



Synthesis and characterization of novel styryl-substituted oligothiénylenevinylenes

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Abstract—A number of 3-monosubstituted bis(thienylvinyl)thiophenes, suitable for the preparation of electronically-variable poly(thienylenevinylene)s have been synthesized for the first time. These materials have been characterized by both NMR spectroscopy and mass spectrometry, and a single crystal X-ray structure analysis of (*E,E*)-3-(5,5-dimethyl[1,3]dioxin-2-yl)-2,5-bis(2-thien-2-ylvinyl)thiophene has shown that the planarity of the terthienylenevinylene chain is maintained on substitution at the 3 position of the central thiophene ring. UV/visible spectroscopy measurements are reported and cyclic voltammetric measurements show that, with the exception of (*E,E,E*)-2,5-bis(2-thien-2-ylvinyl)-3-(2-(4-dimethylaminophenyl)vinyl)-thiophene, electroactive films are produced on electrochemical oxidation of the monomers.

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1. Introduction

Since their discovery in 1977,^{1,2} conjugated polymers and oligomers have been extensively investigated for use in applications such as solar cells, actuators, light emitting diodes and non-linear optical materials.³ Prominent among the conjugated materials studied to date are the oligo- and polythiophenes. These materials have good chemical stability in both their oxidized and reduced states, and a wide variety of functionality can be readily built onto the monomers whether thiophene, bithiophene, or terthiophene.^{4–10}

The introduction of vinylene bridges between thiophene moieties improves the electronic properties of the resulting thienylenevinylene polymers^{11–16} by decreasing the aromaticity and enhancing both the planarity¹⁷ and the effective conjugation length.^{15,18,19} However, the introduction of more than one vinylene bridge leads to a decrease in chemical stability with no significant improvement in the electronic properties,²⁰ as does the introduction of an acetylene bridge.¹⁴ The HOMO–LUMO gap in thienylenevinylene polymers decrease with increasing number of carbons in the conjugated chain and large red shifts in λ_{\max} are observed.¹⁸ This gives rise to the possible fabrication of conjugated polymers that are transparent in the visible region of the electromagnetic spectrum and which might be

used in the fabrication of LEDs operating in the infrared. Furthermore, the increased electron affinity associated with a low-lying LUMO level allows for the fabrication of LEDs with stable metal electrodes.⁹

Another way in which the electronic properties of thiophene oligomers and polymers may be tuned is to introduce functionality to the polymer chain, typically in the form of aromatic substituents. Thus, poly(3-arylthiophenes) have improved doping capacity and cyclability compared with polythiophene,^{21,22} and fusing benzene to thiophene leads to poly(isothianaphthene), the prototypical small band gap polymer.²³ In contrast to the planar-fused benzene ring of the isothianaphthene, the 3-aryl substituents are twisted out of the plane of the polymer backbone, reducing their electronic impact as well as disrupting the polymer interchain interactions. The styryl group is an alternative and readily accessible aromatic functionality, which should not have these disadvantages and may enhance a planar morphology. Attempts to polymerise styrylthiophenes, however, have not been so successful. Electrochemical homopolymerization of 3-styrylthiophene resulted in a nonconductive material, presumably through side-chain polymerization, and other styryl derivatives showed similar behaviour.²⁴ However, electrically conductive polymers have been obtained by copolymerisation of styryl-substituted thiophenes with 3-methylthiophene,²⁵ and an improvement in the photoconductivity of polythiophene was accomplished on copolymerisation of thiophene and 3-(4-nitrostyryl)thiophene.²⁶ Copolymers of bithiophene and *para*-substituted (*E*)-3-styrylthiophenes have also been

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shown to produce photovoltaic responses in photoelectrochemical cells.²⁷ Whilst these copolymerizations undoubtedly lead to improvement in desirable polymer properties, their irregular and random structure makes it difficult to deconvolute the role of the substituent in these improvements.

An alternative approach to the formation of regioregular styryl-functionalised oligo- and polythiophenes is to polymerize styryl substituted terthiophene monomers and towards this end we have reported the syntheses of a range of terthiophenes functionalized at the 3'-position with styryl moieties.^{4,5,28–31} We have demonstrated that the styryl functionality can control oligomer regioregularity and provides advantages in some applications. However, styrylterthiophenes largely form dimers on oxidative polymerization as a result of 'polaron trapping'.⁶ Given the decreased aromaticity in thiylenevinylene polymers,¹⁷ this effect may not be so pronounced in styrylthiylenevinylens and consequently polymers rather than dimers may be produced.

With the eventual aim of producing conjugated styryl-substituted oligo(thiylenevinylene)s we describe in this paper the synthesis of six novel (*E,E,E*)-3'-styrylbis(thienylvinyl)thiophenes and report on their spectral and electrochemical properties. It should be noted that to the best of our

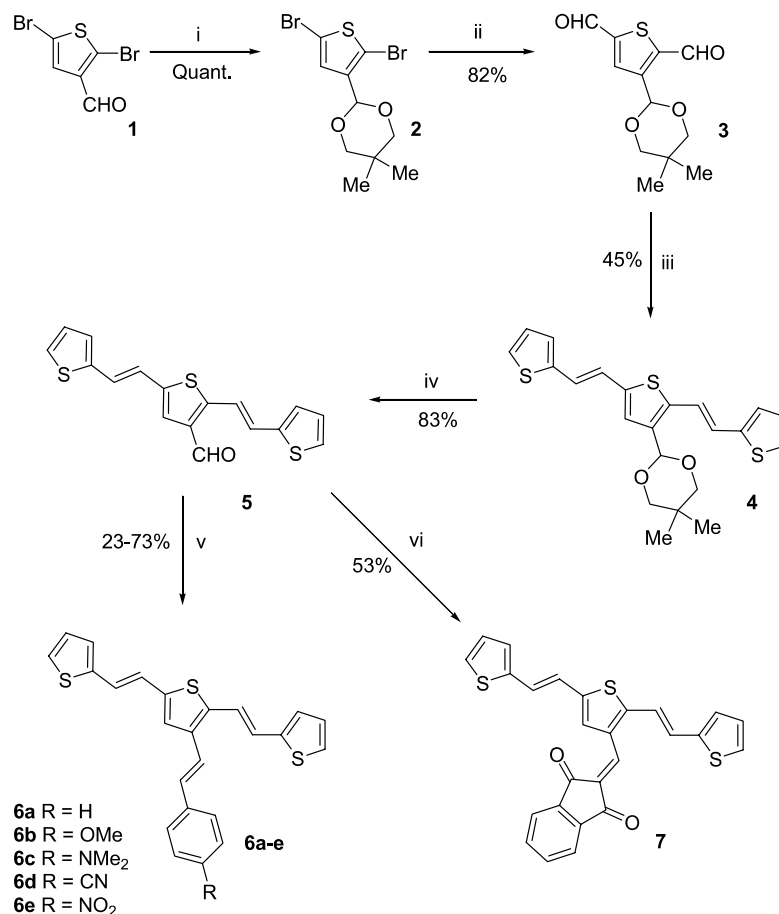
knowledge, no examples of 3-vinyl substituted bis(thienylvinyl)thiophenes have been reported to date. The facile synthesis of thiylenevinylene-3-carboxyaldehyde **5** reported here potentially provides access to a wide variety of other bis(thienylvinyl)thiophene substituents.

2. Results and discussion

2.1. Synthesis

Several methods have been used to syntheses oligothiylenevinylens including the McMurry reaction,^{18,32–34} Wittig condensation,^{33,35,36} Wittig–Horner condensation,^{18,19,37–39} and others.^{11,12,16,40–42} Of these, the Wittig condensation is economic and straightforward and allows the ready introduction of a wide variety of donor/acceptor-functionalized aromatic substituents.

The precursor to the bis(thienylvinyl)thiophene backbone, protected trialdehyde **3** (Scheme 1), was synthesised in 80% yield, by lithiation of the dibromo derivative **2** using a slight excess of *n*-butyl lithium, followed by DMF formylation. No monosubstituted product was observed and increasing the lithiation time above 30 min did not improve the reaction yield. The styryl functionality was introduced in an analogous manner to that used for terthiophenes,⁵ with



Scheme 1. (i) 2,2-Dimethyl-1,3-propanediol, PTSA, toluene, reflux, quantitative; (ii) *n*-BuLi, DMF, THF, -78°C , 82%; (iii) thiophen-2-ylmethyltriphenylphosphonium bromide, DBU, THF, reflux, 45%; (iv) TFAA, dichloromethane, rt, 83%; (v) phosphonium salt, DBU, THF, reflux, 23–73%; (vi) 1,3-indandione, piperidine, dichloromethane, rt, 53%.

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