



Self-assembled monolayers of aromatic pyrrole derivatives: Electropolymerization and electrocopolymerization with pyrrole



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ABSTRACT

Four different 4-(pyrrol-1-yl)-benzenethiol derivatives with/without methyl groups in the 2,5-position of the pyrrole ring and the 3,5-position of the phenyl ring as well as 4-(carbazole-9-yl)-benzenethiol were deposited as self-assembled monolayers on gold to improve the properties of (co)polymerized poly(pyrrole) layers. To understand the behavior of the different systems, the electrochemical properties of the dissolved molecules as well as of the respective monolayers were studied in detail before the copolymerization with pyrrole. As expected, the derivatives without methyl groups at the pyrrole ring as well as the carbazole derivative showed reproducible polymerization from solution and within the monolayer. Infrared reflection-absorption spectroscopy was employed to study the chemical situation within the films before and after electropolymerization. Copolymerization with pyrrole was very effective for 4-(pyrrol-1-yl)-benzenethiol and 4-(pyrrol-1-yl)-3,5-dimethylbenzenethiol monolayers. The poly(pyrrole) films were characterized by scanning electron microscopy and by atomic force microscopy, which revealed significantly smoother and more homogenous surface structures for the films copolymerized onto monolayers of the derivatives without methyl groups at the pyrrole ring as compared to poly(pyrrole) films deposited on bare gold. As evidenced by electrochemical impedance spectroscopy, the capacity at the copolymerized films is decreased as a consequence of the reduction in roughness, while the conductivity at the metal/polymer interface increases due to the covalent attachment through an aromatic system. For the 2,5-dimethylated pyrrole derivatives and for the carbazole derivative there were no such observations.

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1. Introduction

Poly(pyrrole) (PPy) and its derivatives receive enormous interest as flexible and conductive π -conjugated polymers, especially in applications for organic electronics [1–3], supercapacitors [4,5], transparent electrode materials [1], flexible electrodes [6], molecularly imprinted sensors [7–9], biosensors [7,10–12], and mechanical actuators [13,14]. There are diverse options to polymerize pyrrole (Py), of which the electrochemical polymerization [1,2,15,16] is the most elegant and atom-economic way, permitting the control of film thickness and morphology and thus the production of high quality polymer films [1,15–18].

A generally accepted mechanism [19,20] for the electrochemical polymerization of Py derivatives involves the oxidation of monomers in the vicinity of an anode, where the resulting radical cations first dimerize and deprotonate. The dimer is then

reoxidized and couples with another radical cation. The process of deprotonation and reoxidation continues with the formation of oligomeric species. Once the chain length of oligomers exceeds the solubility limit for the respective solvent, precipitation occurs and nuclei deposit on the anode. [19,20].

Chemical and structural defects, generated during this polymerization reaction, are important due to their reverse correlation to the conductivity of the PPy films. Since the oxidation potential of PPy is lower than that of the monomer, overoxidation of PPy is an inevitable consequence [20]. Published results [20,21] show that overoxidation is a major source of chemical defects in PPy films involving the formation of oxygen functionalities, such as carbonyl and hydroxyl groups [21], as a consequence of electropolymerization. Coupling through the 3/4-position of the pyrrole ring is also likely to be a significant source of structural defects [22,23], because coupling in the 3/4-position leads to a break of the conjugation along the polymer backbone, thus increasing the band gap [20] and resulting in lower conductivity. When substituents in the 3/4-position of the monomers are present, the crystallinity of the resulting polymers increases, but the molecular weights

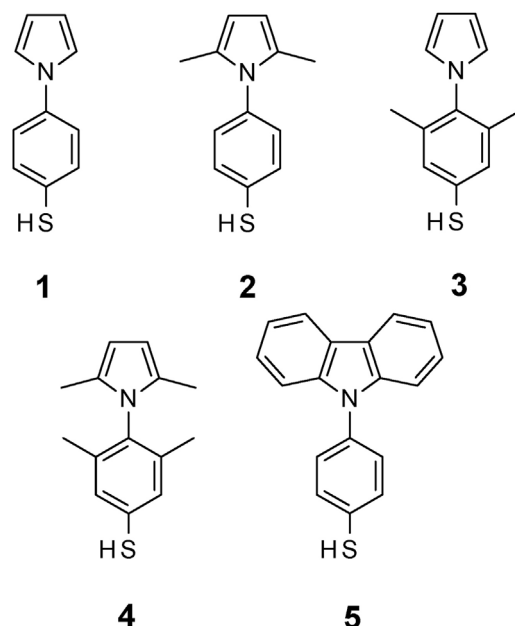
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typically decrease, reducing the conductivity [19]. These and other structural defects lead to delamination and decreased smoothness, which are the main causes of failure in micro-machined PPy devices [13,14]. Additionally, it is well known that smooth PPy surfaces [24] are more suitable for electronic applications [6]. Thus smooth and covalently bound PPy films might be beneficial by reducing shear stress and friction of micro-actuators for example. Moreover covalently bound PPy will enhance the functionality and robustness of molecularly imprinted sensors that make use of pyrrole as functional and/or matrix monomer [25].

One rational approach to attain efficient surface immobilization of such polymer films would be their covalent attachment e.g. by starting from self-assembled monolayers (SAMs) that contain suitable monomer head groups. SAMs are covalently bound to their substrates, can be designed for the specific applications and have defined packing geometries and densities [26]. Based on this concept, Willcutt et al. [27–30] and Wu et al. [31] investigated the electropolymerization of 1-(pyrrol-1-yl)alkan- ω -thiolates on gold. Further studies of 1-(pyrrol-1-yl)ethan-2-thiol and 1-(pyrrol-3-yl)ethan-2-thiol by Smela et al. [32–36] investigated the impact of substitution position on the polymerization of pyrrole-containing SAM precursors. In extension of the concept, Willcutt et al. [29] and Smela et al. [35] studied the deposition of PPy on pyrrolylalkanethiols. Their findings revealed that for SAMs with short alkyl chain linkers or with the pyrrole moiety attached other than in the 1-position, copolymerization with pyrrole was not possible. Moreover if the linker chains were longer, the packing density increased, the copolymerization became possible and the resulting deposited PPy films were rather smooth, but their conductivity was quite low [29,35].

The aim of this study was to obtain smooth, conductive and covalently bound PPy films on modified metal substrates by the use of SAMs with aromatic linkers to increase the quality of packing and to enhance conductivity compared to published results. Furthermore the effect of pre-orientation and the effect of blocking of the 2/5-position of the pyrrole moiety on (co) polymerization performance should be investigated. For this, we designed and synthesized a series of aromatic pyrrole and carbazole derivatives (Scheme 1) to overcome several known limitations: 1) Our series should allow for an adjustment of packing density, since it was demonstrated for the previously investigated pyrrolylalkanethiols [27–31] that the success of adhesion promotion is dependent on alkyl chain length [29,31] and hence quality of packing [31,35]. 2) Aromatic phenyl linkers are generally advantageous in terms of enhanced conductivity because of the lowered band gap [37]. 3) To leave more space for the pyrrole monomers from solution to participate in the copolymerization, we synthesized **3** and **4** with methyl groups in the 3- and 5-positions of the phenyl ring which should increase the distance between the pyrrole moieties in the respective SAMs. 4) To confirm that blocking of the 2/5-position of the pyrrole moiety will inhibit the electrocopolymerization and thus lead to less conductive films especially due to preference of reaction in 3/4-position, compounds **2** and **4** were elaborated. 5) 4-(Carbazol-9-yl)-benzenethiol (**5**) was synthesized as a reference system where polymerization of the SAM should occur, but copolymerization with pyrrole should not.

This study describes the successful electrochemical polymerization of such pyrrolyl-benzenethiols as well as their copolymerization with pyrrole on gold for the first time. The electrochemical properties of the precursors **1–5**, their corresponding SAMs of **1–5** on gold and the copolymer films of PPy with the SAMs of **1–5** on gold were investigated. In addition, the structure, morphology, and adhesion of the copolymerized films were investigated by infrared reflection-absorption spectroscopy (IRRAS), atomic force microscopy (AFM), scanning electron microscopy (SEM), and tape tests.



Scheme 1. – Structural formulae of the investigated compounds: 4-(pyrrol-1-yl)-benzenethiol (**1**), 4-(2,5-dimethylpyrrol-1-yl)-benzenethiol (**2**), 3,5-dimethyl-4-(pyrrol-1-yl)-benzenethiol (**3**), 3,5-dimethyl-4-(2,5-dimethylpyrrol-1-yl)-benzenethiol (**4**), 4-(carbazol-9-yl)-benzenethiol (**5**).

2. Experimental

2.1. Chemicals and syntheses

All chemicals were commercial materials of the highest available purity (analytical grade), and they were used as received. The syntheses of **1–4** will be published elsewhere [38]. In short, for the preparation of **1** and **2** commercially available 4-aminothiophenol was reacted either with 2,5-dimethoxytetrahydrofuran in acetic acid to give **1** in good yield or with 2,5-hexanedione and *p*-toluenesulfonic acid (PTSA) in toluene to give **2** in fair yield. The syntheses of **3** and **4** were accomplished by starting from 4-amino-3,5-dimethyl-phenylthiocyanate which could be obtained in excellent yield by thiocyanation of commercially available 4-amino-3,5-dimethylbenzene via reaction with bromine and potassium thiocyanate [39]. The phenylthiocyanate was then reacted either with 2,5-dimethoxytetrahydrofuran and PTSA in toluene or with 2,5-hexanedione and PTSA in toluene to obtain the respective pyrrole derivatives in excellent and very good yield, respectively. The following reduction of the thiocyanate groups by LiAlH_4 gave both thiols, **3** and **4**, in excellent yield. Carbazolythiol **5** was synthesized especially for this project. Its synthesis is given in the supporting information. It was realized in low yield by Lewis-acidic deprotection of 9*H*-carbazol-9-(4-*tert*-butylsulfanyl)benzene which in turn was synthesized via an Ullmann-type reaction from 1-bromo-4-(*tert*-butylsulfanyl)benzene [40] in good yield. The solid state structures of the thiol as well as of the intermediate are given in the supporting information (Fig. S1). Electrolytic solutions were prepared from fractionally distilled propylene carbonate (PC). Pyrrole (Alfa Aesar) was fractionally distilled under Ar atmosphere twice before use and stored in Schlenk tubes under Ar and exclusion of light. 11-Mercaptoundecanoylferrocene was synthesized according to published procedures [41]. Experiments were performed at ambient temperature.

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