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Towards functionalized poly(terthiophenes): regioselective synthesis of oligoether-substituted bis(styryl)sexithiophenes†

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A variety of new bis(oligo(oxyethylene)styryl)sexithiophenes have been prepared by chemical oxidation of ether-substituted styrylterthiophenes with $FeCl_3$. In all cases dimers are formed in high yields, rather than the expected polymers. In addition, although three different regioisomers can potentially be formed from such an oxidation, the isolable products are shown to consist of only the head-to-head regioisomer. Theoretical calculations on alkoxystyrylterthiophenes show that this can be understood in terms of an uneven electron spin density distribution at the two α-positions available for polymerization. Electron density calculations on the resulting head-to-head alkoxystyrylsexithiophenes show that the spin density is concentrated in the core of the molecule rather than at the α-positions, a result that explains the absence of significant amounts of higher oligomers.

Introduction

Oligothiophenes possess electronic and optical properties that facilitate their use in electroluminescent devices,[1] sensors,[2] solar cells,[3] organic laser diodes[4] and field effect transistors.[5–7] In particular regioregular oligomers are especially useful as they possess enhanced magnetic, optical and electrochemical properties when compared with their regiorandom analogues.[5,8–11] Non-symmetrical thiophene monomers can couple in a ‘head-to-head’, ‘head-to-tail’ or ‘tail-to-tail’ manner, and the resulting oligothiophenes consist of multiple regioisomers.[10] Regioregularity is easier to control in shorter oligothiophenes and, in many applications, sexithiophenes are preferred over polydisperse polythiophenes, as they show superior electronic properties.[6,12,13] Unsubstituted α-sexithiophene, however, is only sparingly soluble and is thus difficult to process.[14] Attention has, therefore, been focused on synthesizing sexithiophenes substituted with solubility-enhancing groups.

β-Substituted sexithiophenes have been prepared by a number of synthetic methods. Palladium-catalyzed cross-coupling methods involve the reaction between a halogenated thiophene, and organotin (Stille coupling[15]) or boronic acid (Suzuki coupling[16]) substituted thiophenes.[17,18] While many groups have used this approach,[19–21] it is synthetically complex and undesired side reactions can include homocoupling, reduction, elimination, isomerization, and reaction of functional substituents.[17] Kumada coupling uses either a palladium or nickel catalyst and involves the reaction of a thiophene Grignard reagent with a halogenated thiophene. Published substituted sexithiophene syntheses utilizing the Kumada reaction have particularly low yields (8–20%).[22,23] In addition, the selective bromination of thiophenes and oligothiophenes is difficult,[24] and the multiple products usually produced are not always separable.[25] A regiospecific reductive homocoupling can also be carried out using α-brominated terthiophenes in the presence of a nickel catalyst formed *in situ* from nickel dichloride, triphenylphosphine and zinc. This approach was used by Bäuerle *et al.* to couple 3′-didodecyloterthiophene, although the yield was poor (33%).[25] Homocoupling between lithiated terthiophenes is effective when the starting monomer is symmetrical,[26] but produces a mixture of regioisomeric products when used on a mono-substituted terthiophene.[27]

While β-substitution has been effective in producing more soluble materials, the introduction of substituents directly attached to the oligomer backbone can cause steric hindrance, reducing conjugation and deleteriously affecting electronic properties.[14,21] In order to overcome this, sexithiophenes have been produced that incorporate substituents at the two terminal α-positions. These ‘end-capped’ sexithiophenes have commonly been made by dimerisation of an α-substituted terthiophene, the substituent enforcing regioselectivity and preventing further polymerization. This homocoupling reaction has been achieved between lithiated terthiophenes in the presence of $CuCl_2$[7,28,29] or other catalysts,[30] and between brominated terthiophenes under various reaction conditions.[31,32] Regioselectively-functionalized sexithiophenes have also been made by metal-catalyzed cross-coupling of terthiophenes, although this is necessarily a more complex synthetic method as two differently functionalized terthiophenes must be made.[14] Further strategies involve the reaction of a central bithiophene unit with two ‘end’ bithiophenes in Stille[14,33] or Kumada[34] couplings.

While these approaches are effective, they involve substantially more complex chemistry than polymerization of monomers using $FeCl_3$, a method often employed for the formation of polythiophenes due to its simplicity of use and low cost. Such polymerizations generally give high molecular weight polymers,[35] however the exact structure of polymers formed from non-symmetrical monomers can often be difficult to determine.[36,37] In order for polymers prepared by chemical oxidation to be regioselective, there must be a sufficiently large difference in the spin–charge density of the radical cation

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† Electronic supplementary information (ESI) available: ^1H NMR spectra of styryl-15-crown-5 terthiophene (**1**) and 15-crown-5 terthiophene dimer $(\mathbf{1})_2$ and characterization data for compounds $(\mathbf{2})_2$, $(\mathbf{4})_2$, $(\mathbf{5})_2$, $(\mathbf{7})_2$ and $(\mathbf{8})_2$. See http://www.rsc.org/suppdata/ob/b5/b502791h/

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generated in the oxidative polymerization process between the two available α-positions.[10,38] There are few examples of chemical oxidation producing regioisomerically pure sexithiophenes in the literature. Mustafa and Shepherd[22] oxidized 4-trimethylsilyl-2,2′:5′,2″-terthiophene with ceric ammonium nitrate and isolated only the 'head-to-head' dimer, however the yield was extremely low (8%). Goldoni *et al.* investigated the effects of alkylsulfanyl substitution on the chemical polymerization of thiophenes,[39,40] and showed that the incorporation of an alkylsulfanyl moiety at the 3-position of thiophene leads to regioselective polymerization due to the deactivating effect felt at the 5-position. While yields were reasonable for the trimer (62%), they decreased with increasing oligomer size so that the hexamer could only be obtained in a poor 5% yield.[40] Applying the same methodology to 3-butylsulfanyl bithiophene gave a good yield (70%) of a single sexithiophene isomer in one step.[39] A single isomer of a methylated sexithiophene was obtained by Engelmann *et al.* after $FeCl_3$ oxidation (65%), however this was due to the methylation of all six β-positions and one α-position of the monomer so that only one product was possible.[41]

The position of oxygen atoms can have a marked effect on regioregularity, as demonstrated by the asymmetric reactivity of 3-alkoxy thiophenes.[42,43] When treated with $FeCl_3$, only low molecular weight material is obtained from 3,3″-dipentoxyterthiophene. However, in the isomeric compound 4,4″-dipentoxyterthiophene, the α-positions next to the alkoxy substituents are activated, and treatment with $FeCl_3$ under similar conditions produces a high molecular weight material.[44] The same effect was also observed for bithiophene.[45]

In all of these examples the substituents affecting the regioselectivity and extent of polymerization are located directly on the thiophene ring. To the best of our knowledge, there have been no investigations carried out on the $FeCl_3$ polymerization of 3′-styryl-substituted terthiophenes, and it is unclear from the literature what effect substitution on the central terthiophene ring would have on the regioselectivity and extent of polymerization.

Previously we have synthesized a range of terthiophenes functionalized at the 3′-position with substituted-styryl moieties.[46–52] These monomers were designed to form conducting polymers with applications in photovoltaics, sensors, and actuators. In particular, monomers containing crown ether or polyether chains are precursors to polythiophenes that could have applications as ion-sensors.[47–49,52] It will be shown, however, that both chemical and electrochemical oxidations of polyether-substituted monomers result in dimers, rather than polymers, as the only soluble product. Furthermore, the dimers consist of only the head-to-head regioisomer. The disubstituted sexithiophenes thus formed are highly soluble, and possess a fully conjugated polyether moiety. Combined with the high yields of the reaction, the straightforward synthesis and purification, and the low-cost of the reagents used, we believe that these materials could have wide utility in a variety of applications.

Results and discussion

Synthesis

The monomers investigated in this work are shown in Fig. 1. Monomers **10** and **11** were included as reference materials against which the behaviour of the polyethers could be compared. Polymerizations were carried out using similar conditions to those of Wang *et al.*,[53] whereby a $CHCl_3$ suspension of $FeCl_3$ is added slowly to a $CHCl_3$ solution of the monomer. The solution is then left to stir at room temperature for a considerable length of time, to allow complete conversion of the monomer to the polymer. The polymer is simultaneously precipitated and dedoped by treatment with methanol, then recovered by filtration. Extraction in a soxhlet apparatus with methanol removes oligomers, and also ensures complete dedoping of the polymer.

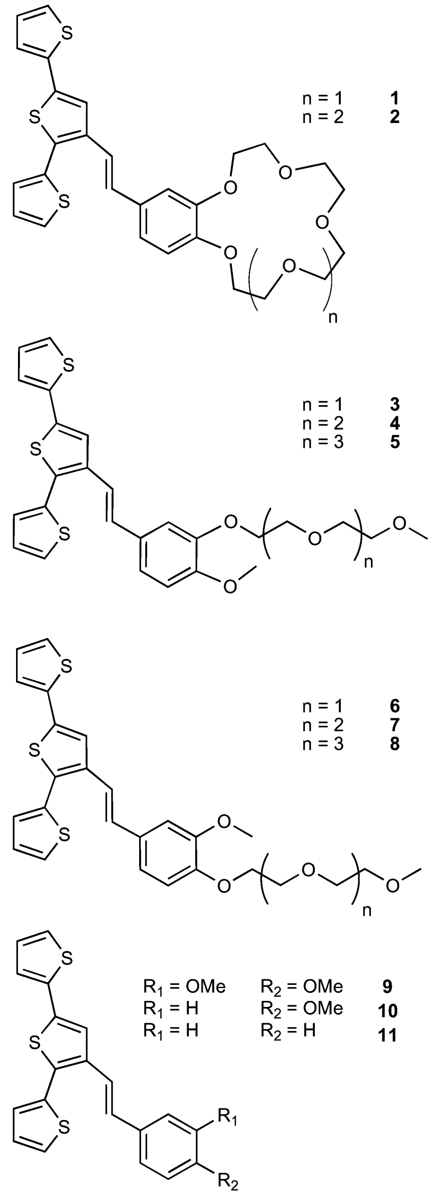


Fig. 1 Styryl-substituted terthiophene monomers.

Application of the above general polymerization method to monomers **1** to **9** resulted in the isolation of a red powder with percentage yields between 59 and 93% that was soluble to a greater or lesser extent in CH_2Cl_2, together with small amounts of insoluble material. It was not possible to characterize the insoluble material using available spectroscopic techniques but it seems likely that it could be either a higher oligomer, or cross-linked material. Yamamoto and Hayashi[54] found that on $FeCl_3$ oxidation of thiophenes substituted with aromatic rings, cross-linked material was produced due to oxidation of the benzene ring, as well as the thiophene ring. Monomers **10** and **11** gave much lower yields of CH_2Cl_2 soluble material (24% and 9%, respectively) than were obtained for dialkoxystyryl-substituted monomers.

Characterization of the soluble material

The solubility of the sexithiophenes in CH_2Cl_2 increases markedly with increasing length of the attached polyether chain and they consist solely of head-to-head linked dimers as will be demonstrated by considering the characterization of the soluble product $(\mathbf{1})_2$ of the oxidation of styryl-15-crown-5 terthiophene **1**. Analysis of $(\mathbf{1})_2$ by FAB-MS suggested that the product consisted solely of dimer (m/z = 1078.20). The NMR spectra of the aromatic region of **1** and $(\mathbf{1})_2$ are included in the electronic supplementary material†. A comparison of these spectra provides clear evidence for the nature of the dimerization; the doublet of doublets at δ 7.41 assigned to the head α-proton of terthiophene **1**[49] is absent in the dimer spectrum indicating head-to-head coupling (Scheme 1). This is supported by the loss of the head β-assigned doublet of doublets at δ 7.13 seen in the spectrum of the monomer and the appearance of a doublet for the equivalent proton in the spectrum of the dimer.

Further analysis of the 2-D ^{1}H connectivity information obtained from COSY confirmed that the product was the head-to-head linked dimer, and ^{13}C NMR spectra are also consistent with this conclusion. ^{1}H and ^{13}C measurements on the dimers $(\mathbf{2})_2$ to $(\mathbf{8})_2$ inclusive, show that for these oligomers also, the only product is the head-to-head dimer. Unlike the polyether dimers, compounds $(\mathbf{9})_2$, $(\mathbf{10})_2$, and $(\mathbf{11})_2$ are quite insoluble in CH_2Cl_2. ^{13}C and 2D experiments were, therefore, not practicable for these compounds but the ^{1}H NMR spectra of $(\mathbf{9})_2$ and $(\mathbf{10})_2$ were consistent with head-to-head linked dimers. No useful NMR data of any kind could be obtained for $(\mathbf{11})_2$ because of its extremely low solubility.

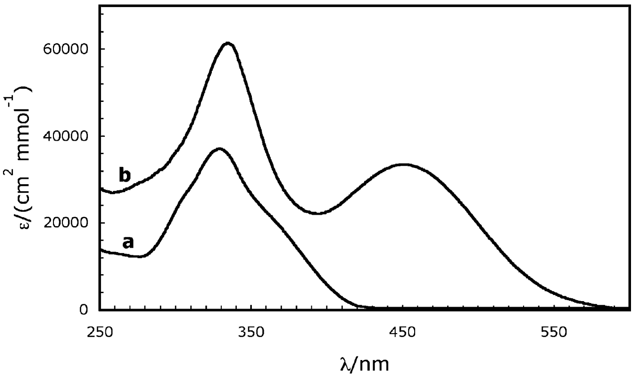
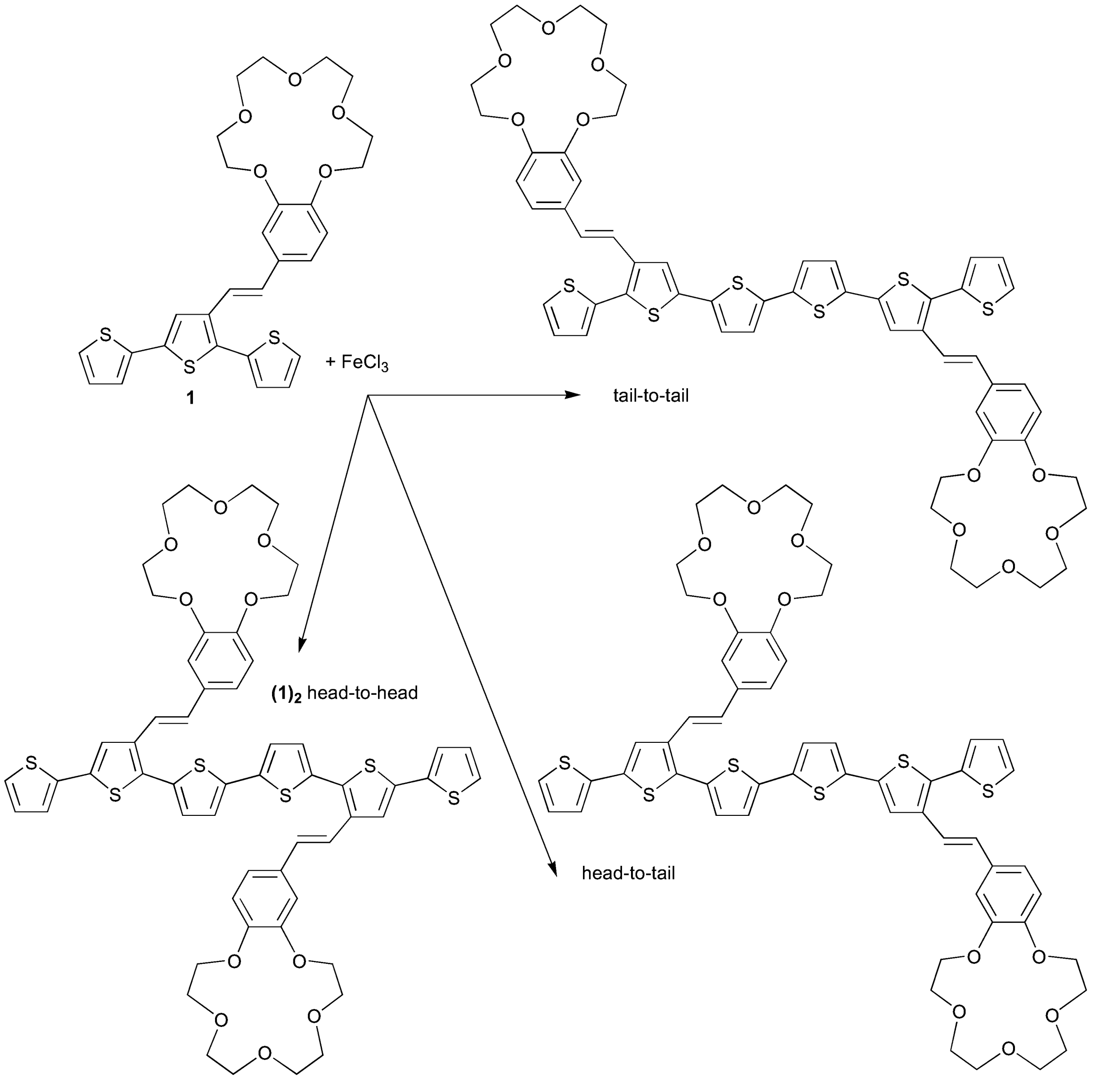


Fig. 2 Electronic absorption spectra of (a) **1** and (b) $(\mathbf{1})_2$ in CH_2Cl_2 solution.

The electronic spectra of the oligomers is also consistent with the presence of dimers as the sole product. This can be seen from the spectra for **1** and $(\mathbf{1})_2$ shown in Fig. 2. All the dioxystyryl substituted monomers have absorption maxima at 329(1) nm with shoulders at 304(1) nm and 365(1) nm as a result of three π to π^* transitions.[55] The corresponding dimer spectra show two bands as expected for styryl-substituted sexithiophenes.[56] The low energy band varies in position between 445 and 459 nm and is due to the HOMO–LUMO transition associated with the sexithiophene chromophore and the high energy band at 336(1) nm associated with the styryl chromophore.[56] The molar extinction coefficient for this latter transition is approximately twice that of the corresponding chromophore in terthiophene **1** as expected (see Fig. 2).

Electronic absorption spectra were also obtained for thin films of the dimers produced by casting from CH_2Cl_2 solution; this data is given along with the corresponding solution data in Table 1. The red shift seen in the low energy absorption band on going from the solution to the solid state is characteristic



Scheme 1 Possible regioisomeric products formed on dimerization of **1**.

Table 1 Dimer solution and solid state UV–VIS data

Compound	CH_2Cl_2 solution λ_{max}/nm (logε/(cm^2 mmol^{-1}))	Thin film λ_{max}/nm
(1)$_2$	336(4.82), 450(4.59)	357, 499
(2)$_2$	336(4.83), 446(4.56)	346, 480
(3)$_2$	335(4.83), 452(4.61)	353, 528
(4)$_2$	335(4.81), 446(4.57)	348, 500
(5)$_2$	336(4.80), 451(4.61)	343, 485
(6)$_2$	336(4.78), 459(4.62)	380, 511
(7)$_2$	336(4.82), 448(4.60)	349, 489
(8)$_2$	337(4.81), 454(4.63)	345, 478
(9)$_2$	336(4.80), 445(4.55)	343, 510, 555 (shoulder)

of soluble polythiophenes, and has been attributed to a conformational change from a flexible coil-like structure in solution to a more rigid rod-like conformation in the solid state.[53] While the solution data does not show a clear trend, the solid state absorption peaks show a significant blue shift in the low energy band shifts with increasing polyether chain length. This is likely to be a steric rather than an electronic effect, with the longer polyether chains causing the molecules to adopt a less planar conformation, leading to a decrease in the conjugation length.

The λ_{max} values given in Table 1 are as high as those reported for some polymerized terthiophene derivatives comprising up to 21 thiophene rings[53,57] implying that the effective conjugation lengths of the longer oligomers may be as short as six thiophene rings. Thus, the sexithiophenes synthesized here could potentially have electrochemical properties as good as those of considerably longer oligothiophenes.

Characterization of oxidation products

In order to probe the nature of the dimerization, the oxidation and subsequent reduction of the various monomers was investigated by UV–VIS–NIR spectroscopy. Spectra were measured over the wavelength range 190–1500 nm using spectroscopy-grade acetonitrile as solvent. Monomer concentrations used were 2.3×10^{-5}–2.8×10^{-5} M, giving maximum absorbances of 0.8–1.2 AU. The monomer spectrum was recorded prior to the addition of oxidant. 5–10 μL aliquots of a solution of 0.4 M copper perchlorate in acetonitrile were added to give an oxidant to monomer ratio of 50 : 1 and the spectrum of the oxidized product recorded. Two drops of 2% aqueous hydrazine were then added to reduce the product and the solution thoroughly mixed before a final spectrum was recorded. Similar results were obtained for all the dioxy-substituted monomers **1–9**, and representative spectra observed when the above procedure was carried out on monomer **1** are shown in Fig. 3.

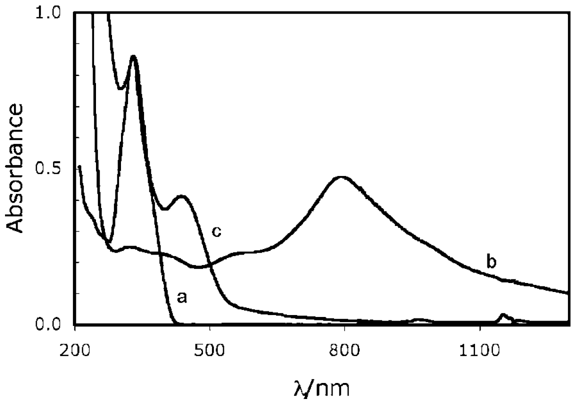


Fig. 3 Electronic absorption spectra obtained during the oxidation of **1** showing (a) neutral monomer, (b) oxidized species and (c) reduced product.

It is clear from Fig. 3 that reduction of the oxidized species with hydrazine does not regenerate the original terthiophene. Instead, two bands are observed at 331 and 437 nm consistent with the presence of the neutral **(1)**$_2$, *i.e.* the species formed in the oxidation reaction is the σ-dimerised terthiophene and not the terthiophene itself.

There are several possibilities for the origin of the bands observed in the spectrum of the oxidized species: the monomer radical cation $3T^{\bullet+}$, the π-dimer radical cation $(3T^{\bullet+})_2$, the dimer radical cation $6T^{\bullet+}$, and the dimer dication $6T^{2+}$. The π-dimer radical cation $(3T^{\bullet+})_2$ observed in acetonitrile by Hill *et al.*[58] is extremely unlikely in this case for two reasons. First, the π-dimers were only observed in terthiophene derivatives that were substituted at their α-positions, precluding the otherwise rapid formation of σ-dimers, and second, π-dimers were only present at low oxidant concentrations, with the compounds being further oxidized to dications on addition of more oxidant. In the present study, since a 50-fold excess of Cu(II) oxidant is present, it is unlikely that π-dimers will exist. It also seems improbable that monomer radical cations would be observed, given the propensity of terthiophene radical cations to rapidly couple.[12] Thus, the most likely species in solution are the dimer radical cation and/or the dimer dication. A detailed analysis of the oxidation process and the various species present during the course of the investigation has been published elsewhere.[56] A notable feature of the oxidized spectrum shown in Fig. 3 is the absence of a free carrier tail; an observation consistent with the absence of long chain conducting polymers.

Attempts to obtain polymers by chemically oxidizing the sexithiophenes were unsuccessful. On addition of the oxidant, similar spectra to those obtained on oxidation of the terthiophenes were observed, and on reduction with hydrazine the original sexithiophene spectrum was recovered.

Electrochemistry

In order to investigate whether the sexithiophenes produced in the chemical oxidations could be induced to react further, electrochemical oxidation of both the terthiophene monomers and dimers was also investigated. Cyclic voltammograms for monomer **1** are shown in Fig. 4.

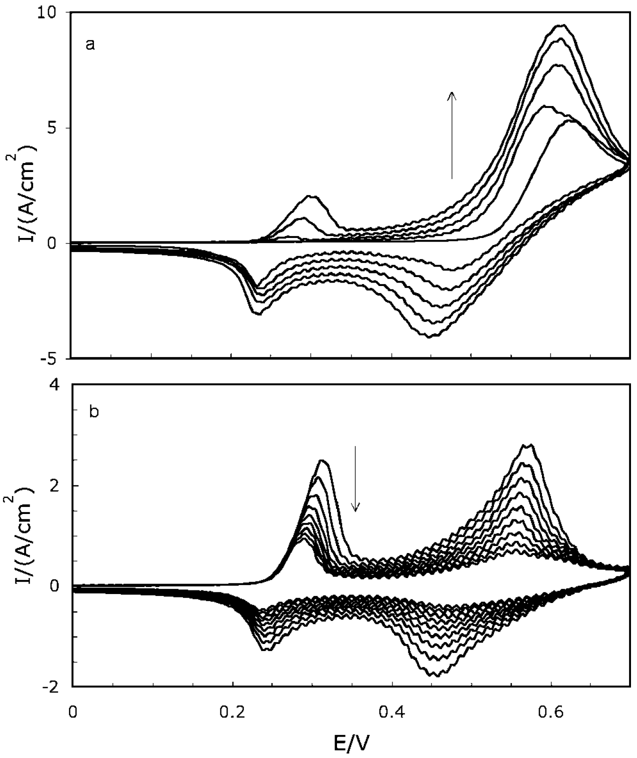


Fig. 4 (a) Growth CV of a 10 mM solution of terthiophene **1** in 0.1 M TBAP. (b) Post polymerization CV in 0.1 M TBAP.

The growth CV (Fig. 4a) clearly shows the formation of an electroactive species with two reversible redox peaks. On the first scan, only one oxidation peak is seen at 0.64 V. On subsequent scans, two oxidation peaks are observed at 0.28 and at 0.64 V. The corresponding reduction peaks occur at 0.22 and 0.47 V. The oxidation peak at 0.64 V is due to oxidation of the monomer to its radical cation. Terthiophene radical cations are known to be very reactive and will couple rapidly with a terthiophene molecule to form a dimer radical cation.[12] The oxidation potential required to oxidize terthiophene to its radical cation is higher than the oxidation potential required to oxidize sexithiophene, so that the newly formed neutral sexithiophene is oxidized immediately to its dication as it is formed. The two peaks observed during the reduction cycle are, therefore, likely to be due to the reduction of the sexithiophene dication to the radical cation, and then the radical cation to the neutral species. On further oxidation cycles, dimer is present and the new oxidation peak at 0.28 V due to oxidation of the dimer to its radical cation. MALDI-MS analysis of this solution indicated the presence of dimer, but no higher oligomers. The red adherent film formed on the electrode surface was subjected to post-polymerization cyclic voltammetry in monomer-free electrolyte solution (Fig. 4b). The post-polymerization CV in TBAP shows the same two sets of redox peaks evident in the growth CV. After the first scan, during which any trapped monomer could be oxidized/polymerized, these peaks are similar in size, as would be expected for a reversible redox system. This CV strongly resembles that seen by Zotti *et al.* for 3′-pentoxy-3,3″-dioctyl-[2,2′5′,2″]-terthiophene, where only dimers were formed on electropolymerization.[59] A gradual decrease in current occurs on post-polymerization cycling in monomer-free electrolyte (Fig. 4b), caused by a slow dissolution of the product in acetonitrile, as indicated by the gradual yellow coloration of the electrolyte solution and eventual recovery of the mirror surface on the platinum working electrode.

Films were also grown onto ITO-coated glass, for analysis by UV–VIS–NIR spectroscopy. Separate films were grown in the neutral and oxidized state, and their spectra are shown in Fig. 5. The λ_{max} peaks in the spectrum of the neutral film occur at 348 and 480 nm. These values correlate well with those obtained for a film of the pure dimer (357, 499 nm; see Table 1) produced by casting the sexithiophene directly onto ITO glass, providing further evidence that under these conditions, only dimerization is occurring. In the oxidized spectrum there is also an absence of a free carrier tail as previously observed for the corresponding chemical oxidation (Fig. 3).

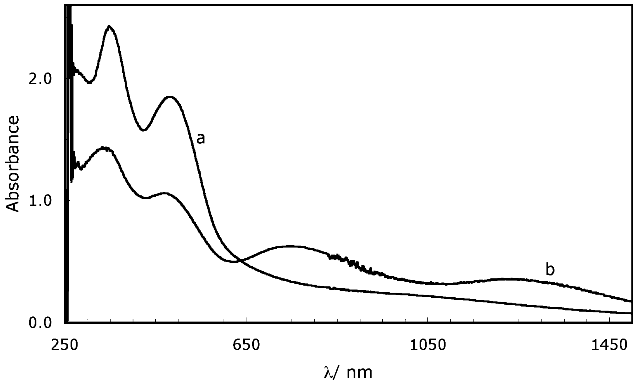


Fig. 5 UV–VIS–NIR spectra of film produced by the electrochemical oxidation of terthiophene **1** in the neutral (a) and oxidized (b) forms.

An SEM image of a reduced film electrochemically grown from terthiophene **1** onto ITO-coated mylar is shown in Fig. 6. It is clear that upon electropolymerization under these conditions, a continuous film is not produced. Indeed, the numerous discrete coral-like structures seen are indicative of oligomeric species.

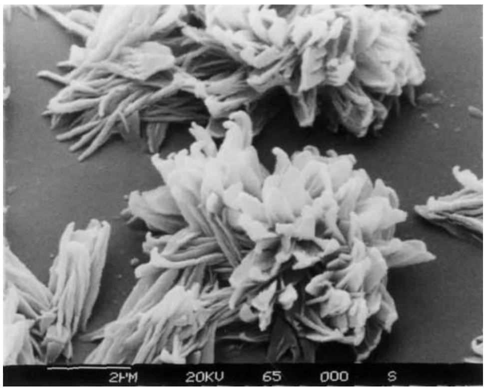


Fig. 6 SEM of reduced film produced from the electrochemical oxidation of terthiophene **1** onto ITO-coated mylar.

An attempt was also made to electropolymerize the chemically produced sexithiophene dimers. The experiments were carried out in CH_2Cl_2 containing 0.1 M TBAP at monomer concentrations of between 0.5 and 1.0 mM. In all cases, oxidation and reduction peaks were seen but there was no increase in current with scan number or any visible film deposited on the working electrode surface, and the redox peaks corresponded to those observed in the CV of the monomer.

Theoretical calculations on monomers

The observed regioregularity in the sexithiophene products can only be explained by a difference in reactivity between the two available terthiophene α-positions. This leads to the conclusion that the head α-position is more reactive than the tail position, and therefore coupling occurs more quickly at this position.

Spin-density calculations on the radical cations of the styryl **11**, methoxystyryl **10** and dimethoxystyryl terthiophene **9** were carried out to establish the effect of successive substitution of methoxy groups in the styryl moiety on the electron densities in the terthiophene ring system. In view of the UV–VIS results, dimethoxystyrylterthiophene will serve as a good model for all the dioxyterthiophenes. The method B3LYP/6-31G(d)[60] was used to calculate the spin densities during each geometry optimization. The spin densities calculated for the head α (5) and tail α (5″) positions are given in Table 2, along with the ratio of these two values.

The polymerization of substituted thiophenes depends both on electronic and steric effects.[61] However, by utilizing terthiophenes substituted on the central ring, any steric barriers to polymerization should be eliminated. In the absence of steric interactions, coupling occurs preferentially between carbon atoms with the highest spin densities,[38,43] a spin density ratio greater than 2.0 indicating a strong directing influence of the radical cations.[38] It can be seen from the data in Table 2 that the dimethoxystyryl compound **9** could be expected to give a greater proportion of head-to-head linked dimer than compounds **10** or **11**. This is reflected in the yields of the corresponding chemical polymerizations, where the dioxystyryl-substituted terthiophenes **1–9** produce excellent yields of head-to-head linked dimer. It is unlikely that any tail-to-tail dimer will form, due to the low electron spin-densities at the tail α-position. It is feasible that some head-to-tail dimer may have

Table 2 Calculated spin density values for styryl-substituted terthiophenes **9–11**

Compound	Spin density (head α-position)	Spin density (tail α-position)	Spin density ratio (head/tail)
11	0.196	0.130	1.52
10	0.164	0.094	1.74
9	0.135	0.074	1.83

Table 3 Calculated spin density values for styryl-substituted sexithiophenes $(\mathbf{9})_2$–$(\mathbf{11})_2$

Compound	Spin density (α)	Spin density ring A	Spin density ring B	Spin density ring C	Spin density (styryl)
Sexithiophene	0.085	0.114 (22%)	0.185 (36%)	0.217 (42%)	—
$(\mathbf{11})_2$	0.062	0.079 (15%)	0.158 (31%)	0.208 (41%)	0.067 (13%)
$(\mathbf{10})_2$	0.053	0.067 (13%)	0.147 (29%)	0.196 (39%)	0.090 (18%)
$(\mathbf{9})_2$	0.048	0.060 (12%)	0.137 (28%)	0.182 (37%)	0.112 (23%)

formed during chemical polymerization, however the lack of isolation of such a compound implies that if it was formed, then it must have reacted further. This could be the origin of some of the insoluble fraction isolated from the oxidation reactions. However, it is also possible that the insoluble fraction could have resulted from oxidation of other parts of the molecule.[54]

Theoretical calculations on dimers

In order to investigate the unusual stability of the sexithiophenes, spin density calculations were carried out on the radical cations of $(\mathbf{9})_2$, $(\mathbf{10})_2$, and $(\mathbf{11})_2$. The spin densities, totalled for each thiophene ring, are given in Table 3, and those for dimethoxystyrylterthiophene $(\mathbf{9})_2$ are shown in Fig. 7.

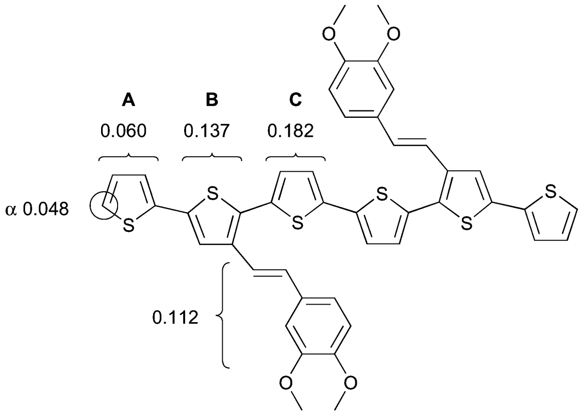


Fig. 7 Spin density calculations for dimer $(\mathbf{9})_2$.

It can be seen from Table 3 that the percentage of spin density on the crucial unsubstituted α-position decreases on incorporation of the styryl moiety, then further decreases on addition of oxygen atoms. At the same time, the proportion of spin density residing on the inner rings and the styryl moiety is increasing with respect to the spin at the α-position. This points to more localized charge defects for the dioxystyrylsexithiophenes. It appears that while the sexithiophene radical cation is being formed on oxidation, there is insufficient electron spin density at the α-position for further coupling to occur. Instead, the majority of the spin density is confined to the four inner terthiophene rings and the styryl moieties. Calculations were also performed on two isomeric compounds containing longer polyether chains. The results for these compounds are the same as for $(\mathbf{9})_2$, indicating that the extension of the polyether chain has little effect on the electronic properties of the system.

Conclusions

Chemical polymerizations using $FeCl_3$ on a range of styryl-substituted terthiophenes result in the formation of regioregular head-to-head dimers. Theoretical calculations support the argument that this is due to an asymmetric reactivity of the two available α-positions of the terthiophene monomers caused by uneven electron spin density distribution, rather than by any steric effects. Electron spin density is considerably higher at the head α-position, causing dimerization to occur preferentially in a head-to-head fashion. The difference in the electron spin density between the head and tail α-positions is less marked for methoxystyryl terthiophene **10** and styryl terthiophene **11**, and this is reflected in the much lower yields of dimer obtained from these reactions. Electrochemical polymerization of the polyether-substituted monomers gave red adherent coatings in most cases. However, these films were shown by SEM to be non-coherent, and by UV–VIS–NIR to consist only of dimers. The dimers themselves undergo electrochemical oxidation and reduction, but do not couple or form films on the working electrode surface. Theoretical calculations on the sexithienyl species showed only a small percentage of spin density resident on the available α-position. This explains the lack of reactivity of these compounds, and why polymerization of terthiophene monomers stops at the sexithiophene dimer. In light of these results, we have begun work on similarly substituted terthiophenes that also incorporate alkoxy substituents at the 4 and 4″-positions, in order to facilitate polymerization. Preliminary work indicates that these compounds polymerize to a far greater extent.[50]

Experimental

^1H NMR spectra were obtained at 400.13 MHz using Bruker 400 Avance running X-WIN NMR software. The chemical shifts are relative to TMS or to the residual proton signal in deuterated solvents ($CDCl_3$ δ 7.27). ^{13}C NMR shifts are relative to $CDCl_3$ (δ 77.0) or CD_2Cl_2 (δ 53.1). Chemical shifts are reported as position (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), relative integral, coupling constant (J Hz) and assignment. Full structural assignments were assisted by the acquisition of appropriate data from 2D experiments (COSY, HMQC, HMBC).

UV–VIS–NIR spectra were collected on a Shimadzu UV-3101PC UV-VIS-NIR Scanning Spectrophotometer controlled by a PC running Shimadzu software. AR, HPLC or spectroscopy grade solvents were always used.

Electrochemical measurements were made using an Autolab Potentiostat Galvanostat controlled by a PC using Autolab GPES software. All cyclic voltammograms were recorded at room temperature with a sweep rate of 100 mV s^{-1}, starting and finishing at the cathodic limit. The working electrode was a platinum disk with an area of 0.0201 cm^2, the counter electrode was platinum mesh, and the reference electrode Ag/AgCl. All measurements were carried out in acetonitrile with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte.

HRMS (FAB and EI) was carried out using a Varian VG70-250S double focusing magnetic sector mass spectrometer.

Melting point determinations were performed on a Cambridge Instruments Kofler hot-stage, and are uncorrected.

Column chromatography was performed using Merck Kieselgel 60 (230–400 mesh), and thin-layer chromatography using precoated silica gel plates (Merck Kieselgel^{60} F_{254}).

Spin density calculations were performed during geometry optimisations using DFT methods (the B3LYP functional and the 6-31G(d) basis set) and the Gaussian 03 program.[62]

The reagents and solvents used in this work came from many different sources, and were generally AR grade. Chromatography solvents were laboratory grade and were distilled before use. H_2O was reverse osmosis for most applications. Higher purity H_2O was obtained by distilling Milli-Q H_2O off activated charcoal. Dry degassed CH_2Cl_2 and DMF were prepared by distillation of AR grade solvent over CaH_2 under a N_2 atmosphere. Dry toluene, ether, benzene and THF were prepared by passing argon-degassed solvent through activated alumina columns. N_2 (oxygen-free) was passed through a KOH drying column to remove moisture.

General procedure for formation of sexithiophenes $(\mathbf{1})_2$–$(\mathbf{9})_2$

5″-Bis-{2-(2′-[2″,2‴5‴,2⁗]terthiophen-3‴-yl-vinyl)-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecene} (1)₂. 2-(2′-[2″,2‴5‴,2⁗]Terthiophen-3″-yl-vinyl)-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecene **1** (0.1638 g 0.303 mmol) was dissolved in dry CH_2Cl_2 (5 mL) under N_2 before anhydrous $FeCl_3$ (0.2603 g, 1.605 mmol) in dry CH_2Cl_2 (10 mL) was added slowly. The reaction mixture was left to stir for 50 hours before being poured into MeOH (100 mL), causing a red precipitate to form. The precipitate was collected on a 0.45 µm HVLP membrane filter (Millipore) and dried under vacuum, then extracted with CH_2Cl_2 for 22 hours in a soxhlet apparatus. The CH_2Cl_2 was concentrated and the product precipitated with MeOH, collected on a membrane filter as previously and dried under vacuum. This yielded 5″-bis-{2-(2′-[2″,2‴5‴,2⁗]terthiophen-3‴-yl-vinyl)-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecene} $(\mathbf{1})_2$ as a red solid, melting point = 213–215 °C, (0.1188 g, 73%).

Electronic spectrum (CH_2Cl_2) λ_{max} nm/(log ε) 336.0 (4.82), 450.0 (4.59).

Electronic spectrum (thin film) λ_{max} nm 357.0, 499.0.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.66–3.72 (m, 16H, $OCH_2$9, 10, 12, 13); 3.85–3.87 (m, 8H, $OCH_2$7, 15); 4.10–4.16 (m, 8H, $OCH_2$6. 16); 6.87 (d, 2H, ^3J = 8.2 Hz, ArH4); 7.04 (d, 2H, ^3J = 16.3 Hz, H_{vinyl}1′); 7.06–7.10 (m, 4H, ArH1, 3); 7.08 (dd, 2H, ^3J = 5.1, ^4J = 3.6 Hz, ThH4⁗); 7.17 (d, 2H, ^3J = 3.8 Hz, ThH3″); 7.26 (d, 2H, ^3J = 3.8 Hz, ThH4″); 7.27 (dd, 2H, ^3J = 3.6, 1.2 Hz, ThH3⁗); 7.28 (d, 2H, ^3J = 16.3 Hz, H_{vinyl}2′); 7.31 (dd, 2H, ^3J = 5.1, ^4J = 1.2 Hz, ThH5⁗); 7.46 (s, 2H, ThH4″).

^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 68.3 OCH_2; 68.5 OCH_2; 68.9 OCH_2; 69.0 OCH_2; 69.8 OCH_2; 69.8 OCH_2; 70.4 OCH_2; 70.4 OCH_2; 111.3 ArC1; 113.2 ArC4; 119.2 C_{vinyl}2′; 119.8 ArC3; 122.1 ThC4″; 123.9 ThC3⁗; 124.2 ThC4″; 124.7 ThC5⁗; 127.2 ThC3″; 127.7 ThC4⁗; 130.0 ArC2; 130.2ThC2‴; 130.5 C_{vinyl}1′; 134.2 ThC2″; 135.7 ThC5‴; 136.3 ThC2⁗; 136.6 ThC3″; 137.1 ThC5″; 148.9 ArC4; 149.0 ArC18.

HRMS (FAB) M^+ calc 1078.2041, found 1078.1985.

4′,3⁗-Bis-(2⁗″-{4⁗‴-methoxy-3⁗‴-[2⁗⁗-(2⁗⁗′-methoxy-ethoxy)-ethoxy]-phenyl}-vinyl)-[2,2′5′,2″5″,2‴5‴,2⁗5⁗,2⁗′]sexithiophene (3)₂. Treatment of **3** with $FeCl_3$ yielded the title compound as a red solid, melting point = 172–173 °C (87%).

Electronic spectrum (CH_2Cl_2) λ_{max} nm/(log ε) 334.5 (4.83), 451.5 (4.61).

Electronic spectrum (thin film) λ_{max} nm 289.5, 352.5, 528.0.

^{1}H NMR (400.1 MHz, CD_2Cl_2) δ 3.32 (s, 6H, 2⁗⁗′OCH_3); 3.50–3.52 (m, 4H, $OCH_2$2⁗⁗′); 3.63–3.66 (m, 4H, $OCH_2$1⁗⁗′); 3.81–3.84 (m, 4H, $OCH_2$2⁗⁗); 3.86 (s, 6H, ArOCH_3); 4.16–4.19 (m, 4H, $OCH_2$1⁗⁗); 6.89 (d, 2H, ^3J = 8.3 Hz, ArH5⁗‴); 7.04 (d, 2H, ^3J = 16.0 Hz, H_{vinyl}2⁗″); 7.08 (dd, 2H, ^3J = 5.2 Hz, ^4J = 3.5 Hz, ThH4, 4⁗′); 7.09 (s, 2H, ArH2⁗‴); 7.12 (dd, 2H, ^3J = 8.3 Hz, ^4J = 1.9 Hz, ArH6⁗‴); 7.16 (d, 2H, ^3J = 3.7 Hz, ThH3″, 4‴); 7.26 (d, 2H, ^3J = 3.7 Hz, ThH4″, 3‴); 7.26 (dd, 2H, ^3J = 3.6 Hz, ^4J = 1.1 Hz, ThH3, 3⁗′); 7.27 (d, 2H, ^3J = 16.2 Hz, H_{vinyl}1⁗″); 7.31 (dd, 2H, ^3J = 5.1 Hz, ^4J = 1.1 Hz, ThH5, 5⁗′); 7.46 (s, 2H, ThH3′, 4⁗).

^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 55.5 ArOCH_3; 58.3 2⁗⁗′OCH_3; 68.1 $OCH_2$1⁗⁗; 69.3 $OCH_2$2⁗⁗; 70.2 $OCH_2$1⁗⁗′; 71.6 $OCH_2$2⁗⁗′; 111.0 ArC2⁗‴; 111.5 ArC5⁗‴; 119.1 C_{vinyl}1⁗″; 119.8 ArC6⁗‴; 122.1 ThC3′, 4⁗; 123.9 ThC3, 3⁗′; 124.2 ThC4″, 3‴; 124.7 ThC5, 5⁗′; 127.2 ThC3″, 4‴; 127.7 ThC4, 4⁗′; 129.8 ArC1⁗‴; 129.9 ThC5′, 2⁗; 130.5 C_{vinyl}2⁗″; 134.2 ThC2″, 5‴; 135.7 ThC2′, 5⁗; 136.3 ThC2, 2⁗′; 136.6 ThC4′, 3⁗; 137.1 ThC5″, 2‴; 148.2 ArC3⁗‴; 149.4 ArC4⁗‴.

HRMS (FAB) M^+ calc 994.1830, found 994.1871.

4′,3⁗-Bis-(2⁗″-{3⁗‴-methoxy-4⁗‴-[2⁗⁗-(2⁗⁗′-methoxy-ethoxy)-ethoxy]-phenyl}-vinyl)-[2,2′5′,2″5″,2‴5‴,2⁗5⁗,2⁗′]sexithiophene (6)₂. Treatment of **6** with $FeCl_3$ yielded the title compound as a red solid, melting point = 128–130 °C (82%).

Electronic spectrum (CH_2Cl_2) λ_{max} nm/(log ε) 336.0 (4.78), 458.5 (4.62).

Electronic spectrum (thin film) λ_{max} nm 291.0, 380.0, 510.5.

^{1}H NMR (400.1 MHz, CD_2Cl_2) δ 3.35 (s, 6H, 2⁗⁗′OCH_3); 3.53–3.55 (m, 4H, $OCH_2$2⁗⁗′); 3.66–3.68 (m, 4H, $OCH_2$1⁗⁗′); 3.82–3.84 (m, 4H, $OCH_2$2⁗⁗); 3.90 (s, 6H, ArOCH_3); 4.13–4.15 (m, 4H, $OCH_2$1⁗⁗); 6.89 (d, 2H, ^3J = 8.9 Hz, ArH5⁗‴); 7.06 (d, 2H, ^3J = 16.7 Hz, H_{vinyl}2⁗″); 7.08 (dd, 2H, ^3J = 5.1 Hz, ^4J = 3.6 Hz, ThH4, 4⁗′); 7.06–7.09 (m, 4H, ArH2⁗‴, 6⁗‴); 7.17 (d, 2H, ^3J = 3.8 Hz, ThH3″, 4‴); 7.25 (d, 2H, ^3J = 3.8 Hz, ThH4″, 3‴); 7.27 (dd, 2H, ^3J = 3.6 Hz, ^4J = 1.2 Hz, ThH3, 3″””′); 7.30 (d, 2H, ^3J = 16.3 Hz, H_{vinyl}1⁗″); 7.31 (dd, 2H, ^3J = 5.1 Hz, ^4J = 1.1 Hz, ThH5, 5”””′); 7.46 (s, 2H, ThH3′, 4”””).

^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 55.5 ArOCH_3; 58.3 2⁗⁗′OCH_3; 68.0 $OCH_2$1⁗⁗; 69.2 $OCH_2$2⁗⁗; 70.2 $OCH_2$1⁗⁗′; 71.6 $OCH_2$2⁗⁗′; 109.3 ArC2⁗‴; 112.9 ArC5⁗‴; 119.2 C_{vinyl}1⁗″; 119.3 ArC6⁗‴; 122.1 ThC3′, 4”””; 124.0 ThC3, 3”””′; 124.2 ThC4”, 3””′; 124.8 ThC5, 5”””′; 127.2 ThC3”, 4””′; 127.7 ThC4, 4”””′; 130.0 ThC5′, 2”””; 130.2 ArC1⁗‴; 130.5 C_{vinyl}2⁗″; 134.2 ThC2”, 5””′; 135.7 ThC2′, 5”””; 136.3 ThC2, 2”””′; 136.6 ThC4′, 3”””; 137.1 ThC5”, 2””′; 148.2 ArC4⁗‴; 149.3 ArC3⁗‴.

HRMS (FAB) M^+ calc 994.1830, found 994.1826.

4′,3⁗-Bis-[2⁗″-(3⁗‴,4⁗‴-dimethoxy-phenyl)-vinyl]-[2,2′5′,2″5″,2‴5‴,2⁗5⁗,2⁗′] sexithiophene (9)₂. Treatment of **9** with $FeCl_3$ yielded the title compound as a red solid, melting point = 216–218 °C (79%).

Electronic spectrum (CH_2Cl_2) λ_{max} nm/(log ε) 275.0 (4.48), 335.5 (4.80), 445.0 (4.55).

Electronic spectrum (thin film) λ_{max} nm 284.5, 342.5, 510.0, 555.0.

HRMS (FAB) M^+ calc 818.0781, found 818.0794.

Further characterisation was not possible due to the insolubility of the material in a wide variety of common solvents.

Characterization data for compounds $(\mathbf{2})_2$, $(\mathbf{4})_2$, $(\mathbf{5})_2$, $(\mathbf{7})_2$ and $(\mathbf{8})_2$ is included in the electronic supplementary material.†

Compounds $(\mathbf{10})_2$ and $(\mathbf{11})_2$ were insufficiently soluble to allow structural characterization.

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