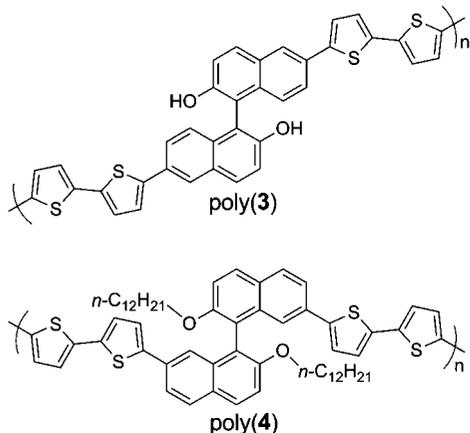


**Figure 4.** Structures of the isomeric polymer, poly(**3**), with 6,6′-connected oligothiophenes and the O-alkylated version, poly(**4**).
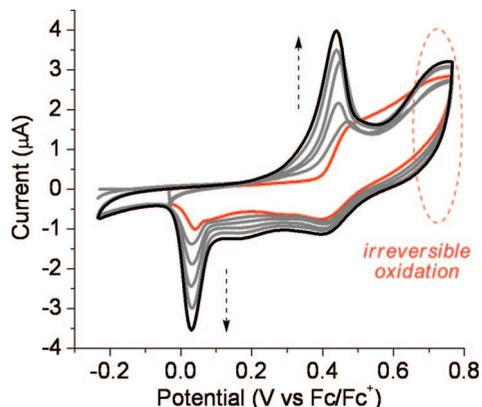


**Figure 5.** Repeated cyclic voltammograms of **6** on a Pt button electrode in CH$_2$Cl$_2$ with 0.1 M TBAPF$_6$ as a supporting electrolyte under ambient conditions.

**Scheme 4. Model Compounds and Their Oxidative Cyclization$^a$**
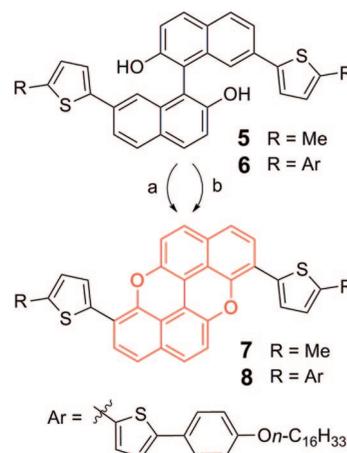


$^a$ Conditions: (a) electrochemical oxidation; (b) NOBF$_4$, CH$_2$Cl$_2$, room temperature.

the chemical transformation of poly(**2**). Poly(**4**) showed two distinct one-electron redox waves, which were stable even at high potentials (Supporting Information). The "blocked" oxygens could not proceed to affect cyclization by the mechanism proposed in Scheme 3.

In order to confirm that oxidative cyclization gives rise to a PXX structure, model compounds were synthesized. Compounds **5** and **6** have a binaphthol core that is functionalized with nonpolymerizable mono- and bithiophene moieties, respectively. Their syntheses were similar to the electropolymerizable monomer **2**; Stille coupling between dibromobinaphthol and corresponding stannylthiophenes produced the desired model compounds in moderate yields.

The electrochemical oxidation of model compounds was performed via cyclic voltammetry (Figure 5 and Supporting Information). In both cases, the CVs revealed irreversible chemical transformations after oxidation, wherein the oxidized thienyls promote cyclization of the binaphthol core. However, the behavior of resulting products was different. Only small currents at the lower potential are observed in the case of monothienyl **5**, whereas more conjugated **6** showed increasing currents as the scan repeated (Figure 5). We suspected the latter is due to the highly insoluble nature of the extended PXX structure **8**. In addition, we observed in the CV a significant separation of peak potentials between oxidation and reduction of the resulting product, which may be attributed to a strong π−π interaction and solid-state structural changes of planar PXX with electrochemical cycling.

The most conclusive evidence for the formation of the PXX structure comes from the mass spectroscopy data of model
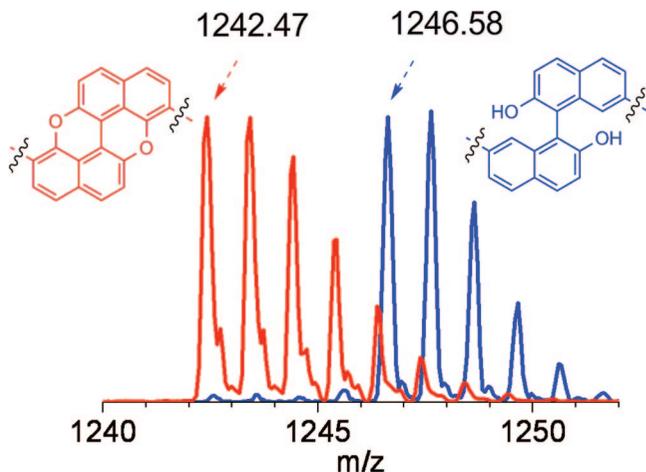
**Figure 6.** MALDI-TOF spectra of **6** (blue line) and its oxidized product (red line).

compounds taken after oxidation. Compounds **5** and **6** were subjected to chemical oxidation by NOPF$_6$ in CH$_2$Cl$_2$ at room temperature (Scheme 4). Anhydrous methanol addition furnished the reduced precipitations, and the isolated products were characterized. Figure 6 shows the MALDI-TOF spectra of binaphthol **6** and its oxidized product **8**. A mass difference of four strongly supports our oxidative cyclization scheme, which results in the expulsion of four hydrogens. High-resolution mass spectroscopy (HR-MS) of compound **5** before and after chemical oxidation also revealed a 4-hydrogen difference. The UV−vis spectrum of cyclized compound **7** revealed a highly rigid and delocalized structure (Supporting Information, Figure S5). There is a significant red shift in peak maxima (330 nm for **5**, 471 nm for **7**), and vibrational fine structure is observed for **7**. These results are consistent with our oxidative cyclization scheme.

## Conclusion

We reported a new electrochemical transformation of bi-naphthol to give *peri*-xanthenoxanthenes (PXX) in conducting polymers and model compounds. This oxidative cyclization produces a highly planar polycyclic heteroaromatic structure (i.e., PXX) in thiophene-based conducting polymers. The introduction of PXX units transforms a moderately conducting segmented polymer into a highly conducting fully conjugated PXX-containing polymer. Model compound studies conclusively proved the proposed oxidative cyclization scheme.

**Supporting Information Available:** Detailed descriptions on the syntheses of all compounds and experimental procedures for electrochemical measurements; electropolymerization of **3** and **4** and the CVs of resulting polymers; electrochemical oxidation of model compound **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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