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The variety of reactions of radical cations derived from 2-diphenylaminothiophene oligomers

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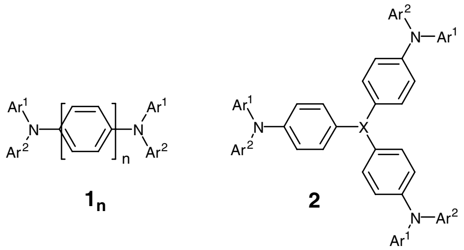
Dedicated to Professor Dr. Juergen Fabian to the occasion of his 70th birthday

Abstract—ESR spectroelectrochemical measurements of 2-diphenylamino-substituted oligothiophenes $\mathbf{8_m}$ proved the existence of radical cations $\mathbf{8_m}^{+\cdot}$ upon oxidation. Their stability and dimerization depend significantly on the number **m** of thiophene units. The radical cations $\mathbf{8_1}^{+\cdot}$ and $\mathbf{8_2}^{+\cdot}$ are very reactive and dimerize spontaneously to yield either 2,5-bis(diphenylamino)-2,2′-bithiophene $\mathbf{10_2}$ or 2,5-bis(diphenylamino)-5,5′-bis(2-thienyl)-3,3′-bithiopene $\mathbf{11_2}$, respectively. In contrast, the radical cations $\mathbf{8_3}^{+\cdot}$–$\mathbf{8_5}^{+\cdot}$ are highly stable and do not dimerize at all.

Recently several types of *N*-perarylated amines, for example, phenylene-1,4-diamines $\mathbf{1_1}$, benzidines $\mathbf{1_2}$ and the so-called starburst compounds **2** (see Scheme 1) received a strong interest as to their use in hole conducting layers in organic devices.[1] Owing to their property to form amorphous glasses in which the charged species exhibit a high stability and a pronounced mobility, they can be used as materials of a reasonable electrical conductivity useful for manufacturing several types of opto-electronic devices, such as organic field-effect transistors,[2] organic light-emitting diodes,[3] organic solar cells,[4] and photocopiers.[5]



Scheme 1. Some examples of hole-transport materials.

The application of the above-mentioned *N*-perarylated amines is different from the use of simple triarylamines **3** in these fields. Compounds like the parent triphenylamine **3a** (and some other derivatives with, at least, one unsubstituted aniline moieties) do not form highly stabilized charged species and yield, therefore, several types of reaction products such as benzidines **4**[6] or carbazoles **5**[7] by oxidation. The corresponding radical cations $\mathbf{3}^{+\cdot}$ and the dications $\mathbf{3}^{2+}$, respectively, have been demonstrated to be the reactive species responsible for these consecutive reactions (see Scheme 2).[8]

A similar situation is found for 2-diarylaminothiophenes **6**. These compounds can be regarded as heterocyclic triarylamine analogues and have been prepared by certain synthetic methods recently.[9,10] The charged species generated by oxidation like, for example, the radical cation $\mathbf{6}^{+\cdot}$ are highly reactive as well.[11] However, different from the triphenylamine series, the radicals were transformed into the corresponding 5,5′-bis(diarylamino)-2,2′-bithiophene derivatives **7**, even if their aryl groups are unsubstituted aniline moieties.[12]

Keywords: 2-Diphenylamino-substituted oligothiophenes; ESR spectroelectrochemistry; Cyclic voltammetry; Radical cations; Dimerization.

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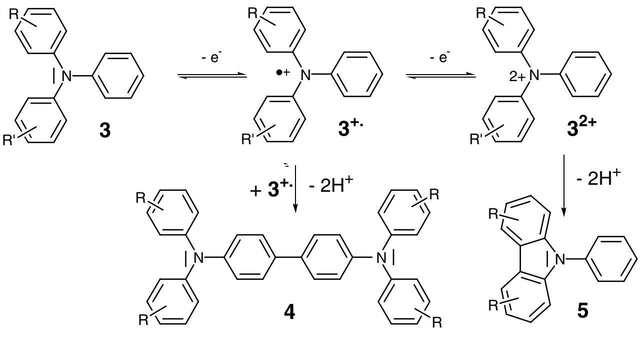
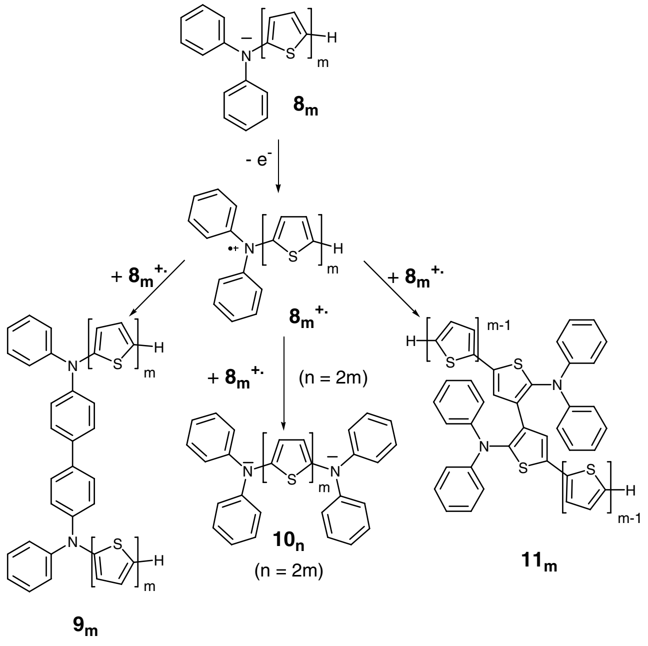


Scheme 2. Oxidation of triphenylamines.

Because the oxidative coupling of 2-diarylaminothiophenes **6** opens a versatile synthetic route to 5,5′-bis(diarylamino)-2,2′-bithiophenes **7**[12] it seems to be of high interest to extend this method to the synthesis of higher homologues of these electroactive compounds[13] by oxidation of some homologues of **6**. However, we found that these compounds do not yield the corresponding 5,5′-bis(diarylamino)-2,2′-bithiophene homologues by chemical oxidation (see Scheme 3).

To understand this result, ESR spectroelectrochemical studies were performed for some of these compounds. Such measurements are well suited to estimate the spin distribution in organic paramagnetic species. They have been used recently to explain the differences in the coupling activity of radical cation $\mathbf{3}^{+\cdot}$ derived from diarylamines[14] as compared to the radical cation $\mathbf{6}^{+\cdot}$ derived from diarylaminothiophenes.[11] Here we focus on the elucidation of oxidized species and their electronic properties for structures derived from some 2-diphenylaminothiophene homologues $\mathbf{8_m}$ with $\mathbf{m} = 2$–5. These compounds have been prepared by a simple palladium-catalyzed heteroaryl-heteroaryl Stille-type coupling reaction of 2-diphenylamino-5-tributylstannylthiophene or its 2,2′-bithiophene homologue with 2-bromothiophene or 5-bromo-2,2′-bithiophene according to a recently reported procedure (see Scheme 4).[15,16]

The electrochemical oxidation of the 2-diphenylamino-substituted oligothiophenes $\mathbf{8_m}$ was followed by in situ ESR spectroscopy and gives a behavior of these compounds depending on the number **m** of their thiophene units.[17] This is indicated both by the cyclovoltammograms (see Figs. 1 and 2) and the ESR spectra (see Fig. 3).

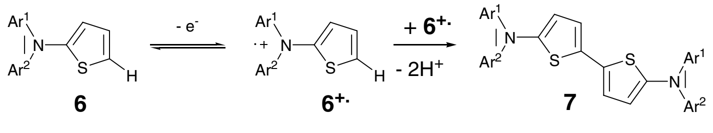


Scheme 4. Oxidation of 2-diphenylamino oligomers.

The cyclovoltammogram of $\mathbf{8_1}$ gives an irreversible one electron oxidation peak at +0.47 V versus Fc/Fc$^+$ which indicates the formation of the very unstable radical cation $\mathbf{8_1}^{+\cdot}$. It immediately dimerizes to form a sigma dimer. This dimer can be detected in the back scan of the first sweep (see Fig. 1a) where two peaks at +0.04 V and −0.07 V appear. Subsequently, the sigma dimer primarily formed is transformed into the α,α′-bis(diphenylamino)-2,2′-bithiophene $\mathbf{10_2}$ by deprotonation. Therefore, the structure $\mathbf{12}^{2+}$ is to be attributed to this sigma dimer. In the second forward scan two new voltammetric peaks at +0.01 V and +0.14 V appear. These peaks are caused by the oxidation of the (dehydro)dimer $\mathbf{10_2}$, which was formed in the preceding deprotonation step. It is now transformed reversibly into its radical cation $\mathbf{10_2}^{+\cdot}$ and the dication $\mathbf{10_2}^{2+\cdot}$.[9] Because the dimer $\mathbf{10_2}$ is more electron rich than its monomer $\mathbf{8_1}$ it can deliver two electrons at electrode potentials lower than those for $\mathbf{8_1}$. The radical cation $\mathbf{10_2}^{+\cdot}$ formed is detected by in situ ESR spectroscopy in the second forward scan. The ESR spectrum exhibits seven lines ($2a_N = 0.46$ mT; $4a_H = 0.40$ mT) and is identical with the spectrum observed recently for the radical cation $\mathbf{10_2}^{+\cdot}$, which was generated by electrochemical oxidation of $\mathbf{10_2}$.[18]

In contrast to $\mathbf{8_1}$, a reversible oxidation peak at +0.2 V versus Fc/Fc$^+$ (see Fig. 1b) was found for $\mathbf{8_2}$. In the anodic reaction a well-defined five line ESR spectrum was observed (see Fig. 3) resulting from 2 equiv nitrogen atoms with splitting constants $2a_N = 0.55$ mT. It is not the spectrum expected for the radical cation $\mathbf{8_2}^{+\cdot}$ but it refers to a reaction product.

As far as a thiophene–thiophene coupling of two cation radicals $\mathbf{8_2}^{+\cdot}$ would occur in analogy to the coupling of



Scheme 3. Oxidation of 2-diarylaminothiophenes.

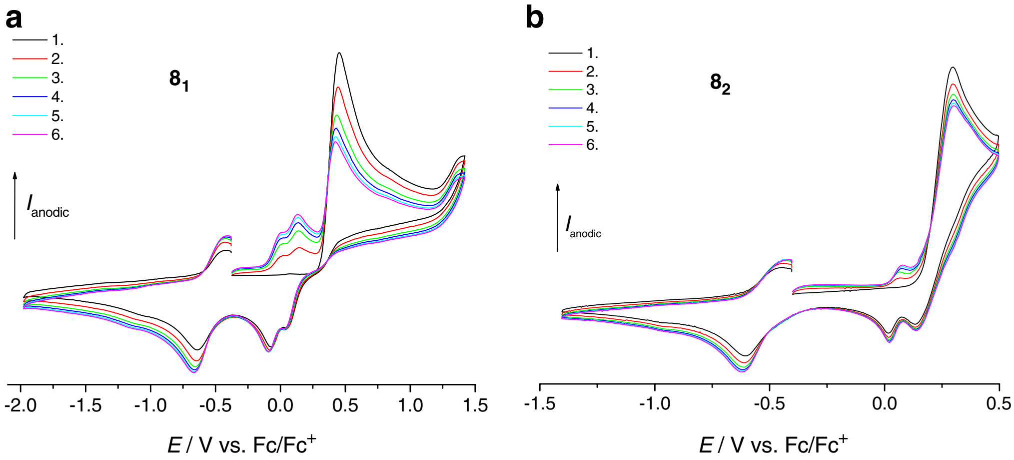


Figure 1. Cyclic voltammograms (six cycles) (a) of compound $\mathbf{8}_1$ and (b) of compound $\mathbf{8}_2$.

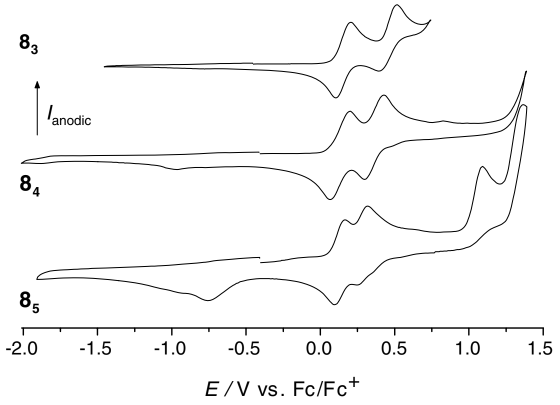


Figure 2. Cyclic voltammograms of compounds $\mathbf{8}_3$–$\mathbf{8}_5$.

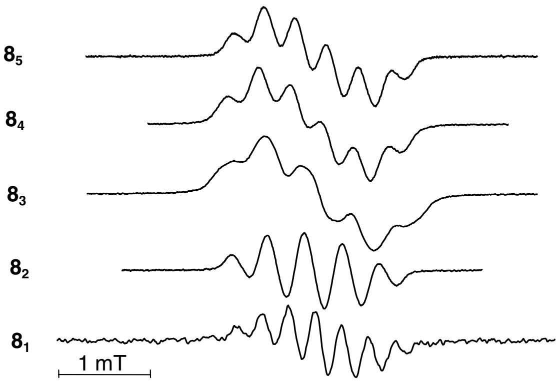
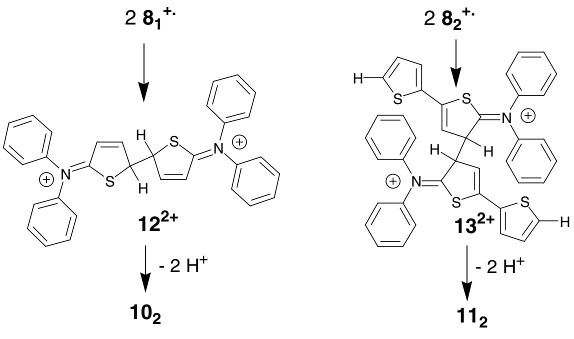


Figure 3. ESR spectra of cation radicals generated by oxidation of $\mathbf{8}_1$–$\mathbf{8}_5$.

two cation radicals $\mathbf{8}_1^{+\cdot}$ the formation of compound $\mathbf{10}_4$ ('tetramer') is expected to result in a nine line ESR spectrum ($2a_N = 0.29$ mT; $2a_H = 0.27$ mT), as recently observed for the radical cation $\mathbf{10}_4^{+\cdot}$ generated from the α,α′-bis(diphenylamino)-substituted quarterthiophene $\mathbf{10}_4$.[18] Because this spectral pattern is not observed, the dimerization of $\mathbf{8}_2^{+\cdot}$ follows another route. At a first glance, a radical cation $\mathbf{9}_2^{+\cdot}$ with a benzidine structure has to be taken into consideration. However, in such a benzidine cation radical the nitrogen splitting would dominate the spectrum,[19] which is not found experimentally. Instead of this a *C–H* coupling in a thiophene moiety a *C–N* coupling is detected (see Fig. 3). Thus, the formation of a sigma dimer of structure $\mathbf{13}^{2+}$ has to be taken into account. This dimer is subsequently transformed into the 2,2′-bis(diphenylamino)-3,3′-bithiophene $\mathbf{11}_2$ and its radical cation $\mathbf{11}_2^{+\cdot}$, which is obviously responsible for the experimental ESR spectrum (Scheme 5).

By oxidation of $\mathbf{8}_3$ two reversible peaks were found at +0.15 and +0.47 V versus Fc/Fc$^+$ (see Fig. 2). The ESR spectrum, which was simultaneously recorded in the first oxidation peak, is split into five lines. It differs in its pattern from the spectrum measured for the oxidation product of $\mathbf{8}_2$ and can be attributed unambiguously to the radical cation $\mathbf{8}_3^{+\cdot}$. This radical is rather stable and does not exhibit any tendency to dimerize under the given experimental conditions.

A similar behavior was observed for $\mathbf{8}_4$ and $\mathbf{8}_5$. In cyclic voltammetry these compounds give two reversible peaks at +0.13 V and +0.32 V and at +0.13 and +0.28 V (vs Fc/Fc$^+$), respectively (see Fig. 2). The ESR spectra measured in situ (see Fig. 3) point to the formation of the radical cation $\mathbf{8}_4^{+\cdot}$ and $\mathbf{8}_5^{+\cdot}$ as well as the dicationic spe-



Scheme 5. Structure of sigma dimers intermediately formed.

cies $\mathbf{8}_4^{2+}$ and $\mathbf{8}_5^{2+}$. The latter are generated in the second electrochemical oxidation step.

To summarize these ESR data the radical cations $\mathbf{8}_3^{+\cdot}$ to $\mathbf{8}_5^{+\cdot}$ are, in contrast to the radical cations $\mathbf{8}_1^{+\cdot}$ and $\mathbf{8}_2^{+\cdot}$, rather stable and do not exhibit any tendency to dimerize or to react under the given experimental conditions. This result is in agreement with the above mentioned behavior of higher 2-diphenylaminothiophene homologues $\mathbf{8}_\mathbf{m}$ ($\mathbf{m} > 2$) which do not yield corresponding dimers $\mathbf{10}_\mathbf{n}$ (with $\mathbf{n} > 1$) in a preparative scale by a reaction with common oxidizing reagents.

Acknowledgements

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16. 2-Diphenylamino-substituted oligothiophenes $\mathbf{8}_3$–$\mathbf{8}_5$ have been synthesized according to a synthetic protocol described in.[15] The analytical data of 2-diphenylaminothiophene ($\mathbf{8}_1$) and of 5-diphenylamino-2,2′-bithiophene ($\mathbf{8}_2$) are documented therein. The analytical data of the other 2-diphenylamino-substituted oligothiophenes are as follows: *Diphenyl-[2,2′:5′,5″]tertiophen-5-yl-amine* ($\mathbf{8}_3$) Mp 146 °C. ^{1}H NMR (in $CDCl_3$), δ-values (assignment): 6.76 (dd, $J = 3.9$ Hz, 1H), 6.96 (t, $J = 3.6$ Hz, 1H), 7.00–7.06 (m, 2H), 7.08–7.11 (m, 2H), 7.17 (d, $J = 3.6$ Hz, 1H), 7.19–7.22 (m, 5H), 7.28–7.33 (m, 5H). ^{13}C NMR (in $CDCl_3$), δ-values: 121.7, 122.9, 123.5, 124.0, 124.2, 124.9, 125.0, 126.6, 127.6, 128.5, 129.0, 129.9, 133.8, 135.8, 148.3, 151.5. Calculated for $C_{24}H_{17}NS_3$ (415.49) C, 69.36; H, 4.12; N, 3.37, S, 23.15; found C, 69.91; H, 3.28; N, 3.28; S, 23.15. *m/z*: 415. *Diphenyl-[2,2′;5′,2″;5″;2‴]quarterthiophen-5-yl-amine* ($\mathbf{8}_4$) Mp 165 °C. ^{1}H NMR (in $CDCl_3$), δ-values (assignment): 6.58 (d, $J = 3.9$ Hz, 1H), 6.95 (t, $J = 3.0$ Hz, 2H), 7.00–7.09 (m, 6H), 7.17–7.22 (m, 6H), 7.26–7.32 (m, 4H). ^{13}C NMR (in $CDCl_3$), δ-values: 121.6, 123.0, 123.6, 124.1, 124.4, 124.8, 124.9, 125.1, 125.2, 128.6, 129.9, 131.4, 133.9, 135.9, 136.8, 136.9, 137.6, 137.8, 148.3, 151.6. Calculated for $C_{28}H_{19}NS_4$ (497.72): C, 67.57; H, 3.85; N, 2.81; S, 25.77; found C, 67.80; H, 3.99; N, 2.55; S 25.48. *m/z*: 497. *Diphenyl-[2,2′;5′,2″;5″;2‴;5‴,2⁗]quinquethiophen-5-yl-amine* ($\mathbf{8}_5$) Mp 225 °C. Calculated for $C_{32}H_{21}NS_5$ (579.85): C, 66.28; H, 3.65; N, 2.42; S, 27.65; found C, 66.20; H, 3.70; N, 2.25; S, 27.09. *m/z*: 579.
17. The cyclic voltammograms were obtained at platinum working and counter electrodes. A silver wire served as pseudoreference electrode. CV measurements were carried out in a glove box using a Princeton Applied Research (PAR 270) universal electrochemical system. Ferrocene was used as an internal potential marker. Cyclovoltammetric and ESR spectroelectrochemical measurements were carried out in 0.1 M tetrabutylammonium tetrafluoroborate (Fluka, dried in vacuum at 70 °C) in dichloromethane (Fluka). ESR spectra were recorded by the ELEXYS spectrometer (Bruker, Germany). A PG 284 potentiostat/galvanostat (HEKA Electronik, Lambrecht, Germany) was used for potential control in the spectroelectrochemical experiments.
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