ORGANIC LETTERS

2003
Vol. 5, No. 11
1817−1820

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

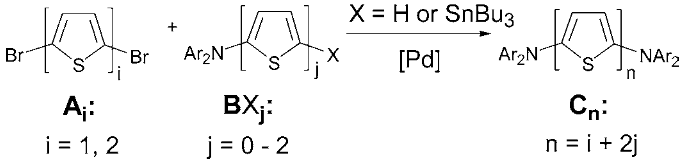
Ahcene Tabet, Anke Schröder, Horst Hartmann,* Dirk Rohde,† and Lothar Dunsch†

University of Applied Sciences, Geusaer Strasse, D-06217 Merseburg, Germany, and
IFW Dresden, Abtl. Elektrochemie und leitfähige Polymere, Dresden, Germany

horst.hartmann@cui.fh-merseburg.de

Received February 24, 2003

ABSTRACT



A series of α,α′-bisdiarylamino-capped oligothiophenes C_n were prepared by the palladium-catalyzed reaction of the dibromo compounds A_i with diarylamines, *N*,*N*-diarylamino-substituted thiophenes or 2,2′-bithiophenes BX_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 structures[1] 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 $\mathbf{4}_{\boldsymbol{n}}\mathbf{a}$[5] or electron-accepting cyano or perfluorohexyl groups $\mathbf{4}_{\boldsymbol{n}}\mathbf{b}$[6] and $\mathbf{4}_{\boldsymbol{n}}\mathbf{c}$,[7] respectively, have been prepared and studied recently. Moreover, oligothiophenes $\mathbf{5}_{\boldsymbol{n}}\mathbf{d}$ with pyrrolidino 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 **2** or **3** with 2,5-dihalothiophene $\mathbf{1}_1$ or 5,5′-dihalo-2,2′-bithiophene $\mathbf{1}_2$. The same 2,5-dihalo compounds $\mathbf{1}_{\boldsymbol{i}}$ have also been used as starting materials for the synthesis of the first two members of diarylamino-capped oligothiophenes of the general structure $\mathbf{9}_{\boldsymbol{n}}$ ($n = 1$ or 2)[9,10] if they were allowed to react with diarylamines. The 2,5-

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† IFW Dresden, Abtl. Elektrochemie und leitfähige Polymere.

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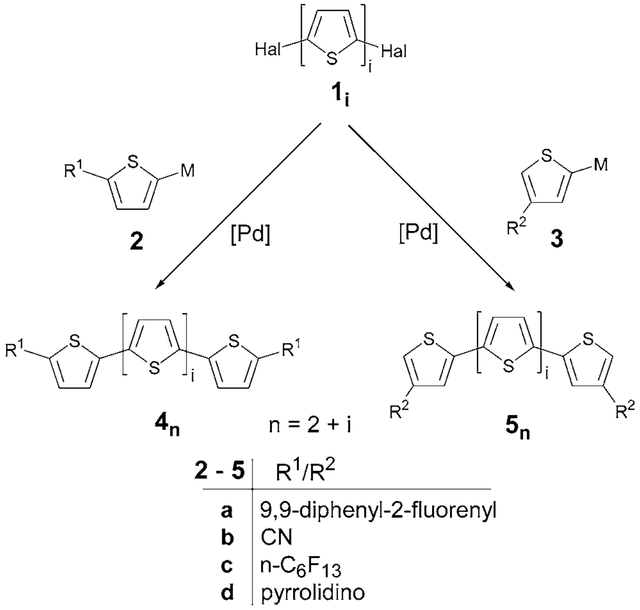
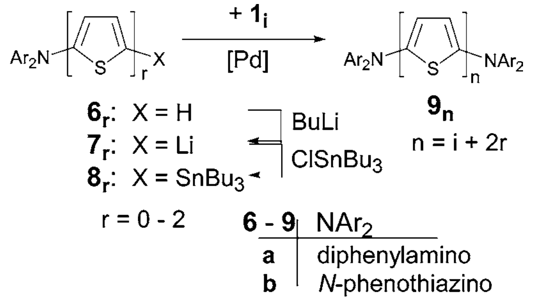
10.1021/ol034322u CCC: \$25.00

Scheme 1



dihalo compounds $\mathbf{1}_i$ 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 $\mathbf{6}_1$ and 5′-diarylamino-substituted 2,2′-bithiophenes $\mathbf{6}_2$ have been used. Whereas the 2-diarylaminothiophenes $\mathbf{6}_1$ were described in the literature and have been prepared either by a heavy-metal-catalyzed coupling reaction of diarylamines $\mathbf{6}_0$ with 2-bromothiophene[12] or by thermal decarboxylation of 2-diarylaminothiophene-5-carboxylic acids,[13] the 5′-diarylamino-substituted 2,2′-bithiophenes $\mathbf{6}_2$ are unknown as yet. We have synthesized these compounds by a palladium-catalyzed coupling reaction of 2-bromothiophene with the stannylated 2-diarylaminothiophenes $\mathbf{8}_1$, which were available from their parent 2-diarylaminothiophenes $\mathbf{6}_1$ via a metalation reaction with BuLi, subsequently followed by stannylation of the lithium compounds $\mathbf{7}_1$ primarily obtained by using tributylstannyl chloride.The stannylated thiophenes $\mathbf{8}_1$ and their homologues $\mathbf{8}_2$, which were available by the same reaction sequence starting from the 5′-diarylamino-2,2′-bithiophenes $\mathbf{6}_2$, can be coupled with 2,5-dibromothiophene $\mathbf{1}_1$ or 5,5′-dibromo-2,2′-bithiophene $\mathbf{1}_2$ (Hal = Br)[14] to yield the higher homologues ($n > 2$) of the series $\mathbf{9}_n$. Thus, the compounds $\mathbf{9}_3$ and $\mathbf{9}_4$ have been prepared by a palladium-catalyzed coupling reaction of the stannylated 2-diarylaminothiophenes $\mathbf{8}_1$ with the dibromo compounds $\mathbf{1}_1$ or $\mathbf{1}_2$, respectively. In analogy, the compounds $\mathbf{9}_5$ and $\mathbf{9}_6$ have been prepared by the same palladium-catalyzed coupling reaction of the stannylated compound $\mathbf{8}_2$ with the dibromo compounds $\mathbf{1}_1$ or $\mathbf{1}_2$.

Scheme 2



The resulting α,α′-diarylamino-capped oligohiophenes $\mathbf{9}_n$ 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 $\mathbf{9}_n\mathbf{a}$ 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).

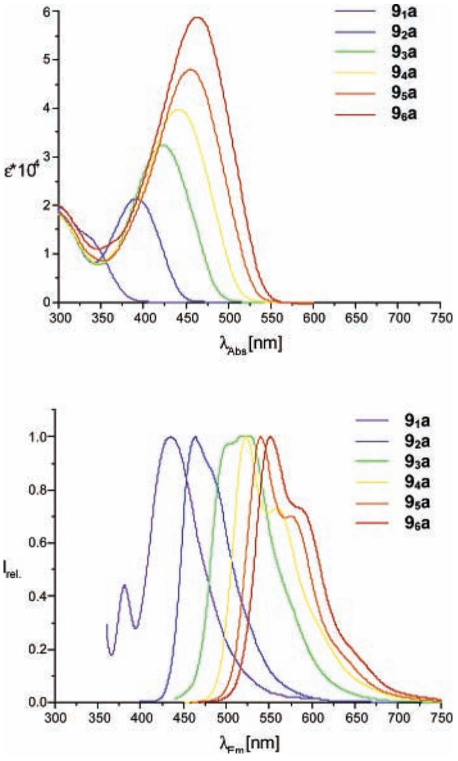


Figure 1. Absorption and emission spectra of α,α′-diphenylamino-capped oligothiophenes $\mathbf{9}_n\mathbf{a}$, measured in toluene

All prepared α,α′-diarylamino-capped oligohiophenes $\mathbf{9}_n$ are fluorescent. The quantum yields of the fluorescence in

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Table 1. Data of Compounds $\mathbf{9}_n$

compd	yield (%)	T_m (°C)	T_g (°C)	T_r (°C)	$\lambda_{abs}{}^a$ (log ϵ)	$\lambda_{em}{}^a$	Φ^b	$\lambda_{em}{}^c$	$E_{ox}{}^1$ [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 platinium 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′-diarylamino-capped oligohiophenes $\mathbf{9}_n$ 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′-diarylamino-capped oligothiophenes $\mathbf{9}_n$. These studies were focused on the diphenylamino-substituted compounds $\mathbf{9}_n\mathbf{a}$ only. The results are given in Table 1. They demonstrate, that the oxidation potentials of the α,α′-diarylamino-capped oligothiophenes $\mathbf{9}_n\mathbf{a}$ 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 $\mathbf{9}_n\mathbf{a}$ 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 compounds $\mathbf{9}_1\mathbf{a}$−$\mathbf{9}_3\mathbf{a}$ differ from each other and from the one of the compounds $\mathbf{9}_4\mathbf{a}$−$\mathbf{9}_6\mathbf{a}$. The first two oxidation potentials seem to fuse for the compound $\mathbf{9}_3\mathbf{a}$.

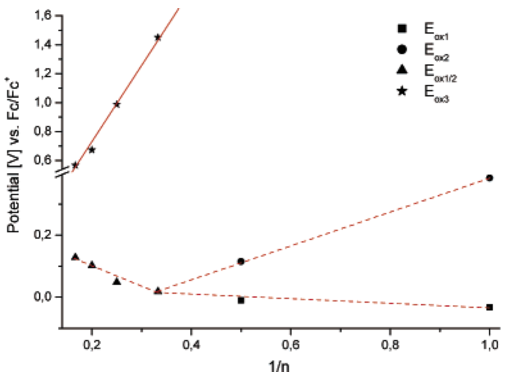

Figure 2. Dependence of the oxidation potentials of the α,α′-diarylamino-capped oligothiophenes $\mathbf{9}_n\mathbf{a}$ on the reciprocal number of thiophene rings.

In a similar manner, the character of the oxidation processes of the α,α′-diphenylamino-capped oligothiophenes $\mathbf{9}_n\mathbf{a}$ is changed as *n* increases. Whereas the compounds $\mathbf{9}_1\mathbf{a}$ and $\mathbf{9}_2\mathbf{a}$ 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 $\mathbf{9}_1\mathbf{a}$ and $\mathbf{9}_3\mathbf{a}$ in Figure 3 in which the cyclic voltammograms are 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 $\mathbf{9}_n\mathbf{a}$ 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.

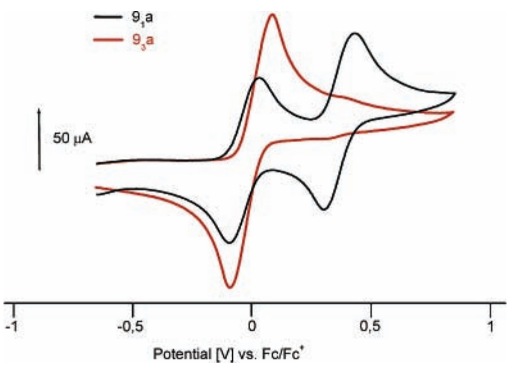

Figure 3. Cyclic voltammograms of compound $\mathbf{9}_1\mathbf{a}$ and $\mathbf{9}_3\mathbf{a}$ measured in benzonitrile (1×10^{-3} M), containing 0.1 m tetrabutylammonium hexafluorophosphate, with a scan rate of 100 mV/s.

The thermal properties of the α,α′-diarylamino-capped oligohiophenes **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.

Acknowledgment. The authors thank the Deutsche Forschungsgemeinschaft for financial support.

Supporting Information Available: Experimental procedure for the α,α′-diarylamino-capped oligothiophenes **C_n** and their NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL034322U