

# Oxidative Bond Formation in Dithienyl Polyphenylenes: Optical and Electrochemical Consequences

Colin J. Martin,<sup>[a]</sup> Belen Gil,<sup>[a]</sup> Sarath D. Perera,<sup>[a,b]</sup> and Sylvia M. Draper\*<sup>[a]</sup>

**Keywords:** Thiophenes / Electrochemistry / C–C coupling / Photophysics / Sulfur

A new set of dithienyl polyphenylenes was prepared with a view of developing sulfur-containing polyaromatic hydrocarbons (PAHs) by oxidative cyclodehydrogenation. The first of these, 1,2-bis(5-methyl-2-thienyl)-3,4,5,6-tetra-(4-*tert*-butylphenyl)benzene (**1**) was sterically hindered at the 5-positions of the thienyl rings and under Lewis acid catalyzed cyclodehydrogenation gave monomeric intramolecularly fused dithienyl **3**, which was spectroscopically and structurally characterized. Under the same conditions, three unhindered dithienyl polyphenylenes, 1,2-(thienyl)-3,4,5,6-tetra-(4-*tert*-butylphenyl)s **2**, **5**, and **6**, underwent both thiophene-di-

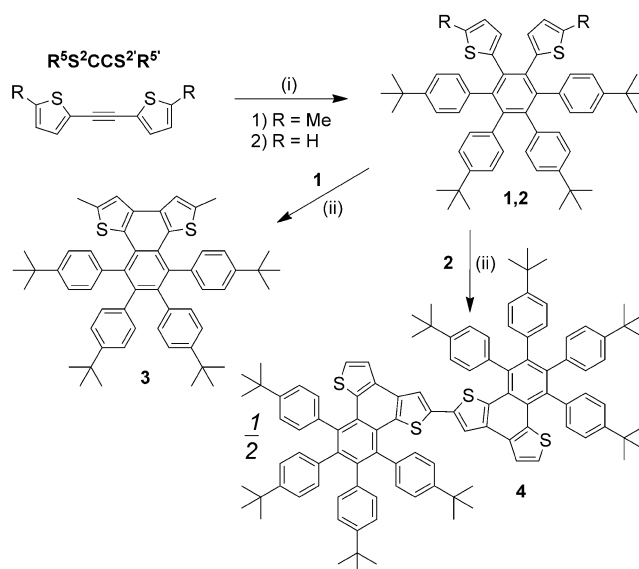
rected intra- and intermolecular C–C bond fusions. The resulting dimers **4**, **7**, and **8** were identified through a series of <sup>1</sup>H, <sup>13</sup>C, and 2D NMR experiments. The electrochemical and photophysical properties of the dimers were examined. Their optical properties reflect the coplanarity or otherwise of their cojoined parts. The electrochemical oxidation of the dithienyl polyphenylene precursors showed a relationship between the ease of oxidation and the availability of the 2- and 5-positions on the thienyl rings. Using spectroelectrochemical methods the electrochemically oxidized and chemically oxidized products were compared.

## Introduction

The chemical and electrochemical oxidation of thiophene systems has been extensively studied<sup>[1–4]</sup> due to the ease with which thiophenes undergo intermolecular dehydrogenation to form polymers.<sup>[3,5,6]</sup> The propensity of thiophene systems toward the formation of insoluble products along with the difficulty of controlling the properties of the resulting polymers have led to the strategy of using monomers containing multiple thiophene units.<sup>[7,8]</sup> Substituted bithienyl-, dithienylethene-, and thiophene-oligomer monomers have given better control over both the band gap and the conductivity of the polymers formed upon oxidation. In all of these systems, the focus has been on the effect of the structural changes to the monomer on the resulting polymer.<sup>[4,6]</sup> In comparison, little attention has been paid to the design of molecular systems containing multiple thiophene units where both inter- and intramolecular oxidations are possible.<sup>[9]</sup> Building on our recent work on monothienyl polyphenylenes<sup>[10]</sup> and our established expertise in dehydrogenation and carbon–carbon bond-forming processes,<sup>[11–13]</sup> we now present synthetic strategies for the generation of a series of dithiophene-containing polyaromatic compounds. A full discussion of the photochemical and electrochemical properties of the new molecules is provided.

## Results and Discussion

In recently published work, we presented a monothienyl polyphenylene that upon oxidation gave a dimeric S-doped hexabenzocoronene; the photochemical properties of which were dependent on the twist of each coronene unit around the newly formed dimer bond.<sup>[10]</sup> Here we report a series of disulfur polyphenylenes, similar in structure to our pre-



**Scheme 1.** Synthetic route to thienyl polyphenylenes **1–4**. Reagents and conditions: (i) Tetrakis(4-*tert*-butylphenyl)cyclopentadienone, Ph<sub>2</sub>CO, 300 °C melt, 90 min, 41% (for **1**), 66% (for **2**); (ii) FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>NO<sub>2</sub>, 25 °C, 40 min, 90% (for **3**), 55% (for **4**).

[a] School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland  
Fax: +353-1-671-2826  
E-mail: smdraper@tcd.ie

[b] The Chemistry Department, Open University of Sri Lanka, Nugegoda, Sri Lanka

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejoc.201100332>.

viously reported nitrogen-containing polyphenylenes. The latter are known to undergo Lewis acid catalyzed oxidation to give heterosuperbenzene systems [N-HSB].<sup>[11]</sup>

The prevalence of intermolecular dehydrogenations in thienyl oxidation<sup>[14,15]</sup> and the consequent problem of multiple isomeric products initially led us to sterically block the site for intermolecular dehydrogenation. To this end, a bithienylacetylene with methyl substituents MeS<sup>2</sup>CCS<sup>2'</sup>Me was synthesized and subsequently reacted with *tert*-butyl-substituted tetraphenylcyclopentadienone to give **1** (Scheme 1).

Cyclodehydrogenation of this bis(methylthienyl) polyphenylene was carried out by using FeCl<sub>3</sub> as oxidant and Lewis acid to give **3** (Scheme 1). Mass spectral analysis of **3** shows the loss of two hydrogen atoms, consistent with the one exclusive 3–3' intramolecular C–C bond fusion apparent in the single-crystal X-ray structure (Figure 1, C62–C72).

In the crystal packing of **3** (Supporting Information, Figure S1) there are two orientations of the molecule, each one layering on top of the other so as to avoid steric interactions between the tertiary butyl groups. Unlike with other polyphenylenes,<sup>[16]</sup> no  $\pi$ – $\pi$  interactions are seen between the molecules in each layer (a minimum  $\pi$ – $\pi$  distance of 4.95 Å is observed).

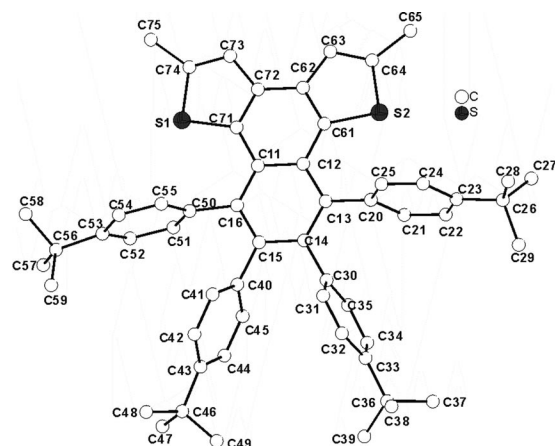
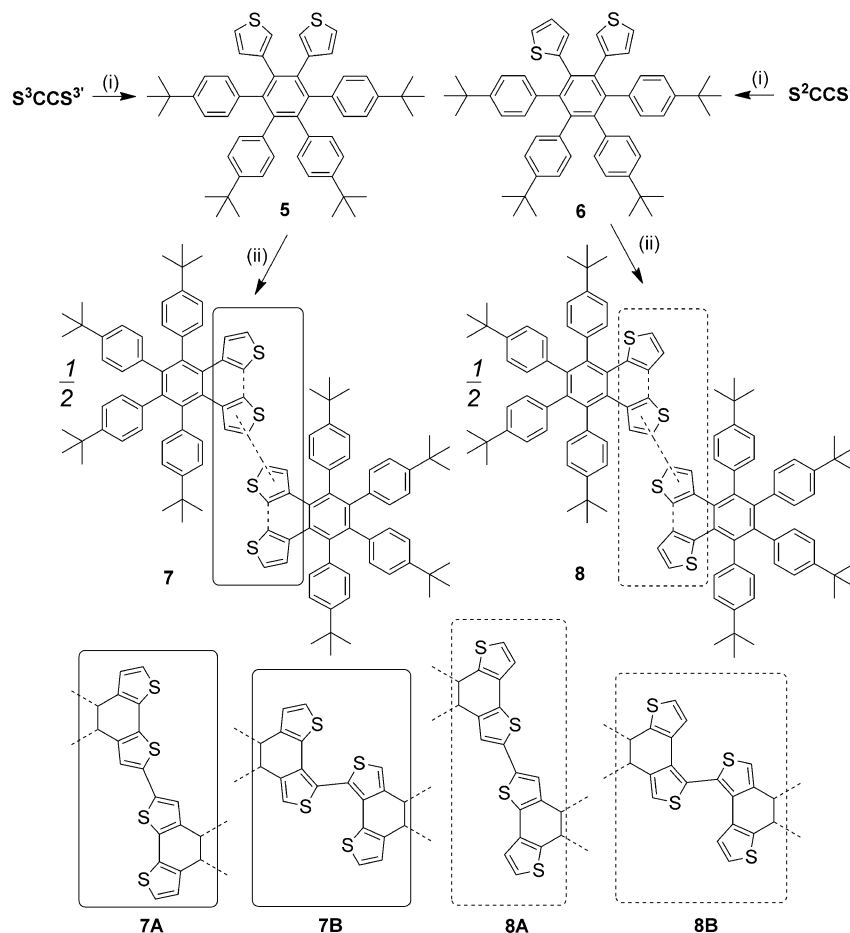


Figure 1. Single-crystal X-ray molecular structure of **3**. H atoms are omitted for clarity.

To examine the reactivities of unhindered dithienyl polyphenylenes under dehydrogenation conditions, symmetric S<sup>2</sup>CCS<sup>2'</sup> and S<sup>3</sup>CCS<sup>3'</sup> and asymmetric S<sup>2</sup>CCS<sup>3'</sup> dithienylacetylenes were prepared by Sonogashira coupling of the appropriate thienyl bromides.<sup>[17]</sup> Using these alkynes, three



Scheme 2. Synthetic route to partially cyclized thiophene systems **7** and **8**. Reagents and conditions: (i) Tetrakis(4-*tert*-butylphenyl)cyclopentadienone, Ph<sub>2</sub>CO, 300 °C melt, 90 min, 66% (for **5**), 66% (for **6**); (ii) FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>NO<sub>2</sub>, 25 °C, 40 min, 60% (for **7**), 52% (for **8**).

new dithienyl polyphenylene precursors were prepared (Scheme 1, Scheme 2).

2,2'-Dithiophene **2** was oxidized to give **4** (Scheme 1), whose mass spectrum shows the loss of six hydrogen atoms and the formation of a dimer. This is in agreement with the formation of three new C–C bonds, of which one is involved in dimer formation. The  $^1\text{H}$  NMR spectrum of **4** (Figure 2) reveals that the compound has only lost hydrogen on each of the thiophene moieties. Unlike other reported polyphenylenes,<sup>[10]</sup> no oxidation occurred at the phenylene rings. Three thiophene protons remain: an AB pattern at  $\delta = 7.44$  and 7.32 ppm and a singlet at  $\delta = 7.41$  ppm. The appearance of these signals, supported by additional NMR spectroscopic data, conclusively led to the structure of dimeric species **4** (Scheme 1). Hence dimerization occurred at the 5,5'-positions as expected from standard thiophene reactivities.<sup>[18]</sup> Comparing the  $^1\text{H}$  NMR spectrum with that of blocked species **3** (Figure 2) it can be seen that in both cases the remaining thienyl hydrogen atoms resonate between  $\delta = 7.45$  and 7.15 ppm. These downfield shifts are indicative of thienyl environments in which the S atoms point toward the *ortho* phenyl rings of the polyphenylene (Figure 1) and indicate that the orientation of the thienyl rings in **3** and **4** is the same.<sup>[13]</sup>

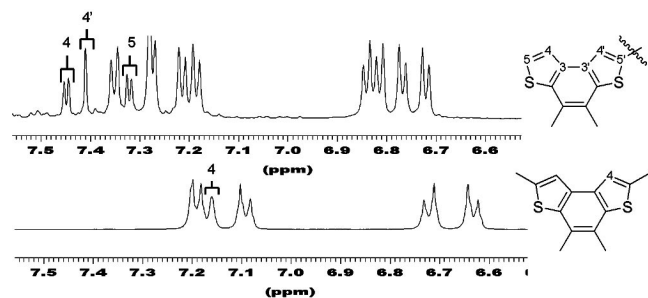


Figure 2.  $^1\text{H}$  NMR spectra (25 °C, 600 MHz,  $\text{CDCl}_3$ ) of **3** (top) and **4** (bottom).

A more complex set of polyphenylene bond fusions was possible on the dehydrogenation of 3,3'- and 2,3'-dithienyl polyphenylenes **5** and **6** (Scheme 2). However, the  $^1\text{H}$  NMR spectra of **5** and **6** were also dominated by the expected thienyl and phenyl ring signals, suggesting the formation of similar dimeric products. This conclusion is further supported by the mass spectroscopic data, which again indicate the formation of three new C–C bonds one of which was the result of dimerization.

For **7**, a total of four dehydrogenated dimers are possible; however, only one of these is formed (Figure 3, Scheme 2). The upfield shift in the  $^1\text{H}$  NMR spectrum of two of the thiophene signals (between  $\delta = 6.45$  and 6.25 ppm) indicates that in this case the thienyl sulfur atoms point away from their neighboring phenyl rings, that is, the *ortho* phenyl groups shield the thienyl protons that point towards them.<sup>[13]</sup> The data are therefore consistent with only two possible dimers **7A** and **7B** (both shown in Scheme 2). Of these, **7A** is preferred, as in this case both the intermolecular and intramolecular oxidations have occurred at the

more reactive 2- and 5-positions on the thiophene rings. The more complex asymmetry of precursor **6** dictates that here there are significantly more dimeric products possible on dehydrogenation (12 in total); however, NMR spectroscopy (Figure 3) again indicates the formation of only one of two possible isomers (Scheme 2, **8A** and **8B**). The  $^1\text{H}$  NMR spectrum clearly shows thienyl ring protons resonating at both high and low field, suggesting inward and outward pointing thienyl S atoms.

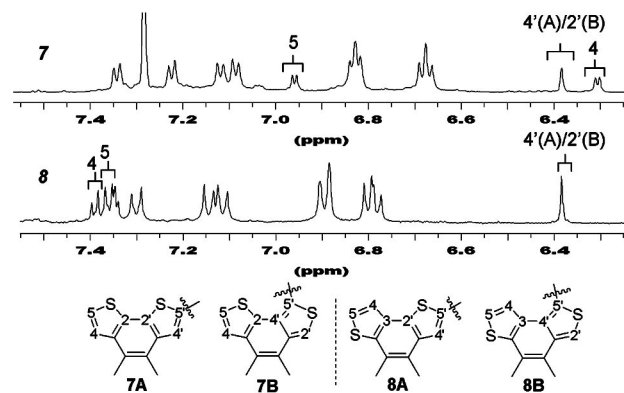


Figure 3.  $^1\text{H}$  NMR spectra of **7** and **8** (25 °C, 600 MHz,  $\text{CDCl}_3$  **7**,  $[\text{D}_2]-1,1,2,2$ -tetrachloroethane **8**).

In the absence of structural data, definitive characterization of compounds **7** and **8** has not been possible; however, it can be concluded that clean and single products were formed in both cases. Further exposure of **7** and **8** to conditions of dehydrogenation resulted in either no reaction ( $\text{FeCl}_3$ ) or decomposition ( $\text{AlCl}_3$ ).

## Photophysical Measurements

The systematic structural variation in this family of novel S-containing polyaromatics lent itself to a study of their optical properties as a function of planarity and the position of their thienyl S atoms. The absorption spectra of monomers **1**, **2**, **5**, and **6** (Supporting Information, Table S1, Figure S2) present broad unstructured bands, typical of nonplanar polyphenylenes.<sup>[19]</sup> The molecules present two broad, weak emission bands (Supporting Information, Table S2): one at high energy, which was attributed to the polyphenylene core (360–390 nm),<sup>[20,21]</sup> and one at low energy, which was attributed to the thiophene rings (420–520 nm; Supporting Information, Table S1, Figure S3).<sup>[22–25]</sup> The molecules are clearly structurally flexible in both the ground and excited states.

Dimeric systems **4**, **7**, and **8** also present a set of high-energy absorptions (Figure 4,  $\lambda = 350$ –450 nm) that are consistent with reported values for fused thienyl systems.<sup>[26]</sup> In addition, their spectra contain a shoulder, similar to the one observed in monothiophene hexabenzocoronenes,<sup>[18]</sup> that extends to lower energies. It corresponds to the increased conjugation arising from the two fused thienyl units in the dimer when they are coplanar (Scheme 3B).<sup>[14]</sup>

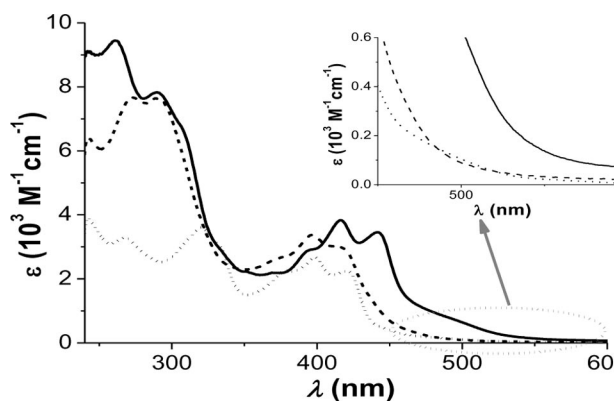


Figure 4. UV/Vis spectra (chloroform,  $10^{-5}$  M) of **4** (---), **7** (—), and **8** (···).



Scheme 3. Twisted (A) and planar (B) conformations as observed in dimeric systems **4**, **7**, and **8**.

The absorptivity of the tail is greatest for **7** in solution, indicating that the planar conformation (Scheme 3B) is more easily attained in this case. The sharp-structured absorption bands (around  $\lambda = 350$ – $450$  nm) observed for all three dimers support the idea of a high-energy barrier for the rotation of monomeric subunits through the newly formed bond.<sup>[22–25]</sup>

Systems **4**, **7**, and **8** are luminescent in the solid state and in solution at room temperature and at 77 K. They exhibit dual luminescence, which varies with concentration (Supporting Information, Table S3). In dilute solution (chloroform,  $10^{-5}$  M; Figure 5), the excitation spectra correspond to the absorption spectra but with the absence of the low-energy absorption shoulder, suggesting a highly twisted conformation (Scheme 3A).<sup>[22–25]</sup> At higher concentrations, a new low-energy band appears (between 525 and 575 nm) matching the tail described in the UV/Vis spectra (Figure 5) and suggesting a planar conformation. This concentration dependence is thought to be due to excited-state molecules aggregating more readily than those in the ground state, giving rise to excimeric species.<sup>[25,27,28]</sup>

The emission spectra of the dimers (at low concentration, Figure 6; Supporting Information, Table S3) show a high-energy band at similar energy to the emission (Supporting Information, Table S2) attributed to the thienyl rings of the starting materials. This implies that there is no increase in the delocalization of electronic density upon dimerization, and it is consistent with a twisted conformation in dilute solutions (Scheme 3A). In more concentrated solutions (chloroform,  $10^{-3}$  M), **4**, **7**, and **8** have a new broad lower-energy emission (Figures 5b and 6b; Supporting Information, Table S3) sometimes mixed with the high-energy bands attributed to the twisted conformation.

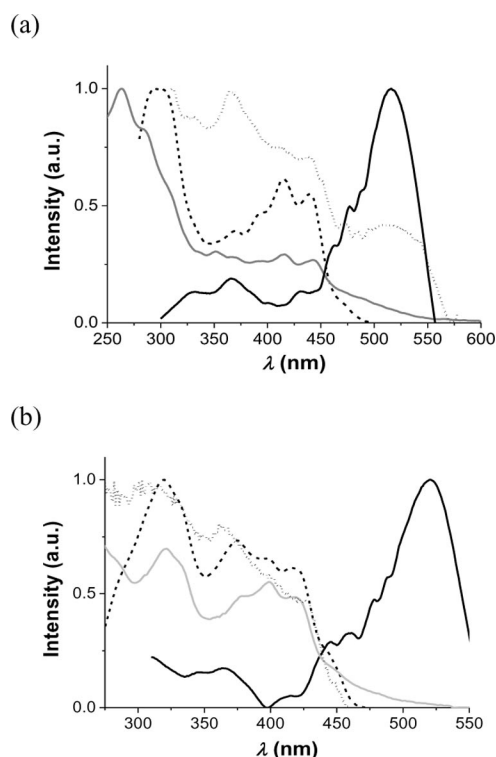


Figure 5. UV/Vis and excitation spectra of (a) **4** and (b) **7** at room temperature. UV/Vis (—, grey solid line), solid state (···), chloroform ( $10^{-3}$  M; —, solid black line), chloroform ( $10^{-5}$  M, ---).

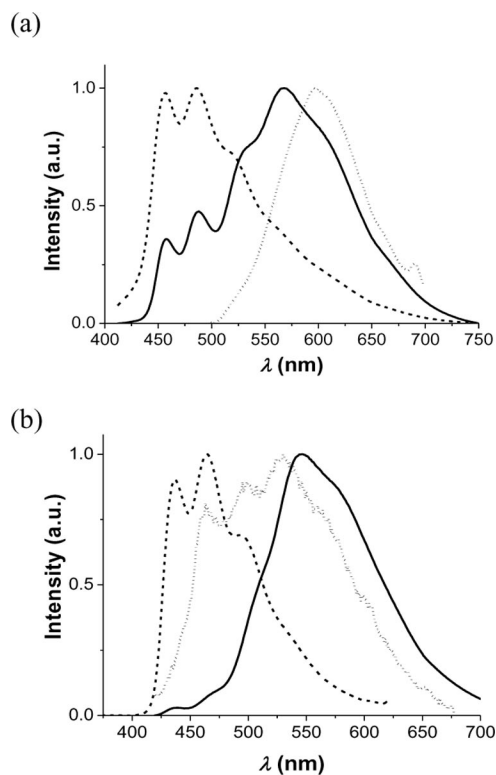


Figure 6. Emission spectra of (a) **4** and (b) **7** at room temperature. Solid state (···), chloroform ( $10^{-3}$  M, —), chloroform ( $10^{-5}$  M, ---).

Although all three dimeric systems **4**, **7**, and **8** present excimeric emissions at high concentration, the nature of their excited states is different. In **4**, the emission comes from a singlet state (nanosecond range), whereas for **7** and **8** the emission is of triplet-state origin (microsecond range).

The difference in the lifetimes seems to indicate that systems **7** and **8** can form more stable excimers, as they adopt a planar conformation more readily (Scheme 3). This is further demonstrated in the solid state where the emissions of **7** and **8** are slightly redshifted relative to those of the concentrated solutions (Figure 6b). For **4**, however, the excitation spectra of the solid state and dilute solutions coincide (Figure 6a). The blueshift between the emissions in the solid state and dilute solutions (Figure 6b) seems to indicate a twisted conformation (Scheme 3A) for **4** even in the solid state.

Excimeric species only form in the dimeric systems. In the case of monomeric **3**, the emission spectrum does not show any change with concentration, having only a sharp band at 400 nm and a tail to longer wavelengths (to 600 nm). At low temperature, a second structured band is also observed (495, 525 nm) that can be attributed to emission from the triplet state (Supporting Information, Figure S4).

## Electrochemical Measurements

The partially fused dithiophene-containing systems **4**, **7**, and **8** undergo no oxidation within the potential windows in both chloroform and acetonitrile. Each polyphenylene (**1**, **2**, **5**, and **6**; Schemes 1 and 2) undergoes a single irreversible oxidation to form a stable species (chloroform,  $10^{-2}$  M). The lowest oxidation potential is observed for 3,3' symmetric species **5** (+1.34 V), where both 2–2' intramolecular and 5–5' intermolecular bond formations are possible.

An increase in oxidation potential to +1.44 V is seen for **6** possibly due to the more electrochemically demanding 2–3' or 2–4' intramolecular bond fusions available. For both **1** and **2** a further increase in oxidation potential is seen, resulting from the 3,3' intramolecular bond formations required in these systems; however, in **1** where the 5-positions are blocked, a decrease in the intensity of the oxidation was observed.

Such a trend implies that electrochemical oxidation to give C–C bond fusion occurs preferentially at the 2,5-positions of each thiophene; this data mirrors the chemically obtained products where intramolecular 2,2' bond formation occurs ahead of intramolecular 2,3' fusion (where a choice is available). The presence of the phenyl substituents in our compounds acts to preclude electrochemical polymerization or indeed further chemical oxidation of any of the compounds as a result of steric effects and the effect of substitution on the electron density at the relevant thiophene polymer-linking positions.<sup>[29]</sup>

To study the products of these high-voltage oxidations, the UV/Vis spectra of polyphenylenes **1**, **2**, **5**, and **6** were observed as the solutions were oxidized by an open poten-

tial of +1.60 V. In the case of the 2,3'-thiophene precursor **6**, the available sites for intramolecular bond formation are 3–2' and there is also a possible 5–5' intermolecular bond. In the UV/Vis spectrum (Figure 7a) we see the formation of weak absorptions at 396 and 419 nm after 20–25 min, which are similar to those seen in dimeric product **8** (Supporting Information, Table S1).

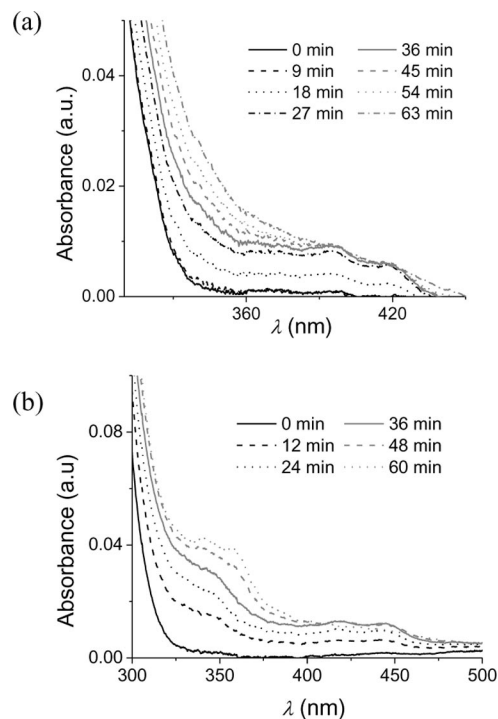


Figure 7. The changes in the UV/Vis spectrum of (a) **6** and (b) **5** as an open potential of +1.6 V is applied (chloroform,  $10^{-4}$  M) (vs.  $\text{Fc}/\text{Fc}^+$ ).

The formation of these peaks, similar to those seen in the dimeric species, is even more pronounced in the case of **5** (Figure 7b) where the absorptions are observed after 25 min at 416 and 444 nm; in **5** the thiophenes can undergo a 2–2' intramolecular oxidative bond formation along with a 5–5' intermolecular one. Assuming this has occurred in the electrochemical oxidation there are still unoxidized 5-positions on the thiophene dimer that could undergo further oxidative bond formation. This could explain the appearance of a new set of absorption bands, after 60 min, in the same region (350–375 nm) as that seen for oligothiophenes containing three or four thienyl units.<sup>[30]</sup>

For **2**, electrochemical oxidation results in no change in the UV/Vis spectrum; as this was the most chemically reactive species towards  $\text{FeCl}_3$  this result seems surprising. If the available oxidation sites (Table 1) are as predicted, intramolecular oxidation of **2** can occur exclusively at the 3-position on the thiophene ring. As electrochemical oxidation has been widely reported to drastically favor those involving at least one 2/5-position on the ring<sup>[3]</sup> it can be assumed that under electrochemical conditions the 5–5' intermolecular oxidation occurs preferentially over the 3–3' intramolecular one. Oxidation of **2** will not lead to intramolecu-

lar bond formation, and as such, the product does not contain the new absorptions observed in the cases of **5** and **6**. In the case of **1** in which all the 2/5-positions of the thiophenes are blocked, no observable change in the spectrum was seen after 75 min.

Table 1. Irreversible oxidation potentials of **1**, **2**, **5**, and **6** (chloroform,  $10^{-2}$  M) vs.  $\text{Fc}/\text{Fc}^+$ .

| Polyphenylene precursor | Oxidation [V] | Available sites for electrochemical oxidation |
|-------------------------|---------------|-----------------------------------------------|
| <b>1</b>                | +1.56         | 3,3' intra                                    |
| <b>2</b>                | +1.52         | 3,3' intra, 5,5' inter                        |
| <b>6</b>                | +1.44         | 2,3' or 2,4' intra, 5,5' inter                |
| <b>5</b>                | +1.34         | 2,2' intra, 5,5' inter                        |

In order to investigate if the products formed from the electrochemical oxidations of **5** and **6** were similar to those seen upon chemical oxidation, the fluorescence spectra of the electrochemical products were examined at low concentration (chloroform,  $10^{-4}$  M) and compared to those of the chemical products (i.e., **7** and **8**).

In both cases an increase in fluorescence intensity was observed upon electrochemical oxidation. For **5**, a new vibrationally structured fluorescence spectrum was observed. The maxima at 462 and 489 nm closely match those in the emission spectrum of **7**, the product from chemical oxidation (Figure 8a). For **6**, electrochemical oxidation produces an emission spectrum with maxima at 432 and 460 nm (Figure 8b), and again these are very similar to the emissions observed for **8**, the product from chemical oxidation.

## Conclusions

Examination of oxidative carbon–carbon bond formations within dithienyl polyphenylenes has led to the synthesis of novel monomeric and dimeric sulfur containing polyaromatic products. The reactivity of dithienyl polyphenylene precursors **1**, **2**, **5**, and **6** shows a preference for the formation of thiophene–thiophene inter- and intramolecular carbon–carbon bonds over intramolecular thiophene–phenylene bonds where possible. This leads to the formation of partially fused species **3**, **4**, **7**, and **8** upon chemical oxidation. Electrochemical oxidation gives only bond formation at the more reactive 2- and 5-thiophene positions to give products that have been monitored spectroelectrochemically.

Dimeric species **4**, **7**, and **8** have optical properties that vary with concentration as a result of the orientation of the systems about the newly formed dimer bond. Blocked fused monomer **3** does not show the same optical properties as the dimers, but instead shows a single luminescence at room temperature.

## Experimental Section

**General Methods:** 2,3,4,5-Tetrakis-(4-*tert*-butylphenyl)cyclopentadienone was synthesized according to a literature procedure.<sup>[31]</sup> Flash chromatography was performed by using silica gel (Aldrich Chemical) as the stationary phase. IR spectra were recorded neat or for **7** and **8** in KBr with a Perkin–Elmer Spectrum 100 FTIR spectrometer fitted with a Universal ATR accessory. NMR spectra were recorded with a Bruker Avance DPX 400 spectrometer operating at 400.13 MHz for  $^1\text{H}$  and at 100.62 MHz for  $^{13}\text{C}$ , or for **4**, **7**, and **8** with a Bruker Avance II 600 NMR spectrometer operating at 600.13 MHz for  $^1\text{H}$  and at 150.90 MHz for  $^{13}\text{C}$ ; all samples were standardized with respect to TMS. ESI MS were recorded with a micromass LCT electrospray mass spectrometer, EI MS were recorded with a Waters GCT Premier electron impact mass spectrometer, MALDI MS were recorded with a MALDI-Q-ToF Premier mass spectrometer. Accurate MS were referenced against leucine enkephalin ( $555.6\text{ g mol}^{-1}$ ) and were reported within 5 ppm. UV/Vis absorption spectra were recorded with a Shimadzu UV-2450 UV/Vis recording spectrophotometer. All electrochemical experiments were performed with a CH Instruments potentiostat model 660B. Cyclic voltammograms were measured on 0.01 M solutions of the compounds in acetonitrile or chloroform, and open potential experiments were carried out on 1 mM solutions of the compounds in chloroform. Tetra-*n*-butylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ , 0.1 M) was used as supporting electrolyte, a glassy carbon working electrode, a Pt wire counterelectrode and a SCE reference electrode were used. Potentials are quoted vs. the ferrocene/ferrocenium couple (0.0 V), and all potentials were referenced to internal ferrocene added at the end of each experiment. All solutions were continuously degassed for 10 min by nitrogen bubbling before the experiments were performed and a flow of nitrogen was

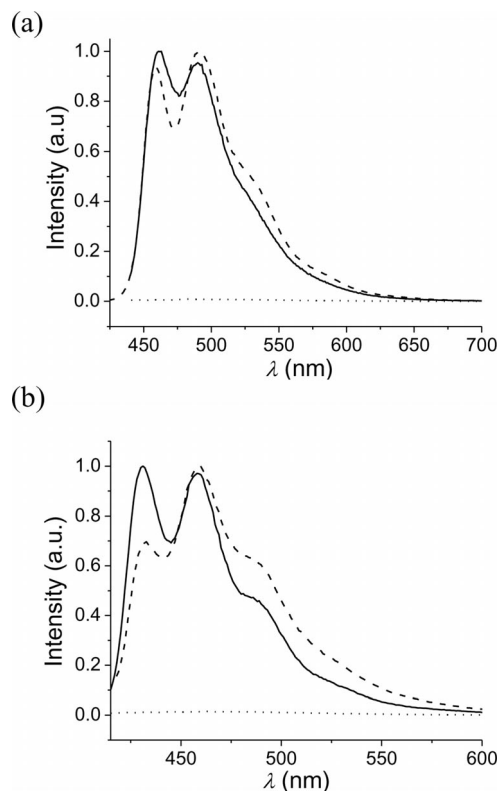


Figure 8. The fluorescence emission on the electrochemical oxidation of (a) **5** at  $\lambda_{\text{exc}} = 421\text{ nm}$  and (b) **6** at  $\lambda_{\text{exc}} = 394\text{ nm}$ , before (—) and after (---) +1.6 V was applied for 40 min. (chloroform,  $10^{-4}$  M) vs.  $\text{Fc}/\text{Fc}^+$ ; along with the relevant chemically oxidized products **7** (a, —) and **8** (b, —). (Note: in both cases the spectra have been normalized, the emission before oxidation is normalized relative to the emission after oxidation).

maintained over the solution for the duration of the experiments. Emission and excitation spectra were obtained with a Fluorolog FL-3-11 spectrofluorimeter, in which lifetime measurements were performed with an IBH Datastation HUB 5000F. All samples were degassed under an argon atmosphere prior to the experiment being carried out.

CCDC-782261 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**2-Thienyl-3-thienylacetylene (S<sup>2</sup>CCS<sup>3</sup>):** To a mixture of benzytriethylammonium chloride (25 mg, 0.11 mmol), copper(I) iodide (34 mg, 0.13 mmol), tetrakis(triphenylphosphane) palladium(0) (110 mg, 0.09 mmol), 2-bromothiophene (0.305 mL, 3.15 mmol), and 4-(3-thienyl)-2-methyl-3-buten-2-ol (0.59 g, 3.32 mmol) in benzene (10 mL) was added 5.5 N NaOH (8 mL, 0.044 mmol). The mixture was stirred at 80 °C for 3 d, and it was then cooled to room temperature. A solution of saturated ammonium chloride (40 mL) was added, and the solution was stirred for 1 h. The phases were separated, and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate, and the solvent was evaporated. The product was purified by column chromatography on silica (hexane/dichloromethane, 3:2) to give a white solid (0.21 g, 1.11 mmol, 34%). M.p. 75–76 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 7.55 (dd, <sup>4</sup>J<sub>H,H</sub> = 1.0, 3.0 Hz, 1 H, H<sub>Th'</sub>), 7.33 (dd, <sup>4</sup>J<sub>H,H</sub> = 3.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 5.0 Hz, 1 H, H<sub>Th'</sub>), 7.30 (m, 2 H, 2\*H<sub>Th</sub>), 7.22 (dd, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 5.0 Hz, 1 H, H<sub>Th'</sub>), 7.03 (dd, <sup>3</sup>J<sub>H,H</sub> = 3.0, 5.0 Hz, 1 H, H<sub>Th</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 131.4 (C<sub>Th</sub>), 129.3 (C<sub>Th'</sub>), 128.4 (C<sub>Th'</sub>), 126.8 (C<sub>Th</sub>), 126.7 (C<sub>Th</sub>), 125.1 (C<sub>Th'</sub>), 122.8 (C<sub>Th/quat</sub>), 121.5 (C<sub>Th/quat</sub>), 87.8 (C<sub>acetyl</sub>), 81.7 (C<sub>acetyl</sub>) ppm. IR (neat): ν̄ = 2163 (C≡C), 1213, 1118, 866, 849, 824, 774, 699, 689, 619 cm<sup>-1</sup>. MS (EI, acetonitrile): *m/z* = 189.9916 [M]<sup>+</sup> (calcd. 189.9911). C<sub>10</sub>H<sub>6</sub>S<sub>2</sub> (190.28): calcd. C 63.12, H 3.18; found C 62.96, H 3.21.

**Synthesis of Bisacetylenes S<sup>3</sup>CCS<sup>3</sup>, S<sup>2</sup>CCS<sup>2</sup>, and MeS<sup>2</sup>CCS<sup>2</sup>Me:** To a mixture of the appropriate bromothiophene (20 mmol), 2-methyl-3-buten-2-ol (2.0 mL, 20 mmol), benzytriethylammonium chloride (71 mg, 0.31 mmol), copper(I) iodide (100 mg, 0.53 mmol), and tetrakis(triphenylphosphane) palladium(0) (200 mg, 0.17 mmol) in benzene (10 mL) was added 5.5 N NaOH (8 mL, 0.044 mmol), and the mixture was stirred for 3 d. More bromothiophene (20 mmol) in benzene (8.0 mL) was added, and the solution was heated to 80 °C and stirred at this temperature for 3 d. The mixture was then cooled to room temperature. A solution of saturated ammonium chloride (40 mL) was added, and the solution was stirred for 1 h. The phases were separated, and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate, and solvent was evaporated. Purification by column chromatography on silica (hexane) gave the desired products as white solids.

**MeS<sup>2</sup>CCS<sup>2</sup>Me:** Yield: 1.84 g (8.43 mmol, 42%). M.p. 55–56 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 7.07 (d, <sup>3</sup>J<sub>H,H</sub> = 3.5 Hz, 2 H, H<sub>Th</sub>), 6.67 (qd, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.8 Hz, 2 H, H<sub>Th</sub>), 2.50 (d, <sup>4</sup>J<sub>H,H</sub> = 0.8 Hz, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 142.3 (C<sub>Th/quat</sub>), 132.2 (C<sub>Th</sub>), 125.4 (C<sub>Th</sub>), 120.7 (C<sub>Th/quat</sub>), 85.8 (C<sub>acetyl</sub>), 15.5 (CH<sub>3</sub>) ppm. IR (neat): ν̄ = 2190 (C≡C), 1487, 1439, 1200, 1159, 1044, 804, 789, 720 cm<sup>-1</sup>. MS (EI, acetonitrile): *m/z* = 218.0225 [M]<sup>+</sup> (calcd. 218.0224).

**S<sup>3</sup>CCS<sup>3</sup>:** Yield: 1.52 g (7.99 mmol, 40%). M.p. 76–77 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 7.54 (dd, <sup>4</sup>J<sub>H,H</sub> = 1.5, 3.0 Hz, 2 H, H<sub>Th</sub>), 7.32 (dd, <sup>4</sup>J<sub>H,H</sub> = 3.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 5.0 Hz, 2 H, H<sub>Th</sub>), 7.21 (dd, <sup>4</sup>J<sub>H,H</sub> = 1.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.5 Hz, 2 H, H<sub>Th</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H}

NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 129.4 (C<sub>Th</sub>), 128.1 (C<sub>Th</sub>), 124.9 (C<sub>Th</sub>), 121.7 (C<sub>quat/Th</sub>), 85.7 (C<sub>acetyl</sub>) ppm. IR (neat): ν̄ = 2161 (C≡C), 1352, 1076, 960, 868, 828, 774, 693 cm<sup>-1</sup>. MS (EI, acetonitrile): *m/z* = 189.9916 [M]<sup>+</sup> (calcd. 189.9911). C<sub>10</sub>H<sub>6</sub>S<sub>2</sub> (190.28): calcd. C 63.12, H 3.18; found C 63.21, H 3.21.

**S<sup>2</sup>CCS<sup>2</sup>:** Yield: 0.51 g (2.68 mmol, 14%). M.p. 73–74 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 7.33 (dd, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 5.0 Hz, 2 H, H<sub>Th</sub>), 7.30 (dd, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.5 Hz, 2 H, H<sub>Th</sub>), 7.03 (dd, <sup>3</sup>J<sub>H,H</sub> = 3.5, 5.0 Hz, 2 H, H<sub>Th</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 131.7 (C<sub>Th</sub>), 127.2 (C<sub>Th</sub>), 126.7 (C<sub>Th</sub>), 122.4 (C<sub>Th/quat</sub>), 85.7 (C<sub>acetyl</sub>) ppm. IR (neat): ν̄ = 2186 (C≡C), 1433, 1407, 1199, 1041, 1028, 850, 825, 694 cm<sup>-1</sup>. MS (EI, acetonitrile): *m/z* = 189.9919 [M]<sup>+</sup> (calcd. 189.9911). C<sub>10</sub>H<sub>6</sub>S<sub>2</sub> (190.28): calcd. C 63.12, H 3.18; found C 63.83, H 3.07.

**Synthesis of Thienyl-Substituted Benzenes:** A mixture of the relevant acetylene (0.32 mmol), 2,3,4,5-tetrakis(4-*tert*-butylphenyl)-cyclopentadienone (150 mg, 0.25 mmol), and benzophenone (0.5 g) were heated for 90 min at 300 °C while attached to an air condenser, giving a brown mixture. After cooling to room temperature, this was purified by flash chromatography (SiO<sub>2</sub>; hexane/diethyl ether, 9:1) to give the product as a light colored solid (**1** and **2**, grey; **5**, white; **6**, brown). These were recrystallized from a mixture of chloroform and methanol (2 mL of each).

**1:** Yield: 82 mg (0.10 mmol, 41%). M.p. 245–246 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 6.92 (d, <sup>3</sup>J<sub>H,H</sub> = 8.3 Hz, 4 H, H<sub>Ar</sub>), 6.80 (m, 8 H, 2\*H<sub>Ar</sub>), 6.62 (d, <sup>3</sup>J<sub>H,H</sub> = 8.6 Hz, 4 H, H<sub>Ar</sub>), 6.27 (m, 4 H, 2\*H<sub>Th</sub>), 2.26 (s, 6 H, CH<sub>3</sub>), 1.16 (s, 18 H, CMe<sub>3</sub>), 1.10 (s, 18 H, CMe<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 147.9 (C<sub>quat</sub>), 147.5 (C<sub>quat</sub>), 141.7 (C<sub>quat</sub>), 141.6 (C<sub>quat</sub>), 139.8 (C<sub>quat</sub>), 139.7 (C<sub>quat</sub>), 137.8 (C<sub>quat</sub>), 137.6 (C<sub>quat</sub>), 134.2 (C<sub>quat</sub>), 130.8 (C<sub>Ar</sub>), 130.5 (C<sub>Ar</sub>), 128.8 (C<sub>Th</sub>), 123.7 (C<sub>Th</sub>), 123.3 (C<sub>Ar</sub>), 123.0 (C<sub>Ar</sub>), 34.2 (CMe<sub>3</sub>), 34.0 (CMe<sub>3</sub>), 31.3 (C<sub>Th</sub>), 31.2 (CH<sub>3</sub>), 15.2 (CH<sub>3</sub>) ppm. IR (neat): ν̄ = 2960, 1511, 1460, 1391, 1361, 1269, 1118, 1019, 830, 797, 571 cm<sup>-1</sup>. MS (ESI, acetonitrile): *m/z* = 821.4197 [M + Na]<sup>+</sup> (calcd. 821.4191).

**2:** Yield: 124 mg (0.16 mmol, 66%). M.p. 270–271 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 7.02 (dd, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 5.0 Hz, 2 H, H<sub>Th</sub>), 6.92 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 4 H, H<sub>Ar</sub>), 6.83 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 4 H, H<sub>Ar</sub>), 6.81 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 4 H, H<sub>Ar</sub>), 6.66 (d, <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz, 4 H, H<sub>Ar</sub>), 6.63 (dd, <sup>3</sup>J<sub>H,H</sub> = 3.5, 5.0 Hz, 2 H, H<sub>Th</sub>), 6.51 (dd, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.5 Hz, 2 H, H<sub>Th</sub>), 1.16 (s, 18 H, CMe<sub>3</sub>), 1.11 (s, 18 H, CMe<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 147.6 (C<sub>quat</sub>), 147.2 (C<sub>quat</sub>), 141.6 (C<sub>quat</sub>), 141.4 (C<sub>quat</sub>), 141.4 (C<sub>quat</sub>), 137.1 (C<sub>quat</sub>), 137.0 (C<sub>quat</sub>), 133.4 (C<sub>Th/quat</sub>), 130.4 (C<sub>Ar</sub>), 1F.0 (C<sub>Ar</sub>), 128.6 (C<sub>Th</sub>), 125.1 (C<sub>Th</sub>), 125.0 (C<sub>Th</sub>), 122.9 (C<sub>Ar</sub>), 122.7 (C<sub>Ar</sub>), 33.7 (CMe<sub>3</sub>), 33.6 (CMe<sub>3</sub>), 30.8 (CH<sub>3</sub>), 30.7 (CH<sub>3</sub>) ppm. IR (neat): ν̄ = 3031, 2958, 2901, 2866, 1510, 1461, 1390, 1362, 1269, 1019, 827, 699 cm<sup>-1</sup>. MS (ESI, acetonitrile): *m/z* = 793.3842 [M + Na]<sup>+</sup> (calcd. 793.3878).

**5:** Yield: 125 mg (0.16 mmol, 66%). M.p. 253–254 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 6.90 (d, <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz, 4 H, H<sub>Ar</sub>), 6.85–6.82 (m, 6 H, H<sub>Th</sub> and H<sub>Ar</sub>), 6.74 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 4 H, H<sub>Ar</sub>), 6.65 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 4 H, H<sub>Ar</sub>), 6.56 (dd, <sup>4</sup>J<sub>H,H</sub> = 1.5, 3.0 Hz, 2 H, H<sub>Th</sub>), 6.51 (dd, <sup>4</sup>J<sub>H,H</sub> = 1.0, <sup>3</sup>J<sub>H,H</sub> = 5.0 Hz, 2 H, H<sub>Th</sub>), 1.16 (s, 18 H, CMe<sub>3</sub>), 1.11 (s, 18 H, CMe<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 147.4 (C<sub>quat</sub>), 147.1 (C<sub>quat</sub>), 140.6 (C<sub>quat</sub>), 140.4 (C<sub>quat</sub>), 140.3 (C<sub>quat</sub>), 137.3 (C<sub>quat</sub>), 137.2 (C<sub>quat</sub>), 134.9 (C<sub>quat</sub>), 130.5 (C<sub>Ar</sub>), 130.2 (C<sub>Ar</sub>), 130.0 (C<sub>Th</sub>), 123.9 (C<sub>Th</sub>), 122.9 (C<sub>Ar</sub>), 122.6 (C<sub>Ar</sub>), 122.1 (C<sub>Th</sub>), 33.7 (CMe<sub>3</sub>), 33.6 (CMe<sub>3</sub>), 30.8 (CH<sub>3</sub>), 30.7 (CH<sub>3</sub>) ppm. IR (neat): ν̄ = 1511, 1461, 1392, 1362, 1269, 1202, 1119, 1018, 853, 803, 763 cm<sup>-1</sup>. MS (ESI,

acetonitrile):  $m/z = 771.4048$  [ $M + H$ ]<sup>+</sup> (calcd. 771.4058). C<sub>54</sub>H<sub>58</sub>S<sub>2</sub> (771.17): calcd. C 84.10, H 7.58; found C 84.29, H 7.53.

**6:** Yield: 120 mg (0.16 mmol, 66%). M.p. 248 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 7.00$  (d, <sup>3</sup>J<sub>H,H</sub> = 5.0 Hz, 1 H, H<sub>Th</sub>'), 6.91 (m, 4 H, 2\*H<sub>Ar</sub>), 6.86 (dd, <sup>3</sup>J<sub>H,H</sub> = 2.9, 5.0 Hz, 1 H, H<sub>Th</sub>'), 6.81 (m, 6 H, 3\*H<sub>Ar</sub>), 6.75 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 2 H, H<sub>Ar</sub>), 6.66 (m, 4 H, 2\*H<sub>Ar</sub>), 6.64–6.59 (m, 3 H, 2\*H<sub>Th</sub> and 1\*H<sub>Th</sub>'), 6.44 (d, <sup>3</sup>J<sub>H,H</sub> = 3.5 Hz, 1 H, H<sub>Th</sub>'), 1.16 (s, 18 H, CMe<sub>3</sub>), 1.12 (s, 18 H, CMe<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 147.5$  (C<sub>quat</sub>), 147.4 (C<sub>quat</sub>), 147.2 (C<sub>quat</sub>), 147.1 (C<sub>quat</sub>), 142.0 (C<sub>quat</sub>), 141.3 (C<sub>quat</sub>), 140.7 (C<sub>quat</sub>), 140.4 (C<sub>quat</sub>), 140.2 (C<sub>quat</sub>), 137.2 (C<sub>quat</sub>), 137.2 (C<sub>quat</sub>), 137.1 (C<sub>quat</sub>), 135.8 (C<sub>quat</sub>), 132.4 (C<sub>quat</sub>), 130.4 (2\*C<sub>Ar</sub>), 130.1 (C<sub>Ar</sub>), 130.0 (C<sub>Ar</sub>), 129.9 (C<sub>Th</sub>), 128.4 (C<sub>Th</sub>'), 125.0 (C<sub>Th</sub>'), 124.9 (C<sub>Th</sub>'), 124.0 (C<sub>Th</sub>'), 122.9 (C<sub>Ar</sub>), 122.8 (C<sub>Ar</sub>), 122.6 (2\*C<sub>Ar</sub>), 122.1 (C<sub>Th</sub>), 33.7 (CMe<sub>3</sub>), 33.6 (CMe<sub>3</sub>), 30.8 (CH<sub>3</sub>), 30.7 (CH<sub>3</sub>) ppm. IR (neat):  $\tilde{\nu} = 2957, 2863, 1461, 1361, 1270, 1153, 1102, 1019, 828$  cm<sup>-1</sup>. MS (ESI, acetonitrile):  $m/z = 771.4050$  [ $M + H$ ]<sup>+</sup> (calcd. 771.4058).

**General FeCl<sub>3</sub> Cyclodehydrogenation Procedure:** The relevant di-thienyl benzene (0.065 mmol) was dissolved in dry dichloromethane (20 mL) and an excess of FeCl<sub>3</sub> (0.189 g, 1.12 mmol, 20 equiv.) in nitromethane (3 mL) was added dropwise under bubbling nitrogen. The mixture was stirred for 40 min to give a brown solution. This was quenched with methanol (30 mL), poured into water, extracted into chloroform, dried with MgSO<sub>4</sub>, and concentrated.

**3:** Purified by column chromatography on silica (dichloromethane/hexane, 1:3). Yield: 47 mg (0.058 mmol, 90%). M.p. >320 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 7.18$  (d, <sup>3</sup>J<sub>H,H</sub> = 6.5 Hz, 4 H, H<sub>Ar</sub>), 7.16 (s, 2 H, H<sub>Th</sub>), 7.09 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 4 H, H<sub>Ar</sub>), 6.72 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 4 H, H<sub>Ar</sub>), 6.63 (d, <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz, 4 H, H<sub>Ar</sub>), 2.36 (s, 6 H, CH<sub>3</sub>), 1.24 (s, 18 H, CCH<sub>3</sub>), 1.0 (s, 18 H, CCH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 150.3$  (C<sub>quat</sub>), 146.8 (C<sub>quat</sub>), 141.2 (C<sub>quat</sub>), 139.1 (C<sub>quat</sub>), 137.3 (C<sub>quat</sub>), 136.8 (C<sub>quat</sub>), 136.5 (C<sub>quat</sub>), 134.6 (C<sub>quat</sub>), 133.8 (C<sub>quat</sub>), 131.5 (C<sub>Ar</sub>), 130.4 (C<sub>Ar</sub>), 125.1 (C<sub>quat</sub>), 124.4 (C<sub>Ar</sub>), 122.3 (C<sub>Ar</sub>), 118.7 (C<sub>Th</sub>), 34.1 (CMe<sub>3</sub>), 33.6 (CMe<sub>3</sub>), 31.0 (CH<sub>3</sub>), 30.7 (CH<sub>3</sub>) ppm. IR (neat):  $\tilde{\nu} = 2957, 1520, 1388, 1361, 853, 789, 696$  cm<sup>-1</sup>. MS (MALDI, acetonitrile):  $m/z = 796.4168$  [ $M$ ]<sup>+</sup> (calcd. 796.4136).

**4:** Purified by silica glass plate (dichloromethane/hexane, 1:4). Yield: 27 mg (0.018 mmol, 55%). M.p. >320 °C. <sup>1</sup>H NMR (600 MHz, [D<sub>2</sub>]-1,2-dichloroethane, 25 °C, TMS):  $\delta = 7.44$  (d, <sup>3</sup>J<sub>H,H</sub> = 5.5 Hz, 2 H, H<sub>Th</sub>), 7.41 (s, 2 H, H<sub>Th</sub>'), 7.35 (d, <sup>3</sup>J<sub>H,H</sub> = 7.7 Hz, 4 H, H<sub>Ar</sub>), 7.32 (d, <sup>3</sup>J<sub>H,H</sub> = 5.2 Hz, 2 H, H<sub>Th</sub>), 7.27 (m-with CHCl<sub>3</sub> peak, 4 H, H<sub>Ar</sub>), 7.21 (d, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, 4 H, H<sub>Ar</sub>), 7.18 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 4 H, H<sub>Ar</sub>), 6.83 (d, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, 4 H, H<sub>Ar</sub>), 6.81 (d, <sup>3</sup>J<sub>H,H</sub> = 8.1 Hz, 4 H, H<sub>Ar</sub>), 6.76 (d, <sup>3</sup>J<sub>H,H</sub> = 8.1 Hz, 4 H, H<sub>Ar</sub>), 6.71 (d, <sup>3</sup>J<sub>H,H</sub> = 8.1 Hz, 4 H, H<sub>Ar</sub>), 1.42 (s, 18 H, CMe<sub>3</sub>), 1.32 (s, 18 H, CMe<sub>3</sub>), 1.08 (s, 36 H, 2\*CMe<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 150.9$  (C<sub>quat</sub>), 150.8 (C<sub>quat</sub>), 147.4 (C<sub>quat</sub>), 147.3 (C<sub>quat</sub>), 140.3 (C<sub>quat</sub>), 140.0 (C<sub>quat</sub>), 138.3 (C<sub>quat</sub>), 137.4 (C<sub>quat</sub>), 137.2 (C<sub>quat</sub>), 136.8 (C<sub>quat</sub>), 136.7 (C<sub>quat</sub>), 135.7 (C<sub>quat</sub>), 135.2 (C<sub>quat</sub>), 134.9 (C<sub>quat</sub>), 134.2 (C<sub>quat</sub>), 131.9 (C<sub>Ar</sub>), 131.8 (C<sub>Ar</sub>), 130.7 (C<sub>Ar</sub>), 130.6 (C<sub>Ar</sub>), 127.7 (C<sub>Th</sub>), 126.5 (C<sub>quat</sub>), 126.0 (C<sub>quat</sub>), 125.7 (C<sub>Ar</sub>), 125.0 (C<sub>Ar</sub>), 124.7 (C<sub>quat</sub>), 122.7 (C<sub>Ar</sub>), 122.6 (C<sub>Ar</sub>), 120.4 (C<sub>Th</sub>), 118.1 (C<sub>Th</sub>'), 117.2 (C<sub>quat</sub>), 34.5 (CMe<sub>3</sub>), 34.4 (CMe<sub>3</sub>), 33.9 (CMe<sub>3</sub>), 33.8 (CMe<sub>3</sub>), 31.5 (CH<sub>3</sub>), 31.3 (CH<sub>3</sub>), 31.0 (2\*CH<sub>3</sub>) ppm. MS (MALDI, chloroform):  $m/z = 1534.7516$  [ $M$ ]<sup>+</sup> (calcd. 1534.7490).

**7:** Purified by silica glass plate (dichloromethane/hexane, 1:4). Yield: 30 mg (0.20 mmol, 60%). M.p. >320 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 7.34$  (d, <sup>3</sup>J<sub>H,H</sub> = 5.2 Hz, 4 H, H<sub>Ar</sub>), 7.22 (d, <sup>3</sup>J<sub>H,H</sub> = 5.3 Hz, 4 H, H<sub>Ar</sub>), 7.11 (d, <sup>3</sup>J<sub>H,H</sub> = 5.3 Hz,

4 H, H<sub>Ar</sub>), 7.08 (d, <sup>3</sup>J<sub>H,H</sub> = 5.3 Hz, 4 H, H<sub>Ar</sub>), 6.96 (d, <sup>3</sup>J<sub>H,H</sub> = 3.8 Hz, 2 H, H<sub>Th</sub>), 6.83 (m, 8 H, 2\*H<sub>Ar</sub>), 6.67 (m, 8 H, 2\*H<sub>Ar</sub>), 6.38 (s, 2 H, H<sub>Th</sub>'), 6.31 (d, <sup>3</sup>J<sub>H,H</sub> = 3.8 Hz, 2 H, H<sub>Th</sub>), 1.44 (s, 18 H, CMe<sub>3</sub>), 1.32 (s, 18 H, CMe<sub>3</sub>), 1.11 (s, 18 H, CMe<sub>3</sub>), 1.10 (s, 18 H, CMe<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 149.6$  (C<sub>quat</sub>), 149.4 (C<sub>quat</sub>), 147.3 (C<sub>quat</sub>), 147.2 (C<sub>quat</sub>), 140.0 (C<sub>quat</sub>), 139.9 (C<sub>quat</sub>), 139.7 (C<sub>quat</sub>), 137.8 (C<sub>quat</sub>), 137.7 (C<sub>quat</sub>), 137.6 (C<sub>quat</sub>), 137.5 (C<sub>quat</sub>), 134.3 (C<sub>quat</sub>), 134.2 (C<sub>quat</sub>), 133.6 (C<sub>quat</sub>), 132.3 (C<sub>quat</sub>), 130.8 (C<sub>Ar</sub>), 130.7 (C<sub>Ar</sub>), 130.6 (C<sub>Ar</sub>), 129.9 (C<sub>Ar</sub>), 128.1 (C<sub>Th</sub>), 127.4 (C<sub>quat</sub>), 127.3 (C<sub>quat</sub>), 127.0 (C<sub>quat</sub>), 126.8 (C<sub>quat</sub>), 125.1 (C<sub>Th</sub>'), 124.8 (C<sub>Ar</sub>), 124.6 (C<sub>Ar</sub>), 122.7 (2\*C<sub>Ar</sub>), 120.7 (C<sub>Th</sub>), 34.7 (CMe<sub>3</sub>), 34.4 (CMe<sub>3</sub>), 34.0 (CMe<sub>3</sub>), 31.9 (CMe<sub>3</sub>), 31.7 (CH<sub>3</sub>), 31.4 (CH<sub>3</sub>), 31.2 (CH<sub>3</sub>), 29.7 (CH<sub>3</sub>) ppm. IR (KBr):  $\tilde{\nu} = 3414, 2963, 1638, 1462, 1363, 1261, 1096, 1022, 801, 610$  cm<sup>-1</sup>. MS (MALDI, acetonitrile):  $m/z = 1534.7457$  [ $M$ ]<sup>+</sup> (calcd. 1534.7409).

**8:** Purified by silica (dichloromethane/hexane, 1:4). Yield: 26 mg (0.017 mmol, 52%). M.p. >320 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 7.33$  (m, 6 H, H<sub>Ar</sub> and H<sub>Th</sub>), 7.27 (m, 4 H, H<sub>Ar</sub> and solv. peak), 7.22–7.16 (m, 10 H, 2\*H<sub>Ar</sub> and H<sub>Th</sub>), 6.82 (m, 8 H, 2\*H<sub>Ar</sub>), 6.70 (m, 8 H, 2\*H<sub>Ar</sub>), 6.44 (s, 2 H, H<sub>Th</sub>'), 1.40 (s, 18 H, CMe<sub>3</sub>), 1.33 (s, 18 H, CMe<sub>3</sub>), 1.11 (s, 18 H, CMe<sub>3</sub>), 1.10 (s, 18 H, CMe<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 150.8$  (C<sub>quat</sub>), 149.4 (C<sub>quat</sub>), 147.3 (C<sub>quat</sub>), 140.2 (C<sub>quat</sub>), 140.0 (C<sub>quat</sub>), 138.0 (C<sub>quat</sub>), 137.7 (C<sub>quat</sub>), 137.5 (C<sub>quat</sub>), 137.4 (C<sub>quat</sub>), 137.2 (C<sub>quat</sub>), 136.9 (C<sub>quat</sub>), 135.4 (C<sub>quat</sub>), 134.9 (C<sub>quat</sub>), 134.2 (C<sub>quat</sub>), 132.8 (C<sub>quat</sub>), 132.6 (C<sub>quat</sub>), 131.9 (C<sub>Th</sub>), 130.8 (C<sub>Ar</sub>), 130.6 (2\*C<sub>Ar</sub>), 128.9 (C<sub>quat</sub>), 128.2 (C<sub>Th</sub>'), 126.7 (C<sub>quat</sub>), 126.0 (C<sub>quat</sub>), 125.1 (C<sub>Ar</sub>), 124.9 (C<sub>Ar</sub>), 124.7 (C<sub>Ar</sub>), 122.7 (C<sub>Ar</sub>), 122.6 (C<sub>Ar</sub>), 120.2 (C<sub>Th</sub>), 34.5 (CMe<sub>3</sub>), 34.4 (CMe<sub>3</sub>), 33.9 (2\*CMe<sub>3</sub>), 31.4 (CH<sub>3</sub>), 31.3 (CH<sub>3</sub>), 31.0 (2\*CH<sub>3</sub>) ppm. IR (KBr):  $\tilde{\nu} = 3414, 2963, 1638, 1462, 1363, 1261, 1096, 1022, 801, 610$  cm<sup>-1</sup>. MS (MALDI, acetonitrile):  $m/z = 1534.7480$  [ $M$ ]<sup>+</sup> (calcd. 1534.7490).

**Supporting Information** (see footnote on the first page of this article): Crystal packing of **3** along with additional photochemical data.

## Acknowledgments

C. J. M. thanks the Science Foundation Ireland award SFI-08RFPCHIE1465 and the Trinity College Ussher fellowship for financial support. S. P. thanks the Science Foundation Ireland award SFI-05PICA1819, and B. G. would like to acknowledge funding from the Marie-Curie EU grant FP5MKTD-014772-SMART. We thank Dr. Martin Feeney, Dr. J. Bernard Jean-Denis, Dr. John O'Brien, and Dr. Manuel Ruether for technical assistance. For X-ray analysis we thank Dr. Sunil Varughese (SFI-05PICA1819) and Dr. Longsheng Wang (FP5MKTD-014472-SMART).

- [1] L. N. Lucas, J. J. D. De Jong, J. H. van Esch, R. M. Kellogg, B. L. Feringa, *Eur. J. Org. Chem.* **2003**, 155–166.
- [2] J. H. Hou, Z. Tan, Y. J. He, C. H. Yang, Y. F. Li, *Macromolecules* **2006**, *39*, 4657–4662.
- [3] R. D. McCullough, *Adv. Mater.* **1998**, *10*, 93–116.
- [4] J. Roncali, *Chem. Rev.* **1997**, *97*, 173–205.
- [5] T. A. Chen, X. M. Wu, R. D. Rieke, *J. Am. Chem. Soc.* **1995**, *117*, 233–244.
- [6] J. Roncali, *Chem. Rev.* **1992**, *92*, 711–738.
- [7] P. Leriche, P. Blanchard, P. Frere, E. Levillain, G. Mahon, J. Roncali, *Chem. Commun.* **2006**, 275–277.
- [8] B. Aydogan, A. S. Gundogan, T. Ozturk, Y. Yagci, *Macromolecules* **2008**, *41*, 3468–3471.
- [9] J. D. Tovar, A. Rose, T. M. Swager, *J. Am. Chem. Soc.* **2002**, *124*, 7762–7769.

- [10] C. J. Martin, B. Gil, S. D. Perera, S. M. Draper, *Chem. Commun.* **2011**, 47, 3616–3618.
- [11] S. M. Draper, D. J. Gregg, R. Madathil, *J. Am. Chem. Soc.* **2002**, 124, 3486–3487.
- [12] D. J. Gregg, E. Bothe, P. Hofer, P. Passaniti, S. M. Draper, *Inorg. Chem.* **2005**, 44, 5654–5660.
- [13] D. J. Gregg, C. M. A. Ollagnier, C. M. Fitchett, S. M. Draper, *Chem. Eur. J.* **2006**, 12, 3043–3052.
- [14] P. Kovacic, K. N. McFarland, *J. Polym. Sci.* **1979**, 17, 1963–1976.
- [15] J. L. Brusso, O. D. Hirst, A. Dadvand, S. Ganesan, F. Cicoira, C. M. Robertson, R. T. Oakley, F. Rosei, D. F. Perepichkat, *Chem. Mater.* **2008**, 20, 2484–2494.
- [16] J. S. Wu, M. D. Watson, N. Tchegbotareva, Z. H. Wang, K. Mullen, *J. Org. Chem.* **2004**, 69, 8194–8204.
- [17] A. Carpita, A. Lessi, R. Rossi, *Synthesis* **1984**, 571–572.
- [18] S. Gronowitz in *The Chemistry of Heterocyclic Compounds*, part 5, Wiley, New York, **1992**, pp. 91–130.
- [19] G. R. Newkome, N. B. Islam, J. M. Robinson, *J. Org. Chem.* **1975**, 40, 3514–3518.
- [20] J. S. Wu, M. D. Watson, L. Zhang, Z. H. Wang, K. Mullen, *J. Am. Chem. Soc.* **2004**, 126, 177–186.
- [21] Y. Y. Lu, J. S. Moore, *Tetrahedron Lett.* **2009**, 50, 4071–4077.
- [22] X. N. Zhang, M. Kohler, A. J. Matzger, *Macromolecules* **2004**, 37, 6306–6315.
- [23] N. DiCesare, M. Belletete, A. Donat-Bouillud, M. Leclerc, G. Durocher, *Macromolecules* **1998**, 31, 6289–6296.
- [24] N. DiCesare, M. Belletete, F. Raymond, M. Leclerc, G. Durocher, *J. Phys. Chem. A* **1997**, 101, 776–782.
- [25] S. A. Lee, S. Hotta, F. Nakanishi, *J. Phys. Chem. A* **2000**, 104, 1827–1833.
- [26] Y. Nishide, H. Osuga, M. Saito, T. Aiba, Y. Inagaki, Y. Doge, K. Tanaka, *J. Org. Chem.* **2007**, 72, 9141–9151.
- [27] Q. Yan, Y. Zhou, B. B. Ni, Y. G. Ma, J. Wang, J. Pei, Y. Cao, *J. Org. Chem.* **2008**, 73, 5328–5339.
- [28] N. DiCesare, M. Belletete, E. R. Garcia, M. Leclerc, G. Durocher, *J. Phys. Chem. A* **1999**, 103, 3864–3875.
- [29] R. J. Waltman, J. Bargon, *Can. J. Chem.* **1986**, 64, 76–95.
- [30] F. Morgenroth, K. Mullen, *Tetrahedron* **1997**, 53, 15349–15366.
- [31] S. Sadhukhan, C. Viala, A. Gourdon, *Synthesis* **2003**, 1521–1525.

Received: March 9, 2011  
Published Online: May 24, 2011