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Synthesis of donor–acceptor substituted oligothiophenes by Stille coupling

M. Manuela M. Raposo,[a,*] A. Maurício C. Fonseca[a] and G. Kirsch[b]

[a]*Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal*
[b]*Laboratoire d'Ingénierie Moléculaire et Biochimie Pharmacologique, UFR SciFA/Université de Metz, 1, bd Arago, Metz Technopôle, CP 87811, 57078 Metz Cedex 3, France*

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Abstract—A synthesis of donor–acceptor-substituted oligothiophenes by Stille coupling is described. The 5′-estanyl derivatives, readily prepared from 5-alkoxy- and 5-amino-2,2′-bithiophenes **7** were coupled with the appropriate aryl or heteroaryl bromides to give the title compounds.

1. Introduction

The interest in future photonic devices such as frequency converters, light modulators and optical switches has led to the development of a variety of organic non-linear optical (NLO) chromophores.[1–3]

In the last few years, thiophene containing donor–acceptor substituted π systems have been extensively investigated.[4–19]

These novel push–pull systems exibit enhanced second-order polarizabilities β compared to biphenyls or stilbenes.[14,16] Donor–acceptor substituted oligothiophenes represent promising candidates for NLO applications.[1–4,13,17,20]

The synthesis of donor–acceptor oligothiophenes may be achieved by several methods such as cross-coupling reactions; Stille,[14–17,21–24] Suzuki,[25] or others[4,6,8,26–28] and by procedures involving thiophene ring formations.[19,29,30]

Recently we have developed an efficient method for the synthesis of 5-amino- and 5-alkoxy-2,2′-bithiophenes.[31] These compounds have proved to be versatile substrates in formylation, dicyanovinylation and tricyanovinylation reactions, permitting the preparation of several new donor–acceptor substituted bithiophenes.[32]

As part of our continuing interest in non-linear optical material[32–36] we report here the use of the readily available 5-amino- and 5-alkoxy-2,2′-bithiophenes in the Stille cross-coupling reaction with phenyl, thienyl and bithienyl bromides to obtain new donor–acceptor substituted oligothiophenes.

The Stille coupling was chosen because it is one of the most versatile methods for C–C bond formation for several reasons: (i) the organostannanes are readily prepared, purified and stored; (ii) the Stille conditions tolerate a wide variety of functional groups (e.g. CO_2R, CN, OH, CHO, NO_2); (iii) the reaction can be performed under mild conditions and (iv) in contrast to the Suzuki reaction, the Stille coupling can be run under neutral conditions.[37,38]

2. Results and discussion

2.1. Synthesis

A series of chromophores was synthesized with either alcoxy- or *N*,*N*-dialkylamino- donors and formyl, nitro and dicyanovinyl acceptors across a conjugated π-bridge containing a bithiophene-benzene, terthiophene or tetrathiophene moiety.

The bithiophenes **9d**, **10a–d**, **11d**, the terthiophenes **12b**, **13–15d** and the quaterthiophene **16d** were synthesized by $Pd(PPh_3)_4$ catalyzed cross coupling reactions of (tributylstannyl)bithiophenes **8a–d** with the acceptor-substituted bromo-aryl or heteroaryl compounds **1a–b**,**d**, **2a–c** and **6**.

The aryl, thienyl and the bithienyl bromides used were activated by electron withdrawing substituents such as

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* Corresponding author. Tel.: +351-253-604381; fax: +351-253-678983; e-mail address: mfox@quimica.uminho.pt

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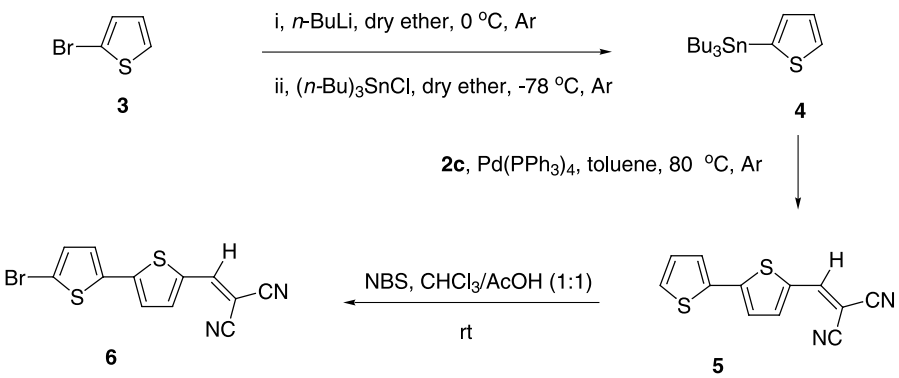
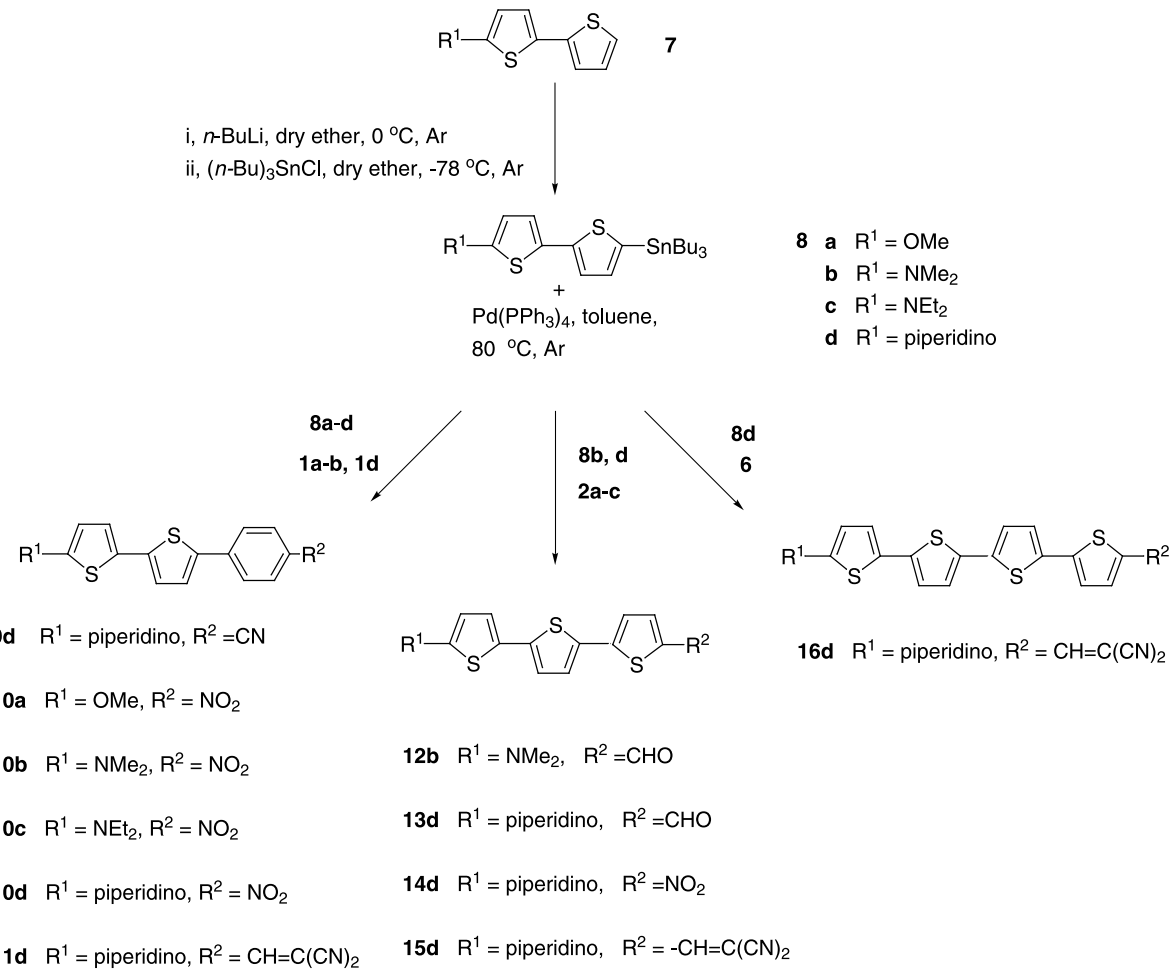


Scheme 1.

formyl, nitro and dicyanovinyl. The bromo derivatives 1-bromo-4-cyanobenzene **1a**, 1-bromo-4-nitrobenzene **1b**, 4-bromo-1-formylbenzene **1c**, 5-bromo-2-formylthiophene **2a** and 5-bromo-2-nitrothiophene **2b** were commercially available. The synthesis of the other bromo derivatives was achieved by several methods. Knoevenagel condensation[39] of the commercial available 4-bromo-1-formylbenzene **1c** and 5-bromo-2-formylthiophene **2a** with malononitrile in refluxing ethanol gave the corresponding dicyanovinyl derivatives 4-bromo-1-dicyanovinylbenzene **1d** and 5-bromo-2-dicyanovinylthiophene **2c** in 87 and 91% yield, respectively.

5′-Bromo-5-dicyanovinyl-2,2′-bithiophene **6** was obtained from 5-dicyanovinyl-2,2′-bithiophene **5** by bromination with NBS in a solution of chloroform–acetic acid (1:1) in 85% yield. Compound **5** was obtained in 55% yield, by Stille coupling of (tributhylstannyl)thiophene **4**[40] under $Pd(PPh_3)_4$ catalysis at 80 °C in toluene. Compound **4** was synthesized from the commercially available 2-bromothiophene **3** in quantitative yield, by lithiation, using *n*-BuLi at 0 °C, followed by transmetalation with tributyltin chloride at −78 °C (Scheme 1).

The bromo derivatives **1d**, **2c** and **6** described earlier were



Scheme 2.

synthesized in order to be coupled under Stille conditions with the stannane bithiophenes **8a–d**.

The synthesis of bithienylstannanes **8a–d** was achieved by metalation of 5-alkoxy- and 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **7a–d**, using *n*-BuLi at 0 °C followed by transmetalation with tributyltin chloride at −78 °C (Scheme 2). The organotin compounds **8a–d** were obtained in good yields (81–90%) and were used in the Stille coupling reactions without further purification.

The Stille reactions were performed in toluene under an argon atmosphere and $Pd(PPh_3)_4$ (2 mol%) was used as palladium catalyst at 80 °C for 8–33.5 h (Scheme 2).

The donor–acceptor oligothiophenes were obtained in moderate to good yields 42–65% (Table 1). Better yields were obtained when more activated aryl or thienyl bromides were used in the Stille couplings. Therefore, bithiophene **10a** was synthesized in 65% yield (Table 1, entry 2) and terthiophene **15d** was obtained in 55% yield (Table 1, entry 10).

The influence of the activation of the aryl or heteroaryl bromides on the yield of the Stille coupling is demonstrated by comparison of the yield of **9d** (43%) (Table 1, entry 1) with the yield of **11d** (56%) (Table 1, entry 6). A better yield was obtained for compound **11d** due to the activation of the bromide **1d** by the dicyanovinyl group.

Waite[41] et al. reported the study of the polarizability and hyperpolarizability of terthiophene **12b** but no analytical data was described for this compound.

2.2. UV–visible study of oligothiophenes

Electronic absorption spectra of all the push–pull compounds **9–16** show an intense lowest energy charge-transfer absorption band in the UV–vis region. The position of this band is strongly influenced by the structure of the compounds, for example by the type of π bridge and the substitution pattern in the donor and acceptor moieties[19] (Table 1).

The influence of the strength of the acceptor group is demonstrated by comparison of the absorption maxima of compounds **13d** and **15d** as the longest wavelength transition is shifted from 456.0 nm in piperidino-T_3-CHO **13d** (Table 1, entry 8) to 545.5 nm in piperidino-T_3-[CH=C(CN)$_2$] **15d** (Table 1, entry 10). The influence of the strength of the donor group is demonstrated by comparison of the absorption maxima of compounds **10a** and **10c** as the longest wavelength transition is shifted from 413.0 nm in methoxy-T_2-4-NO_2-Ph **10a** (Table 1, entry 2) to 474.5 nm in *N*,*N*-diethyl-T_2-4-NO_2-Ph **10c** (Table 1, entry 4).

In general, the stronger the donor and/or acceptor group, the smaller the energy difference between ground and excited states, and the longer the wavelength of absorption.[14] According to Zyss[1] the increase of the β values characteristic of the NLO effects is accompanied by an increase of the λ_{max} in the UV–vis spectra.

Comparison of the electronic absorption spectra of piperidino-T_2-4-NO_2-Ph **10d** (Table 1, entry 5) (λ_{max}=453.0 nm) with piperidino-T_3-NO_2 **14d** (Table 1, entry 9) (λ_{max}=504.0 nm) reveals that the replacement of a benzene ring with a thiophene ring causes a dramatic red shift of the charge-transfer band. This observation clearly indicates that the incorporation of thiophene moieties in push–pull compounds enhances their charge-transfer properties.[4,8,13,20]

2.3. Solvatochromic behavior of oligothiophenes

Solvatochromism is easily quantified by UV–vis spectroscopy and is particularly suitable for the empirical determination of the polarity of a solvent[42,43] on a molecular-microscopic level. To evaluate the intermolecular forces between the solvents and the solute molecules we have measured absorption spectra of six oligothiophenes in 14 solvents of different solvatation character.

The maxima of the wavenumbers ν_{max} for compounds **10d**, **11d**, **12b**, **13d**, **15d** and **16d**, as well as the corresponding wavelength λ are listed in Table 2 and compared with the π^* determined by Kamlet and Taft.

The highest energy transitions are found with non-polar solvents such as hexane and cyclohexane. More polar solvents such as DMF resulted in lower energy transitions. This behavior has been defined as a positive solvatochromic response (between $\Delta\nu$=1333 cm^{-1} for **16d** and $\Delta\nu$= 3758 cm^{-1} for **11d**) that is related to a greater stabilization of the excited state relative to the ground state with increasing polarity of the solvent.

Table 1. Yields and UV–vis absorption spectra of the coupled donor–acceptor oligothiophenes **9–16**

Entry	Bromide	Bithienyl stannane	Product	Yield (%)	Reaction time [h]	λ_{max}[a] [nm] (ε)
1	**1a**	**8d**	Piperidino-T_2-4-CN-Ph **9d**	43	19	420.0 (18,660)
2	**1b**	**8a**	Methoxy-T_2-4-NO_2-Ph **10a**	65	10.5	413.0 (25,750)
3	**1b**	**8b**	*N*,*N*-Dimethyl-T_2-4-NO_2-Ph **10b**	42	19	461.0 (10,050)
4	**1b**	**8c**	*N*,*N*-Diethyl-T_2-4-NO_2-Ph **10c**	44	24.5	474.5 (16,800)
5	**1b**	**8d**	Piperidino-T_2-4-NO_2-Ph **10d**	53	8	453.0 (10,000)
6	**1d**	**8d**	Piperidino-T_2-4-[CH=C(CN)$_2$]-Ph **11d**	56	30	468.0 (21,400)
7	**2a**	**8b**	*N*,*N*-Dimethyl-T_3-CHO **12b**	46	20	465.5 (22,690)
8	**2a**	**8d**	Piperidino-T_3-CHO **13d**	51	17	456.0 (15,260)
9	**2b**	**8d**	Piperidino-T_3-NO_2 **14d**	53	33	504.0 (10,100)
10	**2c**	**8d**	Piperidino-T_3-[CH=C(CN)$_2$] **15d**	55	33.5	545.5 (23,770)
11	**6**	**8d**	Piperidino-T_4-[CH=C(CN)$_2$] **16d**	45	30	510.5 (12,000)

[a] All the UV/vis spectra were run in ethanol.

Table 2. UV–vis absorption maxima of bithiophenes **10d**, **11d**, terthiophenes **12b**, **13d**, **15d** and quaterthiophene **16d** in various solvents in comparison with π^* values by Kamlet and Taft[44]

Solvents	π^*	**10d**		**11d**		**12b**		**13d**		**15d**		**16d**	
		λ_{max} [nm]	ν_{max} [cm^{-1}]	λ_{max} [nm]	ν_{max} [cm^{-1}]	λ_{max} [nm]	ν_{max} [cm^{-1}]	λ_{max} [nm]	ν_{max} [cm^{-1}]	λ_{max} [nm]	ν_{max} [cm^{-1}]	λ_{max} [nm]	ν_{max} [cm^{-1}]
n-Hexane	−0.08	441.5	22,650	437.5	22,857	443.0	22,573	437.5	22,857	532.5	18,779	—	
Cyclohexane	0.00	446.5	22,396	443.0	22,573	448.0	22,321	443.0	22,573	539.0	18,552	—	
Diethyl ether	0.27	448.5	22,296	474.0	21,097	452.0	22,123	444.0	22,522	538.0	18,587	502.0	19,920
Dioxane	0.55	455.0	22,471	495.5	20,181	458.0	21,834	453.0	22,075	539.5	18,535	520.0	19,230
Ethyl acetate	0.55	454.0	22,026	491.5	20,345	457.0	21,881	450.0	22,222	538.5	18,570	513.0	19,493
Tetrahydrofuran	0.58	459.5	21,762	499.0	20,040	461.5	21,668	454.5	22,002	548.0	18,248	521.0	19,193
Acetone	0.71	458.5	21,810	493.5	20,263	461.5	21,668	454.5	22,002	544.5	18,365	515.0	19,417
Acetonitrile	0.75	457.0	21,881	488.5	20,470	462.5	21,621	453.0	22,075	542.0	18,450	503.0	19,880
Dimethylformamide	0.88	470.5	21,253	499.5	20,020	471.0	21,231	463.0	21,598	555.5	18,001	526.5	18,993
Ethanol	0.54	453.0	22,075	468.0	21,367	465.5	21,482	456.0	21,929	545.5	18,331	510.5	19,588
Methanol	0.60	450.0	22,222	468.5	21,344	464.5	21,528	454.5	22,002	539.0	18,552	504.5	19,821
Chloroform	0.58/0.76[45]	457.0	21,881	523.5	19,102	470.5	21,253	468.0	21,367	568.5	17,590	538.0	18,587
Dichloromethane	0.82	467.5	21,390	515.0	19,417	469.0	21,321	462.5	21,621	562.5	17,777	528.0	18,939
Toluene	0.54	459.5	21,762	511.0	19,569	462.0	21,645	454.0	22,026	552.5	18,099	533.0	18,761

Table 3. Correlation of UV–vis absorption maxima of bithiophenes **10d**, **11d**, terthiophenes **12b**, **13d**, **15d** and quaterthiophene **16d** and solvent parameter π^*[a]

Compounds	ν_0 [cm^{-1}]	Regression analysis s[b] [cm^{-1}]	r[b]
10d	22,588	−1120	−0.8084
11d	22,376	−3297	−0.8495
12d	22,415	−1294	−0.9410
13d	22,730	−1252	−0.9037
15d	18,698	−1003	−0.8869
16d[c]	20,019	−1002	−0.9150

[a] Applied solvents (π^* value): *n*-hexane (−0.08), cyclohexane (0.00), diethyl ether (0.27), dioxane (0.55), ethyl acetate (0.55), tetrahydrofuran (0.58), acetone (0.71), acetonitrile (0.75), dimethylformamide (0.88), ethanol (0.54), methanol (0.60), chloroform (0.76), dichloromethane (0.82), toluene (0.54).

[b] Intercept, slope, and correlation coefficient r of the linear solvatation energy relationship.

[c] Without *n*-hexane and cyclohexane.

Because of the pronounced solvatochromism, the good correlation with π^* values for the 14 solvents investigated (r=0.8495) and the long wavelength absorption in the visible range, **11d** seemed to be a very appropriate solvent polarity indicating dye (Table 3). The change in dipole moment on electronic excitation was shown to be oriented parallel to the transition dipole and is moreover constant over the whole charge transfer band.

The great number of aliphatic and dipolar aprotic solvents was chosen to determine the correlation behavior of ν_{max} (**11d**) and π^* because specific interactions were not expected. In fact a good correlation between absorption

Figure 1. Correlation between absorption wavenumbers ν_{max} (**11d**) and the π^* scale according to Kamlet and Taft. Aliphatic and dipolar aprotic solvents (◆), protic solvents (□), chlorinated solvents (△) and aromatic solvents (○).

wavenumbers of **11d** and π^* values (r=0.9431) of the corresponding solvents was obtained (Table 2).

However, as shown in Figure 1, the alcohols, aromatic and chlorinated solvents slightly deviate from this regression line. The behavior in chlorinated and aromatic solvents, which display the lowest energy transitions is noteworthy. Similar behavior has been observed for donor–acceptor molecules of oligothiophenes where the trend was rationalized as a consequence of an intramolecular charge transfer.[14]

The oligothiophene derivatives **9–16** were completely characterized by HRMS, ^{1}H spectroscopy and by IR and UV–vis spectroscopy.

The study of the thermal stability, the electrochemical and the non-linear optical properties of the new oligothiophenes are under way.

3. Experimental

3.1. General

^{1}H NMR spectra were obtained on a Varian Unity Plus Spectrometer at 300 MHz using the solvent peak as internal reference. The solvents are indicated in parenthesis before the chemical shift values (δ relative to TMS). Mp were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer. UV–vis spectra were recorded with a Shimadzu UV/2501/PC spectrophotometer using several solvents analytically pure (Merck). EI mass spectra EI (70 eV) and HRMS were run on a Unicam GC–MS 120. Elemental analysis was carried out on a Leco CHNS-932. Column chromatography was performed on Merck silica gel 60 (Art 9385). Light petroleum refers to solvent boiling in the range 40–60 °C.

All reactions were carried out under an argon atmosphere in dry glassware.

The phenyl and thienyl bromides **1a–c**, **2a–b** and **3** were purchased from Aldrich and used as received.

The synthesis of bithiophenes **7a–d** has been described elsewhere.[31]

3.2. General procedure for the synthesis of dicyanovinyl derivatives 1d and 2c from the corresponding formyl compounds 1c and 2a by Knoevenagel condensation

To a solution of malononitrile (1.2 g, 18 mmol) and the formyl derivatives **1c** and **2a** (15 mmol) in ethanol (50 ml) was added piperidine (1 drop). The solution was heated at reflux for 1 h, then cooled and the solvent was removed under reduced pressure to give the crude dicyanovinyl compounds. The resulting solids were recrystallized to give the title compounds **1d** and **2c**.

3.2.1. 4-Bromo-1-dicyanovinylbenzene 1d. Beige solid (87%). Mp: 160.5–161.6 °C. (ether/n-hexane). IR (nujol) ν 2224 (CN) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.70 (d, 2H, J=8.4 Hz, 2×Ar-H), 7.73 (s, 1H, CH=C(CN)$_2$), 7.78 (d, 2H, J=8.4 Hz, 2×Ar-H). Anal. calcd for $C_{10}H_5BrN_2$: C, 51.52; H; 2.15; N, 12.02. Found C, 51.34; H, 2.46; N, 11.84%.

3.2.2. 5-Bromo-2-dicyanovinylthiophene 2c. Pale orange solid (91%). Mp: 157–158 °C. (ether/n-hexane). UV (acetonitrile): λ_{max} nm (ε, /M^{-1} cm^{-1}) 317.5, (17,000). IR (nujol) ν 3310, 2224 (CN) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.25 (d, 1H, J=4.0 Hz, 4-H), 7.51 (d, 1H, J=4.0 Hz, 3-H), 7.75 (s, 1H, CH=C(CN)$_2$). MS (EI) m/z (%): 240 (M^{+81}Br, 98), 238 (M^{+79}Br, 100), 189 (10), 187 (10), 159 (51). HRMS: m/z (EI) for $C_8H_3{}^{81}BrN_2S$; calcd 239.9180; found: 239.9180. Anal. calcd for $C_8H_3BrN_2S$: C, 40.17; H; 1.26; N, 11.72; S, 13.39. Found C, 40.23; H, 1.49; N, 11.44%).

3.3. Synthesis of 5′-bromo-5-dicyanovinyl-2,2′-bithiophene 6

3.3.1. Synthesis of 2-(tri-*n*-butylstannyl)thiophene 4.[40] Under argon a solution of n-BuLi in hexanes (2.5 ml, 6.14 mmol, 2.5 M) was dropped into a stirred solution of **3** (3.07 mmol) in dry ether at 0 °C. After 1 h the mixture was cooled to −78 °C and a solution of tributyltin chloride (1 g/0.83 ml, 3.07 mmol) in dry ether was slowly added and the mixture was stirred overnight. The mixture was then added to water (50 ml). The aqueous layer was extracted with ether (3×30 ml). The combined organic layers were dried with magnesium sulfate, and the solvent was removed in vacuo to give the title product **4** as a pale brown oil in quantitative yield. ^{1}H NMR ($CDCl_3$) δ 0.80–1.00 (m, 15H, 3×(CH$_2$)$_2$CH_2CH_3)), 1.10–1.50 (m, 12H, 3×(CH_2)$_2$CH$_2$-CH_3), 7.20 (dd, 1H, J=3.3, 1.0 Hz, 3-H), 7.25–7.29 (m, 1H, 4-H), 7.66 (dd, 1H, J=4.7, 1.0 Hz, 5-H). Product **4** was used in the Stille coupling without further purification.

3.3.2. Synthesis of 5-dicyanovinyl-2,2′-bithiophene 5. A degassed solution of the 5-bromo-2-dicyanovinylthiophene **2c** (0.66 g, 2.8 mmol), the thienylstananne **4** (3.07 mmol) and Pd(PPh$_3$)$_4$ (0.056 mmol) in toluene (5 ml) was heated at 80 °C under argon. After 24 h the reaction mixture was cooled to room temperature, filtered and washed with a cold mixture of ether/petrol to give the pure 5-dicyanovinyl-2,2′-bithiophene **5** as a pale orange solid. The organic solution obtained from the filtration was washed with a saturated solution of KF (3×50 ml), water (3×50 ml) and a saturated solution of NaCl (100 ml). The resulting organic layer were dried with magnesium sulfate, and the solvent was removed in vacuo to give a brown oil. Overall yield: 55%. Recrystallization from n-hexane gave the pure 5-dicyanovinyl-2,2″-bithiophene **5** as a pale orange solid. Mp: 166.5–168.5 °C. IR (nujol) ν 2218 (CN) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.18–7.22 (m, 1H, 4′-H), 7.62 (d, 1H, J=4.5 Hz, 3-H), 7.67 (dd, 1H, J=3.8, 1.0 Hz, 3′-H), 7.78 (dd, 1H, J=5.0, 1.0 Hz, 5′-H), 7.89 (d, 1H, J=4.5 Hz, 3-H), 8.64 (s, 1H, CH=C(CN)$_2$).

3.3.3. Synthesis of 5′-bromo-5-dicyanovinyl-2,2′-bithiophene 6. To a stirred solution of 5-dicyanovinyl-2,2′-bithiophene **5** (0.1 g, 0.41 mmol) in a 1:1 (v/v) solution of chloroform–acetic acid (12 ml) was added NBS (0.073 g, 0.41 mmol) at rt. After 24 h the reaction mixture was washed with water (30 ml). The organic layer was dried with magnesium sulfate, and the solvent was removed in

vacuo to give the pure bithiophene **6** as a orange brownish solid (85%). Recrystallization from *n*-hexane gave the title compound as a pale orange solid. Mp: 193–195 °C. UV (acetonitrile): λ_{max} nm (ε, /M^{-1} cm^{-1}) 421.0 (21,290), 308.0 (240). IR (nujol) ν 2222 (CN) cm^{-1}. ^{1}H NMR (DMSO) δ 7.35 (d, 1H, J=4.2 Hz, 3′-H), 7.53 (d, 1H, J=4.2 Hz, 4′-H), 7.61 (d, 1H, J=4.5 Hz, 3-H), 7.88 (d, 1H, J=4.5 Hz, 4-H), 8.65 (s, 1H, C*H*=C(CN)$_2$). MS (EI) *m*/*z* (%): 322 (M^{+81}Br, 99), 320 (M^{+79}Br, 100). HRMS: *m*/*z* (EI) for $C_{12}H_5{}^{81}BrN_2S_2$; calcd 321.9057; found: 321.9058.

3.4. General procedure for the synthesis of 2-alkoxy- and 2-amino-substituted 5-(tri-*n*-butylstannyl)-2,2′-bithiophenes 8a–d

Under Ar a solution of *n*-BuLi in hexanes (1.3 ml, 3.21 mmol, 2.5 M) was dropped into a stirred solution of **7** (2.7 mmol) in dry ether at 0 °C. After 1 h the mixture was cooled to −78 °C and a solution of tri-*n*-butylchlorostannane (2.7 mmol) in dry ether was slowly added and the mixture was stirred overnight. The mixture was then added to water (50 ml). The aqueous layer was extracted with ether (3×30 ml). The combined organic layers were dried with magnesium sulfate, and the solvent was removed in vacuo to give product **8**. Derivatives **8a–d** were used in the Stille couplings without further purification.

3.4.1. 5-Methoxy-5′-(tri-*n*-butylstannyl)-2,2′-bithiophene 8a. Green oil (85%). ^{1}H NMR ($CDCl_3$) δ 0.80–1.00 (m, 15H, 3×$(CH_2)_2CH_2CH_3$), 1.20–1.40 (m, 12H, 3×$(CH_2)_2CH_2CH_3$), 3.90 (s, 3H, OCH_3), 5.80 (d, 1H, J=3.9 Hz, 4-H), 6.87 (d, 1H, J=3.9 Hz, 3-H), 7.00 (d, 1H, J=3.6 Hz, 3′-H), 7.07 (d, 1H, J=3.6 Hz, 4′-H).

3.4.2. 5-*N*,*N*-Dimethylamino-5′-(tri-*n*-butylstannyl)-2,2′-bithiophene 8b. Orange oil (90%). ^{1}H NMR ($CDCl_3$) δ 0.80–1.00 (m, 15H, 3×$(CH_2)_2CH_2CH_3$), 1.10–1.45 (m, 12H, 3×$(CH_2)_2CH_2CH_3$), 2.93 (6H, s, $N(CH_3)_2$), 5.80 (d, 1H, J=3.7 Hz, 4-H), 6.87 (d, 1H, J=3.7 Hz, 3-H), 7.00 (d, 1H, J=3.5 Hz, 4′-H) 7.07 (d, 1H, J=3.5 Hz, 3′-H).

3.4.3. 5-*N*,*N*-Diethylamino-5′-(tri-*n*-butylstannyl)-2,2′-bithiophene 8c. Pale brown oil (90%). ^{1}H NMR ($CDCl_3$) δ 0.80–1.00 (m, 15H, 3×$(CH_2)_2CH_2CH_3$), 1.10–1.45 (m, 12H, 3×$(CH_2)_2CH_2CH_3$), 1.20–1.30 (overlapped t, 6H, 2×CH_2CH_3), 3.25–3.35 (q, 4H, J=6.0 Hz, 2×CH_2CH_3), 5.78 (d, 1H, J=3.9 Hz, 4-H), 6.86 (d, 1H, J=3.9 Hz, 3-H), 7.00 (d, 1H, J=3.6 Hz, 4′-H) 7.05 (d, 1H, J=3.6 Hz, 3′-H).

3.4.4. 5-Piperidino-5′-(tri-*n*-butylstannyl)-2,2′-bithiophene 8d. Pale brown oil (81%). ^{1}H NMR ($CDCl_3$) δ 0.80–1.00 (m, 15H, 3×$(CH_2)_2CH_2CH_3$), 1.20–1.40 (m, 12H, 3×$(CH_2)_2CH_2CH_3$), 1.50–1.80 (m, 6H, 3×CH_2), 3.10–3.20 (m, 4H, 2×NCH_2), 5.98 (d, 1H, J=3.9 Hz, 4-H), 6.86 (d, 1H, J=3.9 Hz, 3-H), 7.00 (d, 1H, J=3.6 Hz, 4′-H) 7.08 (d, 1H, J=3.6 Hz, 3′-H).

3.5. General procedure for palladium-catalyzed cross-couplings of aryl 1a–b, 1d and heteroaryl bromides 2a–c and 6 with stannylbithiophene derivatives 8a–d

To a degassed solution of aryl **1a–b** and **1d**, thienyl **2a–c** or bithienyl **6** bromides (0.5 mmol), and bithienylstanannes **8a–d** (0.55 mmol) in toluene (5 ml) was added $Pd(PPh_3)_4$ (0.01 mmol). The mixture was heated at 80 °C under argon. After the given reactions times (TLC control, Table 1) the reaction mixture was cooled to room temperature and then filtered and washed with cold toluene to give the pure oligothiophenes **9d**, **10a–d**, **11d**, **12b** and **13d–16d**. The isolated solids were recrystallized. The organic solution obtained from the filtration was washed with a saturated solution of KF (3×30 ml), water (3×30 ml) and a saturated solution of NaCl (50 ml). The resulting organic layers were dried with magnesium sulfate, and the solvent was removed in vacuo to give oils which by ^{1}NMR reveal to be the stannanes derivatives used in excess.

3.5.1. 5′-(4″-Cyanophenyl)-5-piperidino-2,2′-bithiophene 9d. Orange solid (43%). Mp: 227–229 °C (ether). UV (EtOH): λ_{max} nm (ε, /M^{-1} cm^{-1}) 420.0 (18,660), 297.0 (7450), 255.0 s (8430), 239.0 (11,130), 215.0 s (13,340). IR (nujol) ν 2219 (CN) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.50–1.80 (m, 6H, 3×CH_2), 3.10–3.20 (m, 4H, 2×NCH_2), 6.00 (d, 1H, J=3.9 Hz, 4-H), 6.92–6.98 (m, 2H, 3 and 3′-H), 7.30 (d, 1H, J=4.2 Hz, 4′-H), 7.63 (br s, 4H, 4×Ar-*H*). MS (EI) *m*/*z* (%): 350 (M^+, 100). HRMS: *m*/*z* (EI) for $C_{20}H_{18}N_2S_2$; calcd 350.0911; found: 350.0916.

3.5.2. 5-Methoxy-5′-(4″-nitrophenyl)-2,2′-bithiophene 10a. Orange solid (65%). Mp: 169–171 °C (ether). UV (EtOH): λ_{max} nm (ε, /M^{-1} cm^{-1}) 413.0 (25,750), 289.0 (8680), 252.0 (1450), 213.0 s (1810). IR (nujol) ν 1593, 1531, 1505, 1351, 1200, 1158, 1111, 1048, 846, 800, 772, 749, 721, 666 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.94 (s, 3H, OCH_3), 6.18 (d, 1H, J=3.9 Hz, 4-H), 6.91 (d, 1H, J=3.9 Hz, 3-H), 7.03 (d, 1H, J=3.9 Hz, 3′-H), 7.37 (d, 1H, J=3.9 Hz, 4′-H), 7.70 (d, 2H, J=9.0 Hz, 2″ and 6″-H), 8.23 (d, 2H, J=9.0 Hz, 3″ and 5″-H). MS (EI) *m*/*z* (%): 317 (M^+, 44). Anal. calcd for $C_{15}H_{11}NO_3S_2$: C, 56.76; H, 3.47; N, 4.41; S, 20.20. Found: C, 56.51; H, 3.52; N, 4.44; S, 19.80. HRMS: *m*/*z* (EI) for $C_{15}H_{11}NO_3S_2$; calcd 317.0180; found: 317.0174.

3.5.3. 5-*N*,*N*-Dimethyl-5′-(4″-nitrophenyl)-2,2′-bithiophene 10b. Orange solid (42%). Mp: 243–245 °C (ethanol). UV (EtOH): λ_{max} nm (ε, /M^{-1} cm^{-1}) 461.0 (10,050), 322.0 (4650), 264.0 (5140), 211.0 s (8540). IR (nujol) ν 1592, 1563, 1534, 1504, 1450, 1425, 1331, 1278, 110, 1056, 919, 848, 795, 748, 688, 666 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.98 (s, 6H, 2×CH_3), 5.81 (d, 1H, J=3.9 Hz, 4-H), 6.94 (d, 1H, J=3.9 Hz, 3-H), 6.96 (d, 1H, J=3.9 Hz, 3′-H), 7.35 (d, 1H, J=3.9 Hz, 4′-H), 7.65 (d, 2H, J=8.9 Hz, 2″ and 6″-H), 8.20 (d, 2H, J=8.9 Hz, 3″ and 5″-H). MS (EI) *m*/*z* (%): 330 (M^+, 100). HRMS: *m*/*z* (EI) for $C_{16}H_{14}N_2O_2S_2$; calcd 330.0497; found: 330.0505.

3.5.4. 5-*N*,*N*-Diethyl-5′-(4″-nitrophenyl)-2,2′-bithiophene 10c. Dark red solid (44%). Mp: 181–183 °C (ethanol). UV (EtOH): λ_{max} nm (ε, /M^{-1} cm^{-1}) 474.5 (16,800), 360.0 (9630), 265.0 (7140). IR (nujol) ν 1591, 1504, 1332, 1280, 1183, 1108, 1057, 847, 791, 750, 722, 666 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.24 (t, 6H, J=7.0 Hz, 2×CH_2CH_3), 3.34 (q, 4H, J=7.0 Hz, 2×CH_2CH_3), 5.79 (d, 1H, J=3.9 Hz, 4-H), 6.92 (d, 1H, J=3.9 Hz, 3-H), 6.98 (d, 1H, J=3.9 Hz, 3′-H), 7.35 (d, 1H, J=3.9 Hz, 4′-H), 7.66 (d, 2H, J=9.0 Hz, 2″ and

6″-H), 8.21 (d, 2H, *J*=9.0 Hz, 3″ and 5″-H). MS (EI) *m/z* (%): 358 (M^+, 100). HRMS: *m/z* (EI) for $C_{18}H_{18}N_2O_2S_2$; calcd 358.0810; found: 358.0810.

3.5.5. 5-Piperidino-5′-(4″-nitrophenyl)-2,2′-bithiophene 10d. Brown solid (53%). Mp: 238–240 °C (ethanol). UV (EtOH): λ_{max} nm (ε, /M^{-1} cm^{-1}) 453.0 (10,000), 322.0 (4720), 316.0 (4710), 266.0 (4700), 213.0 s (8611). IR (nujol) ν 1592, 1504, 1493, 1329, 1275, 1247, 1117, 1066, 843, 796, 686, 666 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.50–1.80 (m, 6H, 3×CH_2), 3.16–3.20 (m, 4H, 2×NCH_2), 5.99 (d, 1H, *J*=3.9 Hz, 4-H), 6.95–6.98 (m, 2H, 3 and 3′-H), 7.35 (d, 1H, *J*=3.9 Hz, 4′-H), 7.66 (d, 2H, *J*=8.9 Hz, 2″ and 6″-H), 8.21 (d, 2H, *J*=8.9 Hz, 3″ and 5″-H). MS (EI) *m/z* (%): 370 (M^+, 100). HRMS: *m/z* (EI) for $C_{19}H_{18}N_2O_2S_2$; calcd 370.0810; found: 370.0814.

3.5.6. 5′-(4″-Dicyanovinylphenyl)-5-piperidino-2,2′-bithiophene 11d. Green solid with metal luster (56%). Mp: 232–233 °C. UV (ethanol): λ_{max} nm (ε, /M^{-1} cm^{-1}) 468.0 (21,400), 360.5 (13,386). IR (nujol) ν 2223 (CN). cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 1.45–1.70 (m, 6H, 3×CH_2), 3.10–3.20 (m, 4H, 2×NCH_2), 6.11 (d, 1H, *J*=4.5 Hz, 4-H), 7.08–7.14 (m, 2H, 3 and 3′-H), 7.69 (d, 1H, *J*=3.9 Hz, 4′-H), 7.90 (d, 2H, *J*=8.4 Hz, 2″ and 6″-H), 7.96 (d, 2H, *J*=8.4 Hz, 3″ and 5″-H), 8.44 (s, 1H, *CH*=C(CN)$_2$). MS (EI) *m/z* (%): 401 (M^+, 100). HRMS: *m/z* (EI) for $C_{23}H_{19}N_3S_2$; calcd 401.1020; found: 401.1022.

3.5.7. 5″-Formyl-5-*N*,*N*-dimethyl-2,2′:5′2″-terthiophene 12b. Brown solid (46%). Mp: 186–188 °C (ethanol) [lit.[41] (mp not quoted)]. UV (EtOH): λ_{max} nm (ε, /M^{-1} cm^{-1}) 465.5 (22,690), 342.0 (9300), 258.0 (12,010), 213.0 s (14,100). IR (nujol) ν 1650 (CHO) cm^{-1}. ^{1}H NMR δ 2.98 (s, 6H, 2×CH_3), 5.80 (d, 1H, *J*=4.4 Hz, 4-H), 6.87 (d, 1H, *J*=4.4 Hz, 4′ or 3′-H), 6.96 (d, 1H, *J*=3.9 Hz, 3-H), 7.17 (d, 1H, *J*=4.4 Hz, 3″-H), 7.22 (d, 1H, *J*=4.4 Hz, 3′ or 4′-H), 7.65 (d, 1H, *J*=4.4 Hz, 4″-H), 9.84 (s, 1H, C*H*O). MS (EI) *m/z* (%): 319 (M^+, 100). HRMS: *m/z* (EI) for $C_{15}H_{13}NOS_3$; calcd 319.0159; found: 319.0156.

3.5.8. 5″-Formyl-5-piperidino-2,2′:5′2″-terthiophene 13d. Brown solid (51%). Mp: 178–180 °C (ether). UV (EtOH): λ_{max} nm (ε, /M^{-1} cm^{-1}) 456.0 (15,260), 332.0 (6000), 257.0 (7570). IR (nujol) ν 1645 (CHO) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 1.50–1.70 (m, 6H, 3×CH_2), 3.05–3.15 (m, 4H, 2×NCH_2) 6.10 (d, 1H, *J*=4.2 Hz, 4-H), 7.05 (d, 1H, *J*=3.9 Hz, 4′-H), 7.09 (d, 1H, *J*=4.2 Hz, 3-H), 7.45 (d, 1H, *J*=4.2 Hz, 3″-H), 7.48 (d, 1H, *J*=3.9 Hz, 3′-H), 7.96 (d, 1H, *J*=4.2 Hz, 4″-H), 9.84 (s, 1H, C*H*O). MS (EI) *m/z* (%): 359 (M^+, 100). HRMS: *m/z* (EI) for $C_{18}H_{17}NOS_3$; calcd 359.0472; found: 359.0482.

3.5.9. 5″-Nitro-5-piperidino-2,2′:5′2″-terthiophene 14d. Dark red solid (53%). Mp: 215–217 °C (ether). UV (EtOH): λ_{max} nm (ε, /M^{-1} cm^{-1}) 504.0 (10,100), 355.0 (2510), 219.0 (4350). IR (nujol) ν 1559, 1509, 1482, 1325, 1274, 1244, 1120, 1074, 1035, 852, 793, 759, 730, 666 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 1.50–1.80 (m, 6H, 3×CH_2), 3.17–3.22 (m, 4H, 2×NCH_2), 5.99 (d, 1H, *J*=3.9 Hz, 4-H), 6.89 (d, 1H, *J*=3.6 Hz, 4′ or 3′-H), 6.97 (d, 1H, *J*=3.9 Hz, 3-H), 7.00 (d, 1H, *J*=4.5 Hz, 3″-H), 7.24 (d, 1H, *J*=3.6 Hz, 3′ or 4′-H), 7.83 (d, 1H, *J*=4.5 Hz, 4″). MS (EI) *m/z* (%): 376 (M^+, 100). HRMS: *m/z* (EI) for $C_{17}H_{16}N_2O_2S_3$; calcd 376.0374; found: 376.0363.

3.5.10. 5″-Dicyanovinyl-5-piperidino-2,2′:5′,2″-terthiophene 15d. Dark purple solid (55%). Mp: 185–187 °C. UV (EtOH): λ_{max} nm (ε, /M^{-1} cm^{-1}) (Ethanol) 545.5 (23,770), 377.0 (10,992). IR (nujol) ν 2218 (CN) cm^{-1}. ^{1}H NMR (DMSO-d_6) 1.50–1.70 (m, 6H, 3×CH_2), 3.10–3.20 (m, 4H, 2×NCH_2), 6.13 (d, 1H, *J*=4.2 Hz, 4-H), 7.09 (d, 1H, *J*=3.9 Hz, 4′ or 3′-H), 7.17 (d, 1H, *J*=4.2 Hz, 3-H), 7.55 (d, 1H, *J*=4.2 Hz, 3″-H), 7.59 (d, 1H, *J*=3.9 Hz, 3′ or 4′-H), 7.86 (d, 1H, *J*=4.2 Hz, 4″-H), 8.57 (s, 1H, *CH*=C(CN)$_2$). MS (EI) *m/z* (%): 407 (M^+, 100). HRMS: *m/z* (EI) for $C_{21}H_{17}N_3S_3$; calcd 407.0585; found: 407.0594.

3.5.11. 5‴-Dicyanovinyl-5-piperidino-2,2′:5′,2″:5″,2‴-tetrathiophene 16d. Dark blue solid (45%). Mp: >230.0 °C (with decomposition). λ_{max} nm (ε, /M^{-1} cm^{-1}) (Ethanol) 510.5 (12,000). IR (nujol) ν 2218 (CN) cm^{-1}. ^{1}H NMR (DMSO-d_6) 1.42–1.70 (m, 6H, 3×CH_2), 3.10–3.20 (m, 4H, 2×NCH_2), 6.10 (d, 1H, *J*=4.2 Hz, 4-H), 7.05 (d, 1H, *J*=4.2 Hz, 4′ or 3′-H), 7.16 (d, 1H, *J*=4.2 Hz, 3-H), 7.34–7.38 (m, 2H, 3′ or 4′-H and 3″-H or 4″-H), 7.64 (d, 1H, *J*=4.2 Hz, 3‴-H), 7.67 (d, 1H, *J*=4.2 Hz, 4″or 3″-H), 7.89 (d, 1H, *J*=4.2 Hz, 4‴-H), 8.62 (s, 1H, *CH*=C(CN)$_2$). MS (EI) *m/z* (%): 489 (M^+, 100). HRMS: *m/z* (EI) for $C_{25}H_{19}N_3S_4$; calcd 489.0462; found: 489.0465.

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