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Notes

Synthesis of a Novel Oligo(*p*-phenylene) Ladder by Sulfide and Sulfonio Groups

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Introduction

π-Conjugated polymers have been extensively studied due to their attractive electronic properties for practical applications such as electrodes of secondary batteries, electroluminescence materials, and nonlinear optics.[1] Since a two-dimensional planar skeleton is stiff and has stable conjugated structure, the synthesis of structurally defined ladder polymers has been a challenging subject in this field.[2] One of the successful synthetic methods consists of two steps that involve the synthesis and cyclization of a functionalized single-stranded precursor. Some ladder polymers with poly(*p*-phenylene) or poly(phenylene sulfide) backbone have been prepared by the groups of Müllen[3] and Tour.[4] The polymers obtained are defect-free; however, they require long alkyl side chain groups in order to improve the solubility.

We have reported the synthesis of poly(arylenesulfonium salt)s by the acid-promoted polycondensation of aryl sulfoxides.[5] The polysulfonium salt as a novel polyelectrolyte shows good solubility in protonic acids (HCOOH, H_2SO_4, CH_3SO_3H) and polar organic solvents (CH_3OH, CH_3CN, DMF, DMSO, etc.). The nucleophilic dealkylation behavior of the polysulfonium salt has also been described in detail,[6] which is important for the application of the polysulfonium salts as a polymeric methylation agent[7] or as a precursor for high molecular weight poly(*p*-phenylene sulfide).[8] This work aims to construct a ladder polymer bridged by sulfonio groups, as a new class of conjugated polymers. In the presence of an extended π-conjugation, two-dimensional planar structures have electronic advantages, for example, as a lower band-gap material.[9] We report herein the synthesis of the first sulfonio-bridged, *p*-phenylene ladder oligomers that have a planar ribbon type structure.

Experimental Section

Materials. 1,2-Dimethoxyethane and acetonitrile were distilled. The commercial products *p*-dibromobenzene, hexyl mercaptan, sodium methanethiolate, sodium methoxide, bromine, iodine, tetraethylammonium bromide, tetrakis(triphenylphosphine)palladium(0), sodium hydrogen carbonate, and trifluoromethanesulfonic acid were used as received. *p*-Phenylene bis(pinacol boronate) was synthesized in the usual manner.[4a]

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded using JEOL JNM-LA500. IR spectra were obtained with a JASCO model IR-810 spectrometer using a potassium bromide pellet or sodium chloride pellet. UV spectra were observed in acetonitrile and formic acid using a Shimadzu UV-2200 spectrometer. Chloroform solutions of the resulting compounds were injected to measure gas chromatography using a Shimadzu GC-14B. The GC mass spectra were recorded on a Shimadzu GCMS-QP5050 instrument with an ionization energy of 70 eV. Elemental analysis was performed on a Perkin-Elmer PE-2400 II and a Metrohm 645 Multi DOSIMAT. Two parallel analyses were performed for each sample.

Synthesis of Oligomers 1a and 1b. 1,4-Dibromo-2,5-bis(methylsulfinyl)benzene (5.76 mmol, 2.07 g), *p*-phenylene bis(pinacol boronate) (5.76 mmol, 1.90 g), sodium hydrogen carbonate (42 mmol, 3.53 g), saturated sodium hydrogen carbonate aqueous solution (9 mL), 1,2-dimethoxyethane (18 mL), and tetrakis(triphenylphosphine)palladium(0) (0.58 mmol, 0.67 g) were put into a 50 mL three-necked round-bottom flask. Nitrogen gas was bubbled, and then the reaction mixture was heated to 90 °C and stirred for 20 h. The solution therefrom was extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate and evaporated to dryness. The crude oligomer was purified by precipitation into methanol from diethyl ether solution. After drying in a vacuum overnight at room temperature, the oligomer **1a** was obtained as an off-white powder, in 85% yield. IR (KBr, cm^{-1}): 3005 (aromatic ν_{C-H}), 2920 (methyl ν_{C-H}), 1630, 1456, 1404 ($\nu_{C=C}$), 1094, 1036, 1011 ($\nu_{S=O}$), 816 (δ_{C-H}), 774, 704. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 2.62 (s, 6H, methyl), 7.53−8.05 (m, 6H, phenyl). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): 40.7 (methyl), 151.5, 138.3, 134.3, 129.2, 122.8 (phenyl).

The oligomerization of 1,4-dibromo-2,5-bis(hexylsulfinyl)benzene and *p*-phenylene bis(pinacol boronate) was carried out in the same manner used to obtain oligomer **1b** (yield 91%). IR (KBr, cm^{-1}): 3012 (aromatic ν_{C-H}), 2955, 2928, 2876 (hexyl ν_{C-H}), 1612, 1456, 1437 ($\nu_{C=C}$), 1096, 1036, 1013 ($\nu_{S=O}$), 820 (δ_{C-H}), 725, 694. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 0.84 (s, 6H, methyl), 1.28−1.75 (m, 16H, methylene), 2.90−3.21 (m, 4H, methylene), 7.53−7.86 (m, 6H, phenyl). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): 13.8, 22.0, 22.6, 27.3, 30.7, 54.1 (hexyl), 115.2, 122.1, 128.0, 129.8, 132.3 (phenyl).

Synthesis of Oligomers 2a and 2b. Oligomer **1a** (1.00 g) was added to cold trifluoromethanesulfonic acid (40 mL) in a 100 mL round-bottom flask. The reaction mixture was stirred at room temperature for 12 h. The mixture was added to 500 mL of cold water with vigorous stirring to precipitate the product. The precipitate was filtered and washed with water several times. Oligomer **2a** was obtained as a brown powder in 84% yield, after drying in a vacuum overnight at room temperature. IR (KBr, cm^{-1}): 3012 (aromatic ν_{C-H}), 2922 (methyl ν_{C-H}), 1632, 1454 ($\nu_{C=C}$), 1256, 638 (ν_{C-F}), 1165 ($\nu_{O=S=O}$), 1032, 1011 ($\nu_{S=O}$). ^{1}H NMR (500 MHz, (CF_3SO_3D, ppm): 2.78 (s, 3H, methyl), 3.15−3.32 (m, 9H, methyl), 7.39−8.41 (m, 13H, phenyl).

The intramolecular ring-closing reaction of oligomer **1b** was carried out in the same manner used to obtain oligomer **2b** (yield 82%). IR (KBr, cm^{-1}): 3012 (aromatic ν_{C-H}), 2948, 2922 (hexyl ν_{C-H}), 1610, 1466 ($\nu_{C=C}$), 1256, 638 (ν_{C-F}), 1165 ($\nu_{O=S=O}$), 1036, 1022 ($\nu_{S=O}$), 725, 694. ^{1}H NMR (500 MHz, (CF_3SO_3D, ppm): 0.89−1.73 (m, 44H, methylene, methyl), 2.70−2.78 (m,

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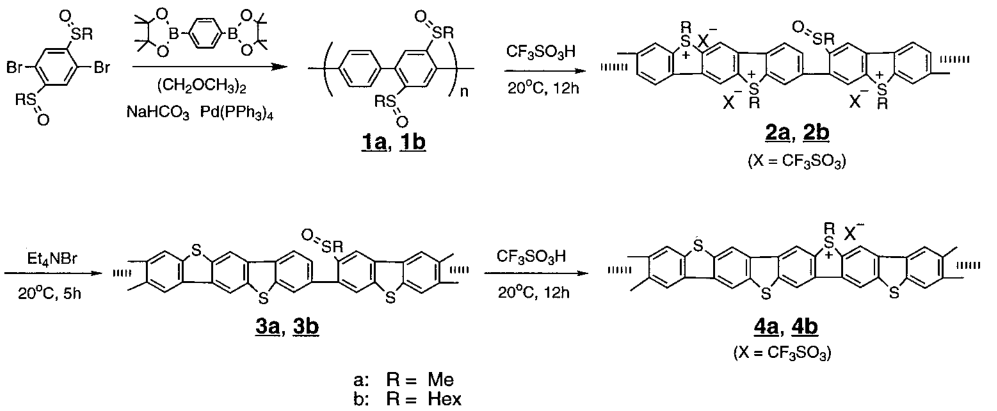
Scheme 1



2H, methylene), 3.25−3.36 (m, 6H, methylene), 7.43−8.50 (m, 13H, phenyl).

Synthesis of Oligomers 3a and 3b. Oligomer **2a** (1.00 g) was dissolved in 80 mL of acetone/acetonitrile (1/1) mixed solvent in a 300 mL round-bottom flask at room temperature. Tetraethylammonium bromide (12.4 mmol, 2.60 g) dissolved in acetonitrile (10 mL) and water (2 mL) mixture was added to the oligomer **2a** solution and stirred vigorously at room temperature for 5 h. The yellow solid oligomer **3a**, which appeared as the result of demethylation, was collected by filtration, washed with water, and dried overnight at room temperature (yield 96%). IR (KBr, cm^{-1}): 3069 (aromatic ν_{C-H}), 2917 (methyl ν_{C-H}), 1634, 1454, 1406 ($\nu_{C=C}$), 1092, 1032, 1011 ($\nu_{S=O}$), 957, 839. ^{1}H NMR (500 MHz, DCOOD, ppm): 2.68 (s, 3H, methyl), 7.24−7.85 (m, 13H, phenyl).

The dealkylation of oligomer **2b** was carried out as described above to obtain oligomer **3b** (yield 90%). IR (KBr, cm^{-1}): 3052 (aromatic ν_{C-H}), 2935, 2926, 2889 (hexyl ν_{C-H}), 1610, 1466, 1405 ($\nu_{C=C}$), 1093, 1036, 1022 ($\nu_{S=O}$), 725, 695. ^{1}H NMR (500 MHz, DCOOD, ppm): 0.89−1.73 (m, 11H, methylene, methyl), 2.68−2.74 (m, 2H, methylene), 7.68−8.26 (m, 13H, phenyl).

Synthesis of Oligomers 4a and 4b. Oligomer **3a** (0.50 g) was added to cold trifluoromethanesulfonic acid (20 mL) in a 100 mL round-bottom flask. The reaction mixture was stirred at room temperature for 12 h. The reaction solution was poured into a 500 mL of cold water with vigorous stirring to precipitate the product. The precipitate was filtered and washed with water several times. Oligomer **4a** was obtained as a brown powder in 84% yield, after drying in a vacuum overnight at room temperature. IR (KBr, cm^{-1}): 3067 (aromatic ν_{C-H}), 2930, (methyl ν_{C-H}), 1634, 1456, 1416 ($\nu_{C=C}$), 1260, 642 (ν_{C-F}), 1172 ($\nu_{O=S=O}$), 841. ^{1}H NMR (500 MHz, CF_3SO_3D, ppm): 3.45 (s, 6H, methyl), 7.62 (s, 6H, phenyl), 8.32 (s, 4H, phenyl).

The intramolecular ring-closing reaction of oligomer **3b** was carried out as described above to obtain oligomer **4b** (yield 79%). IR (KBr, cm^{-1}): 3044 (aromatic ν_{C-H}), 2921, 2904 (hexyl ν_{C-H}), 1646, 1447, 1416 ($\nu_{C=C}$), 1258, 640 (ν_{C-F}), 1159 ($\nu_{O=S=O}$), 840. ^{1}H NMR (500 MHz, CF_3SO_3D, ppm): 0.86−1.42 (m, 22H, methylene, methyl), 3.40−3.53 (m, 4H, methylene), 7.86 (s, 6H, phenyl), 8.24 (s, 4H, phenyl).

Results and Discussion

Synthesis of Alkylsulfinyl-Substituted Oligo(*p*-phenylene)s. To construct a strictly 1,4-phenylene structure, alkylsulfinyl-substituted oligo(*p*-phenylene) (**1a**, **1b**) were prepared based on the Suzuki aryl−aryl coupling reaction[3a,4a,10] between the 1,4-dibromo-2,5-bis(alkylsulfinyl)benzene and *p*-phenylene bis(pinacol boronate) (Scheme 1). This is an important step for the structural regularity of a ladder polymer having extended π-conjugation. The synthesis of the 1,4-dibromo-2,5-bis(alkylsulfinyl)benzene monomer was carried out in good yield in three synthetic steps with *p*-dibromobenzene as the starting material. In the first step, *p*-dibromobenzene was reacted with sodium methanethiolate in the presence of copper(I) chloride as a catalyst to obtain 1,4-bis(methylsulfenyl)benzene. The second step was the bromation of 1,4-bis(methylsulfenyl)benzene with 5 equiv of bromine and a small amount of iodine. The obtained 2,5-dibromo-1,4-bis(methylsulfenyl)benzene was oxidized with nitric acid to yield 2,5-dibromo-1,4-bis(methylsulfinyl)benzene.

The polycondensation of equimolar mixtures of the two monomers was carried out with Pd(0)-catalyst in refluxing 1,2-dimethoxyethane and 1 M aqueous sodium hydrogen carbonate solution for 20 h. The reduction of the sulfoxide group to the sulfide group does not occur during the aryl−aryl coupling reaction as evident by the absence of methyl sulfide protons in the ^{1}H NMR spectra of the oligomers. In the IR spectrum, the strong peaks at 1036 and 816 cm^{-1} are ascribed to the stretching vibration of S=O bond and the stretching vibration of C−H of 1,4-disubstituted phenylene, respectively. The aryl−aryl coupling oligomerization was also confirmed by the reaction between methyl 2-bromophenyl sulfoxide and phenyl pinacol boronate which progressed selectively (without any reduction of sulfoxide group) with high yield (>90%). Unreacted monomer and low molecular weight portions were removed by washing with acetone. The oligomers **1a** and **1b** are obtained as an off-white powder and were soluble in chloroform, diethyl ether, *N*-methylpyrrolidone, formic acid, and sulfuric acid. The degree of oligomerization (*n*) was determined to be 6 for the methylsulfinyl-substituted oligomer (**1a**) and 9 for the hexylsulfinyl-substituted oligomer (**1b**) by means of TOF (time-of-flight) mass spectroscopic analysis. The difference in *n* for the oligomers is due to the lower solubility of the oligomer **1a** in 1,2-dimethoxyethane, the oligomerization solvent. The oligomer yield was >85% in each case.

Intramolecular Ring-Closing Reaction. An intramolecular ring-closing reaction of the resulting oligomers were carried out in three synthetic steps. The reaction was started by the addition of trifluoromethanesulfonic acid to the oligomers **1** at room temperature. To avoid the intermolecular cross-linking reaction, the reaction was carried out at a low concentration (0.5 mM). The intramolecular ring-closing reaction did not proceed completely and afforded oligomers that have sulfonio and sulfoxide groups (**2a**, **2b**). Both the sulfoxide group (1032, 1010 cm^{-1} ($\nu_{S=O}$)) and the counteranion of the sulfonio group ($CF_3SO_3^-$: 1256, 638 cm^{-1} (ν_{C-F})) were detected in the IR spectrum of oligomers. The peaks attributed to the methylsulfinyl and methylsul-

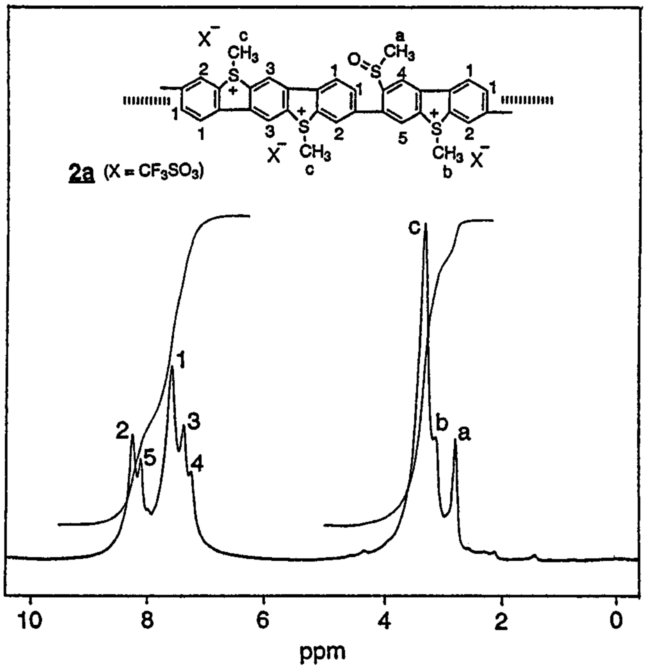


Figure 1. ^{1}H NMR spectrum of **2a** in CF_3SO_3D at 20 °C.

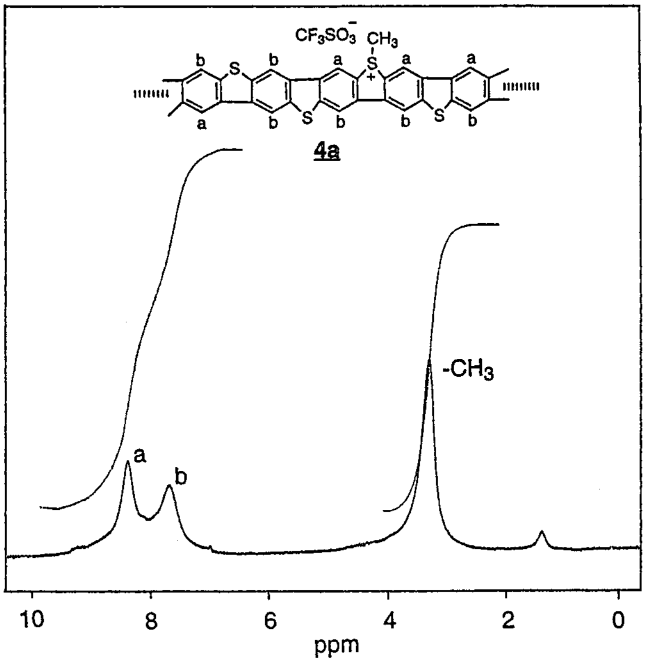


Figure 2. ^{1}H NMR spectrum of laddered oligo(sulfoniophenylene triflate) (**4a**) in CF_3SO_3D at 20 °C.

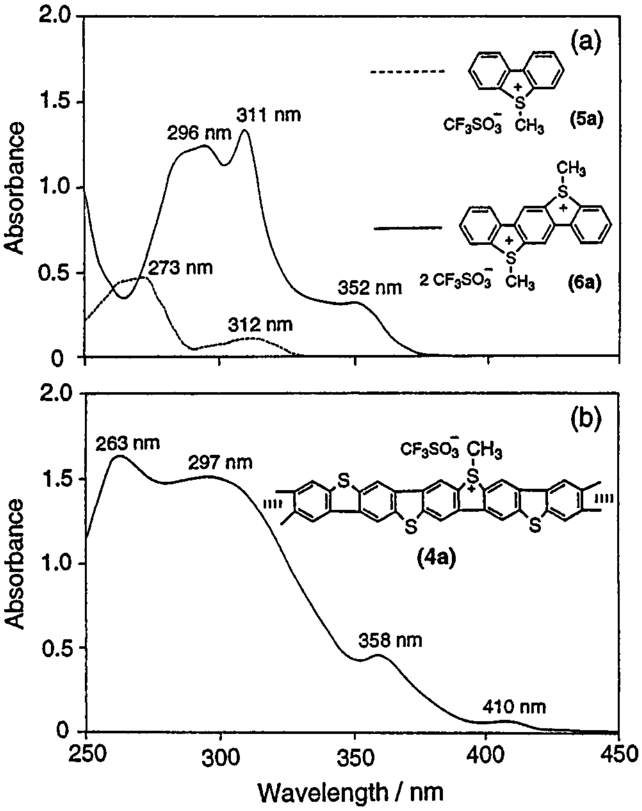


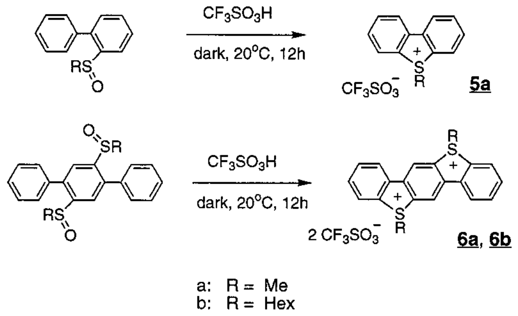
Figure 3. UV–vis spectra of (a) dimer **5a** and trimer **6a** in acetonitrile and (b) laddered oligo(sulfoniophenylene triflate) (**4a**) in formic acid (6.3×10^{-5} M).

fonio protons of oligomer **2a** are observed at 2.78 and 3.32 ppm in the ^{1}H NMR, respectively (Figure 1). From the integration ratio of the two peaks, the conversion of the ring-closing reaction was determined to be 77% for **2a** and 74% for **2b**. The partially ring-closed structure is due to the strong electron-withdrawing property of the sulfonio group bonded to the phenyl ring. The electrophilic substitution by the proton-added sulfoxide (hydroxymethylphenylsulfonio) group to the electron-poor phenyl ring attached to a sulfonio group was hard to proceed.

For the formation of fully laddered structure, the dealkylation of oligomers **2** was carried out by a halide ion in the second step. We have reported previously that nucleophilic dealkylation of sulfonium compounds proceeds selectively at room temperature by treating with Et_4NBr solution.[6] The nucleophilic dealkylation of **2** occurred quantitatively and afforded oligomers **3a** and **3b** that have sulfide bonds and alkylsulfinyl groups. The obtained oligomers are yellow. The bond stretching of the $CF_3SO_3^-$ group in the IR spectrum and the methylsulfonio peak in the ^{1}H NMR spectrum disappeared for the oligomer **3a**. The second intramolecular ring-closing reaction occurred easily for oligomers **3** in trifluoromethanesulfonic acid, because of the electron-donating effect from the neighboring phenylthio group. The ladder oligomers **4a** and **4b** were obtained as a brown powder. The oligomers are soluble in formic acid, sulfuric acid, and trifluoromethanesulfonic acid but insoluble in the common solvents such as methanol, acetone, acetonitrile, and chloroform. The ^{1}H NMR spectrum of the oligomer **4a** is shown in Figure 2. A peak attributed to the methyl protons is observed at 3.45 ppm, which is located at low field. The lack of the peak of methylsulfinyl protons at 2.5 ppm implies the complete cyclization reaction. The IR spectra of the oligomers indicate that they contain $CF_3SO_3^-$ as counter-anions (642, 1260 cm^{-1} (ν_{C-F}) and 1172 cm^{-1} ($\nu_{O=S=O}$)) and methyl groups (2930 cm^{-1} (ν_{C-H})). The sulfoxide group (1010 cm^{-1} ($\nu_{S=O}$)) was not detected.

The intramolecular ring-closing reaction in trifluoromethanesulfonic acid has been also confirmed using 2-methylsulfinylbiphenyl as a model compound (Scheme 2). The reaction proceeded to give dimer **5a** in 100% yield. The intramolecular ring-closing reaction of 2,5-bis(methylsulfinyl)-*p*-terphenyl and 2,5-bis(hexylsulfinyl)-*p*-terphenyl was also carried out to give trimers **6a** and **6b** in good isolated yields (98% and 88%, respectively). The obtained model sulfonium compounds were characterized by IR, UV–vis, and ^{1}H NMR spectra. The

Scheme 2



absorption maximum (λ_{max} = 312 nm) in the electronic spectra of dimer **5a** (Figure 3a) shows a bathochromic shift in contrast to the non-cross-linked diphenylmethylsulfonium triflate (λ_{max} = 231 nm)[11] and 4-(methylsulfenyl)diphenylmethylsulfonium triflate (λ_{max} = 294 nm).[6] The small torsion of the phenyl rings due to the bridging of the sulfonio group results in the expansion of the π-conjugated structure. This effect is more remarkable in the trimer models (**6a** and **6b**) which have a λ_{max} = 352 nm. In Figure 3b is shown the UV–vis spectrum of the ladder oligomer **4a**, which has maxima absorptions at 410 and 358 nm. The absorption spectra of **4a** are more bathochromically shifted than those of the nonbridged poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) (λ_{max} = 317 nm),[6] the model compounds (**5a** and **6a**), and *p*-sexiphenylene (λ_{max} = 318 nm).[12] However, the absorption of **4a** is more hypsochromically shifted than that of the imine-bridged poly(*p*-phenylene) (λ_{max} = 482 nm, solid),[4a] probably because **4a** has more ring strain due to the size of sulfur and its 6–5–6 fused structure.

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Supporting Information Available: Text giving synthetic procedure and characterization data for 1,4-dibromo-2,5-bis(alkylsulfinyl)benzene, 2-methylsulfinylbiphenyl, 2,5-bis(alkylsulfinyl)-*p*-terphenyl, and model compounds (**5a**, **6a**, and **6b**). This material is available free of charge via the Internet at http://pubs.acs.org.

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