

Synthesis and electrochemical properties of new star-shaped thiophene oligomers and their polymers

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The efficient synthesis of some 2,4,6-tris[5-(2,2'-bithienyl)]-1,3,5-triazines and 1,3,5-tris[5-(2,2'-bithienyl)]benzenes and their electrochemical properties are discussed.

Branched conducting polymers with electronically connected nodes are excellent candidates among the family of super-structured conducting polymers. In fact, with such polymers, there should be no need for interchain coupling or interchain electronic transfer in order to insure high electronic conductivity.¹ Moreover, this type of material possesses a three dimensional structure which could also assist the conductivity.

There are few previous reports of this type of conducting polymer because the starting precursors are difficult to synthesise. Previous approaches² were made to reticulated conducting polymers, but electronic conjugation was only weakly, or not at all, insured through the nodes. Also, star-shaped oligomers were used but in low proportions to prepare polythiophene gels which were no longer soluble in classical solvents and had high degrees of swelling.³

Here we present an efficient method for the synthesis of some 2,4,6-tris[5-(2,2'-bithienyl)]-1,3,5-triazine or 1,3,5-tris[5-(2,2'-bithienyl)]benzene derivatives which are precursor of two-dimensional conducting polymers. Their electrochemical properties have been investigated. A new polymer has been synthesised *via* chemical or electrochemical oxidation of 1,3,5-tris[5-(2,2'-bithienyl)]benzene and the charge transfer kinetics inside has been determined by chronoamperometry experiments.

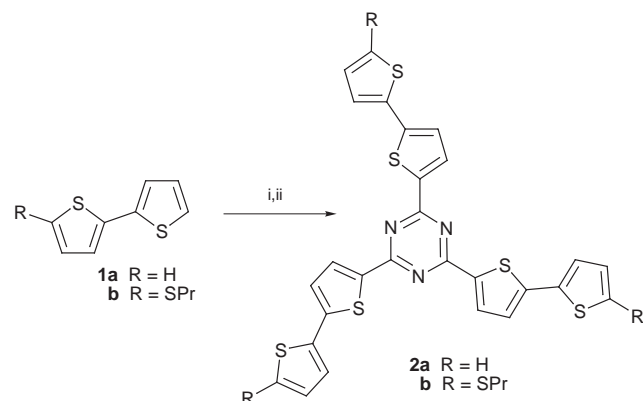
The 2,4,6-tris[5-(2,2'-bithienyl)]-1,3,5-triazine derivatives **2** were obtained by a triple aromatic nucleophilic substitution of 2,2'-dithienyllithium salts on cyanuric chloride (see Scheme 1). This reaction is very efficient⁴ because such substitutions are activated by the mesomer attractive power of the nitrogen atoms, which stabilises the intermediate species. So, 3 equiv. of 2,2'-dithienyllithium salt were added in one portion to 1 equiv. of cyanuric chloride in THF. The crude products were purified by column chromatography with light petroleum-CH₂Cl₂ (1 : 1)

as eluent. Only the tri-substituted products **2**§ were formed with yields close to 90% (**2a**: 95%, **2b**: 90%).

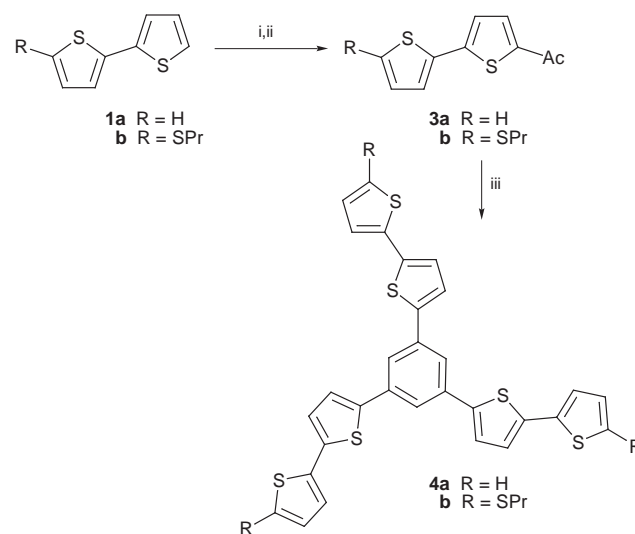
However, the tris(2,2'-bithienyl)benzene derivatives **4** were synthesised *via* an another route, as aromatic nucleophilic substitution on an inactivated benzene is very difficult. Moreover, there is only one report in the literature of 1,3,5-trisubstitution on a tri-substituted benzene.⁵ Therefore, we adapted a recently described procedure based on a triple ketolisation and dehydration of an aromatic methyl ketone with tetrachlorosilane (TCS)-EtOH.⁶ However, this method was developed to afford β -methylchalcone stereoselectively, without polymer formation. The authors obtained some 1,3,5-triarylbenzene derivatives as side products. We modified this reaction so that the major products were the 1,3,5-triarylbenzene derivatives. This was achieved using 5 rather than 1 equiv. of TCS, and increasing the reaction time from the 2–4 h given in the original paper to 18 h. Thus the more general character of this method is demonstrated.

The 5-(2,2'-bithienyl) methyl ketone **3** is made *via* the action of 2,2'-dithienyllithium salts on *N,N*-dimethylacetanilide (see Scheme 2). TCS-EtOH (5 equiv.) was added to 5-(2,2'-bithienyl) methyl ketone in anhydrous toluene under nitrogen atmosphere. The mixture was stirring of 18 h at room temperature (see Scheme 2). It was then poured in water, extracted with CH₂Cl₂, and the organic phase was separated, dried, and the solvent removed under reduced pressure. The residue was purified by column chromatography with light petroleum-CH₂Cl₂ (1:1) as eluent. The pure products **4**§ were obtained with good yield (**4a**: 65%, **4b**: 55%).

All the thiophene oligomers described are electrochemically oxidizable. In the cases of the oligomers **2a** and **4a** (with unblocked α -positions), entirely irreversible voltamograms are obtained whatever the scan rate up to 1000 V s⁻¹ (peak



Scheme 1 Reagents and conditions: i, BuⁿLi; ii, 2,4,6-trichloro-1,3,5-triazine



Scheme 2 Reagents and conditions: i, BuⁿLi; ii, DMA; iii, TCS, EtOH, 18 h, room temp.

potentials at 1 V s^{-1} are 1.41 and 1.02 V vs. SCE for **2a** and **4a**, respectively). This demonstrates the very high reactivity of the electrogenerated cation radicals despite the presence of seven aromatic rings. On the other hand, as expected with oligomers **2b** (oxidation peak potential 1.27 V vs. SCE at 1 V s^{-1}) and **4b** [redox potentiel E° (half sum of reversible peaks in CH_2Cl_2) of 1.00 V vs. SCE is obtained], a return peak is obtained in all cases. As a consequence of the presence of the propylthio group blocking the α -positions, the cation radicals cannot undergo either coupling nor nucleophilic attack due to the steric hindrance of the substituents. It is possible to obtain a standard reversible voltamogram with the benzenic derivative **4b** in CH_2Cl_2 . However, in the case of the triazine **2b**, the return peak always features the oxidation of an adsorbed species whatever the solvent, showing that the propyl chains on sulfur are not sufficient in this case to insure sufficient solubility of the electrogenerated cation radical. Similarly in MeCN the cation radical of **4b** also precipitates. The irreversible dication formation is also observable at potentials of 2.13 and 1.97 V vs. SCE for **2b** and **4b**, respectively.

Upon oxidation of **2a**, no polymer formation was observed whatever the conditions, therefore probably the cation radicals favour nucleophilic attack on the s-triazine nitrogen atoms to coupling. Conversely the oxidation of **4a** gives an electro-deposited polymer, which displays electroactive characteristics analogous to polythiophene, with a broad reversible peak at an average potential of 0.9 V vs. SCE. Chronoamperometry was performed on average thickness films (300 nm) and the diffusion coefficient of the charge transfer is equal to $2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (on the basis of one electron for every four thiophene units and a density of 1.5 g cm^{-3}) which is in accordance with values obtained with other conducting polymers.⁷ Owing to the ease of the monomer synthesis, larger quantities of polymer can

be made by chemical polymerisation with iron(III) chloride. The electrochemical behaviour of the blocked oligomers, especially π -dimer formation, is also being studied.

Notes and References

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§ HRMS analysis **2a**: $M^+ = 573$, **2b**: $M^+ = 795$, **4a**: $M^+ = 570$, **4b**: $M^+ = 792$. All NMR data are in agreement with the proposed structures.

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