JOC Article

Toward Functionalized Conducting Polymers: Synthesis and Characterization of Novel β-(Styryl)terthiophenes

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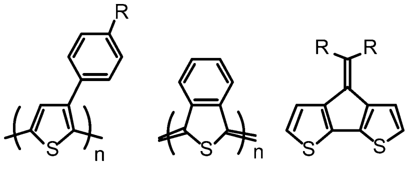
Metal-catalyzed coupling methodologies have been employed in the synthesis of the key building block 3′-formyl-2,2′:5′,2″-terthiophene. Wittig olefinations with this aldehyde have produced five novel β-styryl-substituted terthiophene monomers. These materials have been fully characterized by NMR spectroscopy, microanalysis, mass spectrometry, and X-ray crystal structure analysis. The results from the UV/visible spectroscopy and cyclic voltammetric investigations are reported.

Introduction

Since the Nobel prize-winning discovery by Heeger, MacDiarmid, and Shirakawa[1,2] that doped polyacetylene is conducting, conjugated polymers have been intensely studied.[3] While the initial interest was in the intriguing structure and electronic properties of these materials, subsequent work has been driven by the diversity of potential applications for conducting "plastics".[4,5] Prominent among the conjugated materials studied to date are the oligo- and polythiophenes, since a wide variety of functionality can be readily built on to the parent thiophene, bithiophene, or terthiophene monomers.[6,7] Oligo- and polythiophenes have been investigated as advanced electrode materials;[7] as suitable materials for electronic,[8,9,10] optoelectronic,[8,11,12] and chemosensor[13,14,15] devices; and for photovoltaics.[16,17]

A number of these applications require tailored electronic properties, which influence polymer characteristics, such as p- or n-type doping,[18] redox cycling,[19] band gap,[20,21] and photovoltaic behavior.[22,23] Typically, aromatic substituents have been utilized in this regard. Thus, poly(3-arylthiophenes) (**1**) have improved doping capacity and cyclability over polythiophene,[24,25] and fusing benzene to thiophene leads to poly(isothianaphthene) (**2**), the prototypical small band gap polymer.[26]



(**1**) (**2**) (**3**)

Other conjugated substituents have also been used to influence the electronic nature and resulting properties of polythiophenes. A new variety of low band gap

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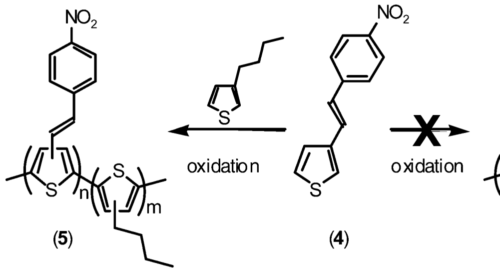
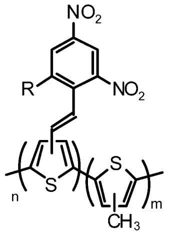
SCHEME 1

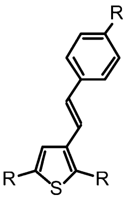


polymers has been developed from the methylenecyclopentadithiophene moiety (**3**).[27,28,29] More recently, Greenwald and co-workers used a styryl substituent in a copolymer (**5**) (Scheme 1) to improve the photoconductivity of polythiophene.[30]

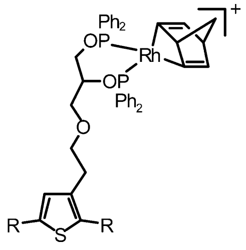
This was not the first time that styryl side chains had been introduced into polythiophene in an attempt to tailor the electronic structure of the polymer. In 1994, Smith et al. reported that electrochemical homopolymerization of (**4**) produced a nonconductive material, presumably through side-chain polymerization.[31] Other styryl derivatives showed similar behavior. However, electrically conducting polymers (**7**) have been obtained by copolymerization of styryl derivatives with 3-methylthiophene.[32] We have recently confirmed and extended these findings.[33] Although copolymers such as **5** and **7** are extremely promising, they have irregular and random structures and provided limited information on the role the conjugated substituents play in influencing the physical and chemical properties of the polymer.



(**7**) n=1, m=4
R=H or NO2



(**8**) R = 2-thienyl



(**9a**) R = H
(**9b**) R = 2-thienyl

An alternative approach to the formation of styryl-functionalized polythiophenes such as **6**, without the complication of the regioirregular alkyl substituent, is to polymerize substituted terthiophenes such as **8**. Since terthiophene polymerizes more readily than thiophene, these polymers should be easier to form and less likely to produce branched structures through the vinylic group. For example, Higgins and Mirkin have found that the terthiophene monomer (**9b**) forms an electroactive material, whereas the analogous thiophene (**9a**) does not.[34] An added advantage to using **8** is that the substituents will be on alternate sides of the polymer chain, reducing steric interactions that may lead to structural irregularities.

To our knowledge, there are no examples of aryl β-conjugatively linked terthiophene derivatives, and therefore, we set out to establish a general methodology to these materials.[35] Since the formation of the aryl alkenic linkage to the terthiophene structure should be readily accessible by Wittig chemistry using a variety of aryl-substituted ylides that have been reported in the literature, the key building block for the syntheses is 3′-formylterthiophene (**10**) (Scheme 2). The chemistry of assembling terthiophene structures using metal-catalyzed aryl-coupling reactions is well-documented, and so it was envisioned that the terthiophene backbone with the necessary functionality at the 3′-position could be efficiently constructed by Kumada coupling[36] (Scheme 2). It is also noteworthy that the Wittig reaction can give rise to cis/trans isomers, which may provide distinct polymers with interesting properties.

Results

1. Synthesis and Characterization. The necessary thiophene precursors, **12** and **17** (Scheme 3), were prepared efficiently and easily from commercially available materials. Monobromination of thiophene (**11**) under mild conditions, following the procedure of Brandsma and Keegstra,[37] gave 2-bromothiophene (**12**) in excellent yield (Scheme 3). Using an adaptation of a procedure from the same paper,[37] 2,5-dibromo-3-formylthiophene (**15**) was synthesized in moderate yield (73%) via a one-step dibromination of 3-formylthiophene (**14**). This reaction can be performed on larger scales (50−100 g) and gives good yields of purified **15** (55−73%). This method improves on those previously reported; Fournari and co-workers[38] used a conventional method to brominate the aldehyde (**14**) in low yield (28%), while Coyle and co-workers[39] used a cumbersome three-step synthesis to convert 3-methylthiophene to the dibromoaldehyde (**15**) in moderate yield (66%). During the course of this work, Gallazzi and co-workers[40] reported that the more recent technique used to brominate oligothiophenes, employing NBS in DMF, could be used to convert **14** to **15**.

Treatment of the dibromoaldehyde (**15**) with neopentyl glycol (**16**) and a catalytic amount of *p*-toluenesulfonic acid in benzene under Dean−Stark conditions provided, after distillation, the acetal (**17**) as a white crystalline solid in quantitative yield. The key advantages of using this 1,3-diol as a protecting group is that the acetal is

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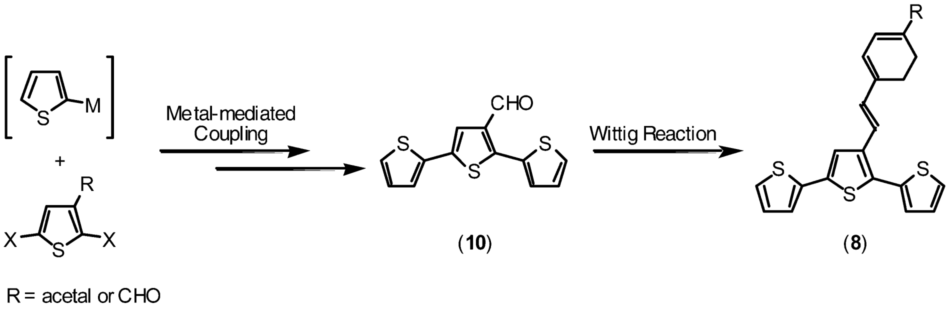
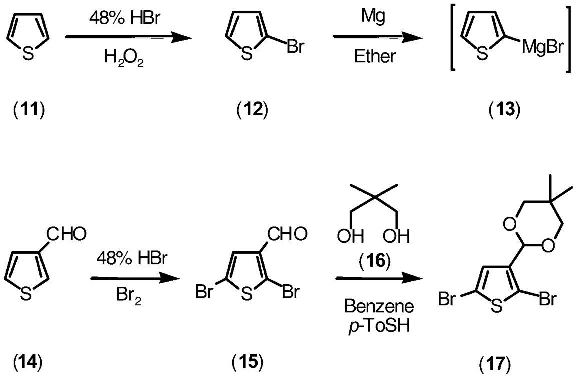
SCHEME 2



SCHEME 3



robust under acidic conditions and has characteristic signals that are easily identifiable in ^{1}H NMR spectra.

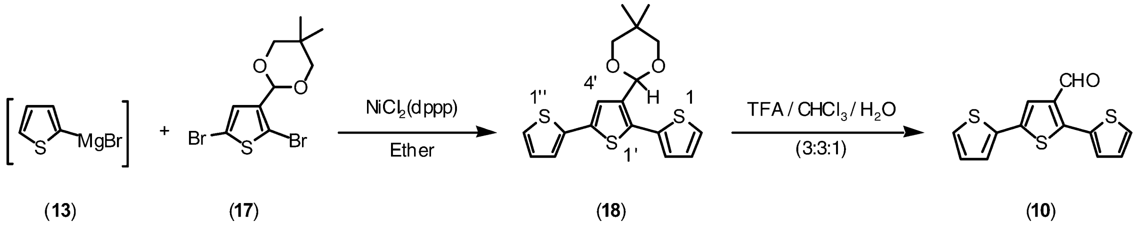
With the necessary precursors available to construct the terthiophene system, small scale (1 g) Kumada coupling reactions were investigated.[36,41,42,43] Treatment of an ethereal solution of 2-bromothiophene with magnesium metal gave 2-bromomagnesiothiophene (**13**) (Scheme 3) with minimal formation of the Wurtz byproduct, 2,2′-bithiophene. Heating the Grignard reagent (**13**) with dibromo acetal (**17**) and $NiCl_2$(dppp) catalyst afforded a complex mixture which, when subjected to radial chromatography, resulted in the isolation of the terthiophene acetal (**18**) in good yield (71%), as well as a small amount of 2,2′-bithiophene and unreacted acetal (**17**) (Scheme 4).

Analysis of the terthiophene acetal (**18**) by ^{1}H and ^{13}C NMR spectroscopy, with the aid of COSY and NOE experiments, allowed the unambiguous assignment of all three thiophene rings. The COSY experiment allowed conclusive assignment of the AMX spin system of each outer thiophene ring. A five bond long-range coupling[44] interaction between H 3″ and the H 4′ was identified. The NOE difference also supported the assignment of the two external thiophene rings. Irradiation of the methine proton of the acetal group indicated a NOE difference of 0.9% and 2.7% between the H 4′ of the center ring and the H 3 denoted as the thiophene ring nearest to the acetal group. The acetal functionality of **18** is clearly identified in the ^{1}H NMR spectrum and all its signals are deshielded due to the π systems of the nearby aromatic rings.

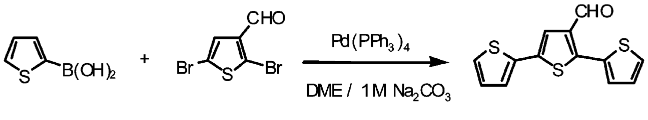
Attempts to remove the acetal group from **18** using conventional procedures[45] resulted in recovery of the acetal or poor conversion to the desired aldehyde material only after long reaction periods (Scheme 4). It was eventually found that the aldehyde could be efficiently deprotected by employing a procedure used by Magnus and co-workers[46] for the removal of diethyl acetals. Treatment of the acetal in a two-phase trifluoroacetic acid/chloroform/water mixture (ratio of 3:3:1) gave, after chromatography, the terthiophene aldehyde (**10**) in excellent yield (95%). The ^{1}H NMR spectrum of **10** at 400 MHz shows an aldehyde proton resonance at 10.08 ppm, while the singlet at 7.57 ppm corresponds to H 4′. COSY and NOESY experiments were used to assign the outer thiophene rings; long-range coupling between H 4′ and H 3″ was detected, while a NOE difference between the aldehyde proton and H 3 of 1.1% was observed. The IR spectrum of **10** shows an absorption band at 1676 cm^{-1}, typical of an aromatic aldehyde.

Unfortunately, attempts to perform the coupling reaction on a preparative scale (>5 g) and isolate suitable quantities of the terthiophene acetal gave discouraging results. Modification of the conditions, by varying the addition time and quantity of the Grignard reagent or prolonged reaction periods, only resulted in poor yields. Attempts to increase the yield by using another nickel catalyst, Ni(dppe)Cl_2, under the conditions used before gave only trace amounts of the desired product. In addition, conventional methods for purifying the terthiophene acetal (**18**) by rapid silica filtration or column chromatography proved laborious and inefficient for large-scale crude mixtures. It was found, however, that adsorption of the crude material onto chromatographic silica gel and extraction with hexane using a Soxhlet apparatus circumvented the need for chromatographic purification. Concentration of this filtrate and cooling

SCHEME 4



SCHEME 5



(19) **(15)** **(10)**

resulted in precipitation of the terthiophene acetal (**18**), which was then recrystallized in 51% yield. Due to the limited success of this Kumada chemistry on a larger scale, alternative coupling methodologies were investigated.

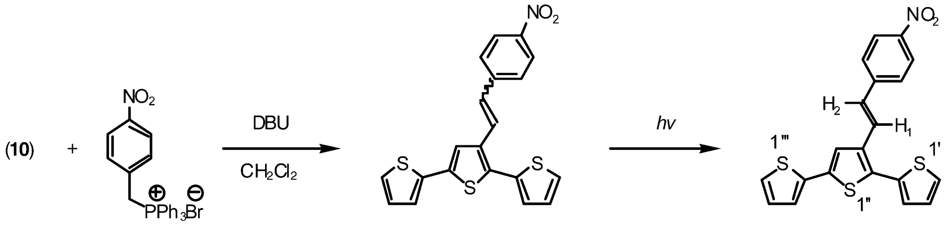
The Suzuki coupling of aromatic halides with aryl boronic acids has been used extensively and is well-documented in the literature.[47,48] Gronowitz and coworkers[49] have successfully shown that 2,2′:5′,2′′-terthiophene can be constructed in satisfactory yield (40%) using the Suzuki coupling methodology. Using this strategy we envisioned that the key precursor, 3′-formylterthiophene (**10**), could be accessed by the reactions represented in Scheme 5, eliminating the need for the protection/deprotection chemistry used in the Kumada coupling approach. Treatment of thiophene (**11**) at low temperature with *n*-butyllithium, followed by reverse addition to trisisopropyl borate and acidic workup gave 2-thienyl boronic acid (**19**) in high yield. Other literature methods describe relatively small-scale syntheses or crude isolation of **19**,[50,51,52] but with this reverse addition high yields and purity can be easily obtained on a multigram scale. A slight excess of the boronic acid (**19**) was treated with the previously prepared dibromoaldehyde (**15**) and tetrakis(triphenylphosphine)palladium catalyst under the Suzuki coupling conditions employed by Gronowitz[49] (Scheme 5). After the requisite aqueous workup and chromatography, terthiophene aldehyde (**10**) was isolated, as well as the monocoupled product, 5-bromo-3-formyl-2,2′-bithiophene (**20**). Interestingly, only one monocoupled product was observed, implying that the first coupling step is regioselective, and this is presumably due to the electronic nature of the nearby aldehyde functionality. Such regioselectivity has also been noted in an analogous system that involves Suzuki coupling with **15**.[53] It was determined that use of an excess of the boronic acid (see Experimental Section) was required to ensure the complete formation of the aldehyde (**10**), which was obtained after purification in excellent yield (76%). This procedure was readily scaled-up to provide a rapid and efficient multigram synthesis of the terthiophene aldehyde building block.

Wittig reactions between 3′-formylterthiophene (**10**) and ylides, derived from various phosphonium salts, gave the target molecules in excellent yields ranging from 80 to 92%. The target materials **23**, **25**, **27**, **29**, and **31**, were successfully characterized using microanalysis, mass spectrometry, IR, NMR, and UV/visible spectroscopy (see later). Wittig olefination involving aryl phosphonium salts with electron-withdrawing groups or no substituent, such as **21**, **24**, or **26**, were best performed by treatment with DBU in the presence of the aldehyde (**10**) in dichloromethane at reflux. In the case of the nitro salt (**21**), using these conditions gave, as expected, a mixture of geometric isomers (**22** and **23**) (Scheme 6). Analysis of the crude mixture by ^{1}H NMR spectroscopy indicated a cis/trans ratio of 1.5:1; this was determined from integration of the vinylic protons of the cis isomer appearing as an AB quartet (6.70 and 6.74 ppm, 12.0 Hz) and the trans isomer consisting of two doublets at 7.05 and 7.49 ppm (16.2 Hz). No attempt was made to isolate the cis isomer, as cis/trans isomerization was found to occur after exposure of a solution of **22** and **23** to sunlight. In practice, the isomerization of **22** to **23** was achieved by irradiating the mixture with a 240-W lamp to afford, after chromatography and recrystallization, the all-trans product **23** as orange crystals (82%). The IR spectrum shows the characteristic absorption bands at 1336 and 1508 cm^{-1} of the nitro group.

Using the same procedure, treatment of the aldehyde (**10**) with (4-cyanobenzyl)triphenylphosphonium bromide (**24**) or benzyltriphenylphosphonium bromide (**26**) under basic conditions gave the target compounds, **25** and **27**, respectively, in excellent yields (Scheme 7). Surprisingly, in each of the crude ^{1}H NMR spectra no cis isomer was observed and both pure trans materials were easily isolated after chromatography and recrystallization as yellow crystalline solids. The IR spectrum of terthiophene (**25**) displays a strong absorption at 2221 cm^{-1}, typical of a cyano function in conjugation with an aryl group.

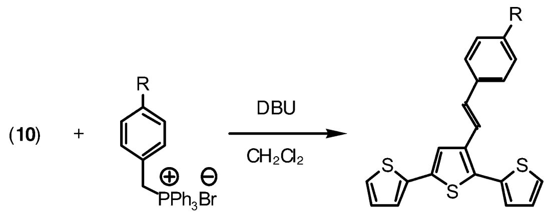
The synthesis of compounds **29** and **31** that contain electron-donating groups on the aryl ring required slightly different reaction conditions than those previously employed. The reaction of excess phosphonium salt, **28** or **30**, with the strong base potassium *tert*-butoxide ensured the generation of the ylide to which the terthiophene aldehyde (**10**) was then added (Scheme 8). This procedure furnished the most satisfactory yields of the pure trans isomers **29** and **31** after an aqueous workup and chromatography (80 and 81%, respectively). The main feature of the IR spectrum of **29** is a C−O−C stretch at 1172 and 1247 cm^{-1}, indicative of the methoxy substituent, while the spectrum of **31** has a strong absorption at 1366 cm^{-1} attributed to the tertiary aromatic amine.

SCHEME 6



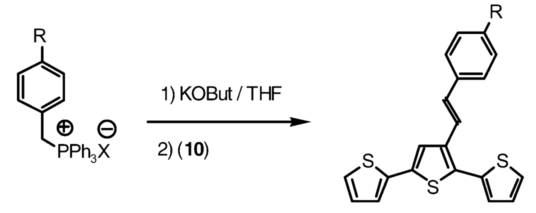
(**21**) (**22** and **23**) (*cis:trans* = 1.5:1) (**23**) (82%)

SCHEME 7



(**24**) R = CN
(**26**) R = H
(**25**) R = CN (92%)
(**27**) R = H (88%)

SCHEME 8



(**28**) R = OMe, X = Cl
(**30**) R = NMe_2, X = I
(**29**) R = OMe (80%)
(**31**) R = NMe_2 (81%)

The absence of cis isomers in all but the reaction of the nitrophenyl phosphonium salt (**21**) is unusual but presumably reflects the influence of the bulky terthiophene aldehyde (**10**) in the transition states of the reactions. In the case of **21**, the presence of the cis isomer could either be caused by $\pi-\pi$ interactions or a favorable interaction of the nitro group on the ylide with a sulfur atom of one of the thiophene rings in the betaine formation of the Wittig reaction.

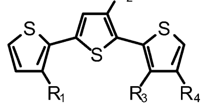
2. NMR Spectroscopy of Aryl-Substituted Terthiophene Materials. Analysis of the target compounds by NMR spectroscopy reveals characteristic signals that are observed in all spectra. Molecules **23**, **25**, **29**, and **31** all contain *para*-substituted aromatic rings. As a result, AA′XX′ patterns are easily distinguished in these spectra. For example, in the proton NMR spectrum of **23** the AA′XX′ spin pattern occurs at 8.16−8.22 and 7.55−7.60 ppm; where the downfield signal is a result of the strong deshielding effect of the nitro group. On the other hand, the spectrum of the phenyl derivative **27**, as expected, is more complicated.

In all the spectra of the target compounds, the vinylic proton resonances appear as two doublets with a coupling of approximately 16 Hz, typical of a trans configuration, with variations in chemical shift, presumably arising from shielding and deshielding effects induced by the R group.

Due to the unsymmetrical nature of the terthiophene compounds, all five molecules have two AMX spin systems that are attributed to the outer thiophene rings. The assignment of the H 3, H 4, and H 5 of each ring was achieved by the extraction of coupling constants and with the aid of COSY experiments. The actual assignment as to which of the two rings is connected to either side of the central ring was established using long-range COSY experiments. Analysis of all the proton spectra for the target compounds reveals the H 4″ as a singlet [e.g. see structure **23** (Scheme 6)] occurring in the range of 7.41−7.45 ppm. The COSY spectra indicate a correlation between the H 4″ and the vinylic proton assigned as H 1. More significantly, H 4″ coupling through five bonds to the proton of an adjacent thiophene ring is observed, which can only be associated with the H 3‴. Conversely, the thiophene ring denoted as being the nearest to the aryl-substituted system shows no evidence for long-range coupling to the H 4″ of the central ring (i.e. six bond coupling). This long range coupling was clearly observed in all the terthiophene systems studied.

Finally, use of HETCOR experiments allowed assignment and distinction between carbon atoms attached to the aryl and thiophene protons, the vinylic protons, and H 4″. Carbon-13 spectra of **29** and **31** also clearly show the key signals of the methoxy substituent at 55.3 ppm and the methyl groups of the amino functionality at 40.4 ppm.

3. X-ray Structure Analysis of *trans*-1-((2′,2″:5″,2‴-Terthiophen)-3″-yl)-2-(4⁗-cyanophenyl)ethene (25). Considering the ongoing interest in synthesizing and utilizing terthiophene block monomers, there is a dearth of X-ray crystallography data for simple β-substituted 2,2′:5′,2″-terthiophenes in the literature. Structural analysis of the parent terthiophene (**32**) in 1989 by Van Bolhuis and co-workers[54] revealed that in the solid state, the thiophene rings are in antiparallel positions and the molecule itself is nearly, but not completely, planar. The two outer thiophene rings, which are coplanar, are



(**32**) R_1=R_2=R_3=R_4=H
(**33**) R_1=R_2=R_4=CH_3, R_3=H
(**34**) R_1=R_3=R_4=H, R_2=Ph
(**35**) R_1=R_3=R_4=H, R_2=CH_3
(**36**) R_1=R_3=CH_3, R_2=R_4=H
(**37**) R_1=R_3=R_4=H, R_2=(2-thienyl)

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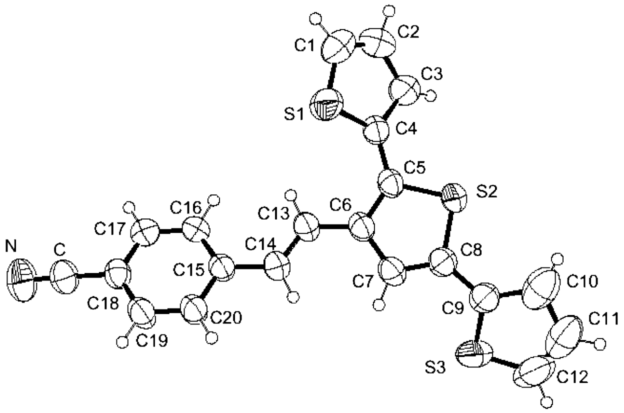

FIGURE 1. X-ray crystal structure of *trans*-1-((2′,2″:5″,2‴-terthiophen)-3″-yl)-2-(4⁗-cyanophenyl)ethene (**25**).

twisted slightly with respect to the central ring with a torsional angle of 6.9°. Later studies by Barbarella and co-workers[55] on the simple β-substituted regioregular thiophene trimer 3,4′,4″-trimethyl-2,2′:5′,2″-terthiophene (**33**) gave similar supporting evidence for an essentially planar structure where the outer thiophene rings are twisted by 7° and 7.8° with respect to the central ring; the thiophene rings themselves are in an anti-arrangement.

However, a significant deviation in the terthiophene crystal geometry has been observed when simple substituents have been directly attached to the β-position of the terthiophene backbone. Kankare and colleagues[56] found it difficult to obtain accurate bond lengths, since a substantial amount of conformational disorder was present in the X-ray data of aryl-substituted terthiophenes. For example, in the case of 3′-phenyl-2,2′:5′,2″-terthiophene (**34**), the thiophene rings were far from coplanar (−156° and 138.4° with respect to the center thiophene ring) and the aryl ring was also twisted at an angle of −116.7°; this presumably occurs due to the close proximity of the nearby thiophene ring. Disorder in the solid-state structures of 3′-methyl-2,2′:5′,2″-terthiophene (**35**), 3,3″-dimethyl-2,2′:5′,2″-terthiophene (**36**), and 5′-(2-thienyl)-2,2′:3′,2″-terthiophene (**37**) has also been reported recently by Chaloner and co-workers.[42] In their studies they found that a range of conformational isomers was present in the solid state and in no case were any of the thiophene rings coplanar, where interplane angles between 29° to 88° were observed. Although there seems to be some variation between early X-ray data and recent findings, these results suggest that conformational disorder is prevalent and the likelihood of disorder is increased by the presence of sterically demanding substituents.

Crystallographic studies on *trans*-1-((2′,2″:5″,2‴-terthiophen)-3″-yl)-2-(4⁗-cyanophenyl)ethene (**25**) provided similar findings to the conformational disorder of the terthiophene systems found by Kankare and Chaloner. The X-ray data of **25** indicates that the outer thiophene rings exist as conformers with the general structure having the antiparallel orientation shown in Figure 1. The presence of these conformers suggests that in solution the rotation of the external thiophene rings about the C(4)−C(5) and C(8)−C(9) bonds is not restricted by a excessively large rotational energy barrier: this is supported by the 2D COSY and NOESY NMR experiments performed on terthiophene systems described in this paper. The torsional angles between the outer rings and the central thiophene ring is −148.6° [S(1a)−C(4)−C(5)−C(6)] for the ring closest the alkene linker, while the other lies at −151.2 [C(7)−C(8)−C(9)−S(3a)]. More importantly, the mean plane through the atoms of the central thiophene ring and the cyano-substituted aryl ring has a dihedral angle of 26.5° as calculated. Thus, it seems that the addition of the alkene spacer allows the aryl and thiophene ring to assume a greater π orbital overlap, which is in stark contrast to the geometry of 3′-phenyl-2,2′:5′,2″-terthiophene (**34**) described earlier.

TABLE 1. Electronic Absorption Spectral Data for Compounds at Room Temperature in $CHCl_3$

compd	λ, nm (log ϵ)
terthiophene (**32**)	355 (4.34)
23	345 (4.57), 411(sh) (4.25)
25	324 (4.65), 355(sh) (4.45)
27	312 (4.57), 353(sh) (4.34)
29	323 (4.74), 362(sh) (4.48)
31	348(br) (4.58)

TABLE 2. Electrochemical Data for Compounds in CH_2Cl_2

	$E°$, V[a]	
compd	initial oxidation potential	polymerization potential
23	1.38	0.90
25	1.24	0.90
27	1.19	0.92
29	1.20	0.86
31	0.83	b
35	1.20	0.81

[a] Versus ferrocene. [b] No visible film seen on the electrode surface.

4. Electronic Absorption Spectra. A survey of the literature indicates that terthiophenes that have aryl substituents directly attached to the 3′ position have been synthesized and their spectroscopic properties studied. Kankare and co-workers[56] have observed that these compounds, such as **34** and **37**, all have a major absorption band occurring around 350 nm that is characteristic of terthiophene (**32**). However, the data obtained for the functionalized terthiophenes prepared in this study, as shown in Table 1 (see Supporting Information), is unusually complex. A DFT study has been undertaken to explain the substituent effects observed, and the results will be published elsewhere.

5. Electrochemistry. Preliminary electrochemical studies have been performed on this series of terthiophenes using cyclic voltammetry. The data obtained for the five styrylterthiophenes is presented in Table 2, with the 3′-methyl-2,2′:5′,2″-terthiophene (**35**) data included for comparison.

The initial oxidation potential of the compounds is found to vary depending on the nature of the substituent. The strong electron-withdrawing substituent, NO_2, is observed to shift the potential of the oxidation to more positive values, while the electron-donating substituent,

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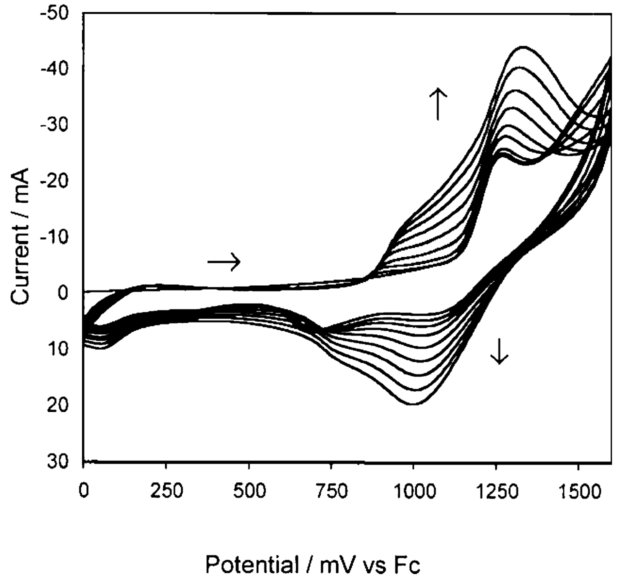

FIGURE 2. Cyclic voltammogram of (**23**), repeated cycles.

NMe$_2$, shifts the potential to less positive values. This effect has been noted before in similarly substituted oligothiophene molecules.[31,33,57,58] Somewhat surprisingly, there was little difference in the oxidation potential of **25**, **27**, and **29**. The first oxidation wave for all compounds showed only a single oxidation peak with no peak attributable to the oxidation of the double bond.[31,33] Repeated cycles showed a growth in current that is consistent with the formation of an electroactive polymer. This differs from the electrochemical polymerization of the analogous thiophene monomers, suggesting that the alkene linker in these terthiophenes is not involved in polymer formation.[31,33] Typically, Figure 2 shows **23** under repeated cycling with formation of an apparent electroactive polymer evident from the appearance and growth of the shoulder at lower potential than the first oxidation potential.[57,58,59,60] The polymerization potential quoted in Table 2 is an indication of the potential at which the shoulder grows in at. In contrast, oxidation of **31** does not appear to form an electroactive polymer. The availability of monomer **23** has, until now, allowed homopolymers to be fabricated for testing in photovoltaic devices.[59] It has been of interest to determine to what extent “high electron affinity” groups, such as nitro, enhance the properties of the polymer that are necessary in photocells.[30]

Conclusion

A combination of Kumada coupling and protection/deprotection chemistry has been employed in the synthesis of 3′-formyl-2,2′:5′,2″-terthiophene (**10**). Attempts to use this route to synthesize this material on a large scale proved complicated. An efficient synthesis that utilizes Suzuki coupling methodology was developed that provides multigram quantities of **10**. Wittig chemistry with **10** has been achieved to give several novel β-(styryl)-substituted terthiophenes. X-ray crystal analysis of **25** confirms that placement of the alkene linkage between the center thiophene and aryl ring reduces the steric interaction, thereby allowing a greater degree of conjugation between the two moieties. This is reflected in the electronic properties of the substituents attached to the aryl ring, which are shown to influence the electronic absorption properties and electrochemistry of the terthiophene monomers. All terthiophene derivatives, **23**, **25**, **27**, and **29**, except **31**, appear to form electroactive polymers.

Current research has been directed at the development of this building block approach for the attachment of a variety of functionality to terthiophene. To date, functionalized polymers have been studied in photovoltaic[59,60] and biological sensor devices.[61] Future work is also directed at the synthesis of materials that may have useful applications in LED, electrocatalytic, and metal ion sensor devices. The results of these findings will be published soon.

Experimental Section

General experimental details are provided in the Supporting Information.

Kumada Coupling Synthesis. 2,5-Dibromo-3-formylthiophene (15). A mixture of thiophene-3-carboxaldehyde (**14**) (1.00 mL, 1.28 g, 11.4 mmol), 48% aqueous hydrobromic acid (3.4 mL), and ether (3 mL) cooled at 0 °C was stirred vigorously while a mixture of bromine (1.18 mL, 3.68 g, 23.0 mmol) and 48% aqueous hydrobromic acid (3.4 mL) was added dropwise. The reaction mixture was then heated at 50 °C and monitored by TLC. After 3 h the mixture was diluted with water (50 mL) and extracted with ether (2 × 50 mL). The organic layers were combined, washed with 10% sodium thiosulfate solution (2 × 15 mL) and water (30 mL), and dried (MgSO$_4$). The solvent was removed under reduced pressure, diluted with dichloromethane/hexane (1:2), and passed through a column of silica to remove baseline material. The residue was vacuum distilled (145 °C/10 mmHg) to give the product **15**, which crystallized upon cooling as a white solid (2.26 g, 73%). Recrystallization from *n*-heptane afforded white fluffy needles that darken on exposure to light and air: mp 46−7 °C (lit.[32] mp 45−6 °C, lit.[33] mp 48−9 °C); ^{1}H NMR (270 MHz) δ 9.79 (s, 1H, CHO), 7.33 (s, 1H, H 4); ^{13}C NMR (67.8 MHz) δ 183.0, 139.1, 128.5, 124.2, 113.3; MS *m/z* 272 (40), 271 (55), 270 (M, 78), 269 (100%), 268 (39), 267 (49), 81 (24), 80 (21); $\upsilon_{\max}$/cm^{-1} 3098, 2856, 1676, 1520, 1176, 1014, 832, 736; electronic spectrum $\lambda_{\max}$ nm/(log ϵ) 252 (4.04), 299 (3.60).

2,5-Dibromo-3-(5,5-dimethyl-1,3-dioxan-2-yl)thiophene (17). A mixture of the aldehyde (**15**) (2.26 g, 8.37 mmol), *p*-toluenesulfonic acid (50 mg, 0.29 mmol), and 2,2-dimethylpropane-1,3-diol (**16**) (0.95 g, 9.12 mmol) in dry benzene (85 mL) was heated under reflux for 1 h using a Dean−Stark apparatus. The reaction mixture was concentrated under vacuum, then diluted with dichloromethane (30 mL) and dried (MgSO$_4$). To this solution was added an equal volume of hexane and the mixture was then passed through a pad of silica to remove the unreacted diol. The filtrate was concentrated and vacuum distilled (120°/0.05 mmHg) to give the acetal (**17**) as a white solid (2.92 g, 98%). Recrystallization from 95% ethanol gave the analytical sample as fluffy white needles: mp 86−7 °C; ^{1}H NMR (270 MHz) δ 7.16 (s, 1H, H 4),

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5.41 (s, 1H, CH), AB quartet, A part of AB, 3.73 (2H, J_{AB} = 11.2 Hz, CH_AH_B) and B part of AB, 3.63 (2H, J_{AB} = 11.2 Hz, CH_AH_B), 1.30 (s, 3H, CH_3), 0.80 (s, 3H, CH_3); ^{13}C NMR (67.8 MHz) δ 139.3, 129.2, 111.4, 110.4, 97.2, 77.6, 30.2, 23.1, 21.9; MS *m/z* 356 (M, 37), 272 (53), 271 (36), 270 (100%), 269 (43), 268 (50), 191 (23), 69 (73); υ_{max}/cm^{-1} 2943, 2854, 1559, 1462, 1437, 1392, 1376, 1360, 1177, 1105, 1010, 991, 977, 958, 926, 830; electronic spectrum λ_{max} nm/(log ϵ) 252 (3.92). Anal. Calcd for $C_{10}H_{12}Br_2O_2S$: C, 33.73; H, 3.40; Br, 44.88. Found: C, 33.85; H, 3.29; Br, 44.83.

3′-(5,5-Dimethyl-1,3-dioxan-2-yl)-2:2′,5′:2′′-terthiophene (18). (a) Small Scale. A stirred mixture of the dibromoacetal (**17**) (1.00 g, 2.81 mmol) and $NiCl_2$(dppp)[62] (50 mg, 0.09 mmol, 3 mmol %) in dry ether (15 mL) was treated dropwise at room temperature with 2-bromomagnesiothiophene (**13**) [generated by reacting 2-bromothiophene (1.09 g, 6.69 mmol) with magnesium (179 mg, 7.36 mmol) in dry ether (9 mL) at ambient temperature over a period of a 30 min]. Once the addition was completed, the mixture was heated under reflux for 4 h. The reaction mixture was cooled and diluted with ether (50 mL) and then quenched with 1 M HCl solution (50 mL). The organic layer was separated and the aqueous layer extracted with ether (3 × 60 mL). The ethereal extracts were combined and washed with water (30 mL), dried ($MgSO_4$), and concentrated in vacuo to give a dark yellow solid. Purification was achieved by radial chromatography to give the materials in order of elution: bithiophene (73 mg), dibromoacetal (**17**) (139 mg), and the terthiophene product (**18**) (624 mg, 71% based on recovered starting material). Recrystallization from ether/hexane afforded an analytical sample as yellow flakes: mp 133 °C; ^{1}H NMR (400 MHz) δ 7.42 (s, 1H, H 4′), 7.37 (dd, 1H, *J* = 5.1, 1.2 Hz, H 5), 7.23 (dd, 1H, *J* = 5.1, 1.2 Hz, H 5′′), 7.21 (dd, 1H, *J* = 3.6, 1.2 Hz, H 3), 7.19 (dd, 1H, *J* = 3.6, 1.2 Hz, H 3′′), 7.10 (dd, 1H, *J* = 5.1, 3.6 Hz, H 4), 7.02 (dd, 1H, *J* = 5.1, 3.6 Hz, H 4′′), 5.53 (s, 1H, CH), AB quartet, A part of AB, 3.79 (2H, J_{AB} = 11.2 Hz, CH_AH_B) and B part of AB, 3.67 (2H, J_{AB} = 11.2 Hz, CH_AH_B), 1.37 (s, 3H, CH_3), 0.82 (s, 3H, CH_3); ^{13}C NMR (67.8 MHz) δ 136.8, 2 × 136.1, 134.2, 133.0, 2 × 127.6, 126.9, 126.5, 124.6, 123.9, 123.4, 97.5, 77.5, 30.3, 23.2, 21.9; MS *m/z* 364 (16), 363 (23), 362 (M$^+$, 100%), 292 (40), 277 (13), 276 (53), 275 (18), 248 (53); υ_{max}/cm^{-1} 3100, 3072, 2952, 2852, 1466, 1459, 1420, 1394, 1362, 1117, 1104, 1013, 981, 837, 820, 709; electronic spectrum λ_{max} nm/(log ϵ) 251 (4.04), 343 (4.28). Anal. Calcd for $C_{18}H_{18}O_2S_3$: C, 59.63; H, 5.00. Found: C, 59.41; H, 5.10.

(b) Large Scale. A stirred mixture of the dibromoacetal (**17**) (5.00 g, 14.0 mmol) and $NiCl_2$(dppp)[58] (250 mg, 0.46 mmol, 3 mmol %) in dry ether (75 mL) was treated dropwise at room temperature with 2-bromomagnesiothiophene (16) [generated by reacting 2-bromothiophene (5.45 g, 33.4 mmol) with magnesium (0.90 g, 37.0 mmol) in dry ether (60 mL) at ambient temperature over a period of 1 h]. Once the addition was completed, the mixture was heated under reflux for 16 h. After this period, the reaction mixture was cooled and diluted with ether (150 mL) and then quenched with 1 M HCl solution (150 mL). The organic layer was removed and the aqueous layer was extracted with ether (3 × 80 mL). The ethereal extracts were combined and washed with water (2 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo to give a dark yellow solid. This crude material was adsorbed onto chromatographic grade silica and then extracted with hexane using a Soxhlet apparatus for 12 h. Upon cooling the filtrate a yellow precipitate was collected and this material was recrystallized from ether/hexane to afford the terthiophene acetal (**18**) (2.58 g, 51%): mp 133 °C.

3′-Formyl-2:2′,5′:2′′-terthiophene (10). A mixture of the terthiophene acetal (**18**) (115 mg, 0.32 mmol), chloroform (4 mL), trifluoroacetic acid (4 mL), and water (1.3 mL) were stirred vigorously at room temperature and monitored by TLC. After 1.5 h the reaction was complete and the mixture was diluted with dichloromethane (30 mL) and the aqueous layer separated. The organic layer was washed with 10% sodium bicarbonate solution (4 × 30 mL), then water (20 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford a brown oil which slowly crystallized on standing. This material was subjected to radial chromatography (CH_2Cl_2/ hexane) to give the title compound (**10**) as a bright yellow solid (83 mg, 95%): mp 68 °C; ^{1}H NMR (400 MHz) δ 10.08 (s, 1H, CHO), 7.57 (s, 1H, H 4′), 7.51 (dd, 1H, *J* = 5.1, 1.2 Hz, H 5), 7.32 (dd, 1H, *J* = 3.6, 1.2 Hz, H 3), 7.30 (dd, 1H, *J* = 5.1, 1.2 Hz, H 5′′), 7.23 (dd, 1H, *J* = 3.6, 1.2 Hz, H 3′′), 7.17 (dd, 1H, *J* = 5.1, 3.6 Hz, H 4), 7.06 (dd, 1H, *J* = 5.1, 3.6 Hz, H 4′′); ^{13}C NMR (67.8 MHz) δ 184.9, 145.8, 137.5, 136.7, 135.4, 132.0, 129.1, 128.6, 128.2, 127.9, 125.7, 124.9, 122.3; MS *m/z* 278 (15), 277 (17), 276 (M$^+$, 100%), 249 (9), 248 (55), 247 (8), 231 (10), 203 (20); υ_{max}/cm^{-1} 3076, 1676, 1386, 1230, 1162, 824, 720, 693; electronic spectrum λ_{max} nm/(log ϵ) 263 (4.20), 322 (4.01), 358 (3.91). Anal. Calcd for $C_{13}H_8OS_3$: C, 56.49; H, 2.92. Found: C, 56.73; H, 2.75.

Suzuki Coupling Synthesis. 2-Thienylboronic Acid (19). A solution of thiophene (**11**) (9.51 mL, 10.0 g, 0.119 mol) in dry THF (120 mL) cooled at −78 °C was treated dropwise with *n*-BuLi (95 mL, 1.24 mol L^{-1}, 0.118 mol). The mixture was stirred at −78 °C for 30 min and then allowed to warm to −20 °C slowly. This mixture was then cooled to −78 °C before the 2-thienyllithium was added to a solution of trisisopropyl borate (38.0 mL, 31.0 g, 0.165 mol) in dry THF (80 mL) also at −78 °C. The reaction mixture was stirred at −78 °C for 1 h before warming the solution to room temperature. The mixture was then treated with 1 M HCl (200 mL) and the organic layer separated. The aqueous layer was then extracted with dichloromethane (5 × 120 mL), and the organic layers were combined and dried ($MgSO_4$). The solvent was then removed under reduced pressure to afford a crude white solid, which was recrystallized from water to give the boronic acid (**19**) as a pure white solid (11.9 g, 78%): mp 125−127 °C (lit.[44] mp 128−130 °C).

5-Bromo-3-formyl-2,2′-bithiophene (20). To a stirred solution of the dibromide (**15**) (1.00 g, 3.68 mmol) and Pd(PPh_3)$_4$ (255 mg, 0.220 mmol) in 1,2-dimethoxyethane (30 mL) was added 2-thiophene boronic acid (1.13 g, 8.83 mmol, 2.4 equiv) and a solution of 1 M Na_2CO_3 (22 mL). The mixture was then heated under reflux for 8 h, cooled, and concentrated under vacuum to remove nearly all of the DME. The crude material was then diluted with DCM (100 mL) and washed with water (2 × 50 mL), and the organic layer was dried ($MgSO_4$). The brown liquid was dissolved in DCM:petroleum ether (1:1) and passed through a pad of silica to remove unwanted baseline materials. This material was then subjected to radial chromatography first with constant elution with 50% toluene/hexane to give the monocoupled product 5-bromo-3-formyl-2,2′-bithiophene (**20**) as a faint yellow solid: mp 76 °C (268 mg, 0.98 mmol, 27%); ^{1}H NMR (400 MHz) δ. 9.97 (d, 1H, *J* = 0.3 Hz, CHO), 7.51 (dd, 1H, *J* = 5.1, 1.2 Hz, H 5′), 7.49 (d, 1H, *J* = 0.3 Hz, H 4), 7.27 (dd, 1H, *J* = 3.6, 1.2 Hz, H 3′), 7.16 (dd, 1H, *J* = 5.1, 3.6 Hz, H 4′); ^{13}C NMR (67.8 MHz) δ 183.9, 148.6, 137.6, 131.0, 129.6, 129.3, 129.2, 128.3, 112.8. Anal. Calcd for $C_9H_5BrOS_2$: C, 39.57; H, 1.84; Br, 29.25; S, 23.48. Found: C, 39.81; H, 1.73; Br, 29.48; S, 23.55; electronic spectrum ($CHCl_3$) λ_{max} nm/(log ϵ) 253 (4.25), 336 (3.86). Elution with EtOAc/hexane (10% and then 20%) gave the terthiophene aldehyde (**10**) (514 mg, 1.86 mmol, 51%) (see earlier experimental for full characterization).

3′-Formyl-2:2′,5′:2′′-terthiophene (10). To a stirred mixture of 2,5-dibromo-3-formylthiophene (**15**) (10.0 g, 37.0 mmol) and tetrakis(triphenylphosphine)palladium [Pd(PPh_3)$_4$][63] (2.55 g, 2.21 mmol, 6 mmol %) in 1,2-dimethoxyethane (300 mL) were added 2-thiophene boronic acid (10.83 g, 84.6 mmol) and a solution of 1 M Na_2CO_3 (220 mL). The reaction mixture was heated under reflux for 5 h. After this period another portion of 2-thiophene boronic acid (2.18 g, 17.0 mmol) was added and

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heating continued for 8 h. The reaction mixture was concentrated and then diluted with dichloromethane (300 mL) and separated. The organic residue was washed with water (2 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo to give a brown liquid. This crude material was dissolved in CH_2Cl_2/hexane (1:1) and passed through a pad of silica to remove baseline material and the palladium catalyst. Further purification was achieved with column chromatography (CH_2Cl_2/hexane), followed by recrystallization from ether to give the title compound (**10**) as a bright yellow solid (7.76 g, 76%): mp 68°. The spectral data of this material is consistent with compound derived from the Kumada coupling synthesis.

Wittig Reactions. *trans*-1-((2′,2″:5″,2‴-Terthiophen)-3″-yl)-2-(4⁗-nitrophenyl)ethene (23). A mixture of the terthiophene aldehyde (**10**) (160 mg, 0.58 mmol), (4-nitrobenzyl)triphenylphosphonium bromide (**21**)[64] (322 mg, 0.67 mmol, 1.2 equiv), and DBU (0.10 mL, 0.67 mmol, 102 mg) in dichloromethane (8 mL) was heated under reflux. After 8 h the reaction mixture was diluted with dichloromethane (60 mL) and washed with a 1 M solution of HCl (2 × 20 mL), 10% sodium bicarbonate solution (20 mL), and water (30 mL). The organic layer was dried and concentrated to give a crude orange solid. This was dissolved in a small quantity of dichloromethane/hexane (1:1) and passed through a column of silica with continued elution with the same solvent system until the yellow/orange material had been collected. Analysis of the material by ^{1}H NMR spectroscopy indicated it consisted of a mixture of the cis and trans isomers in a ratio of 1.5:1. This material was dissolved in dry chloroform (30 mL) and irradiated for 3 h using a 250-W flood lamp. After removal of the solvent, analysis of the sample by ^{1}H NMR spectroscopy indicated it consisted of essentially the trans product. The material was recrystallized from dichloromethane/ether to give **23** as orange crystals (188 mg, 82%): mp 179 °C; ^{1}H NMR (400 MHz) δ 8.22−8.16 (2H, AA′ part of AA′XX′), 7.60−7.55 (2H, XX′ part of AA′XX′), 7.49 (d, 1H, $J = 16.2$ Hz, H 1), 7.44 (dd, 1H, $J = 5.1, 1.2$ Hz, H 5′), 7.41 (s, 1H, H 4″), 7.28 (dd, 1H, $J = 5.1, 1.1$ Hz, H 5‴), 7.22 (dd, 1H, $J = 3.6, 1.1$ Hz, H 3‴), 7.20 (dd, 1H, $J = 3.6, 1.2$ Hz, H 3′), 7.15 (dd, 1H, $J = 5.1, 3.6$ Hz, H 4′), 7.05 (dd, 1H, $J = 5.1, 3.6$ Hz, H 4‴), 7.05 (d, 1H, $J = 16.2$ Hz, H 2); ^{13}C NMR (67.8 MHz) δ 146.7, 143.8, 136.5, 136.3, 135.4, 134.5, 133.9, 127.9, 127.7, 127.4, 126.9, 126.7, 125.9, 125.1, 124.4, 124.1, 121.7; MS *m/z* 397 (17), 396 (26), 395 (M$^+$, 100%), 394 (9), 365 (11), 316 (16), 273 (12), 127 (12); υ_{max}/cm^{-1} 1586, 1508, 1336, 1107, 970, 955, 703, 690; electronic spectrum λ_{max} nm/(log ϵ) 345 (4.57), 411 (4.25). Anal. Calcd for $C_{20}H_{13}NO_2S_3$: C, 60.73; H, 3.31; N, 3.54. Found: C, 60.76; H, 3.08; N, 3.58.

***trans*-1-((2′,2″:5″,2‴-Terthiophen)-3″-yl)-2-(4⁗-cyanophenyl)ethene (25).** A mixture of the terthiophene aldehyde (**10**) (200 mg, 0.72 mmol), (4-cyanobenzyl)triphenylphosphonium bromide (**24**)[65] (398 mg, 0.87 mmol, 1.2 equiv), and DBU (0.13 mL, 0.87 mmol, 132 mg) in dry dichloromethane (20 mL) was heated under reflux. After 3 h the reaction mixture was diluted with dichloromethane (80 mL) and washed with a 1 M solution of HCl (2 × 30 mL), 10% sodium bicarbonate solution (30 mL), and water (40 mL). The organic layer was dried and concentrated to give a crude yellow solid. Analysis of this crude material by ^{1}H NMR spectroscopy indicated it contained the triphenylphosphine oxide byproduct and only the trans product. The material was then subjected to radial chromatography (dichloromethane/hexane) to afford a yellow solid which was recrystallized from ether/pentane to give yellow crystals of **25** (249 mg, 92%): mp 154 °C; ^{1}H NMR (400 MHz) δ 7.64−7.61 (2H, AA′ part of AA′XX′), 7.56−7.53 (2H, XX′ part of AA′XX′), 7.46 (d, 1H, $J = 16.2$ Hz, H 1), 7.44 (dd, 1H, $J = 5.1, 1.2$ Hz, H 5′), 7.42 (s, 1H, H 4″), 7.29 (dd, 1H, $J = 5.1, 1.1$ Hz, H 5‴), 7.23 (dd, 1H, $J = 3.6, 1.1$ Hz, H 3‴), 7.20 (dd, 1H, $J = 3.6, 1.2$ Hz, H 3′), 7.16 (dd, 1H, $J = 5.1, 3.6$ Hz, H 4′), 7.06 (dd, 1H, $J = 5.1, 3.6$ Hz, H 4‴), 7.01 (d, 1H, $J = 16.2$ Hz, H 2); ^{13}C NMR (67.8 MHz) δ 141.8, 136.4, 136.3, 135.4, 134.5, 133.4, 2 × 132.4, 128.1, 2 × 127.9, 127.3, 126.8, 126.7, 2 × 125.0, 124.3, 121.7, 119.0; MS *m/z* 377 (16), 376 (27), 375 (M$^+$, 100%), 374 (14), 342 (7), 341 (7), 273 (15), 127 (10); υ_{max}/cm^{-1} 2221, 1599, 1409, 1172, 966, 949, 818, 698; electronic spectrum λ_{max} nm/ (log ϵ) 324 (4.65), 355 (4.45). Anal. Calcd for $C_{21}H_{13}NS_3$: C, 67.16; H, 3.49; N, 3.73. Found: C, 66.84; H, 3.30; N, 3.83.

***trans*-1-((2′,2″:5″,2‴-Terthiophen)-3″-yl)-2-(phenyl)ethene (27).** A mixture of the terthiophene aldehyde (**10**) (150 mg, 0.54 mmol), benzyltriphenylphosphonium bromide (**26**)[66] (282 mg, 0.65 mmol, 1.2 equiv), and DBU (0.10 mL, 0.65 mmol, 99 mg) in dry dichloromethane (15 mL) was heated under reflux. After 6 h the reaction mixture was diluted with dichloromethane (60 mL) and washed with a 1 M solution of HCl acid (2 × 30 mL), 10% sodium bicarbonate solution (30 mL), and water (40 mL). The organic layer was dried and concentrated to give a crude yellow solid. Analysis of this crude material by ^{1}H NMR spectroscopy indicated it consisted of the desired trans product. The material was then subjected to radial chromatography (dichloromethane/hexane) to afford a yellow oil which crystallized on standing. Recrystallization from ether/pentane gave the product (**27**) as fluffy yellow crystals (168 mg, 88%): mp 93−4 °C; ^{1}H NMR (400 MHz) δ 7.53−7.48 (m, 2H, aryl H), 7.45 (s, 1H, H 4″), 7.40 (dd, 1H, $J = 5.2, 1.2$ Hz, H 5′), 7.38 (d, 1H, $J = 16.1$ Hz, H 1), 7.40−7.34 (m, 2H, aryl H), 7.28 (dd, 1H, $J = 5.1, 1.1$ Hz, H 5‴), 7.30−7.24 (m, 1H, aryl H), 7.24 (dd, 1H, $J = 3.6, 1.1$ Hz, H 3‴), 7.22 (dd, 1H, $J = 3.6, 1.2$ Hz, H 3′), 7.14 (dd, 1H, $J = 5.2, 3.6$ Hz, H 4′), 7.06 (dd, 1H, $J = 5.1, 3.6$ Hz, H 4‴), 7.06 (d, 1H, $J = 16.1$ Hz, H 2); ^{13}C NMR (67.8 MHz) δ 137.4, 136.8, 136.4, 136.0, 135.2, 131.6, 130.4, 128.7, 127.9, 127.8, 127.7, 127.0, 126.5, 126.4, 124.9, 124.2, 122.3, 121.7; MS *m/z* 352 (16), 351 (26), 350 (M$^+$, 100%), 349 (14), 317 (12), 316 (14), 273 (15), 127 (8); υ_{max}/cm^{-1} 3056, 1595, 1506, 1188, 952, 842, 813, 752, 691; electronic spectrum λ_{max} nm/(log ϵ) 312 (4.57), 359 (4.34). Anal. Calcd for $C_{20}H_{14}S_3$: C, 68.53; H, 4.03. Found: C, 68.40; H, 3.81.

***trans*-1-((2′,2″:5″,2‴-Terthiophen)-3″-yl)-2-(4⁗-methoxyphenyl)ethene (29).** A mixture of (4-methoxybenzyl)triphenylphosphonium chloride (**28**)[67] (484 mg, 1.16 mmol, 2 equiv) and KOBu^t (130 mg, 1.16 mmol) in dry THF (10 mL) was heated under reflux for 15 min. To this was added a solution of the terthiophene aldehyde (**10**) (160 mg, 0.58 mmol) in dry THF (10 mL). After 8 h the reaction was stopped, diluted with dichloromethane (60 mL), and washed with a 1 M solution of HCl (2 × 30 mL), 10% sodium bicarbonate solution (30 mL). and water (20 mL). The organic layer was dried ($MgSO_4$) and concentrated to give a crude yellow solid. This solid was dissolved in a small quantity of dichloromethane/hexane (1:1) and passed through a column of silica with continued elution with the same solvent system until the yellow material had been collected. This material was subjected to radial chromatography to give a yellow solid which was recrystallized from ether/pentane to afford the product (**29**) as yellow crystals (175 mg, 80%): mp 94 °C; ^{1}H NMR (400 MHz) δ 7.46−7.44 (2H, AA′ part of AA′XX′), 7.43 (s, 1H, H 4″), 7.40 (dd, 1H, $J = 5.1, 1.2$ Hz, H 5′), 7.27 (dd, 1H, $J = 5.1, 1.2$ Hz, H 5‴), 7.25 (d, 1H, $J = 16.2$ Hz, H 1), 7.23 (dd, 1H, $J = 3.6, 1.2$ Hz, H 3‴), 7.21 (dd, 1H, $J = 3.6, 1.2$ Hz, H 3′), 7.14 (dd, 1H, $J = 5.1, 3.6$ Hz, H 4′), 7.06 (dd, 1H, $J = 5.1, 3.6$ Hz, H 4‴), 7.01 (d, 1H, $J =$ 16.2 Hz, H 2), 6.94−6.88 (2H, XX′ part of AA′XX′), 3.85 (s, 3H, OMe); ^{13}C NMR (67.8 MHz) δ 159.4, 136.9, 136.7, 135.9, 135.4, 130.8, 130.1, 130.0, 127.9, 2 × 127.8, 126.8, 126.2, 124.8, 124.1, 122.2, 119.7, 114.2, 55.3; MS *m/z* 382 (16), 381 (26), 380 (M$^+$, 100%), 379 (8), 303 (7), 273 (6), 272 (5), 127 (8); υ_{max}/cm^{-1} 3104, 1602, 1510, 1247, 1172, 1035, 956, 846, 826, 816, 804, 699;

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electronic spectrum λ_{max} nm/(log ϵ) 323 (4.74), 3.62 (4.48). Anal. Calcd for $C_{21}H_{16}OS_3$ requires C, 66.28; H, 4.24. Found: C, 66.47; H, 4.16.

***trans*-1-((2′,2″:5″,2‴-Terthiophen)-3″-yl)-2-(4⁗-*N*,*N*-dimethylphenyl)ethene (31).** A mixture of (4-*N*,*N*-dimethylbenzyl)triphenylphosphonium iodide (**30**)[68] (597 mg, 1.14 mmol, 2.1 equiv) and KOBu^t (128 mg, 1.14 mmol) in dry THF (10 mL) was heated under reflux for 15 min and then cooled. To this was added a solution of the terthiophene aldehyde (**10**) (150 mg, 0.54 mmol) in dry THF (10 mL) and heated under reflux. After 6 h the reaction was stopped, diluted with dichloromethane (60 mL), and washed with a 1 M solution of HCl (2 × 30 mL), 10% sodium bicarbonate solution (30 mL), and water (20 mL). The organic layer was dried ($MgSO_4$) and concentrated to give a crude yellow solid. This solid was dissolved in a small quantity of dichloromethane/hexane (1:1) and passed through a column of silica with continued elution with the same solvent system until the yellow material had been collected. This material was subjected to radial chromatography to give a yellow oil which crystallized from ether to afford the product (**31**) as yellow crystals (173 mg, 81%): mp 154−5 °C; ^{1}H NMR (400 MHz) δ 7.43 (s, 1H, H 4″), 7.44−7.39 (2H, AA′ part of AA′XX′), 7.37 (dd, 1H, J = 5.2, 1.2 Hz, H 5′), 7.26 (dd, 1H, J = 5.1, 1.2 Hz, H 5‴), 7.23 (dd, 1H, J = 3.6, 1.2 Hz, H 3‴), 7.21 (dd, 1H, J = 3.6, 1.2 Hz, H 3′), 7.20 (d, 1H, J = 16.1 Hz, H 1), 7.12 (dd, 1H, J = 5.2, 3.6 Hz, H 4′), 7.05 (dd, 1H, J = 5.1, 3.6 Hz, H 4‴), 7.00 (d, 1H, J = 16.1 Hz, H 2), 6.76−6.70, 2H (XX′ part of AA′XX′), 3.00, s, 6H, NMe_2. ^{13}C NMR (67.8 MHz) δ 150.2, 137.2, 137.1, 2 × 135.7, 130.7, 129.8, 127.9, 2 × 127.7, 127.6, 126.0, 125.7, 124.7, 124.0, 122.4, 117.6, 112.5, 40.4; MS *m*/*z* 395 (13), 394 (28), 393 (M$^+$, 100%), 392 (9), 316 (5), 197 (9), 196 (4), 40 (4); υ_{max}/cm^{-1} 3064, 1601, 1522, 1366, 1185, 1170, 957, 829, 802, 703; electronic spectrum λ_{max} nm/(log ϵ) 348 (4.58). Anal. Calcd for $C_{22}H_{19}NS_3$: C, 67.13; H, 4.87; N, 3.56. Found: C, 67.13; H, 4.85; N, 3.58.

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Supporting Information Available: General experimental details,^{1}H, ^{13}C, and 2D LRCOSY NMR spectra, X-ray crystallographic data for **25**, cyclic voltammograms and electronic absorption spectra for compounds **23**, **25**, **27**, **29**, and **31** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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