## Synthesis of Phenanthro[9,10-c]thiophenes by 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)-Promoted Cyclo-Oxidation

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A new method to prepare phenanthro[9,10-*c*]thiophenes has been developed. In the presence of triflic acid, 3,4-diaryl thiophenes undergo 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)-promoted cyclo-oxidation. NMR and computational studies indicate that protonation of the thiophene plays a key role in this reaction. The reaction can be used to prepare phenanthro[9,10-*c*]thiophene, as well as derivatives with alkyl, bromo, and methoxy substituents. However, the yields and selectivity of the reaction depend on both the nature and location of the substituents. Bis(3-methoxyphenyl)thiophene reacts under these conditions to give the desired product in 57% yield, while bis(4-methoxyphenyl)thiophene gives no product. Bis(3-bromophenyl)thiophene did not react, but cyclooxidation of bis(4-bromophenyl)thiophene provides the desired product in 34% yield.

Arene-fused thiophenes have been used in polymers for applications in organic field-effect transistors (OFETs), lightemitting diodes (OLEDs) and solar cells (OSCs).<sup>[1]</sup> The bandgap of poly(isothianaphthene) (Figure 1), for example, has been measured at 1.0-1.2 eV, which is almost 1 eV smaller than that of poly(3-hexylthiophene) (P3HT), due to the increased aromatic stabilization in the quinoidal form of the polymer.<sup>[2]</sup>

Phenanthrene-fused thiophenes have aromatic stabilization energies intermediate between those of thiophene and benzo [*c*]thiophene.<sup>[3]</sup> making them promising starting materials for conjugated polymers. Kathirgamanathan and Shepherd examined the polymerization of phenanthro[9,10-*c*]thiophene (1) under electrochemical conditions, and obtained a red conducting material.<sup>[4]</sup> They reported that this polymeric material changes color depending on oxidation state. The polymer was not soluble, and there was no further characterization beyond the electrochemical properties. These results led us to target soluble derivatives of this polymer that can be more completely

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characterized and processed. However, there have been very few reported syntheses of phenanthro[9,10-*c*]thiophene or its derivatives.

The most straightforward approach to the phenanthrothiophenes is by oxidative cyclization of diaryl thiophenes (2, Scheme 1); this route also benefits from the synthetic accessibility of diaryl thiophenes with a variety of substituents.<sup>[5]</sup> However, Schnapperelle and Bach attempted the cyclo-oxidation of compound 2 under a wide variety of conditions, and found no reaction.<sup>[6]</sup> To overcome this problem, they prepared the more complicated desymmetrized chlorodiarylthiophene 3 and successfully converted it to phenanthrothiophene 1 by irradiation with 254-nm light. Other approaches that have been used to make phenanthro[9,10-c]thiophene and derivatives include Hindsburg condensation of a diester sulfide with phenanthroquinone;<sup>[7]</sup> ring closure using sodium sulfide and a phenanthryl dihalide<sup>[8]</sup> or tetrahalide;<sup>[4]</sup> and Stille coupling of a 9-stannafluorene with a dibromothiophene.<sup>[9]</sup> To develop a more efficient and versatile synthesis for substituted phenanthrenes, we decided to reexamine the simple cyclo-oxidation of diarylthiophenes.

Diaryl thiophene derivatives can be synthesized by a variety of methods.<sup>[4,6,8,10]</sup> Dang and Chen reported the efficient syn-



Scheme 1. Approaches to synthesize phenanthro[9,10-c]thiophene



Scheme 2. Synthetic route to diaryl thiophenes.

thesis of diaryl thiophenes in three steps from the bromoacetophenone (4).<sup>[5e]</sup> Based on their approach, we prepared a range of diarylthiophenes (Scheme 2). First, the bromoacetophenone (4a–g) reacts with sodium sulfide to provide the diketone sulfide (5a–g) in high yield. Intramolecular McMurry coupling of the diketone leads to a mixture of diaryl dihydrothiophene and the desired diaryl thiophene. Dang and Chen used CuBr<sub>2</sub> to oxidize this mixture fully to the diaryl thiophene, but we found that subjecting the crude product mixture to 2,3-dichloro-5,6dicyano-1,4-benzoquinone (DDQ) oxidation leads to clean production of the diaryl thiophene (2a–g) in good yield.

To find conditions for the DDQ-promoted cyclo-oxidation of the diaryl thiophenes, several acid catalysts were screened in



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the reaction of compound **2b** (Table 1), based on Rathore's conditions for conversion of activated terphenyls to triphenylenes.<sup>[11]</sup> Methanesulfonic acid and fluoroboric acid provide only trace amounts of the desired product **1b**, while Lewis acid BF<sub>3</sub>-OEt<sub>2</sub> gives none. Triflic acid, however, works well, especially when an excess of DDQ is used. Reducing the temperature to -40 °C improves the yield further, as does increasing the dilution to discourage dimer formation. Under optimized conditions, this reaction can be carried out in 47% isolated yield.

To further investigate the scope of this cyclo-oxidation, several different diaryl thiophenes have been studied (Table 2). These experiments demonstrate that both the substituents and the regiochemistry affect the success of the reaction. Comparing the methoxy-substituted substrates 2c-2e, bis(4-methoxyphenyl) thiophene (2d) gives none of the desired phenanthrothiophene (1 d), with recovery of 43% of starting material, while bis(3-methoxyphenyl) thiophene (2c) undergoes reaction in good yield, although forming an inseparable mixture of both a symmetric and asymmetric product (Scheme 3); bis(3,4-dimethoxyphenyl) thiophene (2e) reacts in high yield to give product 1e. For the bromine-substituted compounds, the selectivity is the opposite: bis(4-bromophenyl) thiophene (2g) reacts in reasonable yield, but reaction of bis(3-bromophenyl) thiophene (2 f) leads to no identifiable products and recovery of 40% of the starting material.





Scheme 3. Reaction of bis(3-methoxyphenyl)thiophene yields an inseparable mixture of two phenanthrothiophenes, the symmetric product 1 c and the asymmetric product 1 c'.



Investigations of the mechanism of the Scholl reaction of diaryl benzenes by King and co-workers implicated a protonated arenium cation as a key intermediate.<sup>[12]</sup> To investigate whether a similar mechanism might be operative here, we calculated the proton affinity of diphenyl thiophene **2a** at various positions. DFT calculations (B3LYP/6-311<sup>++</sup>G\*\*) indicate that the carbon next to sulfur has the largest proton affinity (Figure 2). According to these calculations, the proton affinity of phenanthro[9,10-*c*]thiophene is 14 kcal/mol greater than that of *o*-terphenyl.

NMR experiments support the presence of a protonated arenium intermediate in the triflic acid-catalyzed reaction (Figure 3). Adding 10% triflic acid to a solution of compound **2b** in



Figure 2. Relative proton affinity (kcal/mol) at each unique position in diphenyl thiophene (2 a). Based on DFT calculations (B3LYP/6-311 $^{++}$ G\*\*).



Figure 3. <sup>1</sup>H NMR spectra (11.0–5.0 ppm) of compound 2b (a) in  $CDCI_{3}$ ; (b) in 10% methanesulfonic acid in  $CDCI_{3}$ ; and (c) in 10% trilflic acid in  $CDCI_{3}$ .<sup>[14]</sup>



**Scheme 4.** Proposed mechanism for the formation of phenanthro[9,10-*c*] thiophene.

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CDCl<sub>3</sub> leads to the appearance of a new peak at 5.66 ppm, consistent with a protonated thiophene. In addition, there is an evident loss of symmetry in the molecule, with the peaks corresponding to the protons on the benzene rings splitting into separate signals. These peaks also move to higher frequency (7.5–7.7 ppm vs 7.1–7.3 ppm), consistent with being adjacent to a protonated thiophene. In contrast, addition of the much weaker acid methanesulfonic acid<sup>[13]</sup> to compound **2b** in chloroform leads to no change in the proton NMR peaks, consistent with the poor catalyzing power of MsOH.

The calculations and NMR data are consistent with a ringclosing mechanism that starts with protonation of the thiophene ring at the 2-position to form arenium cation **i** (Scheme 4). Protonation increases the electrophilicity of the benzene ring ortho to the protonated site, leading to nucleophilic attack by the other benzene ring to form intermediate **ii**. Oxidation by DDQ and deprotonation give the final phenanthro[9,10-*c*]thiophene.

In summary, 3,4-diaryl thiophenes can be converted directly into phenanthro[9,10-c]thiophenes when subjected to DDQ oxidation in the presence of triflic acid. This route allows access to a variety of substituted phenanthro[9,10-c]thiophenes. Computational and NMR studies suggest that protonation of the thiophene ring is a key step in the reaction. Further exploration of the reaction scope and mechanism is ongoing.

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## **Conflict of Interest**

The authors declare no conflict of interest.

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- [14] Full  $^1\text{H}$  NMR spectra can be found in the Supporting Information, Figures S1–3.

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## COMMUNICATIONS

Unexpected pleasure: Diaryl thiophenes, previously reported to be inert to 2,3-dichloro-5,6-dicyano-1,4benzoquinone (DDQ), undergo cyclooxidation to the corresponding phenathro[9,10-c]thiophenes in the presence of DDQ and triflic acid. The reaction works in good yield with a variety of substituents on the aryl groups (Br, OMe, *t*-Bu), but it is sensitive to the regiochemistry of substitution.



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