

Charged states in diphenylamino endcapped thiophenes with a 1,4-phenylene core: *In situ* electron spin resonance/ultraviolet–visible–near infrared and nuclear magnetic resonance spectroelectrochemistry and quantum chemical study

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ABSTRACT

The three diphenylamino-endcapped thiophene compounds 1,4-bis-(2-diphenylamino-thiophen-5-yl)-benzene (**A**), 1,4-bis-[2-(phenothiazin-10-yl)-thiophen-5-yl]-benzene (**B**), and 1,4-bis-(5-diphenylamino-[2,2']bithiophen-5'-yl)-benzene (**C**) with a central phenylene core were investigated by *in situ* ESR/UV–vis–NIR and *in situ* NMR spectroelectrochemistry and quantum chemical studies. The computed vertical ionization potentials are 4.85 eV for **A**, 5.39 eV for **B** and 4.80 eV for **C** while the adiabatic ionization potentials are slightly lower 4.45 eV (for **A**), 4.96 eV (for **B**) and 4.47 eV (for **C**). The minimal difference between computed ionization potentials of **A** and **C** and the lower oxidation ability of **B** are in good agreement with the experimental electrochemical findings with the first half-wave anodic potentials 0.69 V (for **A**), 0.81 V (for **B**) and 0.67 V (for **C**), all vs. decamethylferrocene (DmFc⁺/DmFc). For the radical monocations **A**^{•+} and **C**^{•+} the spin delocalisation on the central phenylene moiety was confirmed both experimentally and by theoretical calculations. For the radical cation **B**^{•+}, the presence of a phenothiazinyl moiety is responsible for the delocalization of unpaired electron in the lateral part of this molecule. The stability of the charged states was increased substantially by the incorporation of two further 2,5-thienylene moieties between the central moiety and the side groups in **C**. Detailed spectroelectrochemical studies of the cation radical, dication, trication and tetracation of **C** are in good agreement with the calculated electronic transitions and experimental values for all redox states. *In situ* NMR spectroelectrochemical studies at different temperatures indicate dimerisation reactions of charged 1,4-bis-(5-diphenylamino-[2,2']bithiophen-5'-yl)-benzenes.

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1. Introduction

In the last decades functionalized oligothiophenes found applications in organic field-effect transistors, organic light emitting diodes and solar cells due to their easy structure variation and

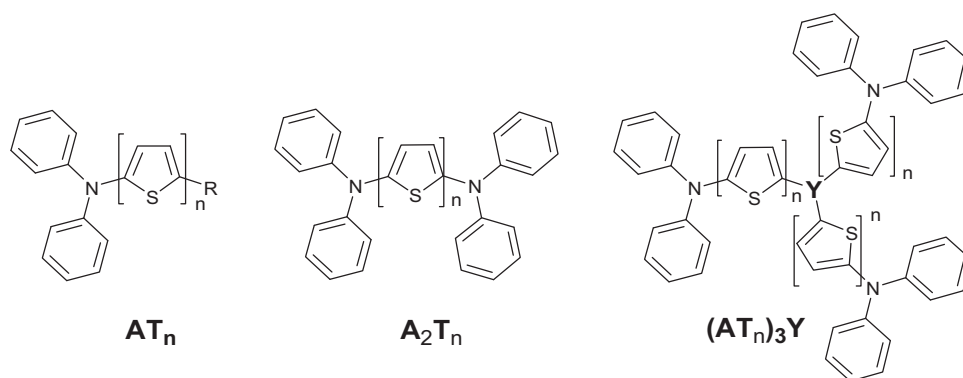
large variety of electronic properties [1–6]. The combination of thiophene derivatives with diphenylamino-groups made these structures useful as hole-transporting materials for optical and microelectronic devices [7,8].

Based on this finding different diarylamino substituted oligothiophenes were synthesized and their redox reactions have been studied by *in situ* spectroelectrochemistry [7–12]. Thus, detailed studies on electron transfer mechanisms and intermediate structures and their products by *in situ* spectroelectrochemistry have been performed recently for stable mono-, di- and trication structures for a series of diphenylamino- and bis(diphenylamino)-capped oligothiophenes **AT_n**, and **A₂T_n**, respectively (Scheme 1) [13,14]. It was shown that the stability of ion radicals strongly depends on the number of thiophene units of the oligomer. Similar results have been obtained for 2-diarylaminothiophene

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Scheme 1. Chemical structure of different diarylamino substituted oligothiophenes.

based starburst compounds $(AT_n)_3Y$ [15]. Increasing the number of thiophene moieties between the central moiety and the side groups stabilizes the charged states [15]. By using *in situ* spectroelectrochemistry the cations, dications, trications, and tetracations of an α,α' -diphenylsexithiophene were studied and it was shown in which way the phenyl terminal groups stabilize even tetracationic species [16]. Further ionization of the corresponding trications and tetracations produces larger changes for the end-phenyl groups and their quinoid character was strongly marked. The weaker quinoid character in the innermost part of the molecule was observed as compared to less ionized species. The large part of the total positive charge over each of the phenyl end-groups was indicated in the trication and tetracation. These theoretical results demonstrate that the two phenyl end-groups have a decisive role in stabilizing the radical trications and tetracations of α,α' -diphenylsexithiophenes [16]. Furthermore the cations, dications, trications, and tetracations of ω,ω' -bis-methylthio-substituted oligo-3,4-propylenedioxythiophenes were studied in the same manner [17].

We have shown the formation of stable radical cations and dications for N,N' -diphenyl- N,N' -(bithiophen-2-yl)-1,4-phenylenediamine. If the 5-position of the thiophene moiety is non-substituted the primarily formed cation radicals dimerise and even further oligomerisation is observed [18]. Similar processes are known for di- and triphenyl amines [19–21].

In this contribution, 1,4-bis-(2-diphenylamino-thiophen-5-yl)-benzene (**A**), 1,4-bis-[2-(phenothiazin-10-yl)-thiophen-5-yl]-benzene (**B**) and 1,4-bis-(5-diphenylamino-[2,2']bithiophen-5'-)-benzene (**C**) consisting of three different groups, namely the diphenylamino-, bithiophene- and central phenylene moiety (Scheme 2), respectively, were studied in detail to get insights into the charge transfer mechanism in dependence on the chemical

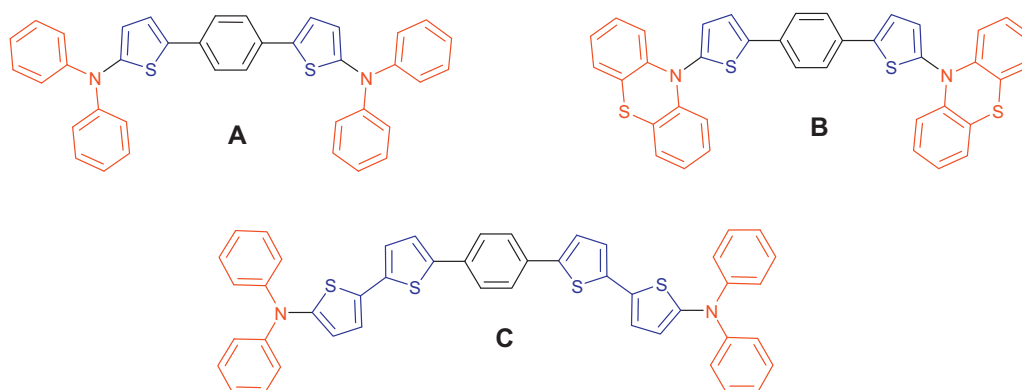
structure and the stability of the formed charged states in such composite π -conjugated compounds. Different voltammetric techniques, *in situ* ESR/vis-NIR and NMR spectroelectrochemistry as well as a theoretical study based on DFT calculations were used to achieve this goal. The strong influence of the central phenylene as well as the terminal moiety on the distribution of the spin density on the corresponding monocation and trication and the formation of different intermediates compared to the homogeneous α,α' -bis(diphenylamino)-capped oligothiophenes A_2T_n is discussed.

2. Experimental

Commercially available dichloromethane (CH_2Cl_2 , Aldrich), and decamethylferrocene (DmFc) (p.a., $\geq 98.0\%$) purchased from Merck were used without further purification. Tetrabutylammonium hexafluorophosphate (TBAPF₆) of puriss. quality (Fluka) was dried under reduced pressure at 70 °C for 24 h and stored in a glove box.

Compounds **A** and **B** were prepared by a Pd-catalysed coupling reaction of two equivalent of 5-stannylated 2-diphenylaminothiophene or 2-(10N-phenothiazinyl) thiophene, respectively, with 1,4-dibromobenzene [12]. The 1,4-bis-(5-diphenylamino-[2,2']bithien-5-yl)-benzene (**C**) was prepared analogously by a Pd-catalyzed reaction of 5'-stannylated 5-diphenylamino-[2,2']bithiophen with 1,4-dibromobenzene (see Supplementary information).

Cyclic voltammograms (CV), square-wave voltammograms (SWV) and fast scan CV were measured in dichloromethane with 0.1 M TBAPF₆ as supporting electrolyte using a one-compartment electrochemical cell with platinum wires as working and counter electrodes and a chlorinated Ag wire as a pseudo-reference electrode. 0.5 mmol dm⁻³ **A**, **B**, **C** solutions in dichloromethane were



Scheme 2. Chemical structure of investigated compounds A, B and C.

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