



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 styrylthiylenevinylenes 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

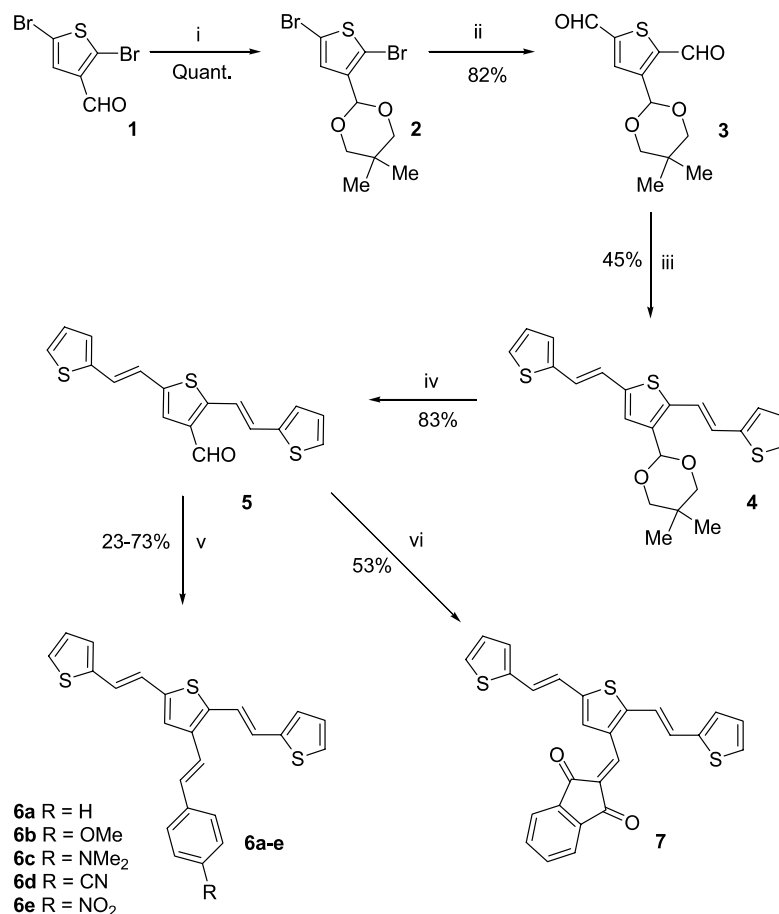
knowledge, no examples of 3-vinyl substituted bis(thienylvinyl)thiophenes have been reported to date. The facile synthesis of thiylenevinylene-3-carboxyaldehyde **5** reported here potentially provides access to a wide variety of other bis(thienylvinyl)thiophene substituents.

2. Results and discussion

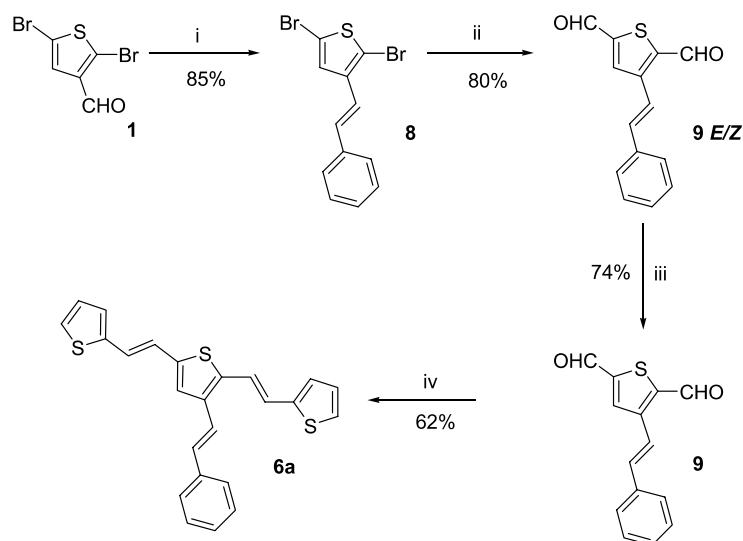
2.1. Synthesis

Several methods have been used to syntheses oligothiylenevinylenes 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%.



Scheme 2. (i) Benzyltriphenylphosphonium chloride, THF, DBU, reflux, 85%; (ii) $-78\text{ }^{\circ}\text{C}$, *n*-BuLi, THF, DMF, 80%; (iii) I_2 3 equiv, dichloromethane, rt, 7 days, 74%; (iv) thiophen-2-ylmethyltriphenylphosphonium bromide, DBU, THF, reflux, 62%.

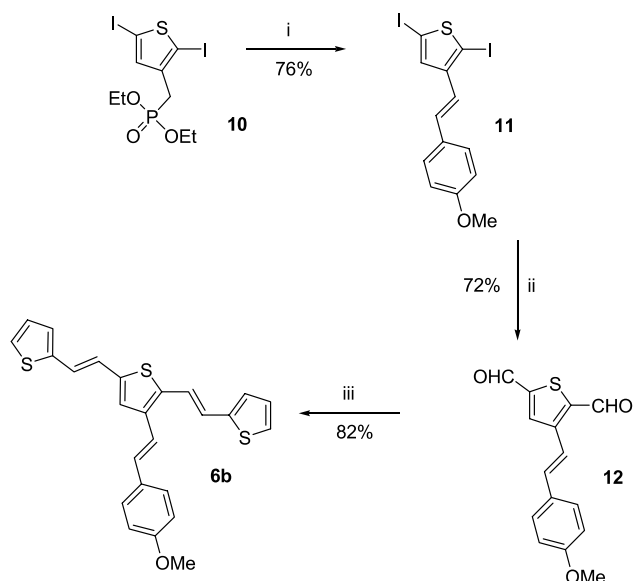
the key intermediate being aldehyde **5**. A Wittig condensation of **3** with thiophen-2-ylmethyltriphenylphosphonium bromide gave **4** as a pure *E,E* isomer. Increasing the reaction time decreased the product yield significantly. The products of monodecarbonylation of the thiophene dicarbaldehyde derivatives, observed previously in the presence of a strong base,²⁰ were not detected here. Deprotection of **4** by trifluoroacetic acid in dichloromethane gave **5** in high yield together with some traces of polymeric side products.

The Wittig condensations between aldehyde **5** and the appropriate phosphonium salts were carried out in boiling THF with DBU as base to give the corresponding 3-styryl derivatives **6a–e**. While **6b–e** were obtained as pure *E* isomers, the phenyl derivative **6a** was obtained as an inseparable mixture of 1:1 *E/Z* isomers, which suggests that the *Z*-isomer of an unsubstituted styryl derivative is more stable than one with an electron withdrawing or donating group. Compound **7** was synthesized, in high yield, by a Knoevenagel condensation of aldehyde **5** with an equimolar amount of 1,3-indandione in THF with piperidine as the base.

Since it proved impossible to separate the *E* and *Z* isomers of **6a** an alternative, but less general, synthetic path was devised (Scheme 2). The styryl functionality was first introduced through a condensation of aldehyde **1** with benzyltriphenylphosphonium chloride to give **8** (85%) as an inseparable *E/Z* 1:1 mixture. The conversion of **8** to an isomeric mixture of the dialdehyde *E/Z* **9** was readily achieved as described for **3** above. Isomerization of *E/Z* **9** was successfully carried out in dichloromethane at room temperature using iodine. After a reaction time of 7 days less than 10% of the *Z* isomer was present, and this was readily removed by chromatography to give pure *E*-**9**. This material, in a Wittig reaction with thiophen-2-ylmethyltriphenylphosphonium bromide, gave **6a** as the pure *E,E,E* isomer.

The yields of compounds **6b,c**, that is, those containing electron releasing groups, is only average to low, so the

approach utilised for **6a** was investigated as an alternative pathway for the synthesis of **6b** (Scheme 3). For these electron donating materials, the styryl functionality was introduced using diiodothiophene phosphonate **10**, previously prepared for the first time in our laboratory.⁴³ This compound was condensed with the appropriate aldehyde, under Horner–Emmons conditions, to give styryl derivative **11** as the *E* isomer with only minor traces of the *Z* isomer. Treatment of **11** with *n*-butyl lithium and DMF gave the dialdehyde **12** in high yield. Double Wittig condensation of **12** with thiophen-2-ylmethyltriphenylphosphonium bromide gave **6b** in high yield as the pure *E,E,E* isomer. The yield by this route, after four steps, is 40%, which is significantly better than that used in Scheme 1 (21%). However, this approach is not suitable for compounds that contain groups sensitive to *n*-butyl lithium.



Scheme 3. (i) 4-Methoxybenzaldehyde, *t*-BuOK, THF, rt, 76%; (ii) *n*-BuLi, DMF, THF, $-78\text{ }^{\circ}\text{C}$, 72%; (iii) thiophen-2-ylmethyltriphenylphosphonium bromide, DBU, THF, reflux, 82%.

2.2. NMR spectroscopy

Analysis of the target compounds by NMR spectroscopy reveals signals that are common to all compounds. Molecules **6b–e** all contain *para*-substituted aromatic rings, that give rise to characteristic AA'BB' or AA'XX' spectra, according to the magnitude of the chemical shift separation between the two types of protons. In cyano derivative **6d**, for example, this is only 0.07 ppm, whereas in nitro derivative **6e** it is 0.58 ppm as a result of the strong deshielding effect of the nitro group on the adjacent protons. The vinylic proton resonances appear as two doublets with a coupling of approximately 16 Hz, typical of an *E* configuration. The nature of the styryl substituent has little, if any, effect on the chemical shifts of the 2- and 5-vinyl protons (see Fig. 1) but there are larger variations in the chemical shifts of the 3-vinyl protons of the styryl groups as a result of shielding or deshielding effects induced by the substituent on the benzene ring. The nature of the vinyl substituent also has little effect on the H4 resonance of the inner thiophene ring, which appears as a singlet over the very narrow range of 7.17–7.19. The proton resonances of the outer thiophene rings exhibit AMX spectra and the assignments of the H3, H4, and H5 protons of each ring was achieved with the aid of COSY experiments. This established a coupling between the H4 proton and the 3-vinyl proton, and a further long range five-bond coupling between the 3-vinyl proton and the 2-vinyl proton was identified in compounds **6a**, **6d** and **6e**. These correlations allow for an unambiguous assignment of the outer thiophene resonances to specific thiophene rings. It is interesting to note that the chemical shifts of the thiophene H5' and H5'' protons are identical in compounds **6a–c**, and differ by only 0.02 ppm in compounds **6d** and **6e**. In the corresponding terthiophene monomers the chemical shifts in these positions differ by between 0.11 ppm (R = NMe₂) and 0.15 ppm (R = CN).⁵

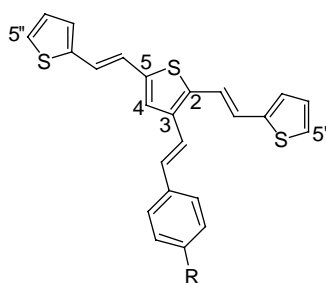


Figure 1. Generalized styryl-substituted bis(thienylvinyl)thiophene structure showing the numbering.

The spectrum of **7** is similar to those of compounds **6a–e**. The main differences are shifts to low fields of the resonances of both the 3-vinyl proton and the thiophene-4H proton by 1 and 1.4 ppm, respectively, both as a result of intramolecular hydrogen bonding between the respective protons and the closest oxygen of the neighbouring indandione ring. The 2-vinyl protons undergo a smaller downfield shift of about 0.2 ppm whilst the chemical shifts of the 5-vinyl protons are little affected, as are the chemical shifts of the outer thiophene protons.

2.3. Electronic absorption spectra

The electronic absorption spectra of compounds **6a**, **6c**, and **6e** are shown in Figure 2. The spectra of compounds **6b** and **6d** are similar in appearance to that of **6a**. All spectra are characterised by an absorption band with a λ_{max} in the range 422 nm (**6d**) to 436 nm (**6e**) indicating that, despite the planarity and therefore increased conjugation of the styryl group, the nature of the *para* substituent on the benzene ring has little effect on the HOMO–LUMO gap in these compounds. Previous work has shown that the position of the absorption maximum of alkyl substituted thienylenevinylene oligomers is largely determined by the number of carbon atoms in the conjugated chain,¹⁸ with λ_{max} for (*E,E*)-2,5-bis(2'-thienylvinyl)-3,4-dibutylthiophene (16 carbon atoms in the conjugated chain) in CH₂Cl₂ being 423 nm. It is clear from the above that the molecular orbitals contributing to this band must be primarily situated along the thienylenevinylene backbone, as has been observed for the corresponding terthiophenes.⁴⁴

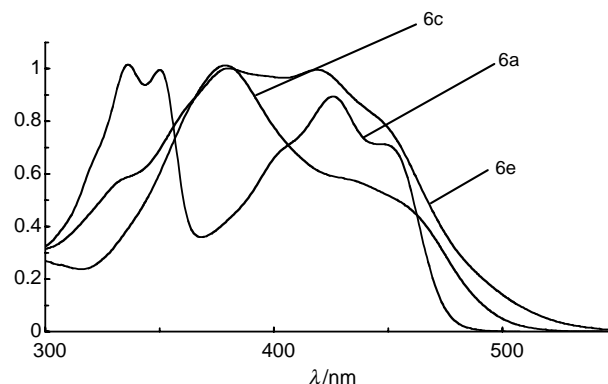


Figure 2. The normalized absorption spectra of **6a**, **6c** and **6e** in CH₂Cl₂ solvent.

Vibronic structure is present in all compounds **6a–e**, as previously reported for thienylenevinylene oligomers,^{18,19,45} although it is much less resolved in **6c**. In **6a**, for example, the 0–0 transition is at 452 nm with vibronic side bands at 428 and 405 nm. The energy difference between successive maxima is thus 0.15 eV, a value consistent with a C=C stretching mode ($\sim 1200 \text{ cm}^{-1}$) strongly coupled to the electronic structure.⁴⁶ The $\sim 0.15 \text{ eV}$ separation between excited state vibrational levels is common to all the styryl-substituted thienylenevinylenes.

The band to lower wavelengths is due to transitions between molecular orbitals associated with the styryl substituent as it is absent in thienylenevinylene oligomers with no styryl substituent. The variation in λ_{max} for this band is much greater than that for the high-wavelength band, ranging from 337 nm for **6a** to 379 nm for **6e**, consistent with the expected influence of the electron donating and withdrawing groups. Vibronic structure is clearly observed in this band in compounds **6a**, **6b**, and **6d**, and less clearly in **6e**. As in the high-wavelength band, the separation between successive maxima corresponds to 0.15 eV and can be associated with a C=C stretching mode.

The spectrum of **7** exhibits two broad bands with λ_{max} values of 378 and 520 nm. The low wavelength band has shoulders at 409 and 431 nm with a ~ 0.15 eV separation between excited state vibrational levels. The band at 520 nm is most likely the result of intramolecular charge transfer.^{47–49}

2.4. X-ray structure analysis of 3-(5,5-dimethyl[1,3]-dioxin-2-yl)-2,5-bis(2-thien-2-ylvinyl)thiophene (**4**)

Attempts to grow single crystals of the target compounds were unsuccessful. However, crystals of sufficient quality for X-ray determination were obtained for compound **4**. The crystal structure of this compound (Fig. 3) illustrates that the planarity of the conjugated terthiophenevinylene chain is maintained on introduction of the β -substituent as observed by Roncali et al.¹⁹ in the only comparable crystal structure of tetra(thiophenevinylene). The dihedral angles between the S(1) and S(2) rings, the S(2) and S(3) rings, and the S(1) and S(3) rings are, respectively, 8.1(2), 7.2(2), and 8.5(2)°, and the thiophene rings are perfectly planar.

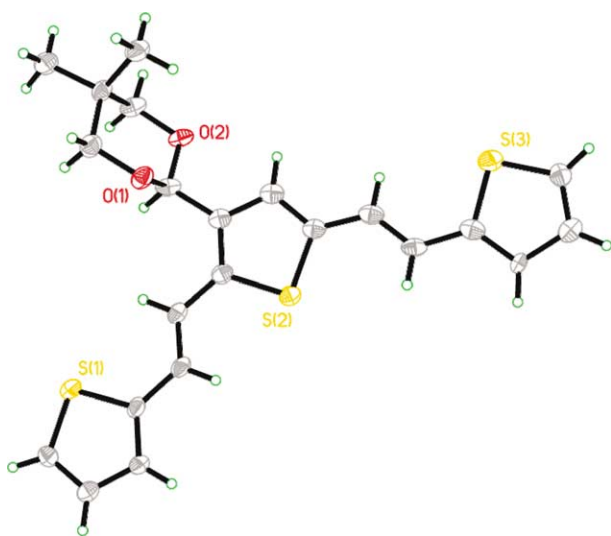


Figure 3. The crystal structure of **4**. Displacement ellipsoids were set at 50% of probability.

For terthiophene ring systems with substituents in the β -position of the central ring, the rings are far from coplanar. For example, in the case of 3'-phenyl-2,2':5',2''-terthiophene,⁵⁰ the two outer rings are twisted by -156 and 138.4° with respect to the central thiophene ring. With a styryl group in the 3-position, the torsion angle between the outer ring closest to the alkene linker on the central thiophene ring is -148.6° and the corresponding angle on the other side of the central thiophene ring is -151.2° .⁵ This steric interaction that leads to a distortion of the thiophene rings has also been observed in other 3-substituted terthiophenes.⁴⁹ Thus, compared with terthiophene oligomers, the addition of the alkene spacers between the rings leads to an increase in the π -orbital overlap along the oligomer backbone.

2.5. Cyclic voltammetry

Cyclic voltammograms (CVs) for compounds **6a–e** are similar in appearance and those for **6e** are shown in Figure 4. The oxidation onset potential of **6a** (0.56 V) is lower than that measured for styrylterthiophene (0.74 V on a microelectrode), due to the greater stability of the bis(thienylvinyl)thiophene radical cation as a result of the extra conjugation introduced by the vinyl linkers. Oxidation onset potentials of 0.56 V are also measured for the compounds **6d**, and **6e** indicating that the reactivity of the 5' and 5'' positions are not significantly affected by electron-withdrawing substituents at the *para*-position on the benzene ring. In contrast, the oxidation onset potential for **6b** is lower at 0.44 V, due to a stabilization of the resulting radical cation by the electron-donating substituent. Subsequent cycles show two oxidation peaks, the peak at potentials less than 0.5 V is the result of oxidation of the deposited electroactive film, and the cathodic peaks are most likely due to reduction of the oxidised film back to neutral material.

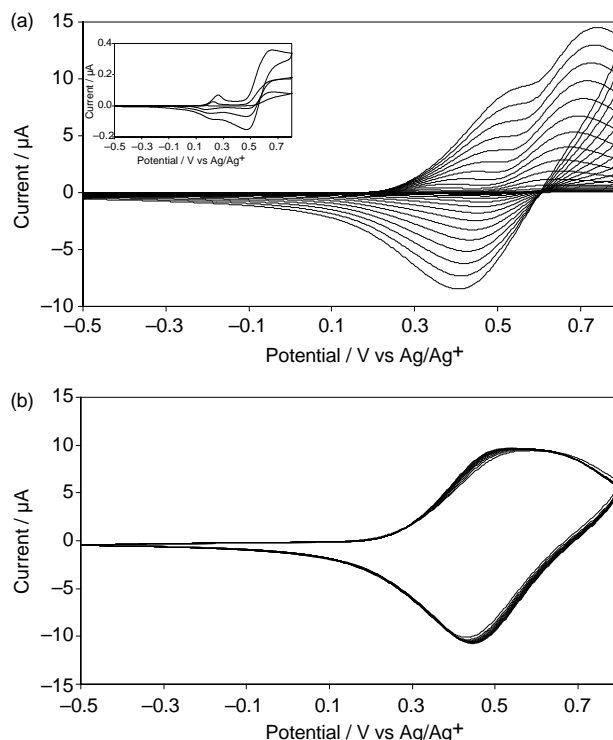


Figure 4. (a) Potentiodynamic growth of **6e** on a Pt microelectrode. Monomer concentration: 5 mM. Supporting electrolyte: 1:1 DCM–acetonitrile/0.1 M TBAP. Scan rate: 100 mV s^{-1} . The insert represents the first three cycles. (b) Post growth cycling of **6e** deposited on a Pt microelectrode. Supporting electrolyte: acetonitrile/0.1 TBAP. Scan rate: 100 mV s^{-1} .

The growth cyclic voltammogram of **6c** is different to that of the other samples. A much lower oxidation onset potential of 0.22 V is observed, and four oxidation and four reduction peaks are produced on the first scan. Subsequent scans show an increase in oxidation onset potential, and a decreasing growth in current with each cycle, indicating the deposition of poorly conducting material. These observations suggest that processes other than polymerisation through the 5' and

5'' positions are occurring, possibly involving the dimethyl-amino substituent.^{51,52}

Post-growth CVs of the electrochemically deposited films (see Fig. 4b for that of **6e**) reveal a considerable variation in the stability of the depositions. Those produced from **6b** and **6e** are quite stable, **6d** gives rise to a film that exhibits a gradual decrease in current with increasing cycle number, and the fall in current is rapid on post cycling of the films produced from **6a** and **6c**.

3. Conclusions

Wittig chemistry provides a convenient and straightforward method for the synthesis of β -styryl-functionalized bis(thienylvinyl)thiophenes. The electronic absorption spectra of all the molecules exhibit red shifts compared to those of the corresponding oligothiophenes as a result of an enhanced planarity, as confirmed by single crystal X-ray structural analysis of (*E,E*)-3-(5,5-dimethyl[1,3]dioxin-2-yl)-2,5-bis(2-thien-2-ylvinyl)thiophen, and the consequent increase in the effective conjugation lengths. The λ_{\max} values fall in a narrow range and are similar to those observed in unsubstituted oligothiophenevinylenes showing that the nature of the styryl substituent has little effect on the HOMO–LUMO gap in these compounds. With the exception of the dimethylamino derivative **6c**, electroactive films are produced on electrochemical oxidation of the bis(thienylvinyl)thiophene monomers. A full investigation into the polymerization of these materials is currently underway.

4. Experimental

4.1. General

NMR spectra were recorded on a Bruker Avance 400 spectrometer using TMS as the internal standard. In some cases not all of the carbon resonances were resolved due to the overlap of peaks. The UV spectra were recorded on a Shimadzu UV3101PC spectrometer using dichloromethane as the solvent. The melting points are uncorrected. All new compounds were determined to be greater than 95% pure by ¹H NMR spectroscopy.

Cyclic voltammograms were recorded in air using an Autolab Potentiostat Galvanostat running Autolab GPES software. A one compartment, three-electrode glass cell was used for all measurements. The cell incorporated a platinum mesh counter electrode, a silver/silver chloride reference electrode, and the working electrode was a platinum microelectrode with a 10 μm^2 surface area. The scan rate used was 100 mV s⁻¹ and the scans were started from the most negative potential. Films were grown using cyclic voltammetry between the limits of -0.5 and 0.8 V in 5 mM monomer solutions in 1:1 DCM–acetonitrile/0.1 M TBAP. Post growth electrochemistry was performed in acetonitrile/0.1 M TBAP monomer-free solutions. All solutions were freshly prepared and solutions were degassed by ultrasonification immediately prior to measurement.

Crystals for X-ray analysis were obtained by slow evaporation of ethanol. Data were collected on a Siemens SMART CCD diffractometer at 273 K with graphite-monochromated Mo K α radiation (λ 0.71073 Å) using $\omega/2\theta$ scans. The structures were determined by means of direct methods⁵³ and refined by the full-matrix least squares technique.⁵⁴ All hydrogen atoms were obtained from the electron differential Fourier map and refined using a riding-model (C–H bonds set to 0.93 Å). Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 271152. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB 2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

2,5-Dibromo-3-thiophenylcarbaldehyde (**1**),⁵ 5,5-dimethyl-2-(2,5-dibromothiophen-3-yl)[1,3]dioxane (**2**)⁵ and thiophen-2-ylmethyltriphenylphosphonium bromide,⁵⁵ were synthesized according to literature procedures. Other reagents used in the syntheses were obtained from commercial sources.

4.1.1. 3-(5,5-Dimethyl-[1,3]dioxan-2-yl)thiophene-2,5-dicarbaldehyde (3). Dibromide **2** (5.10 g, 0.015 mol) was dissolved in dry THF (75 mL), cooled to -78 °C, and a solution of 2.5 mol L⁻¹ *n*-butyl lithium in hexane (14 mL, 0.035 mol) was added dropwise by a syringe. The resulting mixture was stirred at -78 °C for 30 min before a solution of dry DMF (6.60 g, 0.09 mol) in THF (10 mL) was added. The reaction mixture was left to reach room temperature, stirred for 30 min, and poured into 1 mol L⁻¹ hydrochloric acid (150 mL) before being extracted twice with diethyl ether. The organic layer was separated, dried over magnesium sulphate and evaporated to dryness at 50 °C under reduced pressure to give a brownish oil. After purification on silica, using 30% ethyl acetate in hexane as eluent, a colourless oil was obtained (3.11 g, 82%). Recrystallization from hexane at -20 °C gave colourless crystals: mp 69–70 °C; δ_{H} (400 MHz, CDCl₃) 10.35 (1H, s, 2-CHO), 9.97 (1H, s, 5-CHO), 7.91 (1H, s, ThH4), 5.81 (1H, s, diox-H2), 3.81 (2H, d, *J* = 11 Hz, CH₂), 3.70 (2H, d, *J* = 11 Hz, CH₂), 1.29 (3H, s, Me), 0.84 (3H, s, Me); δ_{C} (100.6 MHz, CDCl₃) 184.3, 183.3, 147.1, 145.9, 135.4, 97.2, 77.7, 30.2, 23.1, 21.8; *m/z* (EI) 254 (39, M⁺), 185 (10), 168 (72), 139 (28), 70 (35), 56 (100), 41 (57), 39 (34%); HRMS (EI): M⁺, found 254.06010. C₁₂H₁₄O₂S requires 254.0613; ν_{\max} (KBr) 3320, 3110, 2960, 2865, 1675, 1665, 1545, 1465, 1380, 1365, 1335, 1310, 1225, 1205, 1150, 1110, 1020, 1010 cm⁻¹.

4.1.2. (*E,E*)-3-(5,5-Dimethyl[1,3]dioxin-2-yl)-2,5-bis(2-thien-2-ylvinyl)thiophene (4). Dialdehyde **3** (2.54 g, 0.010 mol) and triphenylthiophen-2-ylmethylphosphonium bromide (9.67 g, 0.022 mol) were dispersed in dry THF (75 mL). DBU (7.5 g, 0.05 mol) was added and the resulting mixture was refluxed under argon for 5 h. The reaction mixture was poured into 1 mol L⁻¹ hydrochloric acid (300 mL) before being extracted twice with dichloromethane. The organic extracts were dried over magnesium sulphate and evaporated to dryness at 50 °C under vacuum to yield a dark-brown oil. Purification on silica, using 30% ethyl acetate in hexane as eluent, and recrystallization from

a dichloromethane/methanol mixture gave fine yellow prisms (1.86 g, 45%): mp 172–174 °C; δ_{H} (400 MHz, CDCl_3) 7.27 (d, 1H, $J=15.7$ Hz, 5-vinyl-H), 7.19 (1H, dd, $J=5.2, 1.0$ Hz, Th- $H5'$), 7.17 (1H, dd, $J=5.2, 1.0$ Hz, Th- $H5''$), 7.08 (1H, s, Th- $H4$), 7.04 (1H, dd, $J=3.6, 1.0$ Hz, Th- $H3'$), 7.03 (1H, dd, $J=3.6, 1.0$ Hz, Th- $H3''$), 7.02 (1H, d, $J=15.7$ Hz, 2-vinyl-H), 7.00 (1H, d, $J=15.8$ Hz, 5-vinyl-H), 6.99 (1H, dd, $J=5.2, 3.6$ Hz, Th- $H4'$), 6.98 (1H, dd, $J=5.2, 3.6$ Hz, Th- $H4''$), 6.93 (1H, d, $J=15.8$ Hz, 5-vinyl-H), 5.52 (1H, s, diox- $H2$), 7.79–3.77 (2H, m, CH_2), 3.67–3.64 (2H, m, CH_2), 1.35 (3H, s, CH_3), 0.81 (3H, s, CH_3); δ_{C} (100.6 MHz, CDCl_3) 142.5, 142.3, 139.8, 138.3, 137.0, 127.7, 126.8, 126.5, 126.2, 124.7, 124.5, 122.6, 121.8, 121.2, 119.5, 97.8, 77.7, 30.2, 23.2, 21.9; m/z (EI) 414 (100, M^+), 344 (15), 328 (24), 317 (14), 266 (12), 97 (10%); HRMS (EI): M^+ found 414.0780. $\text{C}_{22}\text{H}_{22}\text{O}_2\text{S}_3$ requires 414.0782; ν_{max} (KBr) 3105, 3015, 2950, 2860, 1461, 1430, 1400, 1375, 1354, 1330, 1310, 1280, 1235, 1210, 1155, 1105, 1040, 1015, 1000 cm^{-1} .

4.1.3. (*E,E*)-2,5-Bis(2-thien-2-ylvinyl)thiophene-3-carbaldehyde (5). Compound **4** (1.45 g, 3.5 mmol) was dissolved in dichloromethane (15 mL), then trifluoroacetic acid (15 mL) and water (5 mL) were added. The resulting mixture was stirred at room temperature for 1.5 h, placed into the separating funnel and the organic layer collected, washed with water, then with a saturated solution of sodium bicarbonate and dried over magnesium sulphate. The solvent was removed under vacuum at 50 °C and the residue was purified on silica using pure dichloromethane as eluent. The red-orange solid on recrystallization from a dichloromethane–methanol mixture gave fine red needles (0.95 g, 83%): mp 115–116 °C; δ_{H} (400 MHz, CDCl_3) 10.08 (1H, s, CHO), 7.70 (1H, d, $J=16.0$ Hz, 2-vinyl-H), 7.31 (1H, dd, $J=5.0, 1.2$ Hz, Th- $H5'$), 7.26 (1H, s, Th- $H4$), 7.25 (1H, d, $J=16.0$ Hz, 2-vinyl-H), 7.23 (1H, dd, $J=5.0, 1.2$ Hz, Th- $H5''$), 7.17 (1H, dd, $J=3.6, 1.2$ Hz, Th- $H3'$), 7.07 (1H, dd, $J=3.6, 1.2$ Hz, Th- $H3''$), 7.04 (1H, dd, $J=5.0, 3.6$ Hz, Th- $H4'$), 7.01 (1H, dd, $J=5.0, 3.6$ Hz, Th- $H4''$) 7.00 (1H, d, $J=16.0$ Hz, 5-vinyl-H), 6.93 (1H, d, $J=16$ Hz, 5-vinyl-H); δ_{C} (100.6 MHz, CDCl_3) 184.0, 149.8, 141.6, 141.5, 140.0, 136.9, 128.3, 128.0, 127.8, 127.0, 126.9, 126.6, 126.5, 125.3, 123.6, 120.2, 117.8; m/z (EI) 328 (100, M^+), 295 (20), 266 (22), 134 (10), 156 (10%); HRMS (EI): M^+ found 328.0047. $\text{C}_{17}\text{H}_{12}\text{OS}_3$ requires 328.0050; ν_{max} (KBr) 3080, 1660, 1600, 1530, 1505, 1460, 1425, 1385, 1350, 1280, 1195, 1145, 1045 cm^{-1} .

4.2. General procedure for preparation of styryl derivatives 6b–e

Aldehyde **5** (104 mg, 0.32 mmol) and 1.2 equiv of phosphonium salt were dispersed in THF (10 mL). To the suspension DBU (1.0 g, 6.7 mmol) was added and the mixture refluxed overnight under argon. The reaction mixture was then diluted with dichloromethane and washed with 1 mol L^{-1} hydrochloric acid. The organic layer was separated, dried over magnesium sulphate and the solvents were removed under vacuum at 50 °C. The residue was purified on silica using pure dichloromethane as an eluent and recrystallized.

4.2.1. (*E,E,E*)-2,5-Bis(2-thien-2-ylvinyl)-3-(2-(4-methoxyphenyl)vinyl)thiophene (6b). Recrystallization from dichloromethane/methanol yielded yellow needles (69%): mp 171–172 °C; δ_{H} (400 MHz, CDCl_3) 7.46 (2H, d, $J=8.6$ Hz, Ar- H), 7.24 (1H, d, $J=16.1$ Hz, 2-vinyl-H), 7.21 (2H, dd, $J=5.5, 1.2$ Hz, Th- $H5'$, $H5''$), 7.19 (1H, s, Th- $H4$), 7.09 (1H, d, $J=16.0$ Hz, 3-vinyl-H), 7.06 (2H, dd, $J=5.5, 3.6$ Hz, Th- $H3'$, $H3''$), 7.05 (1H, d, $J=16.0$ Hz, 5-vinyl-H), 7.03 (1H, d, $J=16.1$ Hz, 2-vinyl-H), 7.02 (1H, d, $J=16.0$ Hz, 5-vinyl-H), 7.01 (2H, dd, $J=3.6, 1.2$ Hz, Th- $H4'$, $H4''$), 6.92 (2H, d, $J=8.6$ Hz, Ar- H), 6.84 (1H, d, $J=16.0$ Hz, 3-vinyl-H), 3.84 (3H, s, CH_3); δ_{C} (100.6 MHz, CDCl_3) 142.7, 142.2, 139.9, 137.8, 136.3, 130.0, 129.5, 127.8, 127.7, 127.6, 126.4, 126.3, 125.0, 124.7, 124.6, 122.4, 121.9, 121.2, 119.1, 118.2, 55.3; m/z (EI) 432 (100, M^+), 335 (18), 311 (11), 121 (10%); HRMS (EI): M^+ found 432.0673. $\text{C}_{25}\text{H}_{20}\text{OS}_3$ requires 432.0676; λ_{max} nm (ϵ) 343 (48,500), 357 (49,500), 406 sh (28,500), 429 (33,000), 453 (24,000).

4.2.2. (*E,E,E*)-2,5-Bis(2-thien-2-ylvinyl)-3-(2-(4-dimethylaminophenyl)vinyl)thiophene (6c). Recrystallization from dichloromethane/methanol yielded fragile orange plates (23%): mp 205–206 °C; δ_{H} (400 MHz, CDCl_3) 7.42 (2H, d, $J=8.8$ Hz, Ar- H); 7.25 (1H, d, $J=15.6$ Hz, 2-vinyl-H), 7.19 (2H, dd, $J=5.5, 1.2$ Hz, Th- $H5'$, $H5''$), 7.18 (1H, s, Th- $H4$), 7.05 (2H, dd, $J=5.5, 3.6$ Hz, Th- $H3'$, $H3''$), 7.04 (1H, d, $J=16.0$ Hz, 3-vinyl-H), 7.02–6.98 (5H, m, Th- $H4'$, $H4''$, 2 \times 5-vinyl-H, 2-vinyl-H), 6.88 (1H, d, $J=15.6$ Hz, 3-vinyl-H), 6.73 (2H, d, $J=8.8$ Hz, Ar- H), 2.99 (6H, s, NCH_3); δ_{C} (100.6 MHz, CDCl_3) 150.3, 142.7, 142.4, 139.8, 138.5, 135.4, 130.6, 127.8, 127.7, 127.6, 126.3, 126.0, 125.1, 124.6, 124.4, 122.2, 121.4, 121.3, 119.4, 116.1, 112.5, 40.4; m/z (EI) 445 (100, M^+), 348 (19), 222 (10), 134 (52), 105 (24), 91 (33), 69 (22), 57 (31), 49 (44%); HRMS (EI): M^+ found 445.0994. $\text{C}_{26}\text{H}_{23}\text{NS}_3$ requires 445.0993; λ_{max} nm (ϵ) 378 (60,000), 436 sh (33,500).

4.2.3. (*E,E,E*)-2,5-Bis(2-thien-2-ylvinyl)-3-(2-(4-cyano-phenyl)vinyl)thiophene (6d). Recrystallization from dichloromethane/methanol yielded yellow prisms (73%): mp 172–173 °C; δ_{H} (400 MHz, CDCl_3) 7.63 (2H, d, $J=8.4$ Hz, Ar- H), 7.56 (2H, d, $J=8.4$ Hz, Ar- H), 7.29 (1H, d, $J=16.1$ Hz, 3-vinyl-H), 7.24 (1H, d, $J=5.2$ Hz, Th- $H5'$), 7.22 (1H, d, $J=5.2$ Hz, Th- $H5''$), 7.19 (1H, d, $J=15.3$ Hz, 2-vinyl-H), 7.17 (1H, s, Th- $H4$), 7.09 (1H, d, $J=3.6$ Hz, Th- $H3'$), 7.08 (1H, d, $J=15.3$ Hz, 2-vinyl-H), 7.06 (1H, d, $J=3.6$ Hz, Th- $H3''$), 7.03 (1H, dd, $J=5.2, 3.6$ Hz, Th- $H4'$), 7.02 (1H, d, $J=16.0$ Hz, 5-vinyl-H), 7.01 (1H, dd, $J=5.2, 3.6$ Hz, Th- $H4''$), 6.96 (1H, d, $J=16.0$ Hz, 5-vinyl-H), 6.89 (1H, d, $J=16.1$ Hz, 3-vinyl-H); δ_{C} (100.6 MHz, CDCl_3) 142.2, 142.0, 141.8, 140.4, 138.9, 136.3, 132.5, 127.9, 127.8, 127.7, 126.9, 126.8, 126.7, 125.1, 125.0, 124.5, 123.5, 123.1, 122.9, 120.8, 118.4, 110.6; m/z (EI) 247 (100, M^+), 330 (18), 97 (15), 91 (12%); HRMS (EI): M^+ found 427.0526. $\text{C}_{25}\text{H}_{17}\text{NS}_3$ requires 427.0523; λ_{max} nm (ϵ) 346 (49,500), 361 (49,500), 427 (39,000), 451 sh (32,000).

4.2.4. (*E,E,E*)-2,5-Bis(2-thien-2-ylvinyl)-3-(2-(4-nitrophenyl)vinyl)thiophene (6e). Recrystallization from dichloromethane/methanol yielded red plates and blocks (70%): mp 185–186 °C; δ_{H} (400 MHz, CDCl_3) 8.22 (2H, m, Ar- H), 7.61 (2H, m, Ar- H), 7.64 (1H, d, $J=16.1$ Hz,

3-vinyl-*H*), 7.25 (1H, d, $J=4.8$ Hz, Th- $H5'$), 7.23 (1H, d, $J=4.8$ Hz, Th- $H5''$), 7.20 (1H, d, $J=16.0$ Hz, 2-vinyl-*H*), 7.18 (1H, s, Th- $H4$), 7.10 (1H, d, $J=3.6$ Hz, Th- $H4'$), 7.07 (1H, d, $J=16.0$ Hz, 2-vinyl-*H*), 7.06 (1H, d, $J=3.6$ Hz, Th- $H3''$), 7.02 (1H, d, $J=15.6$ Hz, 5-vinyl-*H*), 7.02 (1H, dd, $J=4.8, 3.6$ Hz, Th- $4'$), 7.01 (1H, dd, $J=4.8, 3.6$ Hz, Th- $4''$), 6.96 (1H, d, $J=15.6$ Hz, 5-vinyl-*H*), 6.94 (1H, d, $J=16.1$ Hz, 3-vinyl-*H*); δ_C (100.6 MHz, $CDCl_3$) 146.7, 143.8, 142.2, 142.0, 140.4, 139.4, 136.2, 127.9, 127.8, 127.1, 127.0, 126.7, 125.2, 125.0, 124.4, 124.3, 124.2, 123.3, 123.0, 120.8, 118.3; m/z (EI) 447 (100, M^+), 445 (22), 417 (48), 350 (13), 106 (27), 105 (14), 97 (12), 91 (18), 55 (17), 43 (19%); HRMS (EI): M^+ found 447.0414. $C_{24}H_{17}NO_2S_3$ requires 447.0421; λ_{max} nm (ϵ) 335 (23,500), 379 (39,500), 422 (39,500), 446 sh (32,000).

4.2.5. (*E,E*)-2,5-Bis(2-thien-2-ylvinyl)-3-(1,3-indandion-2-ylmethyl)thiophene (7). Aldehyde **5** (77 mg, 0.23 mmol) and 1,3-indandione (0.034 g, 0.23 mmol) were dissolved in dry THF (10 mL) and piperidine (1 mL, 10 mmol) was added. The colour of the reaction mixture immediately turned to deep red. After stirring overnight at room temperature the reaction mixture was diluted with dichloromethane and washed with 1 mol L⁻¹ hydrochloric acid. The organic layer dried over magnesium sulphate and the solvents were removed under vacuum at 50 °C. The residue was purified on silica using pure dichloromethane as an eluent and recrystallization from dichloromethane/methanol yielded red irregular crystals (57 mg, 53%): mp 186 °C dec; δ_H (400 MHz, $CDCl_3$) 8.60 (1H, s, Th- $H4$), 7.98–7.95 (2H, m, Ar-*H*), 7.96 (1H, s, 3-vinyl-*H*), 7.80–7.78 (2H, m, Ar-*H*), 7.42 (1H, d, $J=15.5$ Hz, 2-vinyl-*H*), 7.32 (1H, d, $J=5.0$ Hz, Th- $H5'$), 7.26 (1H, d, $J=15.5$ Hz, 2-vinyl-*H*), 7.22 (1H, d, Th- $H5''$), 7.19 (1H, d, $J=3.6$ Hz, Th- $H3'$), 7.09–7.03 (4H, m, Th- $H3''$, 5-vinyl-*H*, Th- $H4'$), 7.00 (1H, dd, $J=5.0, 3.6$ Hz, Th- $H4''$); δ_C (100.6 MHz, $CDCl_3$) 190.7, 189.3, 153.2, 142.6, 142.0, 141.6, 140.0, 139.4, 135.1, 135.0, 133.58, 133.55, 130.5, 128.5, 128.1, 127.7, 126.9, 126.8, 126.7, 126.6, 125.2, 123.3, 123.1, 123.0, 120.9, 117.6; m/z (EI) 456 (11, M^+), 307 (24), 289 (12), 155 (26), 154 (100), 137 (57), 136 (67), 120 (12), 107 (24), 89 (22), 77 (23%); HRMS (EI): M^+ found 456.0313. $C_{26}H_{16}O_2S_3$ requires 456.0313; λ_{max} nm (ϵ) 377 (48,500), 400 sh (40,000), 517 (18,000).

4.2.6. 3-(2-Phenylvinyl)-2,5-dibromothiophene (8). Dibromide **1** (9.67 g, 0.036 mol) and benzyltriphenylphosphonium chloride (13.93 g, 0.036 mol) were dispersed in THF (100 mL). To the resulting suspension DBU (10 g, 6.6 mmol) was added and the resulting mixture refluxed overnight under argon. The resulting reaction mixture was diluted with dichloromethane and washed with 1 mol L⁻¹ hydrochloric acid. The organic layer was separated, dried over magnesium sulphate and the solvents removed under vacuum at 50 °C. The residue was purified on silica using 10% ethyl acetate in hexane as eluent to give a yellow oil (10.5 g, 85%): δ_H (400 MHz, $CDCl_3$) 7.51 (2H, m, *E*-Ph-*H*), 7.37–7.35 (3H, m, *E*-Ph-*H*), 7.29–7.23 (5H, m, *Z*-Ph-*H*), 7.23 (1H, s, Th- $H4-E$), 7.01 (1H, d, $J=12.8$ Hz, vinyl-*H-Z*), 6.91 (1H, d, $J=12.8$ Hz, vinyl-*H-Z*), 6.69 (1H, d, $J=16.0$ Hz, vinyl-*H-E*), 6.60 (1H, s, Th- $H4-Z$), 6.33 (1H, d, $J=16.0$ Hz, vinyl-*H-E*); δ_C (100.6 MHz, $CDCl_3$) 139.1, 138.3, 136.6, 136.4, 132.2, 131.3, 130.2, 128.8, 128.7, 128.4,

128.2, 127.8, 127.4, 126.6, 121.6, 120.0, 111.9, 111.6, 110.5, 110.1; m/z (EI) 346 (6, M^+), 344 (12), 342 (7), 184 (100), 139 (11), 92 (12%); HRMS (EI): M^+ found 341.8710. $C_{12}H_8Br_2S$ requires 341.8713.

4.2.7. (*E*)-3-(2-Phenylvinyl)thiophene-2,5-dicarbaldehyde (9). Compound **8** (1.65 g, 4.8 mmol) was dissolved in dry THF (30 mL), cooled to -78 °C and a 2.5 mol L⁻¹ solution of *n*-butyl lithium in hexane (3.8 mL, 9.5 mmol) was added dropwise with a syringe. The resulting mixture was stirred at -78 °C for 15 min then dry DMF (6.6 g, 20 mmol) dissolved in THF (5 mL) was added. The reaction mixture was allowed to reach room temperature for 30 min before being poured into 150 mL of 1 mol L⁻¹ hydrochloric acid and extracted twice with dichloromethane. The organic layers were dried over magnesium sulphate and evaporated to dryness under reduced pressure at 50 °C to yield a dark oil. After purification on silica using dichloromethane as eluent yellow crystals of *E/Z* **9** were obtained (0.92 g, 80%). **Isomerization procedure.** Compound *E/Z* **9** (1.69 g, 7 mmol) was dissolved in dichloromethane (50 mL) and iodine (5.33 g, 21 mmol) was added. The resulting mixture was stirred at room temperature for 7 days then washed with saturated solution of sodium thiosulphate and water. The organic layer was dried over magnesium sulphate, evaporated to dryness and the residue was purified on silica using dichloromethane as eluent. Recrystallization from an ethanol–water mixture yielded thin yellow needles of **9** (1.25 g, 74%): mp 133–134 °C; δ_H (400 MHz, $CDCl_3$) 10.29 (1H, s, 2-*CHO*), 10.03 (1H, s, 5-*CHO*), 8.09 (1H, s, Th- $H4$), 7.69 (1H, d, $J=16.2$ Hz, vinyl-*H*), 7.57–7.55 (2H, m, Ph-*H*), 7.44–7.40 (3H, m, Ph-*H*), 7.24 (1H, d, $J=16.2$ Hz, vinyl-*H*); δ_C (100.6 MHz, $CDCl_3$) 183.4, 182.8, 147.9, 146.1, 141.8, 135.9, 135.7, 133.5, 129.3, 129.0, 127.1, 118.4; m/z (EI) 242 (100, M^+), 213 (22), 185 (62), 184 (37), 165 (11), 152 (20), 141 (16), 92 (10%); HRMS (EI): M^+ found 242.0399. $C_{14}H_{10}O_2S$ requires 242.0402.

4.2.8. (*E,E,E*)-2,5-Bis(2-thien-2-ylvinyl)-3-(2-phenylvinyl)thiophene (6a). Compound **9** (1.21 g, 5 mmol) and thiophen-2-ylmethyltriphenylphosphonium bromide (4.83 g, 11 mmol) were dispersed in dry THF (30 mL). DBU (3.00 g, 19.7 mmol) was added and the mixture was refluxed under argon overnight. The resulting reaction mixture was poured into 1 mol L⁻¹ hydrochloric acid (100 mL) and extracted twice with dichloromethane. The organic layers were dried over magnesium sulphate and evaporated to dryness under reduced pressure at 50 °C. The residue was purified on silica using 20% ethyl acetate in hexane as eluent and recrystallized from dichloromethane–methanol mixture to give irregular yellow-orange blocks (1.24 g, 62%): mp 156–157 °C; δ_H (400 MHz, $CDCl_3$) 7.52 (3H, m, Ph-*H*), 7.37 (1H, d, $J=15.9$ Hz, 3-vinyl-*H*), 7.36 (2H, s, Ph-*H*), 7.27 (1H, d, $J=15.9$ Hz, 3-vinyl-*H*), 7.29–7.20 (4H, m, Th- $H5'$, $H5''$, $H3'$, $H3''$), 7.22 (1H, d, $J=16.0$ Hz, 2-vinyl-*H*), 7.20 (1H, d, $J=15.9$ Hz, 5-vinyl-*H*), 7.19 (1H, s, Th- $H4$), 7.06 (1H, dd, $J=5.2, 3.6$ Hz, Th- $H4'$), 7.02 (1H, d, $J=16.0$ Hz, 2-vinyl-*H*), 7.00 (1H, dd, $J=5.2, 3.6$ Hz, Th- $H4''$), 6.93 (d, 1H, $J=15.9$ Hz, 5-vinyl-*H*); δ_C (100.6 MHz, $CDCl_3$) 142.6, 142.2, 137.4, 127.3, 137.1, 129.9, 128.9, 128.7, 128.3, 127.8, 127.7, 126.5, 125.0, 124.7, 124.6, 122.5, 122.2, 121.1, 120.2, 118.9; m/z (EI) 402 (100, M^+), 311 (12), 305 (21), 292 (10%); HRMS (EI): M^+

found 402.0568. $C_{24}H_{18}S_3$ requires 402.0571; λ_{\max} nm (ϵ): 336 (39,500), 351 (38,500), 406 sh (25,000), 428 (31,000), 451 (24,500).

4.2.9. (E)-3-(2-(4-Methoxyphenyl)vinyl)-2,5-diiodothiophene (11). Compound **10** (4.86 g, 10 mmol) and 4-methoxybenzaldehyde (1.43 g, 11 mmol) were dissolved in THF (50 mL) and cooled to 0 °C. To the resulting solution potassium *tert*-butoxide (2.24 g, 20 mmol) was added, the cooling bath was removed and the resulting mixture stirred at room temperature overnight under argon. The resulting reaction mixture was diluted with dichloromethane and washed with 1 mol L⁻¹ hydrochloric acid. The organic layer was dried over magnesium sulphate and the solvents were removed under vacuum at 50 °C. The residue was purified on silica using 30% dichloromethane in hexane as eluent and recrystallized from ethanol to give fine white needles (3.55 g, 76%): mp 99–100 °C; δ_H (400 MHz, CDCl₃) 7.45–7.43 (2H, m, Ar-*H*), 7.29 (1H, s, Th-*H4*), 6.91–6.89 (2H, m, Ar-*H*), 6.86 (1H, d, $J=16.2$ Hz, vinyl-*H*), 6.75 (1H, d, $J=16.2$ Hz, vinyl-*H*), 3.83 (3H, s, OCH₃); δ_C (100.6 MHz, CDCl₃) 159.7, 145.3, 134.4, 131.1, 129.3, 127.9, 114.2, 78.6, 77.2, 55.3; m/z (EI) 468 (73, M⁺), 342 (13), 214 (100), 199 (21), 171 (48), 107 (10%); HRMS (EI): M⁺ found 467.8543. C₁₃H₁₀I₂OS requires 467.8542.

4.2.10. (E)-3-(2-(4-Methoxyphenyl)vinyl)thiophene-2,5-dicarbaldehyde (12). Compound **11** (2.43 g, 5 mmol) was dissolved in dry THF (20 mL), cooled to -78 °C, and a 2.5 mol L⁻¹ solution of *n*-butyl lithium in hexane (4 mL, 0.010 mol) was added dropwise with a syringe. The resulting mixture was stirred at -78 °C for 15 min, after which, a solution of dry DMF (2.19 g, 0.03 mol) in THF (1 mL) was added. The reaction mixture was allowed to reach room temperature before being poured into 1 mol L⁻¹ hydrochloric acid (150 mL) and extracted twice with dichloromethane. The organic layer was separated, dried over magnesium sulphate and evaporated to dryness under reduced pressure at 50 °C to give a brownish oil. Purification on silica, using dichloromethane as eluent followed by recrystallization from ethanol yielded yellow crystals (0.98 g, 72%): mp 142–144 °C; δ_H (400 MHz, CDCl₃) 10.26 (1H, s, 2-CHO), 10.01 (1H, s, 5-CHO); 8.05 (1H, s, Th-*H4*), 7.54 (1H, d, $J=16$ Hz, vinyl-*H*), 7.50–7.48 (2H, m, Ar-*H*), 7.18 (1H, d, $J=16$ Hz, vinyl-*H*), 6.95–6.92 (2H, m, Ar-*H*), 3.85 (3H, s, OCH₃); δ_C (100.6 MHz, CDCl₃) 183.5, 182.8, 160.5, 147.8, 146.6, 141.0, 135.5, 133.4, 128.5, 128.3, 116.2, 114.4, 55.4; m/z (EI) 272 (100, M⁺), 215 (16), 200 (18), 184 (12), 108 (10%); HRMS (EI): M⁺ found 272.0508. C₁₅H₁₂O₃S requires 272.0507.

4.2.11. (E,E,E)-2,5-Bis(2-thien-2-ylvinyl)-3-(2-(4-methoxyphenyl)vinyl)thiophene (6b). Compound **13** (0.27 g, 1 mmol) and thiophen-2-ylmethyltriphenylphosphonium bromide (0.97 g, 2.2 mmol) were dispersed in dry THF (50 mL). DBU (1.0 g, 6.6 mmol) was added and the mixture was refluxed overnight under argon. The resulting reaction mixture was poured into 1 mol L⁻¹ hydrochloric acid (100 mL) and extracted twice with dichloromethane. The organic layers were dried over magnesium sulphate and evaporated to dryness under vacuum at 50 °C. The residue was purified on silica using 20% ethyl acetate in hexane as

eluent and recrystallized from dichloromethane–methanol mixture to give fine yellow needles of **6b**. (0.35 g, 82%).

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