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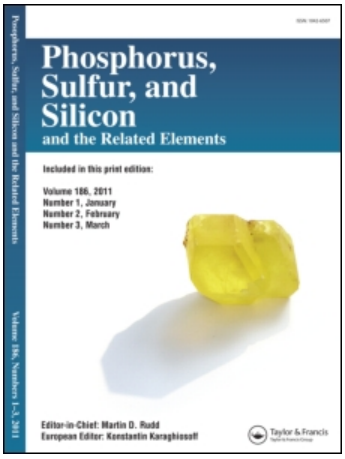

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SYNTHESIS OF α-THIOPHENE OLIGOMERS VIA ORGANOTIN COMPOUNDS

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A versatile synthetic route involving the use of organotin compounds has been applied for the preparation of functionalized oligothiophenes. Thus, substituted α-bithiophenes have been synthesized via the coupling reaction of 2-bromothiophenes with 2-trimethylstannylthiophene. The latter reagent couples with 2,5-dibromothiophenes to give the α-terthiophenes which are also accessible through the reaction of 5-trimethylstannyl-α-bithiophene with 2-bromothiophenes. 2,5-Bis(trimethylstannyl) thiophene and 5,5′-bis(trimethylstannyl)-α-bithiophene react with 2-bromothiophenes to give α-terthiophenes and α-quaterthiophenes, respectively. α-Quaterthiophene is also produced via the reaction of 5-trimethylstannylthiophene with 5,5′- dibromo-α-bithiophene. The coupling reaction of 5-trimethylstannyl-α-bithiophene with 2,5-dibromothiophene affords the α-quinquethiophene. The structures of the new compounds were confirmed by elemental analysis, Mass spectrometry, ^{1}H- and ^{13}C-NMR spectral data.

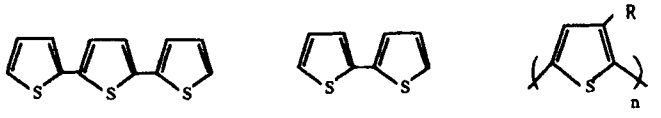
Keywords: Functionalized α-thiophene oligomers; synthesis; 2-stannylthiophenes

INTRODUCTION

2,2′:5′,2"-Terthiophene(**1**),2,2′-bithiophene(**2**), and several of their derivatives are biologically active natural products[1-4]. 2,2′:5′,2"-Terthiophene, the best known member of this series, was found in plants of the family *Compositae (Asteraceae).* It shows nematicidal and fungicidal activity, which is enhanced by near ultraviolet radiation.[3] The distribution, biogenesis and spectral data of naturally occurring thiophenes have been recently reviewed.[4] Furthermore, it was found that thiophene and its higher α-oligomers are of interest as repeating units for the construction of electroconductive polymers. Much of the research has

* Corresponding author.

been focused on modification of the base monomer units, specifically the 3-alkyl derivatives which yield polymers(**3**) with improved conductivity. The synthesis, functionalization and applications of conjugated poly(thiophene) have been recently reviewed.[5]



1 **2** **3**

FORMULA (1)

Thiophene oligomers have been prepared by several methods. Historically, 2,2':5',2"-terthiophene(**1**) was obtained via oxidative coupling of iodothiophene with copper bronze.[6] 2,2':5',2"-Terthiophene(**1**) has been prepared by cyclization of the corresponding 1,4-diketone.[7] α-Quaterthiophene and α-sexithiophene have been prepared by coupling of α-lithiated thiophenes in the presence of cupric chloride or organoboranes.[8] A convenient synthesis has been introduced by Kumada[9] in which a-terthiophene was prepared in 86 % yield by coupling of 2-thienylmagnesium bromide with 2,5-dibromothiophene in the presence of nickel catalyst.

Oligothiophenes bearing electrophilic groups (such as nitro, formyl, acetyl) are desirable for exploration of the chemistry of oligothiophenes via functional group conversions. The present strategy involves an extension of the Stille[10] coupling method to prepare functionalized α-bithiophenes and α-terthiophenes and some higher α-oligothiophenes using tin compounds. Herein, their synthesis and characterization are described.

SYNTHESIS

Lithium and magnesium organometallic compounds have been proven to be very useful intermediates in organic synthesis. However, their high reactivity and the method used for their preparation precludes the presence of most functional groups in these compounds. In view of the known reactivity of electrophilic functional groups like nitro, acetyl and formyl towards organometallic reagents, we chose tin as the activating metal. Organotin compounds have been used in organic synthesis due to the low ionicity of tin-carbon bond as compared with magnesium or lithium carbon bonds. Such organotin compounds allow the direct

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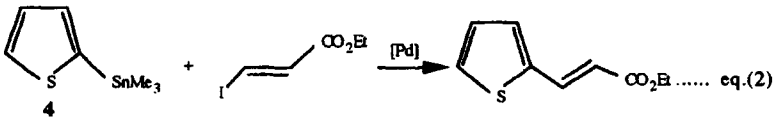
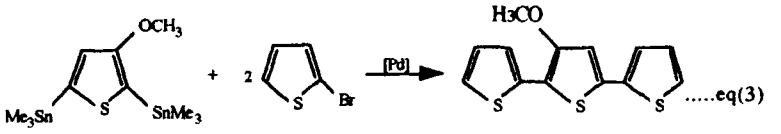
transfer of the organic moiety from the tin metal to the organic substrate in the presence of catalytic amounts of $(Ph_3P)_2PdCl_2$, as shown in equation 1.

$$R_3Sn\text{-}R^1 + R^2\text{-}X \xrightarrow{[Pd]} R^1\text{-}R^2 + R_3SnX \quad \text{..... (eq.1)}$$

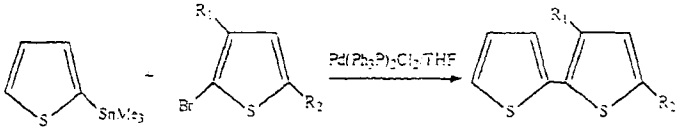
This coupling reaction is regio- and stereoselective; for example 2-trimethylstannylthiophene(**4**) was reacted with ethyl (E)-3-iodoacrylate in the presence of $(Ph_3P)_2PdCl_2$ as a catalyst to give ethyl (E)-3-(2-thienyl)propenoate[11], as shown in equation 2.



Recently, the naturally occurring 3'-methoxy-α-terthiophene was prepared in disappointingly low yield (6 %) from the reaction of 2-bromothiophene and 2,5-bis(trimethylstannyl)-3′-methoxythio phene[12], as show in equation 3.



In the present study, 2-trimethylstannylthiophene(**4**)[13] is found to react with variety of substituted bromothiophenes bearing electron-withdrawing groups in the presence of catalytic amount of dichloro[bis(triphenylphosphin)]palladium (II), [Pd], to give the corresponding bithiophene derivatives (**2,5-8**) in 65-85 % yield as shown in scheme I. The required 2-trimethylstannylthiophene(**4**)[13] was prepared by the reaction of trimethylstannyl lithium[14] with 2-bromothiophene.



4

2: $R_1 = R_2 = H$
5: $R_1 = H$, $R_2 = NO_2$
6: $R_1 = H$, $R_2 = CHO$
7: $R_1 = H$, $R_2 = COCH_3$
8: $R_1 = NO_2$, $R_2 = NO_2$

SCHEME I

Under the same conditions, the reaction of 2-trimethylstannylthiophene(**4**) with 2,5-dibromothiophene, 5,5′-dibromo-α-bithiophene and 2,5-dibromo-3,4-dinitrothiophene gives 2,2′:5′,2"-terthiophene(**1**), 2,2′: 5′,2":5",2′"-quaterthiophene(**9**) and 3′,4′-dinitro-2,2′:5′,2"-terthiophene(**10**), respectively, as shown in scheme (II).

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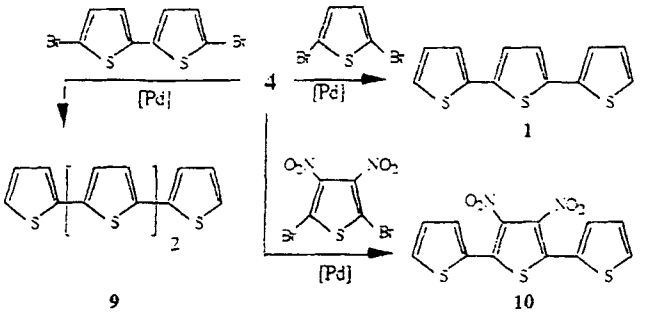
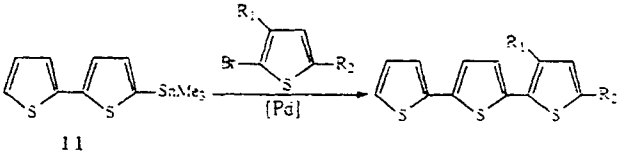


SCHEME II

Similarly, 5-trimethylstannyl-2,2′-bithiophene(**11**), hitherto undescribed, is found to react with a variety of substituted bromothiophenes in the presence of catalytic amount of palladium catalyst, to give the corresponding substituted α-terthiophenes (**12-15**) in 65-85 % yield, as shown in scheme (III).

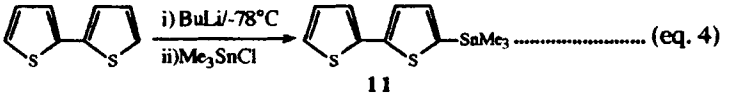


11

1: $R_1 = R_2 = H$
12: $R_1 = H$, $R_2 = NO_2$
13: $R_1 = H$, $R_2 = CHO$
14: $R_1 = H$, $R_2 = COCH_3$
15: $R_1 = NO_2$, $R_2 = NO_2$

SCHEME III

The required 5-trimethylstannyl-2,2′-bithiophene(**11**) was prepared via the metallation of 2,2′-bithiophene with one mole of *n*-butyllithium, followed by addition of trimethylstannyl chloride, as shown in equation 4.



11

It is worth mentioning here, that it was not possibl to prepare 5-trimethylstannyl-2,2′-bithiophene(**11**) via the reaction of trimethylstannyl lithium with 5-bromo-2,2′-bithiophene, since the latter substrate could not be prepared in pure form using published literature methods.[15,16]

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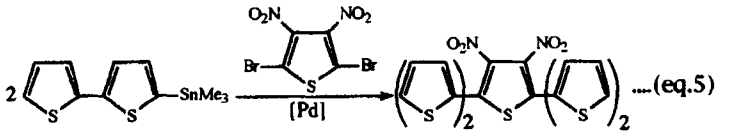
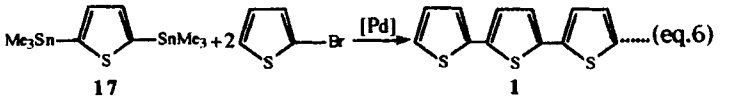
A novel 3",4"-dinitro-2,2′:5′,2":5",2′":5′",2""-quinquethiophene(**16**) has been prepared from the reaction of two moles of 5-trimethylstannyl-2,2′-bithiophene (**11**) with one mole of 2,5-dibromo-3,4-dinitrothiophene in the presence of palladium catalyst,[Pd], as red solid, as shown in equation 5.

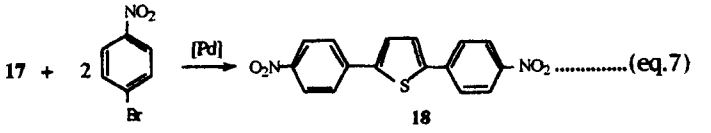


11 **16**

Also, it was found that the reaction of 2,5-bis(trimethyl-stannyl)thiophene(**17**) with 2-bromothiophene and 4-bromonitrobenzene, under palladium catalyzed conditions, gave 2,2′:5′,2"-terthiophene(**1**) and 2,5-di(4-nitrophenyl)thiophene(**18**) as shown in equations 6 and 7, respectively.



17 **1**



18

Similarly, the reaction of 5,5′-bis(trimethylstannyl)-2,2′-bithiophene(**19**) with two moles of each of bromobenzene, 2-bromothiazole and 2-bromothiophene gave the respective 5,5′-diphenyl-2,2′-bithiophene(**20**), 5,5′-di(2-thiazoyl)-2,2′-bithiophene(**21**) and α-quaterthiophene(**9**), as shown in scheme IV.

It is also worth mentioning that this coupling method reported here is quite suitable for obtaining isomerically pure nitro derivatives of α-bithiophene (**5, 8**) and of α-terthiophene (**12, 15**). In contrast, 5-nitro-2,2′:5′,2"-terthiophene (**12**) is formed along with three other isomeric mononitro-α-terthiophenes from the direct nitration of α-terthiophene with fuming nitric acid in the presence of acetic anhydride.[17]

The mass spectra of the bi- and oligothiophenes, prepared in this study, display the correct molecular ions (base peaks in several cases), and the fragmentation modes are in accord with those reported [16,18] for related thiophenes. Their ^{1}H-NMR spectral signals conform with the assigned structures, and are in agreement with literature data [19,20] for the thiophenes.

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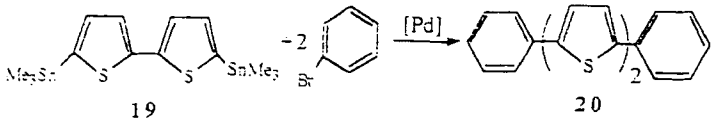

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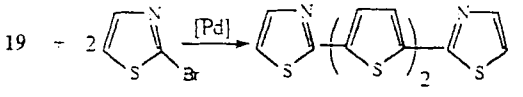

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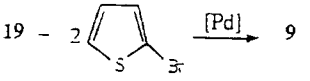

SCHEME IV

Work is in progress to prepare derivatives of the compounds **10**, **15**, **16** and **21** for bioassay.

EXPERIMENTAL

2-Bromothiophene, 2,5-dibromothiophene, 2-bromo-5-thiophenecarbaldehyde, dichloro[1,3-bis(diphenylphosphino)propane] nickle(II), [$NiCl_2$(dppp)], and dichloro[bis(triphenylphosphin)] palladium (II), $(Ph_3P)_2PdCl_2$, were purchased from Acros. Trimethylstannyl chloride and lithium metal (2 % sodium) were purchased from Aldrich. 2,2′-Bithiophene,[9] 5,5′-dibromo-2,2′-bithiophene[20], 2-bromo-5-nitrothiophene,[21] 2-bromo-3,5-dinitro-thiophene[22], 2,5-dibromo-3,4-dinitrothiophene[23] and 2-acetyl-5-bromothiophene[24] were prepared according to literature procedures.

Solvents were dried by using standard procedures. Mass spectra were determined by using a Finnigan MAT 731 spectrometer at 70 eV. NMR spectra were obtained with Brucker AC-300 spectrometer, for solutions in $CDCl_3$. The ^{1}H-

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NMR spectra were calibrated by using signals from the solvents referenced to $(Me)_4Si$. The elemental analysis were determined by M. H. W. Laboratories, Arizona, U.S.A.

2-Trimethylstannylthiophene (4)[13]

A solution of trimethylstannyl lithium[14] in THF, prepared from trimethylstannyl chloride (5.0g, 0.025 mol) and lithium metal (0.6g, 0.09 mol) in dry THF (40 mL) at 0°C under nitrogen atmosphere, was added dropwise at 0°C to a solution of 2-bromothiophene (3.26g, 0.02 ml) in dry THF (30 ml). Stirring was continued overnight at room temperature. THF was evaporated in vacuo, and the residue was extracted with *n*-hexane (3×40mL). Hexane was evaporated to leave oily residue which was purified by vacuum distillation (b.p. 63-64°C/ 2 mmHg). Yield=70 %, Lit.[13] b.p. 97-99°C/33 mmHg).

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2,5-Bis(trimethylstannyl)thiophene (17)[25]

A solution of trimethylstannyl lithium (0.025 mol) in THF, prepared from trimethylstannyl chloride (5.0g, 0.025 mole) and lithium metal (0.60g, 0.09 mol) in dry THF (40 ml) at 0°C under nitrogen atmosphere, was added dropwise at 0°C to a solution of 2,5-dibromothiophene (2.50g, 0.01 mol) in dry THF (30ml). Stirring was continued overnight at room temperature. THF was evaporated in vacuo, and the residue was extracted with n-hexane (3×40ml). Hexane was evaporated to leave white solid which was recrystallized from hexane to give 3.69g (90 %) of product as shiny white needles, m.p 96°C. Lit.[25] m.p 98°C. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.41 (s.2H), 0.41 (s,18H); MS(EI), m/z 410 (M^+). Anal, Calcd for $C_{10}H_{20}SSn_2$: C,29.31; H, 4.92, Found: C, 29.38; H, 4.97.

5- Trimethylstannyl-2,2'-bithiophene(11)

To a solution of bithiophene (5.0g, 0.03 mol.) in dry THF(10 ml) at 0°C was added 12 mL of 2.5M *n*-butyllithium (0.03 mol) in hexane with stirring. Stirring was continued at 0°C for 10 minutes, after which trimethylstannyl chloride (6.0g, 0.03 mol) was added in one portion. Stirring was continued for 30 minutes at room temperature. Solvent was removed under reduced pressure. The oily brown residue was extracted with (3×20 ml) of hexane. Removal of solvent followed by distillation gave (5.9g) 60 % of product as colorless liquid b.p. 63°C (2 Torr.) ^1H NMR ($CDCl_3$, 300 MHz) δ 7.07-7.30 (m, 5H), 0.60 (s, 9H) ; MS(EI), m/z 330 (M^+). Anal. Calcd for $C_{11}H_{14}S_2Sn$: C, 40.15; H, 4.92. Found: C, 40.01; H, 4.80.

5,5'-Bis(trimethylstannyl)-2,2'-bithiophene(19)

This compound was prepared from 5,5'-dibromo-2,2'-bithiophene (3.5g, 0.01 mol) and trimethylstannyl lithium (0.025 mole), as described above for the preparation of 2,5-bis(trimethylstannyl)thiophene to give 3.9g (80 %) of product as shiny white needles, m.p. 75-76°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30 (d, J = 3.3Hz, 2H), 7.10 (d, J = 3.3Hz, 2H), 0.42 (s,18H) ; MS(EI), m/z 494 (M^+). Anal. Calcd. for $C_{14}H_{22}S_2Sn_2$: C, 34.19; H, 4.51. Found: C, 34.36; H, 4.58.

GENERAL PROCEDURES

A three-necked round bottomed flask (100 mL), equipped with condenser, magnetic stirrer and N_2-inlet, was charged with the particular 2-bromothiophene (9.0 mmol), bis(triphenylphosphine) palladium (II) dichloride (0.9 mmole) and dry THF (30 mL). 2-Trimethylstannylthiophene was added, and the reaction mixture was then refluxed for 20 hours with vigorous stirring under N_2-atmosphere. The solvent was removed under vacuum and the residue was extracted with diethyl ether (3×30 mL). The ethereal extracts were washed with water and then with saturated aqueous sodium chloride solution. Ether was than evaporated, and the resulting residue was purified by TLC using silica gel as the adsorbent and benzene-hexane (1:1, v/v) as the eluent.

Yields and melting points of the bithiophenes, terthiophenes and other thiophene oligomers prepared by the above procedure, are listed below:

*2,2'-Bithiophene(**2**):*Yield 64 %, m.p. 33°C (Lit.[9] m.p 33°C).

*5-Nitro-2,2'-bithiophene(**5**):* Yield 87 %, m.p.106°C (Lit.[26] m.p 107°C).

*5-Formyl-2,2'-bithiophene (**6**):* Yield 82 %, m.p.55°C (Lit[27] m.p 58°C).

*5-Acetyl-2,2'-bithiophene (**7**):* Yield 84 %, m.p 109°C (Lit[19] m.p 110°C).

*3,5-Dinitro-2,2'-bithiophene (**8**):* Yield 80 %, m.p.120-121°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.40 (s,1H), 7.71-7.74 (m, 2H), 7.19-7.24 (dd, J = 5.8 Hz, 3.9 Hz, 1H) ; MS(EI), m/z 256(M^+). Anal. calcd for $C_8H_4N_2O_4S_2$: C, 37.50; H, 1.57; N, 10.93; S, 25.02. Found: C, 37.20; H, 1.47; N, 11.08; S, 25.27.

*2,2':5',2"-Terthiophene(**1**):* This compound was prepared from the reaction of 1 mole of 2,5-dibromothiophene with two moles of 2-trimethylstannylthiophene. Yield 42 %, m.p 95-96°C. Compound(**1**) was also prepared from the reaction of 5-trimethylstannyl-2,2'-bithiophene with one mole of 2-bromothiophene. Yield 60 %, m.p. 95-96°C (Lit.[9] m.p. 94-95°C).

*3',4'-Dinitro-2,2':5',2"-terthiophene(**10**):* This compound was prepared from the reaction of 1 mole of 2,5-dibromo-3,4-dinitrothiophene with two moles of 2-trimethylstannylthiophene. Yield 75 %, m.p.135-136°C. ^{1}H NMR ($CDCl_3$,

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300 MHz) δ 7.60-7.64 (dd, J = 5.1 Hz, 1.2 Hz, 1H), 7.54-7.57 (dd, J = 3.8 Hz, 1.3 Hz, 1H) 7.16-7.21 (dd, J = 5.1 Hz, 3.8 Hz, 1H) ; MS(EI), m/z 338 (M^+). Anal. Calcd for $C_{12}H_6N_2O_4S_3$: C, 42.59; H, 1.79; N, 8.25; S, 28.43. Found: C, 42.57; H,1.75; N, 8.08; S, 28.18.

*5-Nitro-2,2':5',2"-terthiophene(**12**):* This compound was prepared from the reaction of one mole of 2-bromo-5-nitrothiophene with one mole of 5-trimethylstannyl-2,2'-bithiophene. Yield 80 %, m.p. 151-152°C (Lit.[17] m.p.150-156°C).

*5-Formyl-2,2':5',2"-terthiophene(**13**):* This compound was prepared from one mole of 2-bromo-5-thiophene carbaldehyde and one mole of 5-trimethylstannyl-2,2'-bithiophene. Yield 77 % m.p.133-134°C. (Lit.[28] m.p.135°C).

*5-Acetyl-2,2':5',2"-terthiophene(**14**):* This compound was prepared from 2-acetyl-5-bromothiophene and 5-trimethylstannyl-2,2'-bithiophene. Yield 85 %, m.p.174-175°C (Lit.[29] m.p.176°C).

*3,5-Dinitro-2,2':5',2"-terthiophene(**15**):* This compound was prepared from the reaction of one mole of 2-bromo-3,5-dinitro thiophene and one mole of 5-trimethylstannyl-2,2'-bithiophene. Yield 70 %, m.p. 136-137°C. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.40 (s, 1H), 7.71(d, J = 4.0 Hz, 1H), 7.36-7.39 (m, 2H), 7.25 (d, J = 4.0 Hz, 1H), 7.09-7.13 (dd, J = 5.1 Hz, 3.8 Hz, 1H) ; MS(EI), m/z 338 (M^+). Anal. Calcd for $C_{12}H_6N_2O_4S_3$: C, 42.59; H, 1.79; N, 8.25; S, 28.43. Found: C, 42.58; H, 1.69; N, 8.20; S, 28.26.

*2,2':5',2":5":2"'-Quaterthiophene(**9**):* This compound was prepared from the reaction of one mole of 5,5'-dibromo-2,2'-bithiophene with one mole of 2-trimethylstannylthiophene. Yield 48 %, m.p. 210-212°C. Alternatively, this compound was prepared from the reaction of two moles of 2-bromothiophene with one mole of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene. Yield 40 %, m.p. 210-212°C (Lit.[9] m.p. 211°C).

*3",4"-Dinitro-2,2':5',2":5",2'":5'",2""-quinquethiophene(**16**):* This compound was prepared from the reaction of one mole of 2,5-dibromo-3,4-dinitrothiophene with two moles of 5-trimethylstannyl-2,2'-bithiophene. Yield 40 %, m.p. 260-262°C. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.10 (d, J = 4.1 Hz, 1H), 7.82-7.84 (m,1H), 7.70-7.73 (m,1H), 7.64 (d, J = 4.1 Hz, 1H), 7.28-7.33 (dd, J = 5.1 Hz, 3.8 Hz, 1H) ; MS(EI), m/z 502 (M^+). Anal. Calcd for $C_{20}H_{10}N_2O_4S_5$: C, 47.79; H, 2.00; N, 5.57; S, 31.89. Found: C, 47.56; H, 1.98; N, 5.45; S, 31.90.

*2,5-Bis(4'-nitrophenyl)thiophene(**18**):* This compound was prepared from the reaction of two moles of 4-bromonitrobenzene and one mole of 2,5-bis(trimethylstannyl)thiophene. Yield 66 %, m.p. 210-211°C (Lit.[30] m.p. 210°C).

*5,5'-Bis(2-thiazoyl)-2,2'-bithiophene(**21**):* This compound was prepared from the reaction of two moles of 2-bromothiazole with one mole of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, Yield 75 %, m.p. 195-196°C. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.78 (d, J = 3.0 Hz, 1H), 7.43 (d, J = 3.6 Hz, 1H), 7.27 (d, J = 3.0

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Hz, 1H), 7.20 (d, J = 3.6 Hz, 1H) ; MS(EI), m/z 338 (M^+). Anal. Calcd for $C_{14}H_8N_2S_4$: C, 50.57; H, 2.43; N, 8.42; S, 38.57. Found: C, 50.82; H, 2.44; N, 8.31; S, 38.27.

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