

Electroactive dendritic π -conjugated oligothiénylenevinylenes

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Electroactive π -conjugated oligothiénylenevinylenes end-capped with dendritic branches of generation one to three have been synthesized.

Thienylenevinylene oligomers (n TVs) have recently emerged as a new class of extensively π -conjugated systems.¹ Whereas at a molecular level n TVs are interesting models of molecular wires, they also open interesting potentialities as advanced materials for electronic and photonic applications. Progress in these areas implies a supramolecular control of interchain interactions in order to develop at will either compact materials with high electron mobility or, in contrast, single molecular wires.

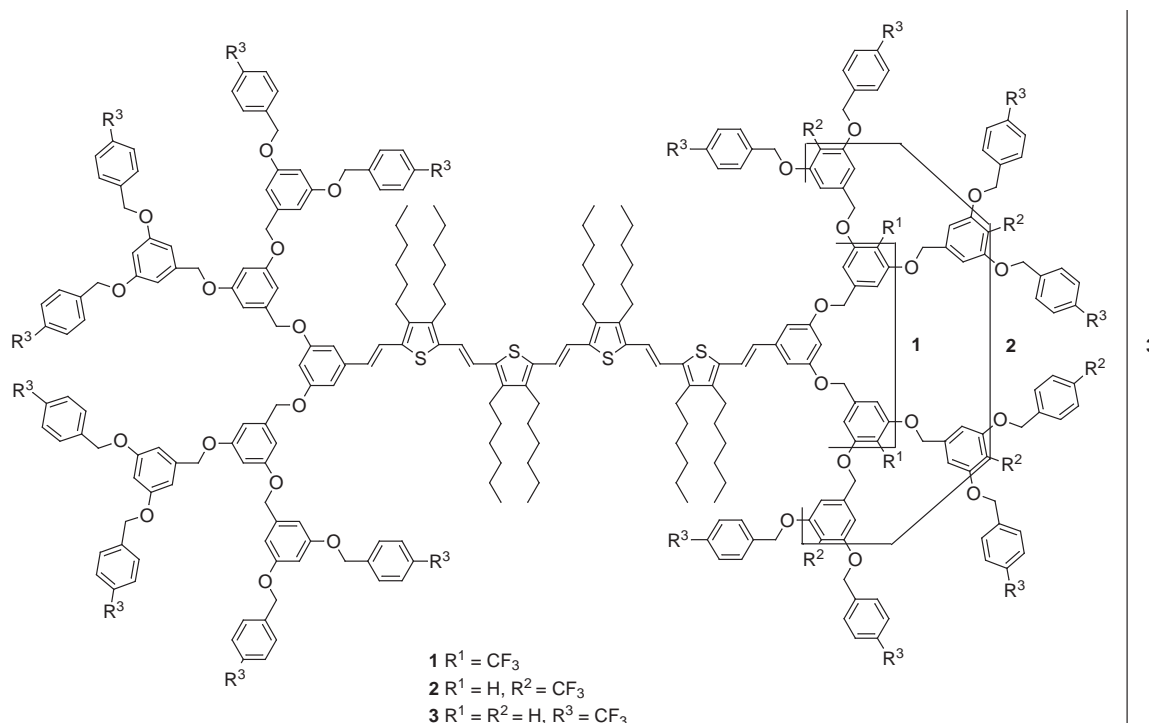
We report here the synthesis of monodisperse electroactive n TVs end-capped with dendritic chains² and preliminary results on their electrochemical behavior. Previous examples of incorporation of linear π -conjugated systems within dendritic structures involved dendrimers with poly(*p*-phenylene)³ and oligotriacetylenes⁴ cores.

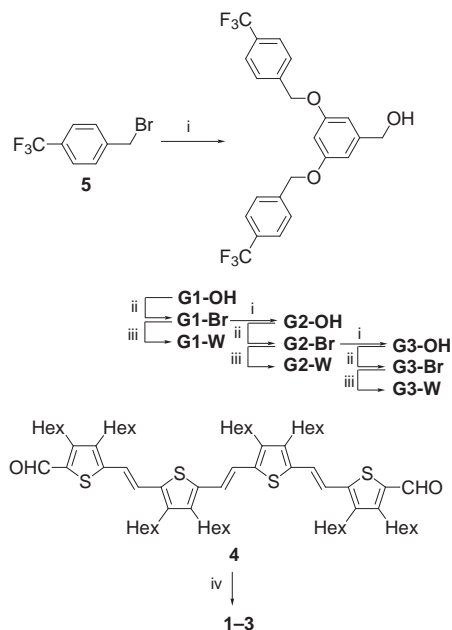
In order to analyze the effect of progressive steric shielding of the n TV system, Fréchet type dendrons⁵ of generation 1, 2 and 3 have been attached at both ends of a tetrathiénylenevinylene (4TV) derived from 3,4-dihexylthiophene to afford the target compounds **1–3**. While the construction of dendrons from 1-trifluoromethyl-4-bromomethylbenzene **5** is based on the Fréchet type convergent approach,⁵ the originality of our strategy lies in the conversion of each generation of dendron into a phosphonate (**Gn-W**) with final assembly of the target system *via* a two-fold Wittig–Horner olefination of dialdehyde **4** with phosphonates **G1-W**, **G2-W** and **G3-W** (Scheme 1).

Reaction between **5** and 3,5-dihydroxybenzyl alcohol in the presence of K_2CO_3 and 18-crown-6 afforded the benzylic alcohol of the first generation (**G1-OH**) which was then converted into the bromomethyl derivative (**G1-Br**) by reaction with PBr_3 . Repetition of the procedure followed by recrystallization at each step gave successively **G2-Br** and **G3-Br** in high yields. Reaction of **G1-Br** and **G2-Br** with diethyl phosphite in the presence of NaH led to phosphonates **G1-W** and **G2-W** while **G3-W** was prepared by reaction of **G3-Br** with phosphite (yields $\geq 90\%$). Compounds **1–3** were obtained in 50–60% yield by double Wittig–Horner olefination of dialdehyde **4** with phosphonates **Gn-W**. The target compounds were fully characterized by 1H and ^{13}C NMR analyses, elemental analyses, FAB and MALDI-TOF mass spectroscopies.[†]

Compounds **1–3** exhibit identical UV–VIS spectra with λ_{max} at 542 nm and $\epsilon_{max} = 100000$. Owing to the extension of the conjugation length by the grafting of two styryl groups, these values are larger than those for the 4TV core and are close to those for 6TV.¹ All spectra exhibit a well-resolved vibronic fine structure which indicates that the increase of **Gn** does not alter the planarity and rigidity of the π -conjugated backbone.

Compounds **1–3** show identical cyclic voltammograms (CV) with two reversible one-electron oxidation waves corresponding to the formation of the cation radical and dication at redox potentials E°_1 and E°_2 of 0.53 and 0.65 V (Fig. 1). Both E°_1 and E°_2 values were fully independent of **Gn**. Furthermore, the linear dependence of the intensity of the first anodic peak of compound **3** vs. the square root of scan rate between 25 and 5000 $mV s^{-1}$ shows that the charge-transfer process between





Scheme 1 Reagents and conditions: i, 3,5-dihydroxybenzyl alcohol, K_2CO_3 , 18-crown-6, acetone; ii, PBr_3 , toluene; iii, **G1-W**, **G2-W**, $HPO(OEt)_2$, NaH, THF, **G3-W**, $P(OEt)_3$, reflux; iv, **Gn-W**, Bu^tOK , THF.

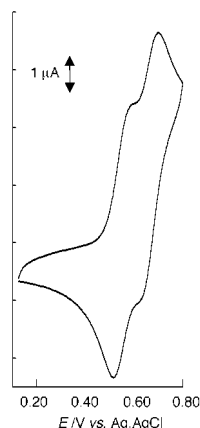


Fig. 1 Cyclic voltammogram for **3** (10^{-4} M) in 0.5 M Bu_4NPF_6/CH_2Cl_2 , Pt electrodes, scan rate 100 mV s^{-1} .

the electrode and the core electrophore is not subject to kinetic limitation. This behavior contrasts with that of redox active

metal centers encapsulated in dendritic structures for which the increase of **Gn** leads to a progressive decrease of the reversibility of the oxidation and/or reduction process and to a positive and/or negative shift of the corresponding potential.⁶ The independence of the electroactivity of the π -conjugated system on **Gn** observed here may be related to the length of the electrophore which prevents complete steric burial within the dendritic structure. We also observed that the E°_1 value for **3** was independent of substrate concentration in the range of 5×10^{-5} to 5×10^{-3} M. This result is consistent with an absence of follow-up reaction of the cation radical such as formation of a π -dimer;⁷ however, this hypothesis needs further confirmation.

Work is now underway to extend this approach to longer *n*TVs and to analyze in more detail the effects of the dendritic branches on inter-chain interactions.

Notes and references

† Selected data for **3**: Mp 201°C ; $\delta_H(\text{CDCl}_3)$ 7.61 (d, 32H, 3J 8.2), 7.50 (d, 32H, 3J 8.1), 7.19 (d, 2H, 3J 15.7), 7.02–6.98 (m, 6H), 6.78 (d, 2H, 3J 15.5, 2), 6.72 (d, 4H, 4J 2.1), 6.68 (d, 8H, 4J 2.0), 6.67 (d, 16H, 4J 2.1), 6.53–6.50 (m, 14H), 5.07 (s, 32H), 4.96 (s, 24H), 2.58 (m, 16H), 1.56–1.29 (m, 64H), 0.94–0.86 (m, 24H); m/z (MALDI-TOF) 5344.56 ($M+2$) [Calc. (found): C, 66.39 (66.96); H, 5.25 (5.20); F, 16.85 (17.06); S, 2.32% (2.40%)].

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