



## Mechanism of 3,4-diarylpyrrole electrooxidation



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### ABSTRACT

The purpose of this study was to investigate 3,4-diarylpyrrole electropolymerization and simultaneous or subsequent intramolecular oxidative coupling leading to poly(phenanthropyrole). Small amounts of  $\pi$ -conjugated products were obtained only under the conditions of increased concentration of the monomer and increased rate of potential sweep, which enabled both processes – monomer oxidation and deprotonation of the  $\sigma$ -dimer. The combined electrochemistry, UV-vis-NIR, ESR and TD-DFT results show, that the  $\alpha,\alpha'$ -coupling of 3,4-diarylpyrrole derivatives is inhibited by the stability of the  $\sigma$ -dimer dication, inhibition of the deprotonation and the reversal of the  $\sigma$  bond formation resulting in regeneration of the monomer. The addition of pyridine did not result in  $\sigma$ -dimer deprotonation in 2- and 2'-position.

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### 1. Introduction

The synthesis of pyrrole derivatives is an important area of heterocyclic chemistry due to the ubiquity of pyrrolic motifs not only in natural products but also in materials chemistry. In the latter context, pyrrole-based polymers are of particular importance, with current research focused on increasing their solubility [1,2], and modification of their optical properties [3,4]. Both effects can be readily tailored through the use of substituted pyrroles. Electropolymerization of substituted pyrroles has been successfully performed, usually using N-substituted pyrroles [5], 3,4-alkylenedioxyppyroles [6], indoles or isoindoles [7]. The electrooxidation of 2,3-diphenylindole results in an almost quantitative transformation into the indole-indolenine dimer, involving linkage through a fused benzene ring [8].

Furthermore, electrochemically prepared polypyrroles suffer from the occurrence of undesired  $\alpha$ - $\beta$  and  $\beta$ - $\beta$  couplings during polymerization [9], and the  $\alpha$ - $\alpha$  coupling selectivity can be achieved by using 3,4-disubstituted monopyrrole precursors [10]. The most common 3,4-disubstituted polypyrroles, prepared using electrochemical method are poly(3,4-dimethoxyppyrole)s [11] and poly(3,4-diethylenedioxyppyrole)s (PEDOP) [12,13]. In turn, 3,4-diarylpyrroles are interesting as precursors to physiologically and biologically active compounds [14]. An important property of these polymers is their ability to be doped through a partial oxidation or

reduction. The use of electrochemical techniques allows to obtain polymers with specified doping degree in a controlled manner via partial oxidation or reduction, which may be implemented through the sign and value of applied potential [15].

The 3,4-diarylpyrrole moiety is a constituent of a wide array of natural products, such as 3-chloro-4-(3-chloro-2-nitrophenyl)-1H-pyrrole (pyrrolnitrin) [16], *Lamellarin* [17] or *Lycogarubin C* [18]. Cyclization of  $\alpha$ -amino carbonyl compounds and aldehydes is a simple method for the preparation of 1,3,4-triarylpyrroles [19]. 3,4-Diarylpyrroles have been developed using the Hinsberg reaction of benzil with dimethyl N-acetylaminodiacetate [20]. The Barton-Zard pyrrole synthesis using nitroalkenes [21], and the van Leusen TOSMIC method [22] are now well established for the preparation of  $\beta$ -arylpyrroles. Other synthetic methods include the reduction of  $\beta$ -nitrostyrene with  $\text{TiCl}_3$  [23], Knorr-type condensations of amino ketones [24], and palladium-catalyzed Suzuki cross-coupling of 3,4-dihydroxyppyrole bis-triflate derivatives [25]. The use of copper or nickel catalysis was recently found to yield highly selective denitrogenative annulations of vinyl azides with aryl acetaldehydes, leading to both 2,4- and 3,4-diaryl substituted pyrroles [26].

3,4-Diarylpyrroles are important precursors to octaaryl- [27,28] and dodecaarylporphyrins [29,30]. Recently, some of us have shown that electron-rich 3,4-diarylpyrroles can undergo a tandem inter- and intramolecular oxidative coupling, providing access to bis(phenanthropyroles) with extended  $\pi$ -conjugation. These bis(phenanthropyroles) are characterized by restricted rotation around the  $\alpha$ - $\alpha$  bond and exhibit strong blue fluorescence and large Stokes shifts [31]. This type of coupling reactivity was earlier

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employed in the synthesis of self-assembling porphyrin-based materials [32]. Literature reports detail various benzo-fused heterocyclic materials [33], characterized by high luminescence quantum yields [34]. Many such derivatives have two-dimensional self-assembled structures [35]. The supramolecular, self-assembly processes, occurring for these systems, are affected by a complex interplay of inter- and intramolecular interactions, non-covalent forces such as hydrogen-bonding, electrostatic or  $\pi$ - $\pi$  stacking, which is also related to the luminous efficiency.

This paper presents an attempt to control 3,4-diarylpyrrole electro-coupling, in order to obtain oligo(phenanthropyrroles). Apparently, the intermolecular coupling is a rapid process and can compete with the intramolecular ring closure, suppressing the formation of monomeric phenanthropyrrole.

Mostly, electropolymerizations of aryl-substituted pyrroles were carried out using: N-aryl-pyrroles [36] or N-aryled and 3,4-substituted pyrroles [37]. Electropolymerization of 3,4-dicarboranyl-functionalized pyrroles has also been reported [38]. 3-Aryl- and 3,4-aryl polymers are often obtained with other heterocyclic compounds such as thiophene derivatives [39,40] or their oligomeric precursors – e.g. 3',4'-diphenyl-2,2':5',2"-terthiophene [41]. Poly(benzothiophene)s can be obtained by electrocopolymerization with benzothiophene and thiophene or pyrrole derivatives [42].

In general, due to the steric hindrance in 3,4-substituted derivatives, straightforward electropolymerization was found to be unfeasible in compared to similar substances with aliphatic substituents [43]. However, poly(3,4-diphenylpyrroles) were grown electrochemically from solutions of acetonitrile containing diphenylpyrrole, tetrahexylammonium poly(styrenesulfonate) and sodium perchlorate, but no information was given concerning the possibility of coupling reactions between substituents [44]. In turn, poly(phenantro[9,10c]thiophene) can be prepared by electrochemical polymerization with  $\text{Bu}_4\text{NPF}_6$  and it showed high conductivity ( $105 \text{ S cm}^{-1}$ ) [45].

The mechanism of electropolymerization of aromatic heterocyclic monomers is still not fully understood and remains a subject of controversy. Tanaka et al. [46] carried out a study of coupling processes between two pyrrole radical cations. They have envisioned two possible routes of the pyrrole coupling involving on the one hand a  $\sigma$ -radical and on the other a  $\pi$ -radical [47]. Diaz proposed the classical route of conducting polymer formation which involved the dimerization of monomeric radical cations at their  $\alpha$ -positions followed by deprotonation of the doubly charged  $\sigma$ -dimer, resulting in aromatic neutral dimer [48]. Other studies have shown that it is not the rate of coupling, but rather the elimination of protons from the  $\sigma$ -dimer, that is the rate-

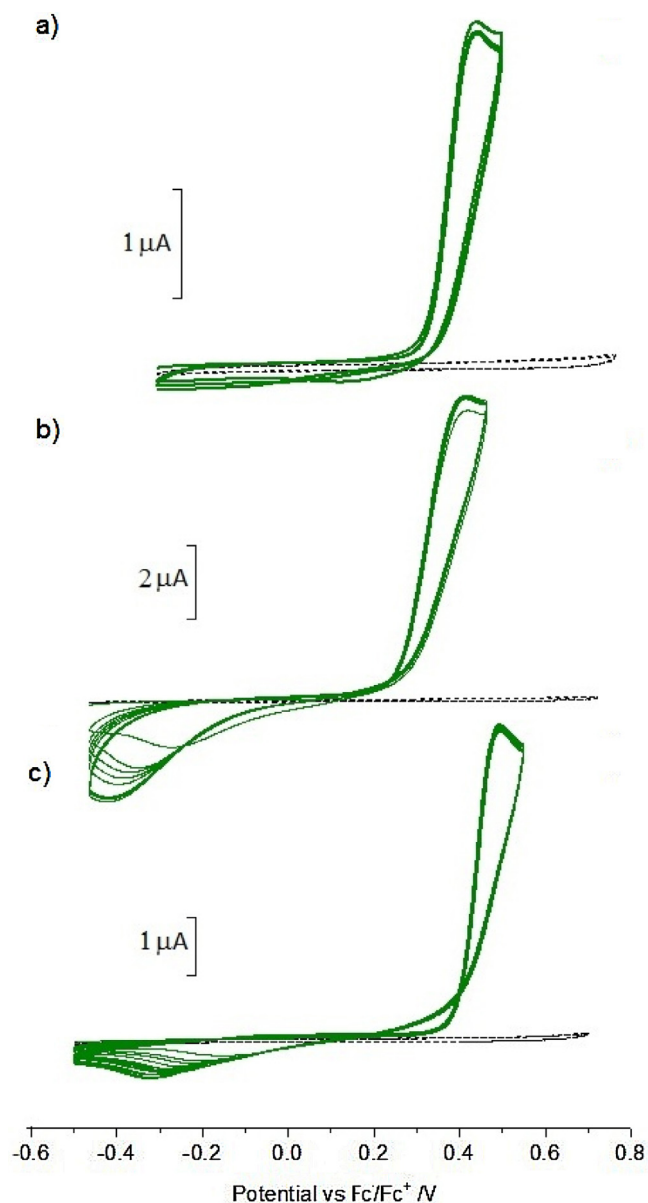
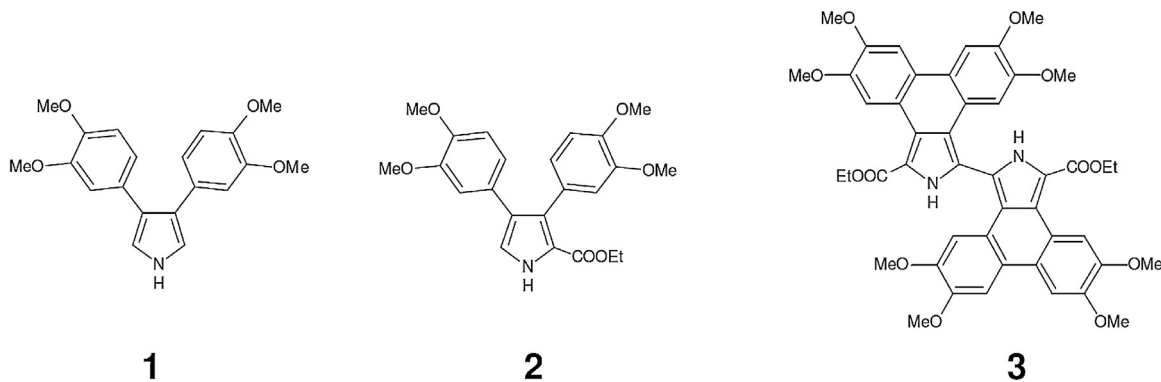


Fig. 1. 1–10<sup>th</sup> CV plots of 1 with: 2.0 mM (a) and 5.5 mM concentration in 0.1 M TBAP/DCM (b) and 2.0 mM in 0.1 M TBAP/ACN (c); potential scan rate:  $50 \text{ mV s}^{-1}$ .



Scheme 1. Structures of 3,4-bis(3,4-dimethoxyphenyl)-1H-pyrrole (1); ethyl 3,4-bis(3,4-dimethoxyphenyl)-1H-pyrrole-2-carboxylate (2) and 5,5',6,6',9,9',10,10'-octamethoxy-2H,2H-[1,1-bidibenzo[e,g]isoindole]-3,3-dicarboxylate (3) compounds subjected to electrooxidation.

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