

Preparation and Characterization of α,α' -Bisdiarylamino-Capped Oligothiophenes

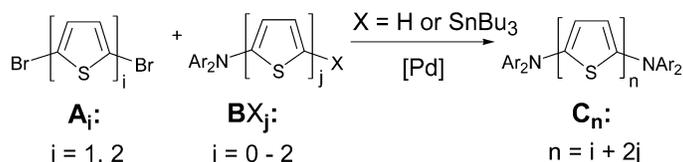
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ABSTRACT



A series of α,α' -bisdiarylamino-capped oligothiophenes \mathbf{C}_n were prepared by the palladium-catalyzed reaction of the dibromo compounds \mathbf{A}_i with diarylamines, N,N -diarylamino-substituted thiophenes or 2,2'-bithiophenes $\mathbf{B}\mathbf{X}_j$. These easily oxidizable compounds exhibit a high tendency to form amorphous glasses and characteristic electrochemical and spectroscopic properties that depend significantly on the number of their thiophene moieties.

Owing to their unique electronic and optical properties, oligothiophenes with well-defined structures¹ are of great interest for new materials used in several fields of applications, such as field-effect transistors,² organic light-emitting diodes,³ or photocopiers.⁴ To diversify the structure and, hence, the properties of the oligothiophenes, the introduction of different terminal groups into their backbone is a growing synthetic interest. For instance, a series of oligothiophenes substituted at their α,α' -positions by 9,9-diphenylfluorene moieties $\mathbf{4}_n\mathbf{a}$ ⁵ or electron-accepting cyano or perfluorohexyl groups $\mathbf{4}_n\mathbf{b}$ ⁶ and $\mathbf{4}_n\mathbf{c}$,⁷ respectively, have been prepared and studied recently. Moreover, oligothiophenes $\mathbf{5}_n\mathbf{d}$ with pyr-

rolidino groups at their β,β' -positions and $n = 0-2$ have also been reported recently. These compounds render, e.g., versatile starting materials for electroactive polymers.⁸ The essential step in the synthesis of the mentioned oligothiophenes consists of a heavy-metal-catalyzed coupling reaction of a metalated thiophene $\mathbf{2}$ or $\mathbf{3}$ with 2,5-dihalothiophene $\mathbf{1}_1$ or 5,5'-dihalo-2,2'-bithiophene $\mathbf{1}_2$. The same 2,5-dihalo compounds $\mathbf{1}_i$ have also been used as starting materials for the synthesis of the first two members of diarylamino-capped oligothiophenes of the general structure $\mathbf{9}_n$ ($n = 1$ or 2)^{9,10} if they were allowed to react with diarylamines. The 2,5-

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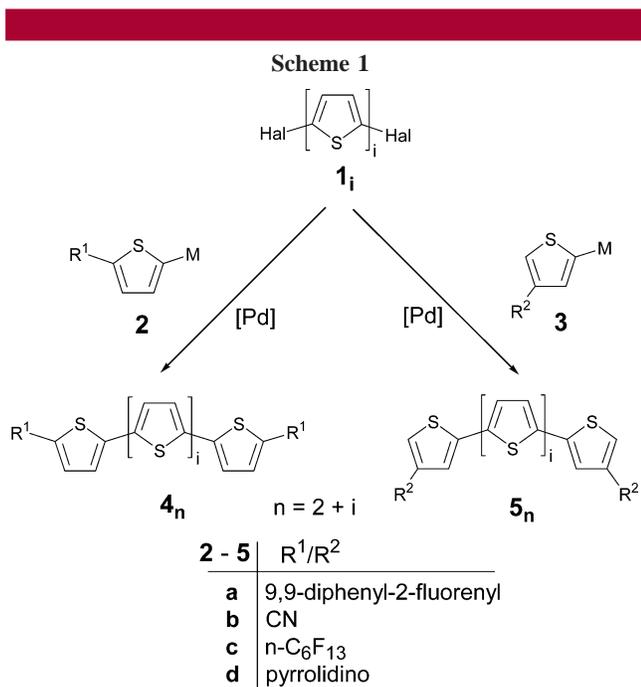
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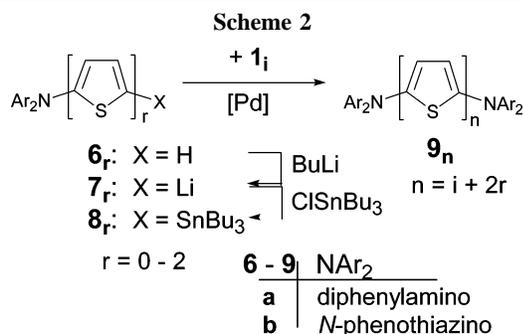
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dihalo compounds 1_i can be also used, as we present here, as starting compounds for higher homologues of this series, which are expected, similar to their lower homologues, to be of essential interest as hole transport materials.¹¹ As starting materials the 2-diarylamino-substituted thiophenes 6_1 and 5'-diarylamino-substituted 2,2'-bithiophenes 6_2 have been used. Whereas the 2-diarylaminothiophenes 6_1 were described in the literature and have been prepared either by a heavy-metal-catalyzed coupling reaction of diarylamines 6_0 with 2-bromothiophene¹² or by thermal decarboxylation of 2-diarylaminothiophene-5-carboxylic acids,¹³ the 5'-diarylamino-substituted 2,2'-bithiophenes 6_2 are unknown as yet. We have synthesized these compounds by a palladium-catalyzed coupling reaction of 2-bromothiophene with the stannylated 2-diarylaminothiophenes 8_1 , which were available from their parent 2-diarylaminothiophenes 6_1 via a metalation reaction with BuLi, subsequently followed by stannylation of the lithium compounds 7_1 primarily obtained by using tributylstannyl chloride. The stannylated thiophenes 8_1 and their homologues 8_2 , which were available by the same reaction sequence starting from the 5'-diarylamino-2,2'-bithiophenes 6_2 , can be coupled with 2,5-dibromothiophene



1_1 or 5,5'-dibromo-2,2'-bithiophene 1_2 (Hal = Br)¹⁴ to yield the higher homologues ($n > 2$) of the series 9_n . Thus, the compounds 9_3 and 9_4 have been prepared by a palladium-catalyzed coupling reaction of the stannylated 2-diarylaminothiophenes 8_1 with the dibromo compounds 1_1 or 1_2 , respectively. In analogy, the compounds 9_5 and 9_6 have been prepared by the same palladium-catalyzed coupling reaction of the stannylated compound 8_2 with the dibromo compounds 1_1 or 1_2 .

The resulting α,α' -diarylamino-capped oligothiophenes 9_n were isolated in 13–45% yields mostly and purified by chromatography at silica. Their measured spectroscopic and electrochemical data depend, as expected, on the number of their thiophene moieties. Thus, the electronic absorption properties of the compounds 9_{na} with $n = 1-6$ are well-correlated to the conjugation length, i.e., their absorption maxima are significantly red-shifted as the number n of their thiophene moieties increases (see Figure 1).

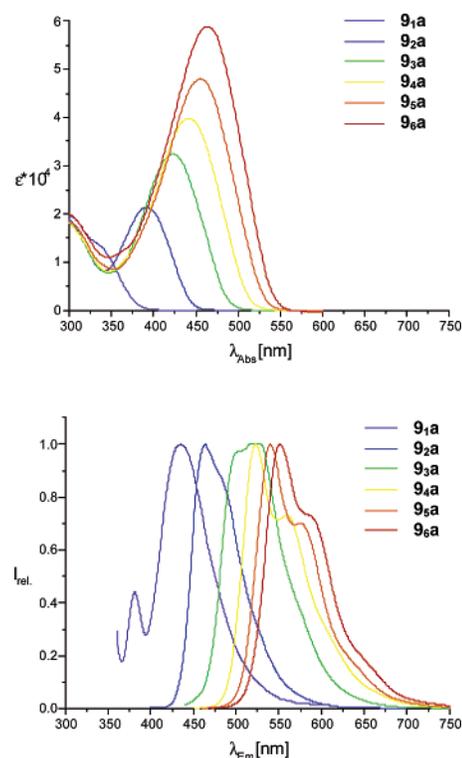


Figure 1. Absorption and emission spectra of α,α' -diphenylamino-capped oligothiophenes 9_{na} , measured in toluene

All prepared α,α' -diarylamino-capped oligothiophenes 9_n are fluorescent. The quantum yields of the fluorescence in

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Table 1. Data of Compounds 9_n

compd	yield (%)	T_m (°C)	T_g (°C)	T_r (°C)	λ_{abs}^a (log ϵ)	λ_{em}^a	Φ^b	λ_{em}^c	E_{ox}^1 [V] ^d (m) ^e	E_{ox}^2 [V] ^d (m) ^e	E_{ox}^3 [V] ^d (m) ^e	m/z
9_{1a}	45	149	38		342 (4.10)	435	0.1	447	-0.03 ^f (1)	+0.38 ^f (1)		419
9_{2a}	13	188	35	102	393 (4.33)	464	100	520	-0.01 ^f (1)	+0.12 ^f (1)		500
9_{3a}	33	181	49	104	423 (4.51)	505	7	563		+0.02 ^f (2)	+1.45 ^h (1)	582
9_{4a}	32	198	-	152	443 (4.60)	523	19	601		+0.05 ^g (2)	+0.99 ^g (1)	664
9_{5a}	17	80	40		455 (4.68)	540	21	629		+0.10 ^g (2)	+0.67 ^g (1)	746
9_{6a}	25	228		127	462 (4.77)	552	21	644		+0.13 ^f (2)	+0.57 ^f (1) ⁱ	829
9_{2b}	14	283		236	369 (3.80)	454	2	461				506
9_{3b}	33	213	68		378 (4.29)	488	5	573				642
9_{4b}	34	250	86	170	414 (4.53)	516	16	588				724

^a In nm, measured in toluene. ^b Measured relative to anthracene. ^c In nm, measured as solid. ^d Measured at a platinum electrode in benzonitrile containing tetrabutylammonium hexafluorophosphate, versus ferrocene/ferrocenium as internal standard, 100 mV/s scan rate. ^e Number of electrons transferred. ^f Reversible. ^g Quasireversible. ^h Irreversible. ⁱ Further irreversible one-electron half-waves at +0.85 and +1.06 V.

toluene range from 0.12% to 100%, and the fluorescence maxima are red-shifted with increasing number of n (Table 1). The fluorescence color can be tuned from light blue to bright green (Figure 1). Remarkably, the α,α' -diaryl-amino-capped oligothiophenes 9_n exhibit a strong emission also in their crystalline state, formed after their recrystallization from cyclohexane, and in their amorphous state obtained after cooling their smelts. The fluorescence maxima in the solid states are slightly red-shifted in comparison to the ones in toluene solution.

Cyclic voltammetry was used to study the electrochemical properties of the α,α' -diaryl-amino-capped oligothiophenes 9_n . These studies were focused on the diphenyl-amino-substituted compounds 9_na only. The results are given in Table 1. They demonstrate, that the oxidation potentials of the α,α' -diaryl-amino-capped oligothiophenes 9_na depend, as expected, on the number n of their thiophene rings, but not in a straightforward manner. Thus, the peak potentials of the first electron transfer increase with n while the other ones decrease.

By plotting the measured oxidation potentials of the compounds 9_na versus the reciprocal number n of thiophene rings linear correlations are obtained (see Figure 2). However, the slopes for the first and second electron transfer of the

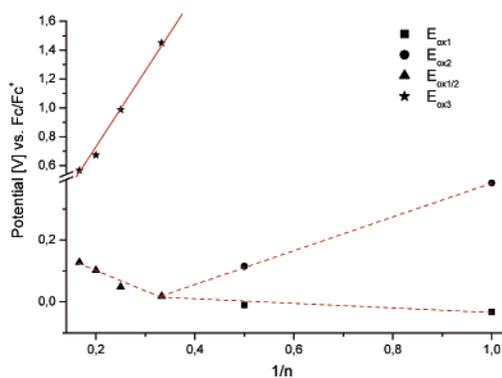


Figure 2. Dependence of the oxidation potentials of the α,α' -diaryl-amino-capped oligothiophenes 9_na on the reciprocal number of thiophene rings.

compounds 9_{1a} – 9_{3a} differ from each other and from the one of the compounds 9_{4a} – 9_{6a} . The first two oxidation potentials seem to fuse for the compound 9_{3a} .

In a similar manner, the character of the oxidation processes of the α,α' -diphenyl-amino-capped oligothiophenes 9_na is changed as n increases. Whereas the compounds 9_{1a} and 9_{2a} exhibit two reversible one-electron oxidation waves, each of their higher homologues exhibits a two-electron as well as a one-electron oxidation wave. This fact is documented in Table 1 and exemplified for the compounds 9_{1a} and 9_{3a} in Figure 3 in which the cyclic voltammograms are

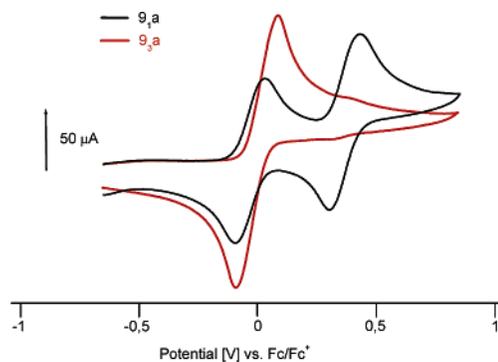


Figure 3. Cyclic voltammograms of compound 9_{1a} and 9_{3a} measured in benzonitrile (1×10^{-3} M), containing 0.1 M tetrabutylammonium hexafluorophosphate, with a scan rate of 100 mV/s.

depicted. They demonstrate that the compounds with lower n tend to donate one electron and the compounds with higher n ($n > 3$) tend to donate two electrons at their first half-wave oxidation potentials. It indicates that the dications of the higher homologues of the thiophenes 9_na are more stabilized than their monocationic radicals suggesting that the coulomb repulsion between the two electrons in the corresponding HOMO is diminished as the number of thiophene rings increases. Detailed studies to confirm this fact and enlighten on the mechanisms for these redox processes are underway and their results will be published in due course.

The thermal properties of the α,α' -diarylamino-capped oligothiophenes $\mathbf{9}_n$ were investigated by differential scanning calorimetry (DSC). All compounds were found to be stable up to 350 °C. As can be seen from Table 1, most of them are able to form amorphous glasses at room temperature after cooling. By repeated heating a distinct glass transition temperature (T_g) was observed for some compounds. These values and the recrystallization temperatures (T_r) found for some compounds are given in Table 1.

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Supporting Information Available: Experimental procedure for the α,α' -diarylamino-capped oligothiophenes \mathbf{C}_n and their NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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