Efficient Synthesis of Alkyl End-Capped Oligoheterocycles via the Use of Palladacycle Catalyst

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The preparation of mixed thiophene/furan oligomers with alkyl groups at α,α′-position by the method which we discovered recently in our lab is presented. Thus, the mixed thiophene/furan oligomers can be prepared in good yields from monoiodoarene in the presence of 5 mol % of palladacycle catalyst and 1.2 equiv of *N,N*-diisopropylethylamine in DMF at 100 °C for 8 h.

INTRODUCTION

Thiophene oligomers have continually attracted much attention to their biological activities[1,2] and as starting materials for the preparation of organic conductors.[3,4] The oligomers of similar structure such as pyrroles and thiophenes are reported and are promising materials for many potential applications.[5,6] However, despite the interesting properties in this field, not many efforts have been undertaken to synthesize the mixed thiophene/furan oligomers with alkyl groups capped at α-position. The presence of the furan unit should enhance the solubility of oligomers compared with their thiophene analogues. Until recently, very few mixed thiophene/furan oligomers have been reported in the literature.[7-13] The utility of oligomers with well defined structures has become apparent and a number of these oligomers, which are usually β-alkylated to enhance solubility, also have been reported recently.[14-19] The α-alkyl end-capped oligomers are particularly useful for obtaining the information on the nature of the charge carriers in the doped polythiophene, since blocking of the α-positions prevents further undesired reactions upon doping. To our knowledge, there are no reports in the literature about the α-alkyl end-capped mixed oligomers containing thiophene and furan units. In this paper, we wish to report an efficient synthesis of mixed thiophene/furan oligomers with alkyl groups capped at α-position by the reductive homocoupling method by palladacycle catalyst which we have discovered in our laboratory recently.[20,21]

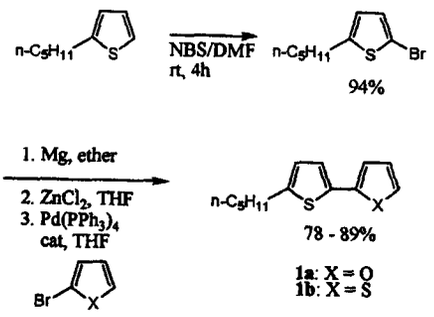
RESULTS AND DISCUSSION

The synthetic routes used to build up oligoheterocycles were the homocoupling of the monoiodoheteroaryl by the use of palladacycle catalyst.[20] The preparation of compounds **1a-b** was in satisfactory yields (73 to 83%) from 2-pentylthiophene by bromination (NBS/DMF), transformed into Grignard and zinc reagents, and followed by crossed coupling with 2-bromofuran or 2-bromothiophene by the aid of $Pd(PPh_3)_4$ catalyst as shown in Scheme I. It is noteworthy that the palladium-catalyzed cross coupling reactions of 2-bromo-5-pentylthiophene with either the corresponding Grignard or organozinc compound of 2-bromofuran and 2-bromothiophene failed. Compounds **1c-d** were synthesized in 78 to 85% yields according to our earlier reports.[21] Thus, (3*Z*)-1-(2-furyl)-3-iodonon-3-en-1-one and (3*Z*)-3-iodo-1-(2-thienyl)non-3-en-1-one were prepared from 1-(2-furyl)non-2-yn-1-one and 1-(2-thienyl)non-2-yn-1-one, respectively, by treatment with TMSCl/NaI/H_2O in MeCN.[22,23] The following cyclization by the use of palladacycle catalyst and *N,N*-diisopropylethylamine as a base can afford compounds **1c-d**. The products **3a-d** were synthesized from **1a-d** via iodination (HgO/I_2) in benzene to give **2a-d** (75 to 99% yields) followed by reductive homocoupling reaction in the presence of 5 mol % of palladacycle catalyst and *N,N*-diisopropylethylamine in dry DMF at 90-100 °C (60 to 81% yields) as shown in Scheme II. The use of $Pd(PPh_3)_4$ as the catalyst in the reductive homocoupling reaction gave only low yields (< 25%). The use of the corresponding monobromoarene or monochloroarene in the above reductive homocoupling reaction failed.

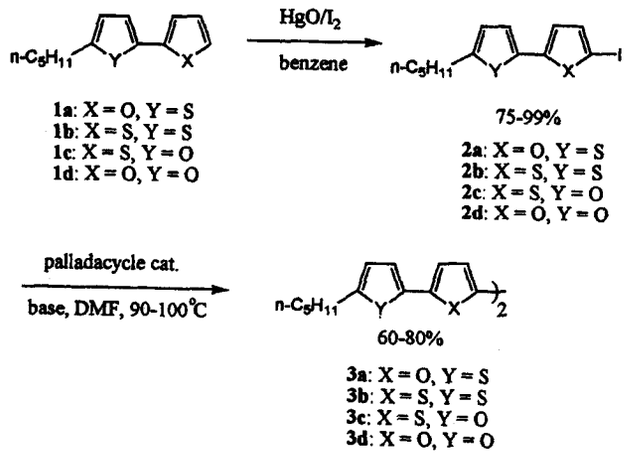
The electrochemical and conducting properties of the α-alkyl end-capped mixed oligomers containing thiophene and furan units are currently under active investigation.

Dedicated to the memory of the late Professor Ta-shue Chou

Scheme I



Scheme II



EXPERIMENTAL SECTION

Precoated silica gel 60F-254 on aluminum plates made by EM chemical company was used for thin-layer chromatography. Purification by column chromatography was carried out with EM silica gel 60 (70-230 mesh ASTM). High-pressure liquid chromatography (HPLC) separation was performed at a flow rate of 0.7 mL/min by the use of two Chemco-Pak 10 × 250 column packed with Chemcosorb 5-ODS-H. GLC analyses were performed by a 3.2 × 3.1 column packed with SE-30 (5% on Chemcosorb W). The purity of each compound was judged to be > 95% by GLC, ^{1}H-NMR or ^{13}C-NMR spectral analyses. Reactions of organometallic compounds were undertaken in oven- and/or flame-dried glassware. Tetrakis(triphenylphosphine)palladium[24] and palladacycle[25] were prepared by published methods. Zinc chloride was dried before use at > 50 °C and at < 1 mmHg for 2 h. All other materials were used without further purification. IR spectra were recorded on a Perkin-Elmer 882 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200 or AC300 spectrometer, chemical shifts were reported in ppm down field from Me_4Si. MS spectra were obtained on HP 5971 or Fisons MD800 GC/MS or VG 70-250S spectrometer.

2-Bromo-5-pentylthiophene

In the absence of light, a solution of NBS (9.82 g , 55.19 mmol) in DMF (40 mL) was added dropwise to an ice-cooled solution of 2-pentylthiophene (8.52 g, 55.19 mmol) in DMF (40 mL), and the mixture was stirred for 4 h at room temperature. To the reaction mixture, water (100 mL) was added and the organic compound was extracted with ethyl acetate (50 mL × 2). The combined organic extract was washed with water (50 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was chromatographed over silica gel using hexane as the eluent to give the title compound (12.07 g, 94%) as a pale yellow liquid: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, J = 7 Hz, 3H), 1.27-1.43 (m, 4H), 1.55-1.70 (m, 2H), 2.73 (t, J = 7 Hz, 2H), 6.52 (d, J = 3.5 Hz, 1H), 6.83 (d, J = 3.5 Hz, 1H) ppm; IR (neat) 1464 (m), 1447 (m), 1045 (w), 956 (w), 790 (m) cm^{-1}; MS *m/z* 234, 232 (M^+), 177, 175, 96, 95; HRMS for $C_9H_{13}BrS$: calcd 231.9921, found 231.9922.

5-Pentyl-2-(2-furyl)thiophene (1a)

Magnesium (0.64 g, 26.46 mmol) turnings and diethyl ether (5 mL) were placed in a flask under nitrogen atmosphere. A crystal of iodine was added to the mixture. Then, 2-bromo-5-pentylthiophene (5.14 g, 22.05 mmol) in diethyl ether (10 mL) was added dropwise at 50 °C. The mixture was refluxed for 2 h and cooled to room temperature at which time $ZnCl_2$ (3.60 g, 26.46 mmol) in THF (30 mL) was added dropwise and stirred at room temperature for 30 min. To the above reaction mixture 2-bromofuran[26] (3.91 g, 26.46 mmol) and 5 mol % of $Pd(PPh_3)_4$ in THF (5 mL) was added dropwise. The reaction mixture was refluxed for 16 h, cooled to room temperature and quenched with saturated NH_4Cl solution. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (30 mL × 2). The combined organic phase was washed with water (25 mL) and brine (25 mL), dried (Na_2SO_4), filtered and evaporated under reduced pressure. The residue was chromatographed over silica gel using hexane as the eluent to afford **1a** (3.51 g, 72.31%) as a pale yellow oil: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, J = 7 Hz, 3H), 1.27-1.43 (m, 4H), 1.66-1.71 (m, 2H), 2.79 (t, J = 7 Hz, 2H), 6.41 (s, 2H), 6.69 (d, J = 3.5 Hz, 1H), 7.05 (d, J = 3.5 Hz, 1H), 7.37 (s, 1H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 13.99, 22.39, 29.99, 31.21, 31.28, 104.12, 111.50, 122.24, 124.55, 131.11, 141.18, 145.13, 149.74 ppm; IR (neat) 1451 (m), 1153 (m), 1012 (m), 974 (m) cm^{-1}; MS *m/z* 220 (M^+), 163,

134, 91; HRMS for $C_{13}H_{16}OS$: calcd 220.0922, found 220.0924.

5-Pentyl-2-(2-thienyl)thiophene (1b)

Using the general procedure described above for the synthesis of **1a**, compound **1b** was prepared from 2-bromo-5-pentylthiophene (1.0 g, 4.29 mmol), magnesium (0.13 g, 5.15 mmol), dry ether (10 mL), $ZnCl_2$ (0.70 g, 5.15 mmol), 5 mol % of $Pd(PPh_3)_4$ and 2-bromothiophene (0.70 g, 4.28 mmol). After column chromatography over silica gel using hexane as the eluent to provide **1b** (0.89 g, 88.11%): ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, J = 7 Hz, 3H), 1.34-1.38 (m, 2H), 1.63-1.73 (m, 2H), 2.78 (t, J = 7 Hz, 2H), 6.67 (d, J = 3.4 Hz, 1H), 6.97-6.99 (m, 2H), 7.09 (d, J = 3.4 Hz, 1H), 7.15 (d, J = 3.4 Hz, 1H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 13.98, 22.39, 30.08, 31.25 (2 Cs), 122.93, 123.34, 123.66, 124.66, 127.63, 134.71, 137.94, 145.33 ppm; IR (neat) 1518 (m), 1486 (m), 1206 (m), 837 (m), 795 (s) cm^{-1}; MS *m/z* 236 (M^+), 207, 179; HRMS for $C_{13}H_{16}S_2$: calcd 236.0693, found 236.0695.

5-Pentyl-2-(2-thienyl)furan (1c)[21]

Pale yellow liquid; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, J = 7 Hz, 3H), 1.32-1.38 (m, 4H), 1.62-1.72 (m, 2H), 2.64 (t, J = 7 Hz, 2H), 6.01 (d, J = 3 Hz, 1H), 6.38 (d, J = 3 Hz, 1H), 6.98-7.01 (m, 1H), 7.14-7.18 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 13.99, 22.40, 27.73, 28.04, 31.36, 105.72, 106.72, 121.61, 123.27, 127.48, 134.33, 147.64, 156.13, 185.72 ppm; IR (neat) 3112 (w), 3076 (w), 2949 (s), 2922 (s), 2849 (m), 1560 (m), 1460 (w), 1428 (w), 1374 (w), 1261 (w), 1193 (w), 1012 (m), 844 (m), 772 (s), 681 (s) cm^{-1}; MS *m/z* 220 (M^+), 219, 163, 162, 134, 91; HRMS for $C_{13}H_{16}OS$: calcd 220.0922, found 220.0922; Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.92; H, 7.50.

2-(2-Furyl)-5-pentylfuran (1d)[21]

Colorless liquid; R_f = 0.55 (Si60 F254, hexane); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, J = 7 Hz, 3H), 1.31-1.37 (m, 4H), 1.61-1.69 (m, 2H), 2.65 (t, J = 7 Hz, 2H), 6.02 (d, J = 2 Hz, 1H), 6.42-6.47 (m, 3H), 7.38 (s, 1H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 13.97, 22.39, 27.73, 28.02, 31.35, 104.07, 105.84, 106.45, 111.21, 141.26, 144.82, 146.98, 156.28 ppm; IR (neat) 3115 (w), 2949 (s), 2931 (s), 2859 (m), 1578 (m), 1455 (m), 1202 (w), 1157 (w), 1007 (s), 776 (s), 722 (s) cm^{-1}; MS *m/z* 204 (M^+), 147, 95, 91; HRMS for $C_{13}H_{16}O_2$: calcd 204.1150, found 204.1150; Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.66; H, 8.12.

5-Pentyl-2-(5-iodo-2-furyl)thiophene (2a)

To a solution of **1a** (2.00 g, 9.09 mmol) in benzene (15 mL) was added alternately in small portions at room temperature, mercuric oxide (1.98 g, 9.09 mmol) and iodine (2.31 g , 9.09 mmol). The reaction mixture was stirred at room temperature for 12 h, extracted with ethyl acetate, and washed with Na_2SO_3 aqueous solution. The organic layer was then dried (Na_2SO_4), the solvent was removed under reduced pressure, and the residue was chromatographed over silica gel using hexane as the eluent to afford **2a** (2.34 g, 74.47%) as a pale yellow oil: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, J = 7 Hz, 3H), 1.33-1.40 (m, 4H), 1.57-1.72 (m, 2H), 2.79 (t, J = 7 Hz, 2H), 6.29 (d, J = 3.4 Hz, 1H), 6.55 (d, J = 3.4 Hz, 1H), 6.67 (dt, J = 3.6, 1.0 Hz, 1H), 7.04 (d, J = 3.6 Hz, 1H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 13.95, 22.37, 29.98, 31.19, 31.25, 85.63, 106.93, 122.12, 122.83, 124.57, 129.91, 145.81, 155.03 ppm; IR (neat) 1638 (m), 1492 (m), 1171 (m), 1105 (m), 1010 (m), 991 (m), 913 (m), 799 (m), 776 (m) cm^{-1}; MS *m/z* 346 (M^+), 289, 191, 134; HRMS for $C_{13}H_{15}IOS$: calcd 345.9888, found 345.9894.

5-Pentyl-2-(5-iodo-2-thienyl)thiophene (2b)

Following the general procedure described above for the synthesis of **2a**, compound **2b** (0.15 g, 99%) was a colorless solid prepared from **1b** (0.10 g, 0.40 mmol), mercuric oxide (0.09 g, 0.40 mmol) and iodine (0.10 g, 0.40 mmol) in benzene (2 mL): ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, J = 7 Hz, 3H), 1.34-1.37 (m, 4H), 1.60-1.70 (m, 2H), 2.77 (t, J = 7 Hz, 2H), 6.66 (d, J = 3.5 Hz, 1H), 6.76 (d, J = 3.5 Hz, 1H), 6.92 (d, J = 3.5 Hz, 1H), 7.12 (d, J = 3.5 Hz, 1H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 13.95, 22.37, 30.08, 31.23 (2 Cs), 70.90, 123.87, 124.32, 124.76, 133.50, 137.53, 143.90, 146.00 ppm; MS *m/z* 362 (M^+), 305, 179, 134; HRMS for $C_{13}H_{15}IS_2$: calcd. 361.9660, found 361.9660.

5-Pentyl-2-(5-iodo-2-thienyl)furan (2c)

Following the general procedure described above for the synthesis of **2a**, compound **2c** (2.04 g, 80.54%) was prepared as a pale yellow oil from **1c** (1.61 g , 7.32 mmol), mercuric oxide (1.58 g, 7.32 mmol), iodine (1.81 g, 7.32 mmol) and benzene (10 mL): ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 13.99, 22.38, 27.66, 28.00, 31.33, 70.88, 106.26, 106.84, 122.82, 137.37, 140.20, 146.53, 156.59 ppm; IR (neat) 1560 (m), 1420 (m), 1014 (m), 778 (m) cm^{-1}; MS *m/z* 346 (M^+) , 289, 163, 134; HRMS for $C_{13}H_{15}IOS$: calcd 345.9888, found 345.9897.

5-Pentyl-2-(5-iodo-2-furyl)furan (2d)

Following the general procedure described above for the synthesis of **2a**, compound **2d** (0.17 g, 74.45%) was prepared as a pale yellow oil from **1d** (0.14 g, 0.70 mmol), mercuric oxide (0.15 g, 0.70 mmol), iodine (0.18 g, 0.70 mmol) and benzene (3 mL): ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.83 (t, J = 7 Hz, 3H), 1.20-1.27 (m, 4H), 1.56-1.60 (m, 2H), 2.56 (t, J = 7 Hz,

2H), 5.95 (s, 1H), 6.30 (s, 1H), 6.38 (s, 1H), 6.48 (s, 1H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 14.00, 22.38, 27.67, 27.98, 31.33, 85.96, 106.57, 106.67, 106.76, 121.86, 143.65, 152.13, 156.63 ppm; MS *m/z* 330 (M^+), 273, 175, 118; HRMS for $C_{13}H_{15}IO_2$: calcd 330.0117, found 330.0118.

5,5′-Bis(5-pentyl-2-thienyl)-2,2′-bifuran (3a)

To a solution of **2a** (0.14 g, 0.41 mmol) and 5 mol % of palladacycle in dry DMF (2 mL) was added *N,N*-diisopropylethylamine (0.06 g, 0.49 mmol). The reaction mixture was stirred under heating at 90 to 100 °C for 8 h. The mixture was cooled to room temperature, water was added and extracted with ethyl acetate (15 mL × 2). The combined organic extract was washed with water (20 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The dark brown residue was chromatographed over silica gel using hexane as the eluent to provide **3a** (0.06 g, 62.76%) as a pale yellow solid: mp: 75-76 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, *J* = 7 Hz, 6H), 1.30-1.40 (m, 8H), 1.67-1.72 (m, 4H), 2.81 (t, *J* = 7 Hz, 4H), 6.48 (d, *J* = 3.5 Hz, 2H), 6.62 (d, *J* = 3.5 Hz, 2H), 6.71 (d, *J* = 3.5 Hz, 2H), 7.11 (d, *J* = 3.5 Hz, 2H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 14.00, 22.40, 30.06, 31.22, 31.31, 106.19, 107.16, 122.48, 124.71, 130.73, 145.02, 145.43, 149.01 ppm; MS *m/z* 438 (M^+), 381, 324, 219, 162; HRMS for $C_{26}H_{30}O_2S_2$: calcd 438.1687, found 438.1691.

5,5′-Bis(5-pentyl-2-thienyl)-2,2′-bithiophene (3b)

The title compound **3b** (0.07 g, 79.55%) was prepared as a pale yellow solid from **2b** (0.14 g, 0.39 mmol), *N,N*-diisopropylethylamine (0.06 g, 0.46 mmol) and 5 mol % of palladacycle in dry DMF (2 mL): mp: 177-179 °C;^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, *J* = 7 Hz, 6H), 1.30-1.40 (m, 8H), 1.60-1.70 (m, 4H), 2.79 (t, *J* = 7 Hz, 4H), 6.68 (d, *J* = 3.5 Hz, 2H), 6.97-7.03 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 13.99, 22.40, 30.15, 31.25, 123.37, 123.55, 124.00, 124.83, 134.45, 135.35, 136.73, 145.66 ppm; MS *m/z* 470 (M^+), 413, 356, 323, 202, 122, 93; HRMS for $C_{26}H_{30}S_4$: calcd 470.1230, found 470.1217.

5,5′-Bis(5-pentyl-2-furyl)-2,2′-bithiophene (3c)

The title compound (0.03 g, 68.60%) was prepared as a yellow solid from **2c** (0.03 g, 0.09 mmol), *N,N*-diisopropylethylamine and 5 mol % of palladacycle in dry DMF (1 mL): mp: 129-130 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, *J* = 7 Hz, 6H), 1.30-1.40 (m, 8H), 1.60-1.70 (m, 4H), 2.65 (t, *J* = 7 Hz, 4H), 6.03 (d, *J* = 3.5 Hz, 2H), 6.39 (d, *J* = 3.5 Hz, 2H), 7.04-7.08 (m, 4H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 14.01, 22.41, 27.72, 28.08, 31.37, 106.08, 106.98, 122.21, 123.85, 132.80, 135.14, 147.21, 156.45 ppm; MS *m/z* 438 (M^+), 381, 324, 295, 219, 162, 73; HRMS for $C_{26}H_{30}O_2S_2$: calcd 438.1687, found 438.1692.

5,5′-Bis(5-pentyl-2-furyl)-2,2′-bifuran (3d)

The title compound (0.09 g, 59.35%) was prepared as a yellow solid from **2d** (0.25 g, 0.76 mmol), *N,N*-diisopropylethylamine (0.12 g, 0.92 mmol) and 5 mol % of palladacycle in dry DMF (2 mL): mp: 71-73 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, *J* = 7 Hz, 6H), 1.33-1.39 (m, 8H), 1.63-1.70 (m, 4H), 2.60-2.72 (m, 4H), 6.05 (d, *J* = 3.5 Hz, 2H), 6.45-6.65 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 300 MHz) δ 14.00, 22.40, 27.71, 28.07, 31.37, 106.05, 106.28, 106.67, 106.98, 144.51, 145.10, 146.20, 156.64 ppm; MS *m/z* 406 (M^+), 349, 292, 203, 146; HRMS for $C_{26}H_{30}O_4$: calcd 406.2144, found 406.2141.

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Key Words

Palladacycle catalyst; Mixed furan/thiophene oligomers; Homocoupling reaction; Palladium catalyst.

REFERENCES

1. Nakayama, J.; Konishi T.; Hoshine, M. *Heterocycles* **1998**, *27*, 1731.
2. Downum, K.; Hancock, R. E. W.; Towers, G. M. N. *Photochem, Photobiol.* **1982**, *3*, 517 and reference cited therein.
3. Kagan, J.; Arora, S. K. *J. Org. Chem.* **1983**, *48*, 4317.
4. Roncali, J.; Garnier, F.; Lemaire , M.; Garrean, R. *Synthetic Metals* **1986**, *15*, 323.
5. Skotheim, T. E. *Handbook of Conductive Polymers*, Marcel Dekker: New York, **1986**.
6. Tsumura, A.; Koezuka, H.; Tsunoda, S.; Ando, T. *Chem. Lett.* **1986**, 863.
7. Wynberg, H.; Sinnige, H. J. M.; Creemers, H. M. J. C. *J. Org. Chem.* **1971**, *36*, 1011.
8. Chen, L. H.; Wang, C. Y.; Luo, T. M. H. *Heterocycles* **1994**, *38*, 1393.
9. Kagan, J.; Arora, S. K. *Heterocycles* **1983**, *10*, 1941.
10. Parakka, J. P.; Cava, M. P. *Synthetic Met.* **1995**, *68*, 275.
11. Carpta, A.; Rossi, R.; Veracini, C. A. *Tetrahedron* **1985**,

41, 1919.
12. Hucke, A.; Cava, M. P. *J. Org. Chem.* **1998**, *63*, 7413.
13. Luo, F. T.; Bajji, A. C.; Jeevanandam, A. *J. Org. Chem.* **1999**, *64*, 1738.
14. (a) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F.; Zinger, B. *Chem. Mater.* **1992**, *4*, 1106. (b) Zinger, B.; Mann, K. R.; Hill, M. G.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1113.
15. (a) Tour, J. M.; Wu, R. L. *Macromolecules* **1992**, *25*, 1901. (b) Guay, J.; Kasai, P.; Diaz, P.; Wu, R. L.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097.
16. (a) Bauerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. *J. Am. Chem. Soc.* **1993**, *115*, 10217. (b) Bauerle, P.; Segelbacher, U.; Gandl, K. U.; Huttenlocher, D.; Mehring, M. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 76. (c) Bauerle, P.; Fischer, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 303.
17. (a) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. *Synth. Met.* **1990**, *39*, 243. (b) Fichou, D.; Horowitz, D. *Mater. Res. Soc. Symp. Proc.* **1990**, *173*, 379.
18. (a) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, 5430. (b) Zotti, G.; Schiaron, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, 5620. (c) Zotti, G.; Berlin, A.; Pagani, G.; Schiaron, G.; Zecchin, S. *Adv. Mater.* **1994**, *6*, 231.
19. (a) Hotta, S.; Waragai, K. *J. Phys. Chem.* **1993**, *29*, 7427. (b) Hotta, S.; Waragai, K. *J. Mater. Chem.* **1991**, 1835. (c) Hotta, S.; Waragai, K. *Synth. Met.* **1991**, *41*, 519.
20. Luo, F. T.; Jeevanandam, A.; Basu, M. K. *Tetrahedron Lett.* **1998**, *39*, 7939.
21. Luo, F. T.; Jevanandam, A.; Bajji, A. C. *Tetrahedron Lett.* **1999**, *40*, 121.
22. Luo, F. T.; Kumar, K. A.; Hsieh, L. C.; Wang, R. T. *Tetrahedron Lett.* **1994**, *35*, 2553.
23. Luo, F. T. *J. Org. Chem.* **1998**, *63*, 5656.
24. Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
25. Herrmann, W. A.; Brossmer, C.; Ofele, K.; Reisinger, C. P.; Priemeier, T.; Beller, M.; Fisher, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844.
26. Keegstra, M. A.; Klomp, A. J. A.; Brandsma, L. *Synth. Commun.* **1990**, *20*, 3371.