

Tetrathiapentalenes: chemical and electrochemical polymerization

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RÉSUMÉ

La polymérisation des 1,3,4,6-tétrathiapentalènes **1a** (R = phényle) et **1b** (R = thiényle) par voie (électro)chimique a conduit aux polymères **6a** et **6b**. Les conductivités électriques mesurées de ces matériaux sont $\sigma_{RT} = 5 \cdot 10^{-3} - 5 \cdot 10^{-1}$ S/cm.

mots-clés: Tétrathiapentalène, polymère conducteur, voltammétrie cyclique.

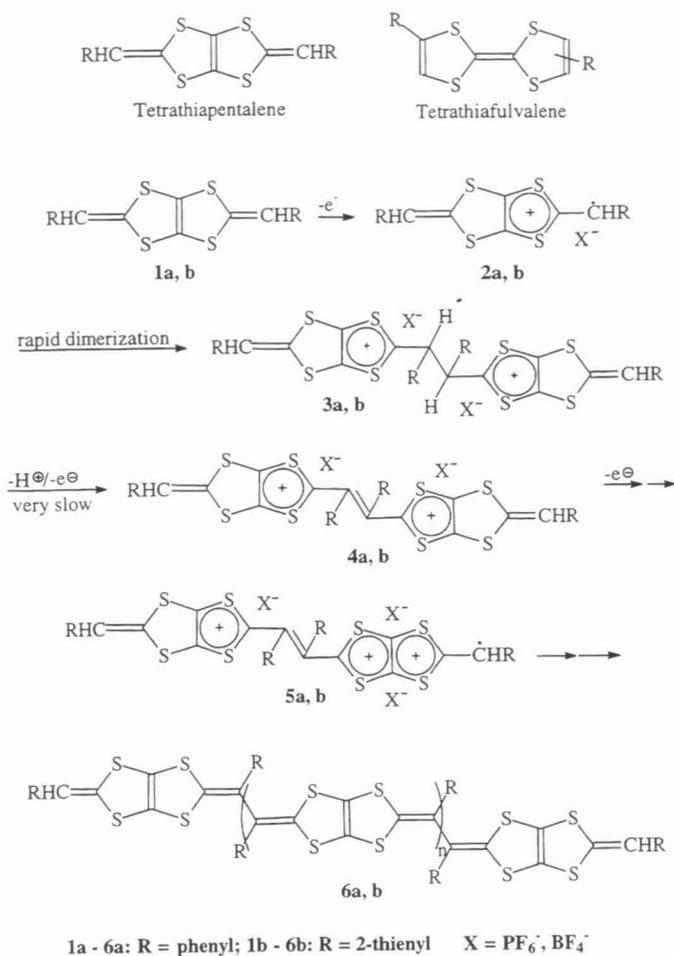
ABSTRACT

The (electro)chemical polymerization of 1,3,4,6-tetrathiapentalenes **1a** (R = phenyl) and **1b** (R = thienyl) gave the polymeric compounds **6a** and **b**. The electrical conductivities of these materials amount to $\sigma_{RT} = 5 \cdot 10^{-3} - 5 \cdot 10^{-1}$ S/cm.

key words: Tetrathiapentalene, conducting polymer, cyclic voltammetry.

Bis-substituted 1,3,4,6-tetrathiapentalenes (TTP) **1a**, **b** represent a new class of sulphur heterocycles and are isomers of the corresponding tetrathiafulvalenes (TTF) (cf Scheme). TTF-based donors form highly stable radical cations [1], whereas TTP-derivatives give rise to very short-lived radical cations upon oxidation which are supposed to rapidly (dehydro)dimerize to the tetrathiafulvalene derivatives **4a**, **b** (**3a**, **b**). These dicationic intermediates can further be oxidized at higher potentials to the highly reactive radical trications **5a**, **b** which can then undergo another radical cation-radical cation coupling reaction to give the tetrameric molecules **6a** and **6b** (n = 2); further repetitions yield eventually the oligomeric/polymeric derivatives **6a** and **6b** (n > 2).

Thus, owing to their bifunctional character, TTP-derivatives [2] are important monomeric precursors to the stepwise construction of oligo- and polymeric tetrathiafulvalenes, such as those illustrated by general formula **6** in Scheme 1.



Scheme 1: Redox behaviour of tetrathiapentalenes

Here we report on the synthesis and properties of the polymers **6a** and **6b**, obtained by (electro)chemical polymerization of the monomers **1a** and **1b** (cf Scheme 1).

Typical multisweep cyclic voltammograms (CV) of **1a** and **1b** are presented in Figure 1. The first (innermost) scans of both CV's show two successive, irreversible redox waves, respectively. The first oxidation waves correspond to the formation of the monoradical cations **2a** and **2b**, respectively, whereas the second, broad waves involve several electron transfer processes, as shown by coulometry. For **1a**, a new signal appears with the second cycle cathodic to the initial first oxidation wave, indicative of the formation of the dimer **3a** (or **4a**), and eventually of the polymer **6a**.

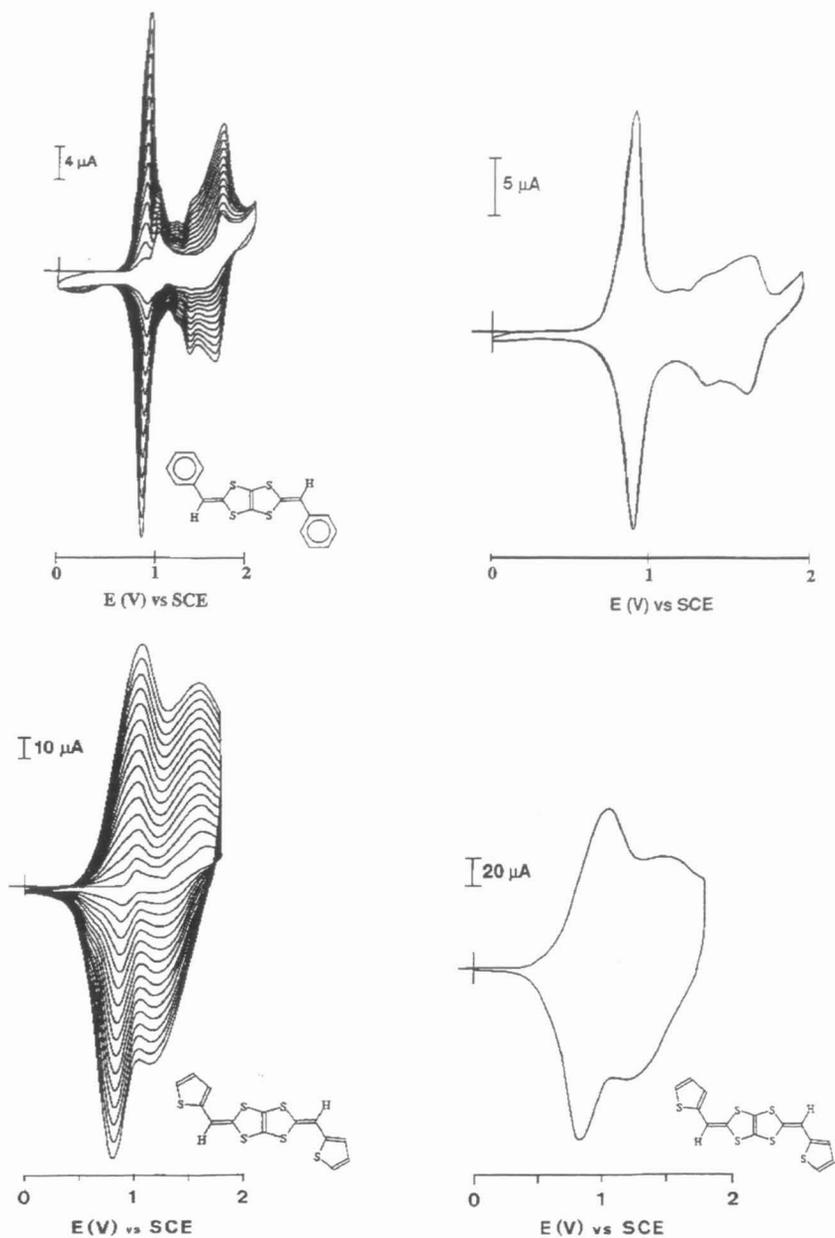


Figure 1: Multisweep cyclic voltammograms of **1a**, **b** ($v = 100$ mV/s, substrat $5 \cdot 10^{-4}$ M, 0.1 M $n\text{-Bu}_4\text{NPF}_6$, Pt-electrodes) (left) and of electropolymerized films of **6a**, **b** in a monomer-free solution ($v = 100$ mV/s, 0.1 M $n\text{-Bu}_4\text{NPF}_6$, Pt-electrode)(right).

For **1b**, no such behaviour could be observed, instead the peak potential of the first oxidation wave shifts to less anodic values as consequence of continued cycling, pointing to the adsorption of an electroactive species on the electrode. Oxidized, black, freestanding films of **6a** and **6b** could indeed be obtained by anodic potential cycling which corroborates the interpretation of the CV's as well as the *formal* oligo-/polymerization mechanism outlined in Scheme 1. CV's of polymeric films deposited on Pt-electrodes in monomer-free solution are displayed in Figure 1. The strikingly different electrochemical behaviour of **1a** and **1b** could be due to the presence of the electroactive thienyl-rings in the latter, however, this aspect requires further clarification.

Table 1: Electrical conductivities and ESR data of polymers **6a** and **6b**.

Polymer	Polymerization	σ_{RT} [S/cm] [*]	ESR ΔH [G]/g
6a [†]	potentiodynamic	$5 \cdot 10^{-3}$	6.0/2.0077
” [‡]	NOBF ₄	$< 10^{-6**}$	4.6/2.0065
6b [†]	potentiodynamic	$4 \cdot 10^{-2} - 5 \cdot 10^{-1}$	5.2/2.0064
” [‡]	NOBF ₄	$3.7 \cdot 10^{-3**}$	9.6/2.0062

*four probe measurements. ** measured on compaction samples. [†]Film. [‡]Powder.

Oxidation of **1a, b** with NOBF₄ gave black powders which were compacted for four-probe conductivity measurements. The electrical conductivities of electropolymerized films of **6a** amount to values of around $5 \cdot 10^{-3}$ S/cm, values obtained on powder samples are much lower. In the case of **6b**, conductivities of films range from $5 \cdot 10^{-2}$ to $5 \cdot 10^{-1}$ S/cm, whereas the conductivity of compaction samples is around 10^{-3} S/cm. A comparison of ESR data obtained on electrochemically synthesized films and powders obtained by oxidation with nitrosonium tetrafluoroborate yielded for both cases linewidths approximately half as broad for the films than for powder samples. In view of the non-negligible anisotropy of the obtained materials, orientation effects could account for this observation. Conductivities and ESR data are summarized in Table 1.

In conclusion, the electrochemical behaviour of disubstituted tetrathiapentalenes **1a** and **1b** has been investigated. It was found that both compounds can indeed be polymerized, either by potential cycling or by oxidation with NOBF₄, giving rise to new, polymeric, electrically conducting solids.

REFERENCES

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