PREPARATION OF A SERIES OF OLIGO[THIOPHENE-2,5-DIYL]VINYLENES

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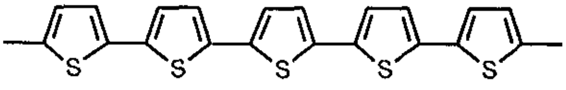
Abstract - Preparation of a series of oligo[thiophene-2,5-diyl]vinylenes (**3**) is reported. Compounds containing an even number of thiophene rings were synthesized by the carbonyl coupling of thiophenecarbaldehydes with a low-valent titanium reagent and those carrying an odd number of thiophene rings by the coupling of thiophenecarbaldehydes with Wittig-Horner (Wittig) reagents. Uv-vis spectral feature of these compounds is also reported.

The chemistry of thiophene oligomers has been attracting much attention because of their biological activities and as starting materials for building molecular electronic devices.[1] Recently, we have reported the preparation of α-type oligothiophenes (**1**)[2] and α,β-type oligothiophenes (**2**)[3] and have been investigating the physico-chemical properties of these compounds to find their applications as molecular electronic devices.[4] In this connection, we have now become interested in the preparation of a series of oligo[thiophene-2,5-diyl]vinylenes (**3**) that have an extended conjugated system which is crucial for building molecular electronic devices. All of the double bonds of **3** must have *E*-geometry for attaining effective conjugation over the whole molecule. Prior to our synthetic study, Kossmehl *et al.* reported the preparation of some of these compounds.[5] We have adopted a different synthetic methodology to prepare a series of these compounds and obtained them satisfactorily in higher purity.



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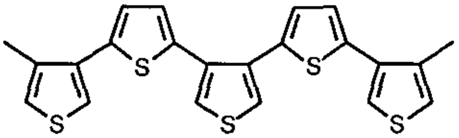

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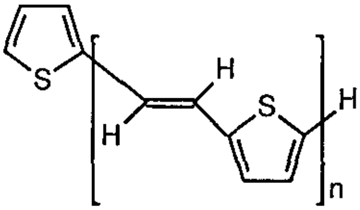

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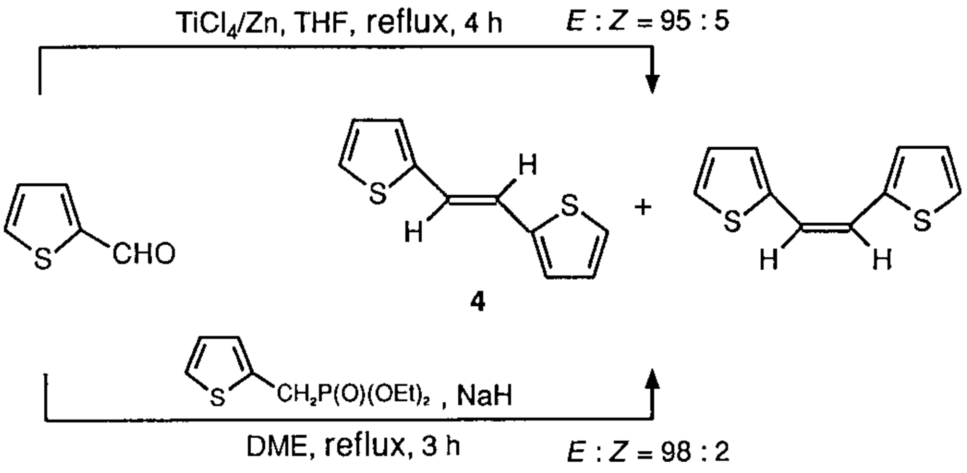
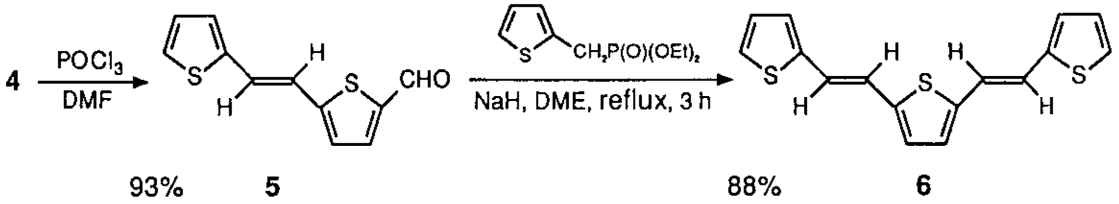
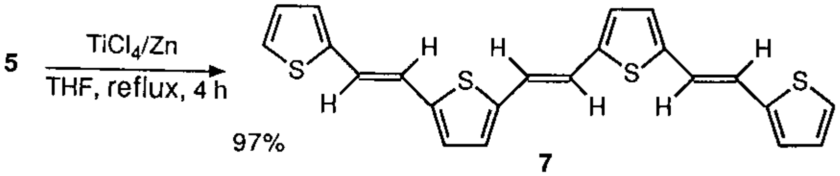
Carbonyl coupling of aldehydes with a low-valent titanium reagent and Wittig-Horner reaction are the methods of our choice that construct the double bond part of **3**. In order to attain effective conjugation over the whole molecule, all of the double bonds of **3** must retain *E*-configuration. We therefore attempted the preparation of 1,2-di-2-thienylethylene by the both methods to determine the stereoselectivity of these reactions. Treatment of thiophene-2-carbaldehyde with a low-valent titanium reagent, prepared from titanium(IV) chloride and zinc powder,[6] in boiling tetrahydrofuran (THF) afforded 1,2-di- 2-thienylethylene nearly quantitatively, which is a mixture of the *E*- and *Z*-isomers in the ratio 95:5. Recrystallization from cyclohexane allowed the isolation of the pure *E*-isomer **4** in 85% yield. The Wittig-Horner reaction of thiophene-2-carbaldehyde with diethyl 2-thienylmethylphosphonate also worked cleanly to give the expected ethylene quantitatively in the *E* and *Z*-isomer ratio 98:2. Recrystallization of the mixture afforded the pure *E*-isomer **4** in 88% yield. The Z-isomer is much more soluble in organic solvents than the *E*-isomer is. We can thus anticipate that *E*-isomers formed in small amounts in other cases can be easily removed by recrystallization from an appropriate solvent to afford pure desirable *E*-isomers. As described below, we have succeeded in the preparation of a series of **3** containing from three thiophene rings and two double bonds (compound **6**) to seven thiophene rings and six double bonds (compound **14**) by using the above two reactions.



E,E-2,5-Bis[2-(2-thienyl)ethenyl]thiophene (6) was prepared in 88% yield as golden yellow leaflets by the Wittig-Horner reaction of diethyl 2-thienylmethylphosphonate with the aldehyde (5), which was obtained by the Vilsmeier formylation of 4 in 93% yield. Its ^{13}C nmr spectrum shows only 8 peaks, thus eliminating the possibility of contamination of the *E,Z*- or *Z,Z*-isomer. ^{1}H Nmr analysis (400 MHz) reaches the same conclusion. The compound (6) was previously synthesized by other methods in lower yields.[5,7]



E,E,E-2,2'-(1,2-Ethenediyl)bis[5-[2-(2-thienyl)ethenyl]thiophene (7) was synthesized in 97% yield as fine red granules by carbonyl coupling of the aldehyde (5) with the foregoing low-valent titanium reagent. The material recrystallized from 1,2-dichloroethane melts at 226-227 °C, while Kossmehl *et al.*[5] obtained this compound by the Wittig reaction and reported its melting point as 199-203 °C. Thus, our compound is purer than that previously reported. Unfortunately the low solubility of the compound in $CDCl_3$ made it impossible to determine its ^{1}H and ^{13}C nmr spectra (400 MHz and 100 MHz, respectively), though mass spectrum shows a correct molecular peak.



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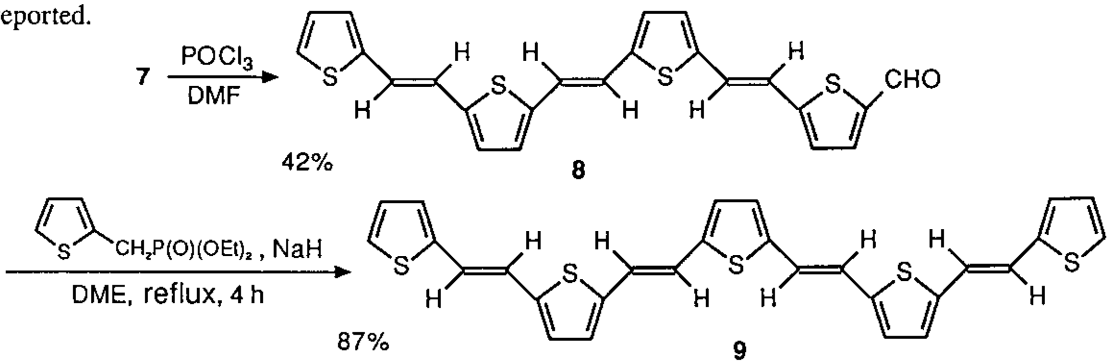
E,E,E,E-2,5-Bis[2-[5-[2-(2-thienyl)ethenyl]-2-thienyl]ethenyl]thiophene (**9**) was prepared in 87% yield as fine purple granules by the Wittig-Horner reaction of diethyl 2-thienylmethylphosphonate with the aldehyde (**8**) that was obtained by the Vilsmeier formylation of **7** in 42% yield. The material recrystallized from xylene twice melts at 251 °C, while Kossmehl *et al.*[5] synthesized it by the other method and reported its meleting point as 235-237 °C. Again our compound is purer than that reported.



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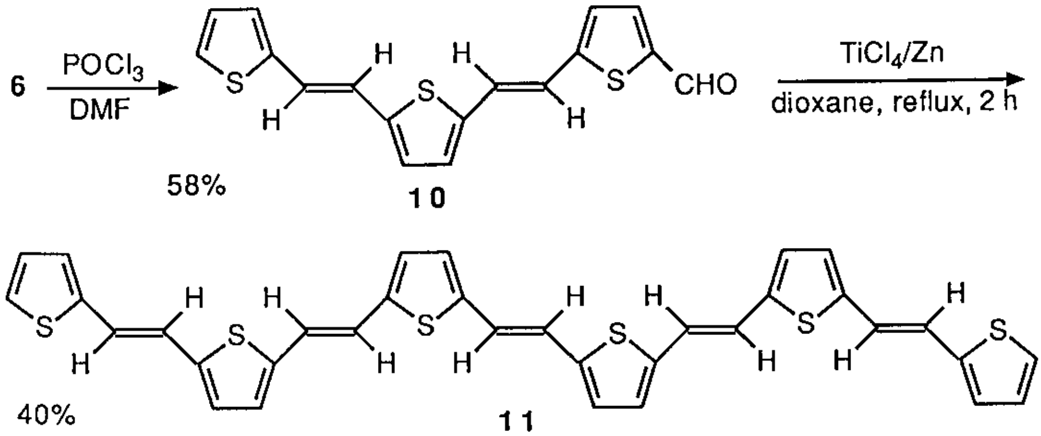
9

A new compound, 2,2'-(1,2-ethenediyl)bis[5-[2-[5-(2-thienyl)ethenyl]-2-thienyl]ethenyl]thiophene (**11**) which contains six thiophene rings was synthesized in 40% yield as dark violet granules by the carbonyl coupling of the aldehyde (**10**), which was prepared by the Vilsmeier formylation of **6** in 58% yield. The compound can be recrystallized from *o*-dichlorobenzene.



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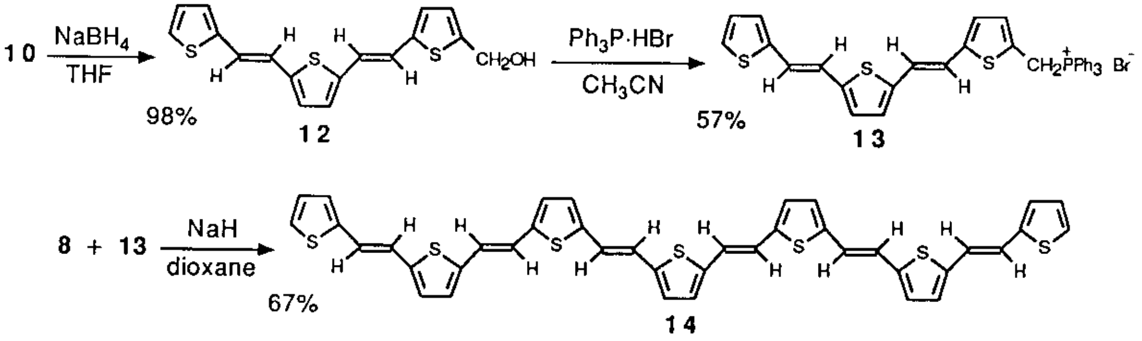
11

2,5-Bis[2-[5-[2-[5-[2-(2-thienyl)ethenyl]-2-thienyl]ethenyl]-2-thienyl]ethenyl]thiophene (**14**) which carries seven thiophene rings was synthesized in 67% yield by the Wittig reaction of the aldehyde (**8**) with the phosphonium ylide produced from the phosphonium bromide (**13**). The bromide (**13**) was prepared in 57% yield by the action of triphenylphosphine hydrobromide on the alcohol (**12**),[8] which was obtained by reduction of the aldehyde (**10**) with sodium borohydride in 98% yield. The compound (**14**) can be recrystallized from a large amount of *o*-dichlorobenzene as dark violet crystals, mp 280-285 °C (decomp.)



Finally we attempted the preparation of 2,2'-(1,2-ethenediyl)bis[5-[2-[5-[2-[5-[2-(2-thienyl)ethenyl]-2-thienyl]ethenyl]-2-thienyl]ethenyl]thiophene (**15**) that possesses eight thiophene rings by the carbonyl coupling of the aldehyde (**8**). The reaction afforded dark solid, recrystallization of which required a huge amount of *o*-dichlorobenzene to give a black powder, mp > 400 °C, in low yield (5%). The compound is practically insoluble in any organic solvents at room temperature; its insolubility made it impossible even to determine uv-vis spectrum. Elemental analysis gave a slightly incorrect result. Thus, no rigid evidence for the formation of **15** is available.

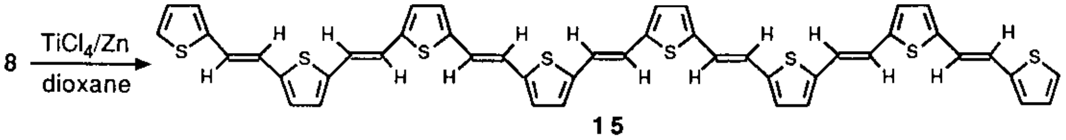


Figure 1 shows uv-vis spectra of oligo[thiophene-2,5-diyl]vinylenes synthesized by us. The shape of absorption of every compound is similar to each other. The absorption maxima are bathochromically shifted regularly with an increasing number of the thiophene rings and double bonds. The molar absorptivities also increase with an increasing number of the thiophene rings. These facts mean that all of the double bond part of these compounds have *E*-geometry and their π-electron system is fully conjugated. It is noteworthy that compounds (**11**) and (**14**) have an extra absorption maximum at 615 and 640 nm, respectively, in addition to the absorptions that are observed with the other compounds. We are currently investigating the physico-chemical properties of these compounds.

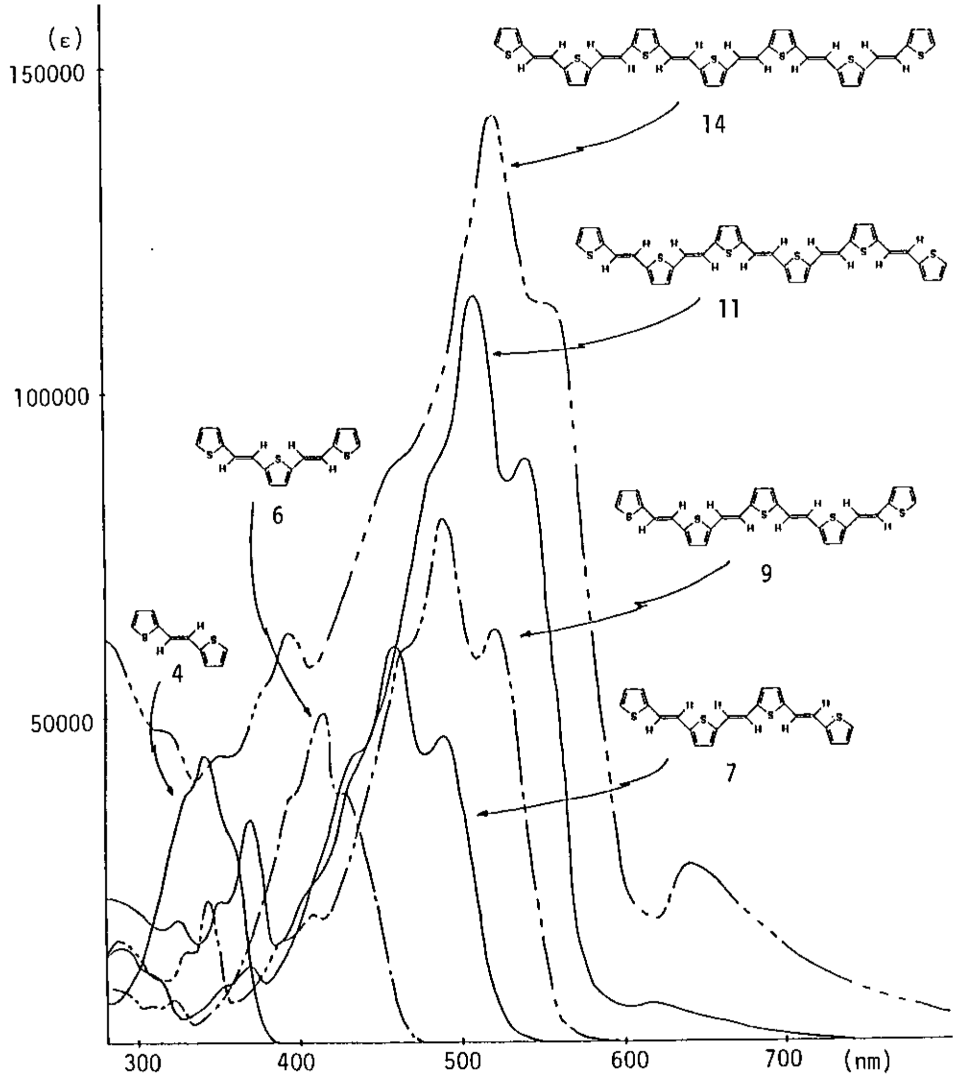


Figure 1. Uv-vis Spectra of Oligo[thiophene-2,5-diyl]vinylenes

EXPERIMENTAL

Melting points were determined on a MEL-TEMP capillary tube apparatus and are uncorrected. Ir spectra were taken on a Hitachi 270-50 spectrophotometer. ^{1}H Nmr spectra were determined on a JEOL PMX-60 or a Bruker AM-400 spectrometer with $CDCl_3$ as solvent and using tetramethylsilane as internal standard and ^{13}C nmr spectra on a Bruker AM-400 spectrometer. Mass spectra were determined on a Shimadzu QP-1000 spectrometer. Uv-vis spectra were determined on a Hitachi 340 spectrophotometer. Column chromatography was carried out using Merck silica gel, Art 7734 (70-230 mesh). Tetrahydrofuran (THF) (containing no stabilizer), dioxane, and 1,2-dimethoxyethane (DME), and *N,N*-dimethylformamide (DMF) were dried over molecular sieves before use. Titanium(IV) chloride and zinc powder were used as purchased.

***E*-1,2-Di-2-thienylethylene (4). a) By Carbonyl Coupling.** To a stirred solution of thiophene-2-carbaldehyde (11.2 g, 0.1 mol) in THF (200 ml) was added titanium(IV) chloride (13 ml, 0.12 mol) over a period of 0.5 h at -18 °C. After stirring at this temperature for 0.5 h, zinc powder (15.7 g, 0.24 mol) was added in small portions over a period of 0.5 h. The mixture was stirred at -18 °C for 0.5 h, warmed to room temperature, and refluxed for 3.5 h. The reaction was quenched by addition of ice-water (150 ml) and the resulting solid was collected by filtration and dried. The solid was dissolved in methylene chloride (150 ml) and the insoluble inorganic material was removed by filtration. The filtrate was evaporated and the residue was recrystallized from cyclohexane to give 9.4 g (85%) of pure *E*-1,2-di-2-thienylethylene (4), mp 133-134 °C (lit.,[9] mp 133-134 °C). The mother liquor of the recrystallization was analyzed by ^{1}H nmr which revealed that this is a mixture of **4** and *Z*-1,2-di-2-thienylethylene in the ratio 7:1 (the olefinic proton of the *Z*-isomer appears at δ 6.50). This means that *E*- and *Z*-isomers were formed in the ratio 95:5.

b) By Wittig-Horner Reaction. To a stirred and ice-cooled solution of diethyl (2-thienylmethyl)phosphonate[10] (2.30 g, 10 mmol) in DME (40 ml) was added sodium hydride (60% dispersion, 0.52 g, 12 mmol) all at once. The mixture was stirred for 0.5 h under ice-cooling and then a solution of thiophene-2-carbaldehyde (1.12 g, 10 mmol) in DME (10 ml) was added dropwise over a period of 0.5 h. The mixture was slowly warmed and refluxed for 3 h. After quenching the reaction by addition of ice-water (50 ml), the mixture was extracted with ether. The extract was washed with water, dried over $MgSO_4$, and evaporated. The residue was recrystallized from cyclohexane to give 1.67 g (88%) of pure **4**. ^{1}H Nmr analysis of the mother liquor of the recrystallization showed that this is a mixture of *E*- and *Z*-isomers in the ratio 4:1. This means that *E*- and *Z*-isomers were formed in the ratio 98:2 in the reaction.

***E*,*E*-2,5-Bis[2-(2-thienyl)ethenyl]thiophene (6). Aldehyde 5.** DMF (20 ml) and phosphorus oxychloride (3.83 g, 25 mmol) were mixed up and stirred for 1 h under ice-cooling. To this mixture was added a solution of **4** (3.84g, 20 mmol) in DMF (50 ml) over a period of 0.5 h. The mixture was slowly warmed to room temperature and then heated at 50 °C for 3 h. The reaction was quenched by addition of ice-water (50 ml) and then aqueous 10% sodium hydroxide (50 ml). The mixture was extracted with benzene. The extract was washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel with benzene as the eluent to give 0.09 g (2%) of **4** and 4.10 g (93%) of **5**, mp 86-87 °C (lit.,[5] mp 88-89 °C).

Preparation of 6 by Wittig-Horner Reaction of 5. To a stirred mixture of sodium hydride (60% dispersion, 1.05 g, 24 mmol) in DME (40 ml) was added a solution of diethyl (2-thienylmethyl)phosphonate (5.60 g, 24 mmol) in DME (10 ml) over a period of 15 min under ice-cooling. After stirring for 30 min at this temperature, a solution of **5** (4.40 g, 20 mmol) in DME (50 ml) was added over a period of 0.5 h. The mixture was gradually warmed and then refluxed for 3.5 h. The reaction was quenched by addition of ice-water (50 ml) and the resulting solid material was collected by filtration, washed with a small amount of methanol, and dried to give 5.29 g (88%) of **6**. The recrystallized material from cyclohexane, golden yellow plates, melts at 150.5-151 °C (lit.,[7] mp 151 °C). ^{1}H Nmr (400 MHz, $CDCl_3$) δ 6.69 (s, 2H), 6.97-6.99 (m, 6H), 7.03 (d, *J*=2.7 Hz, 2H), 7.18 (d, *J*=5.0 Hz, 2H); ^{13}C nmr (100 MHz, $CDCl_3$) δ 121.45 (d), 121.60 (d), 124.48 (d), 126.17 (d), 127.08 (d), 127.72 (d), 141.30 (s), 142.40 (s); uv-vis λ_{max} ($CHCl_3$) (ε) 429 (38500), 416 (50600), 394 (37500), 322 nm (7000).

E,E,E-2,2'-(1,2-Ethenediyl)bis[5-[2-(2-thienyl)ethenyl]thiophene (7). To a stirred solution of **5** (2.20 g, 10 mmol) in THF (60 ml) was added titanium(IV) chloride (1.50 ml, 13 mmol) over a period of 0.5 h under ice-cooling. After stirring for 0.5 h, zinc powder (1.70 g, 26 mmol) was added in small portions over a period of 0.5 h at 0 °C. The mixture was warmed and then refluxed for 4 h. The reaction was quenched by addition of ice-water (50 ml) and the resulting solid material was collected by filtration and dried. The solid material was heated with boiling 1,2-dichloroethane (200 ml) and filtered while still hot. The filtrate was concentrated to *ca.* 30 ml and the resulting red crystals were collected by filtration to give 2.02 g (97%) of **7**. The material recrystallized from 1,2-dichloroethane, red granules, melts at 226-227 °C (lit.,[5] mp 199-203 °C); ms *m/z* 408 (M^+), 149, 105, 98, 97, 91; uv-vis λ_{max} ($CHCl_3$) (ε) 490 (47200), 460 (61000), 435 (44800), 370 nm (12000). Anal. Calcd for $C_{22}H_{16}S_4$; C, 64.66; H, 3.95. Found: C, 64.52; H, 3.83.

E,E,E,E-2,5-Bis[2-[5-[2-(2-thienyl)ethenyl]-2-thienyl]ethenyl]thiophene (9). Aldehyde 8. DMF (80 ml) and phosphorus oxychloride (0.92 g, 6 mmol) were mixed up under ice-cooling. After stirring for 0.5 h at 0 °C, compound (7) (2.04 g, 5 mmol) was added all at one. The mixture was heated at 60 °C for 5 h. The reaction was quenched by addition of ice-water (50 ml) and then 1 *M* sodium hydroxide (50 ml). The resulting solid material was collected by filtration, air-dried, and chromatographed on a column of silica gel. Elution with carbon tetrachloride gave 0.78 g (38%) of **7** and then elution with benzene gave 0.92 g (42%) of **8**, mp 195-196 °C (1,2-dichloroethane); ir (KBr) 1660 (CH=O), 1447, 1415, 1224, 937, 800 cm^{-1}.

Preparation of 9 from 8 by Wittig-Horner Reaction. To a stirred mixture of the finely powdered aldehyde (**8**) (0.65 g, 1.5 mmol) and diethyl (2-thienylmethyl)phosphonate (0.47 g, 2 mmol) in DME (40 ml) was added sodium hydride (60% dispersion, 87 mg, 2 mmol) under ice-cooling. The mixture was stirred for 0.5 h at this temperature, warmed slowly, refluxed for 4 h, and cooled at room temperature. The resulting solid material was collected by filtration, washed with a small amount of DME and then with water, and air-dried to give 0.68 g (87%) of **9** as red-purple powder. Two recrystallizations of the material from xylene gave 0.50 g (64%) of pure **9** as fine purple granules, mp 251 °C (lit.,[5] mp 235-237 °C); ir (KBr) 1226, 1038, 934, 852, 810, 792, 682 cm^{-1}; uv-vis $\lambda_{max.}$ ($CHCl_3$) (ε) 521 (62100), 490 (80700), 463 (59700), 408 (20000), 388 (15700), 344 nm (22400). Anal. Calcd for $C_{28}H_{20}S_5$; C, 65.08; H, 3.90. Found: C, 65.20; H, 3.73.

***E,E,E,E,E*-2,2'-(1,2-Ethenediyl)bis[5-[2-[5-[2-(2-thienyl)ethenyl]-2-thienyl]ethenyl]thiophene (11). Aldehyde 10.** DMF (50 ml) and phosphorus oxychloride (1.60 g, 10 mmol) were mixed up under ice-cooling and stirred for 0.5 h. A solution of **6** (2.56 g, 8.5 mmol) in DMF (30 ml) was added over a period of 0.5 h at 0 °C. The mixture was heated at 60 °C for 5 h. The reaction was quenched by addition of ice-water (50 ml) and aqueous 10% sodium hydroxide (50 ml). The resulting solid material was collected by filtration and chromatographed on a column of silica gel. Elution with carbon tetrachloride gave 0.68 g (27%) of **6** and then elution with benzene gave 1.63 g (58%) of the aldehyde (**10**), mp 158-159 °C (lit.,[5] mp 144-146 °C).

Preparation of 11 by Carbonyl Coupling of 10. To a solution of **10** (1.41 g, 4 mmol) in dioxane (50 ml) was added titanium(IV) chloride (1.1 ml, 9.6 mmol) with a syringe and then was added zinc powder (1.26 g, 19.2 mmol) in small portions at 10 °C. The mixture was stirred for 0.5 h at room temperature and then refluxed for 2 h. The mixture was cooled to room temperature and the resulting solid material was collected by filtration and washed with water and ethanol. The material was boiled with *o*-dichlorobenzene (250 ml) for 1 h and filtered while still hot. The filtrate was cooled to room temperature and the resulting crystalline material was collected by filtration to give 0.50 g (40%) of **11**. One more recrystallization from *o*-dichlorobenzene gave analytically pure **11** as fine dark violet granules, mp 278 °C (dec.); uv-vis λ_{max} ($CHCl_3$) (ε) 615 (7000), 542 (90000), 510 (115000), 480 (86000), 434 (40700), 369 nm (34700). Anal. Calcd for $C_{34}H_{24}S_6$: C, 65.34; H, 3.87. Found: C, 65.20; H, 3.68.

***E,E,E,E,E,E*-2,5-Bis[2-[5-[2-[5-[2-(2-thienyl)ethenyl]-2-thienyl]ethenyl]-2-thienyl]ethenyl]thiophene (14). Alcohol 12.** To a solution of **10** (1.64 g, 5 mmol) in THF (45 ml) was added sodium borohydride (0.19 g, 5 mmol) in small portions under ice-cooling. The mixture was stirred for 4 h at room temperature. Usual workup of the mixture gave 1.63 g (98%) of **12**, mp 144-146 °C (chlorofrom); ir (KBr) 3150 cm^{-1} (OH); ^{1}H nmr (60 MHz, $CDCl_3$) 1.57 (s, 1H, OH), 4.80 (s, 2H, CH_2), 6.90-7.16 (m, 11H).

Phophonium Bromide 13. A suspension of **12** (1.05 g, 3.18 mmol) and triphenylphosphine hydrobromide[8] (1.20 g, 3.50 mmol) in acetonitrile (85 ml) was refluxed for 5 h. The mixture was cooled and the resulting crystalline precipitate was collected by filtration, washed with water, and dried under vacuum to give 1.19 g (57%) of **13**, mp 233-240 °C.

Preparation of 14 from 8 and 13. To a suspension of **13** (0.83 g, 1.27 mmol) in dioxane (30 ml) was added sodium hydride (60% dispersion, 40 mg, 1.26 mmol) all at once under cooling. To this mixture was added the aldehyde (**8**) (0.52 g, 1.15 mmol) all at once. The mixture was slowly warmed and then refluxed for 12 h. The resulting solid was collected by filtration, washed with dioxane and then with water, and dried. The material was recrystallized from *o*-dichlorobenzene (200 ml) to give 0.57 g (67%) of analytically pure **14** as dark violet crystals, mp 280-285 °C (decomp.); ir (KBr) 1285, 1231, 1073, 1038, 930, 851, 792, 683 cm^{-1}; uv-vis λ_{max} (ε) 640 (27800), 560 (113400), 521 (142800), 459 (88000), 394 nm (63700). Anal. Calcd for $C_{40}H_{28}S_7$: C, 65.53; H, 3.85. Found: C, 65.34; H, 3.67.

Attempeted Preparation of *E,E,E,E,E,E,E*-2,2'-(1,2-Ethenediyl)bis[5-[2-[5-[2-[5-[2-(2-thienyl)ethenyl]-2-thienyl]ethenyl]-2-thienyl]ethenyl]thiophene (15). Aldehyde (8) (0.87 g, 2 mmol) was treated with the foregoing low-valent titanium reagent. Workup in a manner similar to that described with **11** gave 0.8 g of the dark solid product. The material was recrystallized from a large amount of *o*-dichlorobenzene to give 42 mg (5%) of black powder, mp > 400 °C; ir (KBr) 1240, 1040, 931, 795, 692, 556 cm^{-1}. The insolubility of the compound in any solvents at room temperature made it impossible to determine its uv-vis spectrum. Anal. Calcd for $C_{46}H_{32}S_8$: C, 65.67; H, 3.83. Found: C, 64.29; H, 3.79.

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