Poly[(dibenzylidene)tetrathiapentalene]—the first linearly extended TTF polymer

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The preparation of the first π-conjugated TTF polymer composed entirely of vinylogous, linearly fused TTF moieties has been achieved by oxidative polymerization of 2,5-di(benzylidene)-1,3,4,6-tetrathiapentalene.

Numerous attempts to incorporate TTF into polymeric backbones have been spurred by the exciting solid state properties of TTF molecular conductors and aimed at a combination of the electrical conductivity exhibited by these radical cation salts with the enhanced processability of a polymer matrix.[1] The TTF polymers reported to date consist of essentially independent TTF entities attached to a conjugated polymer backbone or of linear chains composed of segregated TTF units linked through spacer groups *via* σ or π bonds.[1] In spite of the well-known tendency of TTF to form ordered stacks,[2] the interactions between individual TTF units in polymeric matrices are difficult to control in the solid state. Insufficient through-bond and through-space interactions as a consequence of lacking conjugation and structural disorder in TTF polymers may result in low conductivities in the oxidized state.[1]

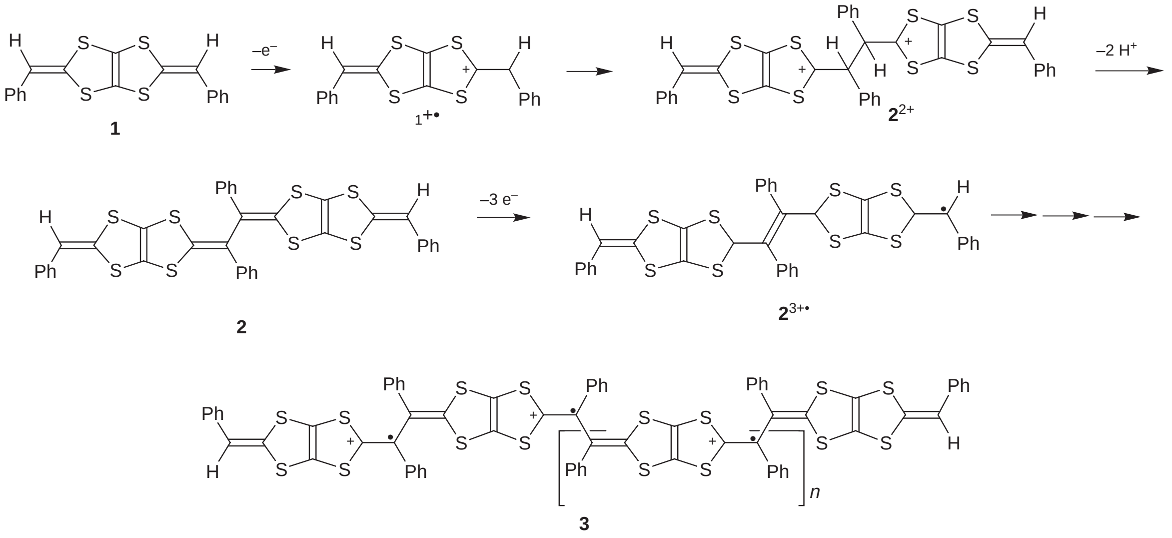
Macromolecular structures composed of fully π-conjugated TTF units could possibly offer an interesting alternative to overcome these inherent drawbacks.[1*f*,*g*,3] Linearly annelated TTF entities appear to be particularly promising in that respect, since the radical cation salts of many dimeric, linearly fused TTF derivatives exhibit metallic conductivity.[4] Despite the exceptional solid state properties of molecular conductors based on dimeric TTF donor molecules, the preparation of polymeric analogues has not yet been reported.

Recently, we have disclosed a novel synthetic approach to vinylogous, extended TTF derivatives starting from tetrathiapentalenes as precursors.[5] Here we report the application of this method to the preparation of poly[(dibenzylidene)tetrathiapentalene] (**3**; PDB-TTP), the first conducting polymeric TTF derivative composed entirely of π-conjugated, linearly annelated TTF units.

The synthetic concept is based on the transformation of the tetrathiapentalene (TTP) precursor **1** into the corresponding bifunctional TTF derivative **2**.[5] Owing to its hybrid TTP/TTF character, compound **2** can undergo oligo- and polymerization reactions *via* radical intermediates, a behaviour which contrasts sharply with that commonly known for TTF vinylogues.[6] Suitable substituents, such as the phenyl rings of **1**, enhance the solubility of the monomer and prevent the growing TTF chain from precipitation and thus from an early termination of the polymerization reaction.

The key step of the oxidative polymerization involves the formation of the highly reactive radical $\mathbf{1}^{+\cdot}$ from 2,5-di(benzylidene)-1,3,4,6-tetrathiapentalene (**1**; DB-TTP), which dimerizes with subsequent dehydrogenation to the TTF derivative **2**.[5] The isolation of the stable intermediate **2** confirms that radica–radical coupling of $\mathbf{1}^{+\cdot}$ occurs *via* the benzylic carbon atoms and thus resembles closely the well-known oxidative dimerization of 1,4-dithiafulvenes to vinylogous TTF derivatives.[7] Contrary to ordinary TTF derivatives, however, **2** can be oxidized to the radical trication $\mathbf{2}^{3+\cdot}$ which through subsequent radical dehydrodimerization and oxidation steps, eventually yields a polymer of general formula **3**. The proposed polymerization mechanism is depicted in Scheme 1 and was established by detailed electrochemical investigations performed on **1** and independently synthesized **2**.[8]

Thin films of **3** were prepared on Pt disk electrodes in anhydrous dichloromethane by repeated potential cycling between 0 and + 1.6 V (**1**: 4 10^{-4} M; $\mathrm{Bu^n{}_4NPF_6}$ 0.1M; $\mathrm{CH_2Cl_2}$;



Scheme 1 Redox polymerization of monomer **1**. The counterions have been omitted for clarity, the polymer **3** is shown in a partially oxidized state. For an estimate of *n* see text.

Pt disc electrode ∅ 3 mm; $v = 100$ mV s^{-1}; 500 cycles) or by potentiostatic electrolysis at + 1.6 V [all potential values *versus* a saturated calomel electrode (SCE)].† The cyclic voltammogram of **1**, recorded during film synthesis, exhibited two irreversible waves (anodic peak potentials *ca.* + 0.8 and + 1.4 V) for the first sweep. Further scans showed the evolution of a new symmetrical redox wave at a less anodic potential (*ca.* + 0.6 V) indicating the formation of a new electroactive species. The peak currents of the latter increased continuously with each subsequent scan thus evidencing progressive deposit growth on the electrode surface.

The electrochemical response of a PDB-TTP film in monomer-free solution. The CV involves a sharp redox wave at a peak potential of *ca.* + 600 mV as well as several coalescing signals between + 900 and + 1500 mV, respectively. For simplicity, the latter will be considered as a single redox wave only. The amounts of charge transferred between 0 to + 700 mV and between + 700 to + 1500 mV are equal, as follows from an integration of the respective peak areas. The symmetrical signal shapes are characteristic of a surface-immobilized reversible redox system and hence in line with the postulated structure **3**.[9]

Results obtained by *in situ* EPR spectro-electrochemistry indicate that each peak potential coincides with a local maximum of the potential-dependent spin density. The relative ratio of the spin populations corresponding to the peak potentials of the first and second redox couple, respectively, is *ca.* 2 : 1. This value, together with the coulometric analysis of the peak areas makes plausible an assignment of the first redox couple to a partial oxidation state **3**, where a linearly extended chain bears one positive charge per vinylogous TTF unit. The removal of further electrons requires the unfavourable localization of positive charges on adjacent dithiole units and occurs in several steps between + 900 and + 1500 mV, where complete oxidation is reached. The resulting increase of the coulombic repulsion shifts the corresponding oxidation potentials towards higher values, simultaneously the number of charge carriers decreases as a consequence of spin recombination.

Continued potential cycling (500 cycles) of films in monomer-free solution between 0 and + 750 mV did not cause any loss in electroactivity, thus demonstrating high stability and pronounced electrochemical reversibility. A switching potential of + 1700 mV reduced the electroactivity by about 50% after 50 scans, presumably as a consequence of overoxidation.

Treatment of **1** with NOPF$_6$ (molar ratio 1 : 1.5) furnished the black, insoluble solid **3** in a yield of 80%, the analytical data of which are in good agreement with the partially oxidized structure **3** containing one counterion per repetitive unit.‡

MALDI-TOF and FAB MS of solid **3** gave intense peaks corresponding to the general formula $m/z = n\,(354)$ with $z = 1$. Fragments with $m/z = 2412$ ($n = 6$), 1416 ($n = 4$) and 1062 ($n = 3$) can unambiguously be assigned to structural elements comprising six, four and three monomer units, respectively. These results provide strong evidence for the presence of a linearly extended structure **3**, since the polymerization of **1** ($m/z = 356$) implies the formal abstraction of two hydrogen atoms per monomer unit within a chain, whereas the two terminal units loose only one hydrogen atom. The lower limit for the average molecular weight of **3** (without counterions) can thus be estimated to amount to at least eight monomer units, corresponding to a molecular weight of 2836 g mol^{-1}. TTF polymers comprising eight monomer units have been described in previous work.[10]

IR spectra of solid **3** exhibit a weak electronic absorption stretching from 3700 to *ca.* 1750 cm^{-1}, a behaviour typical of a semiconductor. Assuming a simple transition between the valence and the conduction band, the corresponding band gap amounts to a value of 217 meV. Intense bands at 1357 and 1248 cm^{-1} closely resemble features characteristic of TTF radical cation salts,[11] and thus corroborate the charged TTF structure **3**. Absorptions at 838 and 557 cm^{-1} confirm the presence of the hexafluorophosphate counterion. EPR spectra of compound **3** display a single, symmetrical line with a width of 6–8 G. The averaged g-factor is 2.0077, the spin density is *ca.* 2×10^{23} spins mol^{-1}. The electrical conductivity, as determined by four-probe measurements on compact samples of **3**, gave values of about 10^{-6} S cm^{-1}. For electrochemically deposited films the conductivities range from 5×10^{-3} to 5×10^{-4} S cm^{-1}. The latter values are among the highest reported to date for polymeric TTF derivatives.[1]

A typical small angle X-ray scattering (SAXS) pattern of compound **3** shows a diffuse scattering background with a sharp superimposed peak at $\boldsymbol{s} = 0.44$ nm^{-1} and a large bump stretching from 0.6 nm^{-1} $\leqslant \boldsymbol{s} \leqslant$ 1.4 nm^{-1} where s is the modulus of the scattering vector. The observed feature is typical of a partially crystalline polymer comprising an ordered, crystalline phase randomly distributed in an amorphous matrix.[12] The single Bragg peak at $\boldsymbol{s} = 0.44$ nm^{-1} indicates the presence of a crystalline phase with a d-spacing of 22.6 Å. The large bump of the intensity curve originates from the scattering contribution of both amorphous and crystalline phases. Wide-angle X-ray scattering (WAXS) data show essentially a considerable amorphous background with a few superimposed diffraction peaks in the range $2° \leqslant 2\Theta \leqslant 25°$ and hence support the macromolecular character of **3**.

In conclusion we have presented the synthesis of the first TTF main-chain polymer composed entirely of linearly fused TTF units starting from a tetrathiapentalene precursor. The synthetic approach is unique in its simplicity and contrasts the multistep procedures described in previous work.[1] Attempts to extend the scope of the synthetic approach and to tailor important polymer properties, such as solubility and conductivity by varying the substituents of the monomeric precursors are currently being investigated and will be presented in due course.

Notes and references

† The redox-potential of the ferrocene/ferrocenium couple under the conditions used is to +0.46 V *vs.* SCE.

‡ Compound **3**, black solid (from CH$_3$CN), mp (decomp.) > 200 °C. Anal: found C, 43.47, H, 2.30. C$_{18}$H$_{10}$S$_4$PF$_6$ requires C, 43.28, H, 2.02%.

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