J. Org. Chem. **1995**, *60*, 2082−2091

Synthesis and Solvatochromic Properties of Donor−Acceptor-Substituted Oligothiophenes

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Received October 21, 1994⊗

The Pd-catalyzed cross coupling reaction of electron donor-substituted thiophenes **1** with electron acceptor-substituted halothiophenes **2**,**10** via organozinc intermediates or organotin compounds **5** to give bi-, ter-, and quaterthiophenes **3**, **4**, **6**, **8**, **12**, **13**, and **14** is described. (Dimethylamino)-bithiophenes **8** with acceptor groups of varying reactivity were prepared via **5d** in 60−80% yield, whereas bithiophenes **6d,e** were obtained as a mixture with phenylthiophenes **7d,e**. Symmetrical substituted byproducts **11** were formed in the conversion of **1b** with bromothiophenes **10** via organozinc compounds yielding oligothiophenes **6b** and **12**. The ter- and quaterthiophenes **13** and **14** were isolated in about 50−70% yield. The electronic interactions between donor and acceptor end groups in the conjugated bithiophenes **3**, **4**, and **8** are expressed in the intensive and markedly solvatochromic CT transitions. The solvatochromic behavior of **3**, **4**, and **8** was determined by linear regression analyses of absorption maxima in 11 solvents, whereby bithiophene **3d** was found to be a very appropriate indicator dye whose absorption wavenumbers $\tilde{\nu}_{max}(\mathbf{3d})$ in aliphatic and dipolar aprotic and—on consideration of the polarizability correction term $d\delta$—in aromatic and chlorinated solvents excellently correlate with the π^* values defined by Kamlet and Taft.

Introduction

For the empirical determination of solvent parameters the solvatochromism of special organic compounds which can be easily quantified by UV−vis spectroscopy is particularly suitable.[2] Of the many types of compounds studied, three have proven to be particularly good model compounds for this purpose because of their pronounced solvatochromic properties: (a) Kosower developed and proposed *Z* values, obtained from the solvent dependent charge transfer (CT) transitions in pyridinium compounds,[3] (b) Dimroth, Reichardt, et al. defined $E_T(30)$ values obtained from the longest wavelength absorption of pyridinium *N*-phenoxides,[4] and (c) Taft, Kamlet, et al. defined the π^* values derived from the long-wavelength absorption of donor−acceptor-substituted benzenes and styrenes.[5]

In solvents of higher polarity the application of pyridinium compounds (*Z* values) is considerably restricted since the CT transition overlaps with the strong $\pi-\pi^*$ absorption. A disadvantage of the $E_T(30)$ values is that the pyridinium *N*-phenoxides normally are strongly basic[6] and can therefore give a specific interaction with protic and Lewis acid solvents.[7] The pyridinium compounds as well as the pyridinium *N*-phenoxides show negative solvatochromism. Dyes displaying positive solvatochromism (bathochromic shifts of the absorption band with increasing solvent polarity) show smaller specific interactions and are therefore generally better suited for the description of solvent polarity parameters in terms of unspecific interactions. Hitherto no universally applicable positive solvatochromic dye is known. The π^* values were obtained from the solvatochromic behavior of seven standard and about 40 auxiliary compounds and defined as an "averaged" π^* scale by Kamlet and Taft. Although this scale in essence reproduces the stabilization of the excited state by electrostatic interactions correctly, in contrast to the $E_T(30)$ and *Z* scales it has no clear and well-understood reference process as basis.[8] The merocyanine dye upon which the χ_R scale is based[9] exhibits positive solvatochromism, but here also specific interactions with protic solvents lead to an additional bathochromic shift that is not caused by the solvent polarity.

In recent years we have studied the photophysical properties of donor−acceptor-substituted polyenes from a fundamental view and for their application in molecular electronics.[10] Since the thermal and photochemical stability of polyenes is inadequate we have extended our investigations to oligothiophenes as conjugated π systems. For thiophene oligomers and polymers the application in electronic devices has already been demonstrated.[11]

In a communication[12] we have reported on the preparation of 5-(dimethylamino)-5′-nitro-2,2′-bithiophene and

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⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1995.

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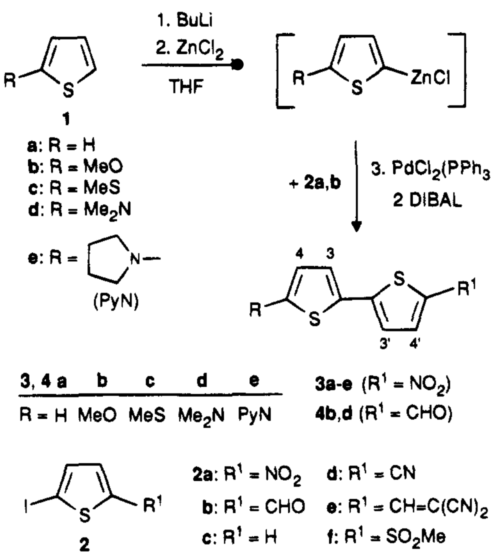
Scheme 1



its pronounced positive solvatochromism which is almost exclusively based on unspecific solvatation interactions and therefore universally applicable to all types of solvents. In the present publication the synthesis of donor−acceptor-substituted bi-, ter-, and quaterthiophenes is described and their solvatochromic properties are discussed.

Results and Discussion

Synthesis of Bithiophenes 3 and 4. The donor−acceptor-substituted bithiophenes **3** and **4** were prepared by Pd(0)-catalyzed cross coupling reactions[13] via zinc-substituted thiophenes. In the first step the donor-substituted thiophenes **1a−e** were lithiated with *n*-BuLi at 0−20 °C. The organolithium compounds were converted with $ZnCl_2$ to the corresponding organozinc compounds which react under Pd(0) catalysis with the acceptor ($R^1 = NO_2$ or CHO)-substituted iodothiophenes **2a,b** to give the bithiophenes **3a-e** and **4b,d** (Scheme 1, Table 1). The catalyst was obtained in situ from $PdCl_2(PPh_3)_2$[14] by reduction with diisobutylaluminum hydride (DIBAL).

Compounds **3a-c** were obtained with yields between 80 and 90% in reaction times of 2−4 h at room temperature (Table 1). On the contrary, the yields for the amino-substituted bithiophenes **3d,e** markedly decrease to 20−25% even in presence of higher amounts of the catalyst (5 mol %) (Table 1). This is due to various side reactions of the organozinc compounds to highly polar and nonisolable byproducts. The same tendency of decreasing yield was observed for formylbithiophene **4d** in comparison with **4b** (Table 1). Moreover, the yield of **4d** was influenced in addition by the lower reactivity of **2b** in comparison with **2a**. The influence of the reactivity of the halide acceptor component was further demonstrated by coupling **1e** with the extremely reactive 2,4-dinitroiodobenzene to give 2-(2,4-dinitrophenyl)-5-pyrrolidinothiophene in 53% yield. From these results it is obvious that the donor as well as the acceptor influence the yield of the cross coupling reactions.

Table 1. Preparation of Bithiophenes 3, 4, 6, and 8 from 1 via the Corresponding Organozinc or Organotin Compounds by Palladium-Catalyzed Coupling Reaction

educts		catalyst[a]	product			
1	2	(mol%)	3, 4, 6, 8	yield[b] (%)	yield[c] (%)	mp (°C)
a	**a**	1	**3a**	80		114[d]
b	**a**	1	**3b**	84		121−122
c	**a**	1	**3c**	87		128
d	**a**	5 (3)[c]	**3d**	20	70	176−177
e	**a**	5 (5)[c]	**3e**	25	82	185−186
b	**b**	1	**4b**	70		55−57
d	**b**	5 (5)[c]	**4d**	8	60	114−115
d	**c**	(5)[c]	**6d**		41[e]	
e	**c**	(5)[c]	**6e**		43[f]	
d	**d**	(5)[c]	**8a**		61	130−131
d	**e**	(5)[c]	**8b**		70	241−242
d	**f**	(5)[c]	**8c**		58	170−171

[a] Related to **1**. [b] Preparation via organozinc compounds by Pd-catalyzed reaction. [c] Catalyst amount and preparation via organotin compounds by Pd-catalyzed reaction. [d] Lit.[15] mp 105−107 °C. [e] Mixture of **6d** and 2-(dimethylamino)-5-phenylthiophene (**7d**) (70:30, determined by ^1H NMR). [f] Mixture of **6e** and 2-phenyl-5-pyrrolidinothiophene (**7e**) (70:30, determined by HPLC and ^1H NMR).

Bithiophenes 3 and 4 via Organotin Compounds 5. We expected an improvement of yields in the preparation of **3d,e** and **4d** by substitution of zinc in the organometallic compounds by boron or tin to give less reactive organometallic components with the hope to avoid side reactions. The synthesis of organoboron compounds, however, failed. The conversion of lithiated **1d** with an excess of boron acid trimethyl ester at −70 °C only gave the starting thiophene **1d** because of protodeboronation during aqueous workup.

Excellent results, however, have been received by using organotin compounds instead of the zinc derivatives[16] (Table 1, Scheme 2). The thiophenes **1d,e** were lithiated with *n*-BuLi at room temperature followed by transmetalation with trimethyltin chloride at −70 °C to give the organotin compounds **5d,e** which could be isolated in 83% yield each after distillation. **5d, e** are fairly insensitive to oxygen and hydrolysis on air. At 60 °C **5d,e** were coupled with the iodothiophene **2a** under $PdCl_2(PPh_3)_2$[14] catalysis to the bithiophenes **3d,e** in 70−82% (Table 1). Similarly, the yield of **4d** was raised from 8% in the zinc-mediated coupling to 60% in the reaction of **2b** with **5d** (Table 1).

Bithiophenes 6 and 8 via Organotin Compounds 5. On the basis of these excellent results we extended the Pd(II)-catalyzed cross coupling reaction of **5d,e** to the synthesis of the bithiophenes **6** and **8** with acceptor groups varying in reactivity (Table 1, Scheme 2).

Analogous to the nitro- and formyl-substituted bithiophenes **3** and **4**, yields of the bithiophenes **8a-c** depend on the reactivity of the acceptor iodothiophenes **2d-f** giving the highest yield with **2e** since the dicyanovinyl group has the highest acceptor strength and the lowest yield with **2c** with hydrogen as substituent.

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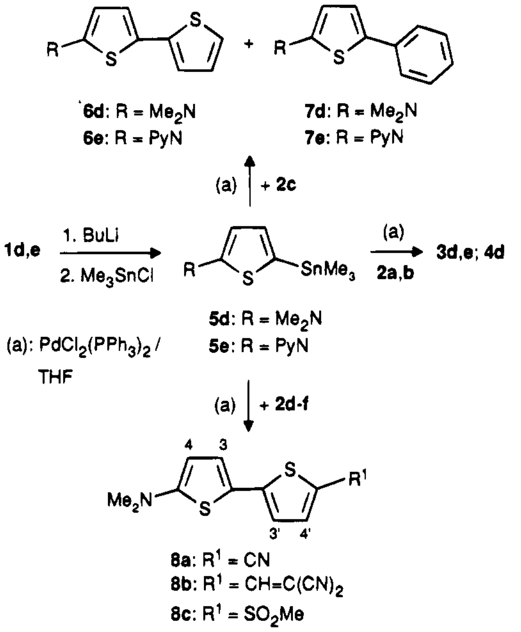
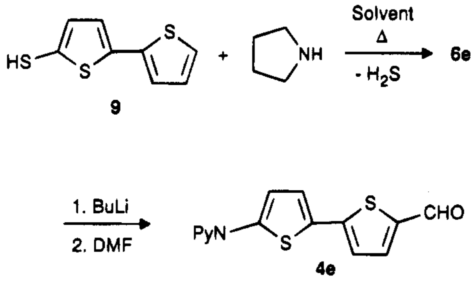
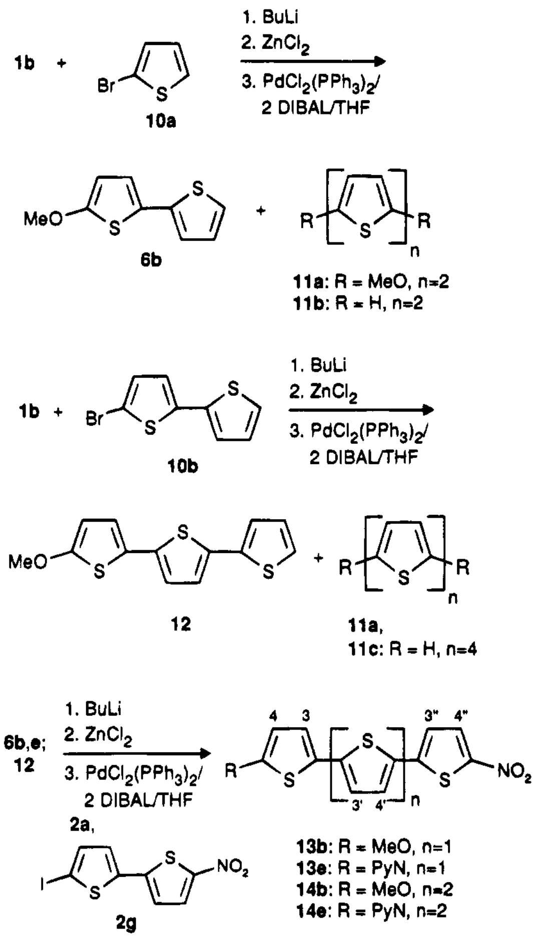
Scheme 2



Scheme 3



Scheme 4



In the coupling reaction of **5d,e** with **2c**, in addition to the bithiophenes **6d,e** the phenylthiophenes **7d,e** were obtained in a ratio **6**:**7** = 70:30 (determined by HPLC and ^{1}H NMR) (Scheme 2, Table 1). Obviously, these byproducts were formed by reaction of **5d,e** with the catalyst. Phenyl migration is a rarely observed side reaction in Pd-catalyzed cross coupling reactions, but some examples have already been described in the literature.[17] Neither by chromatography nor by recrystallization could **6** and **7** be separated. For unambiguous characterization the mixture **6e**/**7e** was lithiated with *n*-BuLi and subsequently formylated with DMF to give **4e** (R = PyN, R^1 = CHO) and **7e**, respectively, which easily could be separated by column chromatography. 2-(Dimethylamino)-5-phenylthiophene (**7d**) was not isolated but characterized by ^{1}H NMR and mass spectroscopy.

An alternative route to **6e** starting from 5-mercapto-2,2′-bithiophene (**9**) is outlined in Scheme 3. **9** was obtained from 2,2′-bithiophene by lithiation with *n*-BuLi at −50 °C followed by reaction with sulfur in 40% yield.[18] The rather low yield is caused by air oxidation of **9** to disulfides[19] and dimerization to sulfides under H_2S elimination during distillation. Pure **9**, which is stable under inert gas, reacts with pyrrolidine either in boiling toluene or boiling xylene to give **6e** in 25 and 37% yield, respectively (Scheme 3). In toluene a substantial amount of bis(2,2′-bithienyl-5-yl) disulfide is formed from unreacted **9** by oxidation during workup.

The bithiophene **4e** was prepared by lithiation of 5-pyrrolidinobithiophene **6e** and subsequent formylation with DMF in 62% yield (Scheme 3).

Preparation of Ter- and Quaterthiophenes 13 and 14. The oligothiophenes **13b,e** and **14b,e** were synthesized starting from the donor-substituted bi- or terthiophenes. The methoxy-substituted oligothiophenes **6b** and **12** were prepared by Pd(0)-catalyzed coupling reaction of **1b** with the bromothiophenes **10a** and **b**[20] (Scheme 4, Table 2).

The use of the nonactivated acceptor-free bromothiophenes **10**, however, leads again to a decrease of the cross-coupling product and to the formation of the symmetrical products **11a**/**11b** and **11a**/**11c**, respectively, in isolated yields of up to 20%. Similar distributions of unsymmetrical (**6b**, **12**) and symmetrical (**11**) products have also been described for Pd-catalyzed thiophene−thiophene cross-coupling reactions using organotin[21] and organozinc compounds.[22] Obviously, symmetrical cou-

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Table 2. Palladium-Catalyzed Preparation of Bi-, Ter-, and Quaterthiophenes 6, 12, 13, and 14 via Organozinc Compounds

educts		catalyst[a] (mol%)	THF (mL)	reaction time (h)	products **12−14**	yield (%)	mp (°C)
1, 6, 12	**2, 10**						
1b	**10a**	1.0	150	24	**6b**	43	*b*
1b	**10b**[c]	5.0	80	3	**12**	53	101−103
6b	**2a**	1.3	50	2−4	**13b**	73	164−165
12	**2a**	1.5	50	5	**14b**	74	199−201
6e	**2a**	5.0	40	2−4	**13e**	48	222
6e	**2g**	5.0	45	4	**14e**	55	>264 dec

[a] Related to **1**, **6**, or **12**. [b] Yellow oil, bp 90 °C/0.1 Torr. [c] Reference 20.

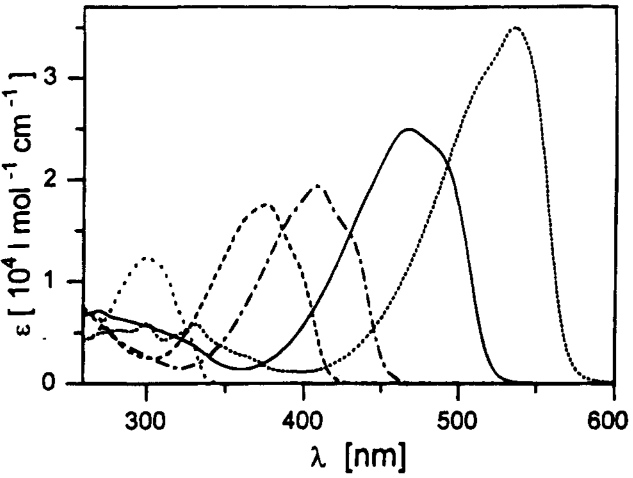

Figure 1. UV−vis absorption spectra of bithiophene (···) in comparison with the donor−acceptor-substituted bithiophenes **3a** (- - -), **3b** (− • −), and **3d** (—) in *n*-hexane and **8b** (···) in cyclohexane at 20 °C.

Table 3. Correlation of UV−Vis Absorption Maxima of Bithiophenes 3,4,8 and Ter- or Quaterthiophenes 13,14 and Solvent Parameter π^* from Equation (1)[a]

compd	λ_{max}[b] (nm) (ϵ (L·mol^{-1}·cm^{-1}))[b]	$\tilde{\nu}_0$[c] (cm^{-1})	regression analysis	
			s[c] (cm^{-1})	r[c]
3a	375 (17 500)	26 620	−1860	−0.9886
3b	408 (19 300)	24 460	−2100	−0.9904
3c	391 (18 300)	25 420	−2200	−0.9811
3d	466 (25 000)	21 210	−3330	−0.9903
3e	499 (27 000)	20 390	−3050	−0.9871
4b	372 (22 700)	26 930	−1130	−0.9083
4d	421 (27 500)	23 650	−1900	−0.9605
4e	440 (33 100)	22 780	−1630	−0.9341
8a	398 (25 400)	25 148	−1417	−0.9853
8b	529 (35 000)[d]	18 917	−1696	−0.9787
8c	389 (22 500)	25 707	−1309	−0.9863
13b	442 (25 000)	22 700	−1540	−0.9468
14b[e]	454 (29 500)	21 990	−1150	−0.8883
13e[e]	505 (23 600)	19 710	−1990	−0.9760

[a] Applied solvents (π^* value): *n*-hexane (-0.08), diethyl ether (0.27), toluene (0.54), ethyl acetate (0.55), THF (0.58), methanol (0.60), acetone (0.71), acetonitrile (0.75), dichloromethane (0.82), DMF (0.88), formamide (1.12).[5b] [b] Absorption maxima and extinction coefficients in *n*-hexane. [c] Intercept, slope, and correlation coefficient *r* of the linear solvatation energy relationship. [d] In cyclohexane. [e] Without formamide.

pling products are always to be expected in reactions of metalated thiophenes with nonactivated acceptor-free halide thiophenes.[1a,22]

In an alternative route, **6b** was prepared in 65% yield by a CuO-catalyzed reaction[23] of sodium methanolate with 5-iodo-2,2′-bithiophene[24] which, however, is difficult to prepare and is less stable.

The terthiophenes **13b**,**e** were obtained in 73 and 48% yield (Table 2) by lithiation of the bithiophenes **6b** and **e**, transmetalation to the corresponding organozinc compounds, and subsequent Pd(0)-catalyzed reaction with **2a**. The quaterthiophene **14b** was prepared in an analogous manner from the terthiophene **12** and **2a** in 74% yield (Table 2). The quaterthiophene **14e** was obtained from bithiophene **6e** and 5-iodo-5′-nitro-2,2′-bithiophene (**2g**), which was formed in the reaction of **3a** with I_2/HgO in acetic acid in 77% yield.

Absorption spectra. Figure 1 represents the absorption spectra of the nitro-substituted bithiophenes **3a**,**b**,**d** with the donor substituents H, MeO, and Me_2N and the (dicyanovinyl)(dimethylamino)bithiophene **8b** in comparison to the unsubstituted bithiophene. The longest wavelength absorption band of these compounds is polarized along the long axis of the molecules and therefore is strongly influenced by the substituents in the 5 and 5′ positions. The bathochromic shift and the increasing intensity with rising donor and acceptor strength is consistent with a charge transfer (CT) character of this transition. Thus, the longest wavelength transition is shifted from 300 nm in bithiophene to 530 nm in **8b**, and the oscillator strength increases from 0.20 (bithiophene) to 0.39 (**8b**).

The high degree of conjugation between the donor and acceptor end groups along the conjugated bridge is also preserved in the ter- and quaterthiophenes as demonstrated by the bathochromic shift of the absorption maxima of **13b**,**e** and **14b** (Table 3) in comparison to terthiophene (λ = 351 nm) and quaterthiophene (λ = 385 nm). This behavior is typical for a pronounced conjugation between the end groups and resembles to that of donor−acceptor-substituted polyenes. On the contrary, oligophenylenes exhibit absorption maxima that maximize for bi- or terphenyls for a given donor−acceptor combination. The difference between these conjugated bridges has been explained by a reduced aromaticity of the oligothiophene which allows greater electronic interactions of the end groups (quinonoid resonance structure) as well as an enhanced π-overlap between the preferentially coplanar thiophene units in comparison to the preferentially twisted phenylene units.[12,25,26] The different degrees of planarity of these π-chain molecules are a result of the more pronounced steric interactions of the two ortho hydrogens in oligophenylenes.

As expected from the absorption spectra of Figure 1 the longest wavelength transition of all donor−acceptor-substituted oligothiophenes exhibits pronounced solvatochromism.

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[2,3] describing the solvent polarity on a molecular-microscopic level.

To evaluate the acting intermolecular forces between the solvents and the soluted molecules we have measured absorption spectra of all compounds in 11 solvents of different solvatation character. Whereas the correlation with $E_T(30)$ and *Z* values was rather poor, a good

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correlation with the π^* parameters defined and evaluated by Kamlet and Taft[5] was obtained. Table 3 summarizes the results of the linear regression analyses of absorption maxima $\bar{\nu}_{max}$ for the oligothiophenes **3**, **4**, **8**, **13**, and **14** in 11 solvents according to eq 1.

$$\bar{\nu}_{max} = \bar{\nu}_0 + s\pi^* \qquad (1)$$

The most important values of the linear relationship between $\bar{\nu}_{max}$ and π^* are the correlation coefficient r and the slope s, which describes the size of solvatochromism from $\pi^* = 0$ (cyclohexane) to $\pi^* = 1$ (DMSO). As shown from Table 3, the greatest value for s ($s = 3330$ cm^{-1}) was found for **3d**.

The correlation coefficients are very high for nitro-substituted compounds but also indicate that the π^* values do not exclude specific interactions as stated by Kamlet and Taft.[5,27] Thus, acceptors other than nitro exhibit a worse correlation to π^* values. This is easily understandable by regarding the compounds which are used by Kamlet and Taft to establish the π^* scale wherein six of the seven standard compounds contain the nitro group.

The decrease of the correlation coefficients of the ter- and quaterthiophenes **13** and **14** is probably based on a diminished size of solvatochromism and broadening of the absorption bands.

Detailed Discussion of the Solvatochromism of Bithiophene 3d. Because of the pronounced solvatochromism, the high correlation with π^* values for the 11 solvents investigated (Table 3) and the long wavelength absorption in the visible range, **3d** seemed to be a very appropriate solvent polarity indicator dye.[12] Contrary to other dyes applied,[2,3] the CT transition of **3d** shows a high intensity and is not masked by other electronic transitions as has been proved by electrooptical measurements.[25] 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 CT band.

The maxima of the wavenumbers $\bar{\nu}_{max}$ for **3d** measured in 34 solvents (four aliphatic, 11 dipolar aprotic, seven aromatic, five chlorinated, and seven hydrogen bond donor solvents) as well as the corresponding wavelength λ are listed in Table 4 in comparison with the π^* values determined by Kamlet and Taft.

The great number of aliphatic and dipolar aprotic solvents was chosen to determine the correlation behavior of $\bar{\nu}_{max}$(**3d**) and π^* because specific interactions were not expected. Indeed an excellent correlation between absorption wavenumbers of **3d** and π^* values of the corresponding solvents according to eq 2 was obtained (Table 4).

$$\bar{\nu}_{max}(\mathbf{3d}) = (21\,166\ \mathrm{cm}^{-1} - 3323\ \mathrm{cm}^{-1})\pi^* \qquad (r = 0.9979) \quad (2)$$

However, as shown in Figure 2, the aromatic and chlorinated solvents slightly deviate from this regression line. Both classes of solvents absorb at shorter wavelength than calculated on the basis of π^* values according to eq 2.

This effect depends on a changed influence of dipolarity and polarizability of the solvent in thiophene and benzene compounds and may be taken into account by a second parameter, the polarizability correction term $d\delta$,[12] which was introduced by Kamlet and Taft[27] (see eq 4).

Table 4. UV–Vis Absorption Maxima $\bar{\nu}_{max}$ and Reduced Absorption Maxima π^* of 5-(Dimethylamino)-5′-nitro-2,2′-bithiophene (3d) at 20 °C in Various Solvents in Comparison with π^* Values by Kamlet and Taft[a]

solvent	$\bar{\nu}_{max}$ (cm^{-1})	λ_{max} (nm)	π^*(**3d**)	π^*(**3d**) + 0.1δ	π^{*a}
n-pentane	21 460	466.0	−0.10	−0.10	
n-hexane	21 450	466.2	−0.10	−0.10	−0.08
cyclohexane	21 186	472.0	−0.02	−0.02	0.00
methylcyclohexane	21 190	471.9	−0.02	−0.02	
triethylamine	20 699	483.1	0.13	0.13	0.14
dibutyl ether	20 350	491.4	0.23	0.23	0.24
diethyl ether	20 161	496.0	0.29	0.29	0.27
butyl acetate	19 566	511.1	0.47	0.47	0.46
dioxane	19 732	506.8	0.42	0.52[b]	0.55
ethyl acetate	19 489	513.1	0.49	0.49	0.55
THF	19 209	520.6	0.57	0.57	0.58
acetone	18 907	528.9	0.66	0.66	0.71
acetonitrile	18 730	533.9	0.71	0.71	0.75
DMF	18 218	548.9	0.87	0.87	0.88
DMSO	17 756	563.2	1.01	1.01	1.00
2-methyl-2-propanol	19 490	513.1	0.49	0.49	0.41
n-butanol	19 357	516.6	0.53	0.53	0.47
2-propanol	19 380	516.0	0.52	0.52	0.48
ethanol	19 238	519.8	0.57	0.57	0.54
methanol	19 055	524.8	0.62	0.62	0.60
formamide	17 325	577.2	1.14	1.14	0.97/1.12[c]
formamide/H_2O 1:1	16 740	597.4	1.31	1.31	
CCl_4	20 433	489.4	0.21	0.26	0.28
trichloroethylene	19 535	511.9	0.48	0.53	0.53
chloroform	18 857	530.3	0.68	0.73	0.58/0.76[c]
dichloromethane	18 688	535.1	0.73	0.78	0.82
dichloroethane	18 636	536.8	0.74	0.79	0.81
mesitylene	19 928	501.8	0.36	0.46	0.41
o-xylene	19 680	508.1	0.43	0.53	
p-xylene	19 833	504.2	0.39	0.49	0.43
toluene	19 694	507.8	0.43	0.53	0.54
benzene	19 600	510.2	0.46	0.56	0.59
chlorobenzene	18 936	528.1	0.66	0.76	0.71
nitrobenzene	17 992	555.8	0.94	1.04	1.01

[a] Reference 5a. [b] Dioxane was treated as aromatic solvent. [c] Reference 5b.

The deviation in alcohols is oriented to longer wavelength and rises with increasing size of the aliphatic chain, e.g., the greatest deviation with $0.08\pi^*$ units is found for 2-methyl-2-propanol (Table 4). The deviation of alcohols can be interpreted either as reduced specific solvation of the amino group or as increased specific solvation of the nitro group relative to the dyes applied for the evaluation of the π^* scale.

In Table 4 the absorption wavenumbers $\bar{\nu}_{max}$(**3d**) as well as the reduced absorption wavenumbers π^*(**3d**) according to eq 3 are listed. The advantage of the

$$\pi^*(\mathbf{3d}) = \frac{\bar{\nu}_{max}^{cyclohexane} - \bar{\nu}_{max}^{solvent}}{\bar{\nu}_{max}^{cyclohexane} - \bar{\nu}_{max}^{DMSO}} = \frac{21126\ \mathrm{cm}^{-1} - \bar{\nu}_{max}^{solvent}}{3337\ \mathrm{cm}^{-1}} \qquad (3)$$

reduced wavenumbers π^*(**3d**) depends on the fact that they are directly comparable to the known π^* values. Both scales are normalized to the same range of polarity with 0.00 for cyclohexane and 1.00 for dimethyl sulfoxide (DMSO).

By introduction of the polarizability correction term $d\delta$ with a d value of −0.1 for the bithiophene **3d** and the δ values used in the literature,[5a,27] $\delta = 0$ for aliphatic and dipolar aprotic solvents, $\delta = 0.5$ for chlorinated aliphatic solvents, and $\delta = 1$ for aromatic solvents, including

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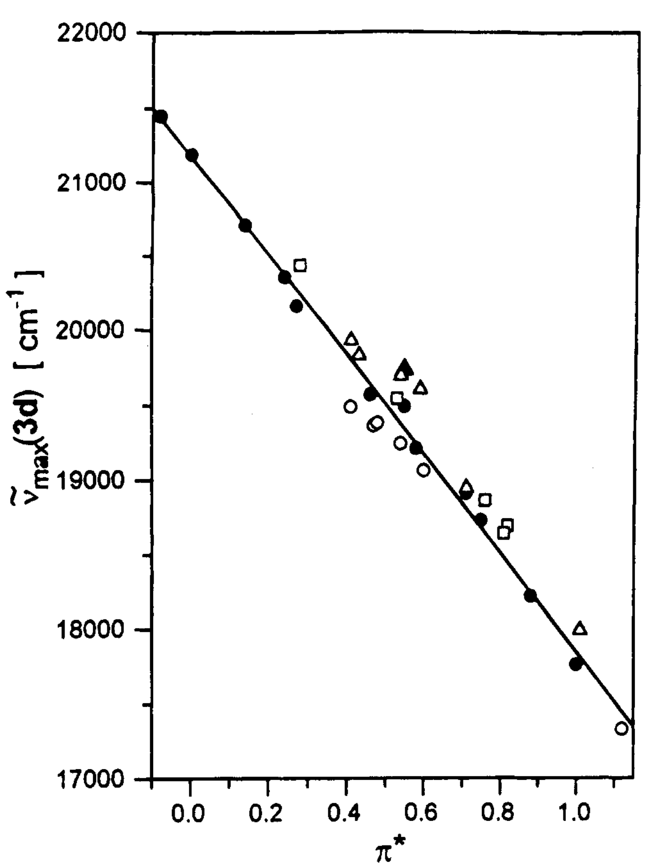

Figure 2. Correlation between absorption wavenumbers $\tilde{\nu}_{max}$(**3d**) and the π^* scale according to Kamlet and Taft. Aliphatic and dipolar aprotic solvents (●), protic solvents (○), chlorinated solvents (□), aromatic solvents (△), and dioxane (▲). The given regression line was obtained using the aliphatic and dipolar aprotic solvents (●).

dioxane, π^* values may be calculated for all types of solvent on the basis of eq 4.

$$\pi^* = \pi^*(\mathbf{3d}) + 0.1\delta \quad (r = 0.9936) \qquad (4)$$

With the excellent correlation π^* values can be determined simply and fast with only one indicator dye, (dimethylamino)nitrobithiophene (**3d**). The standard deviations are in most cases less than 0.03 π^* units, and the highest deviation is given for 2-methyl-2-propanol (0.08 π^* units) (Table 4).

Physicochemical Analysis of the Solvatochromic Behavior of 3d. In a preceding paper we have investigated the nonlinear optical properties[28] of the compounds **3**, **4**, **13**, and **14**, which demonstrate donor–acceptor-substituted oligothiophenes to be very promising candidates for application in poled polymers since they exhibit high dipole moments and very high second-order polarizabilities β.[25] Furthermore, we could show a very good correlation between experimental β values and the values calculated from solvatochromic data by the two-level model.[29] Using this method, excited state dipole moments are available by evaluating the spectral shifts of the absorption band caused by the internal field of the solvent,[30] which is treated based on the Onsager theory.[31] According to this theory only the unspecific polarization (dipolarity and polarizability) and dispersion interactions between the soluted dye molecule and the solvent environment are considered. Thus, this method should be appropriate to evaluate specific interactions of individual solvents or solvent classes which are given by the deviation from the ideal behavior. As prerequisite to apply this method, the indicator dye has to be described for a sufficient number of "ideal" solvents by the evaluation model[32] including the required simplifications, which were discussed in detail by Liptay.[32]

The solvent dependence of the wavenumber $\tilde{\nu}_{max}$ of the absorption band of **3d** was evaluated with the program SOLVDEPE, developed by Liptay,[32b] on the basis of the extended Onsager model[33] on consideration of the polarizability tensor α but neglecting dispersion interactions. The values for the main axes of bithiophene **3d** described as ellipsoid are obtained from the crystal structure[12] and consider the van-der-Waals-radii.[34] The calculation is performed according to eq 5.

$$\tilde{\nu}^{sol}_{max} = \tilde{\nu}_0 - \frac{1}{hc_0} f_z(1 - f_z\alpha_z)^{-1}(\mu_{az} - \mu_{gz})\mu_{gz} - \frac{1}{2hc_0} f'_z(1 - f'_z\alpha_z)^{-1}(\mu_{az} - \mu_{gz})^2 \quad (5)$$

whereby f_z and f'_z, which depend on the dielectric constant and the refractive index, are defined by the ellipsoidal cavity using the extended Onsager model[32,33] and α_z is the polarizability in direction of the ground and excited state dipoles μ_{gz} and μ_{az} (z coordinate = long axis of the ellipsoid).

From the values of ground state dipole moment (μ_g = 26.5 × 10^{-30} Cm),[25] polarizability (α_z = 50 × 10^{-40} C V^{-1} m^2)[35] and interaction semiaxes (a_x = 235, a_y = 335, and a_z = 745 pm, which consider 25 pm for the solvent cavity[32]) and the absorption maxima $\tilde{\nu}^{sol}_{max}$ in aliphatic and dipolar aprotic solvents, for **3d** an excited state dipole moment μ_a results (μ_a = 72.7 × 10^{-30} Cm) which completely corresponds to the value received by electrooptical absorption measurements (μ_a = 73 × 10^{-30} Cm).[25] The correlation coefficient (r = 0.9916) demonstrates that the experimental absorption wavenumbers $\tilde{\nu}_{max}$(**3d**) excellently correlate with the solvent function described by ϵ and n according to eq 5.

On the basis of this correlation, additional solvent effects other than unspecific polarization interactions can be determined by the deviation of the solvents (aromatic, chlorinated, and protic) from the ideal behavior. In Figure 3 the experimental absorption maxima $\tilde{\nu}_{exp}$ (Table 4) are plotted versus the values $\tilde{\nu}_{calc}$ calculated according to eq 5 from dielectric constant ϵ and refractive index n_D of the different solvents using the preceding values for

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(35) The polarizability tensor was obtained by AM1 calculations which were performed by K. Elich, University of Mainz.

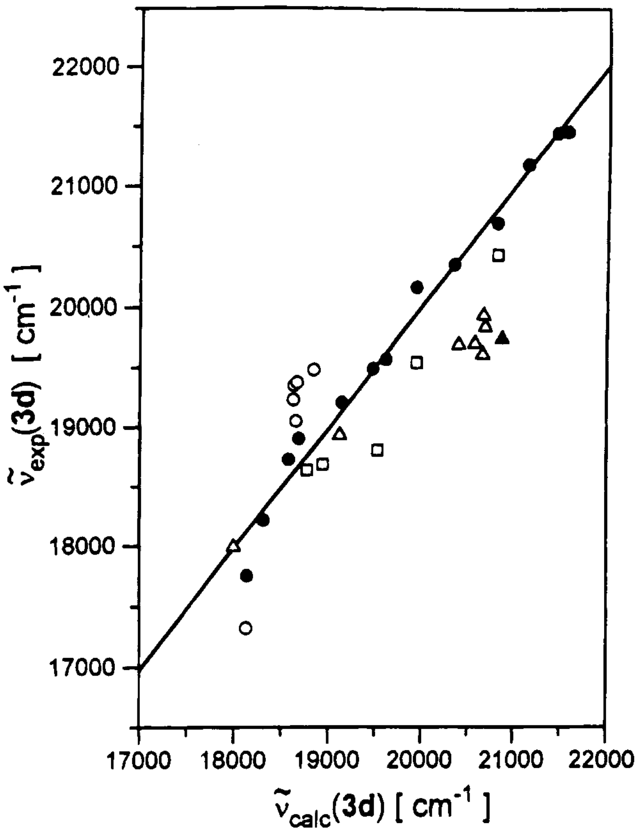

Figure 3. Experimental absorption maxima $\tilde{\nu}_{exp}$(**3d**) versus absorption maxima $\tilde{\nu}_{calc}$(**3d**) calculated according to eq 5 on consideration of μ_g (26.5 × 10^{-30} Cm), μ_a (72.7 × 10^{-30} Cm), α_z (50 × 10^{-40} C V^{-1} m^2) and interaction semiaxes (a_x = 235, a_y = 335, a_z = 745 pm, including 25 pm for the solvent cavity[32]). Aliphatic and dipolar aprotic solvents (●), protic solvents (○), and chlorinated solvents (□) as well as aromatic solvents (△) and dioxane (▲).

dipole moments, polarizability, and radii. Therein the contribution of solvatochromism, which is independent on dipolarity and polarizability, is expressed by deviation from the regression line.

Considerable deviations from the ideal behavior are found for aromatic and protic solvents whereas chlorinated solvents are fairly well described by the given model. The deviation of the aromatic solvents, including dioxane and CCl_4, is explained by an enhanced microscopic polarity caused by quadrupole and higher multipole interactions, which are not accounted for in the macroscopic permittivity ϵ. This viewpoint is confirmed by the fact that the deviations are especially high for those aromatic solvents with low dipolarity (e.g., benzene, toluene) but negligible for the more polar ones (chlorobenzene, nitrobenzene). Hence, there is no evidence for specific $\pi-\pi$ interactions between the dye molecule **3d** and aromatic solvents. Specific interactions by means of H bridges are observed for protic solvents. Thus, the absorption maxima of **3d** in all alcohols deviate from the regression line. As the deviation is given to shorter wavelength as was expected by eq 5 a weak specific solvatation of the amino group by H bridges can be assumed. From the behavior of alcohols we conclude that the π^*(**3d**) values and—in higher portion—the π^* values are indeed influenced by specific interactions with hydrogen bond donor solvents. The contribution of polarity, which is therefore undervalued by the π^* parameter, amounts to 0.14 π^* units for methanol ($\tilde{\nu}_{calc} - \tilde{\nu}_{exp}$ = 400 cm^{-1}) and 0.29 π^* units for butanols ($\tilde{\nu}_{calc} - \tilde{\nu}_{exp}$ = 700 cm^{-1}). In contrary to the explanation by Kamlet and Taft the π^* values of alcohols are affected to 20–40% by H bridge donor interactions. The amount is reduced in **3d** to 15–30%.

Formamide and formamide/water (1:1) clearly deviate in the opposite direction. The same behavior was also observed for other dyes that exhibit positive solvatochromism, e.g., *p*-(dimethylamino)nitrobenzene or *p*-(dimethylamino)nitrostilbene.[1a] Since specific interactions by H bridges may not account for these deviations we assume they are caused by structural changes of these highly associated solvents in the environment of the dye molecules.

In summary, a separation of specific and unspecific solvatation interactions based on the physicochemical analysis of solvent polaritiy is possible and the solvatochromic behavior of **3d** allows the quantification of the hydrogen bonding contribution of the protic solvents to the π^* parameters often used.

Conclusion

The described Pd-catalyzed cross coupling reaction via organozinc or organotin compounds is a general method for the synthesis of donor–acceptor-substituted oligothiophenes. If the acceptor halothiophene is not actived by an electron-withdrawing substituent, the coupling reaction is accompanied by byproducts.

Due to their pronounced solvatochromic properties donor–acceptor bithiophenes and especially aminonitro-substituted bithiophenes are suitable to investigate the solvent polarity by means of their absorption wavenumbers.

Since (dimethylamino)nitrobithiophene (**3d**) excellently correlates with the π^* values defined by Kamlet and Taft, π^* values can be determined simply and fast with only *one* indicator dye according to eqs 3 and 4.

The analysis of the solvatation of **3d** by means of evaluation according to Liptay on the basis of the extended Onsager model proved that π^* values are usable but not perfect as the solvatochromic parameter to express the nonspecific contribution of the solvent polarity.

Experimental Section

General Procedures. Melting points are uncorrected. ^{1}H NMR spectra were recorded with TMS as internal standard using a Bruker AC 250 F (250 MHz) instrument. Mass spectra were obtained with a Varian MAT 711 electron impact spectrometer at 70 eV. Preparative chromatography was carried out on columns packed with silica gel S (Riedel-de Haen, size: 0.032–0.063 mm) or silica gel 60 (Merck, size: 0.040–0.063 mm). UV–vis spectra were recorded with a Perkin-Elmer Lambda 7 spectrometer in 1 cm quartz cuvettes at 20 °C using fractionally distilled solvents dried as described in the literature[36] or UVASOL solvents (Merck).

All reactions were carried out under an argon or nitrogen atmosphere in dried glassware. All solvents were purified and dried, and the starting compounds were distilled or recrystallized.

The 2-substituted thiophenes **1** were prepared as described in the literature:[18,23,37] 2-formyl-5-iodothiophene (**2a**) and

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Table 5. Palladium-Catalyzed Preparation of Bithiophenes 3, and 4 as Well as Physical Data

1 (g) (mmol)	BuLi[a] (mL) (mmol)	$ZnCl_2$ (g) (mmol)	DIBAL[b] (mL) (mmol)	THF (mL)	**2** g (mmol)	**3, 4**	yield (g)
a 0.42 (5.0)	3.3 (5.0)	0.69 (5.0)	0.1 (0.1)	60	**a** 0.97 (3.8)	**3a**[c]	0.64
b 0.57 (5.0)	3.3 (5.0)	0.69 (5.0)	0.1 (0.1)	60	**a** 1.02 (4.0)	**3b**[d]	0.81
c 1.30 (10.0)	6.3 (10.0)	1.36 (10.0)	0.2 (0.2)	60	**a** 2.30 (9.0)	**3c**[d]	2.02
d 1.27 (10.0)	6.3 (10.0)	1.36 (10.0)	1.0 (1.0)	60	**a** 2.05 (8.0)	**3d**[e]	0.41
e 1.22 (8.0)	5.3 (8.0)	1.08 (8.0)	1.0 (1.0)	60	**a** 1.80 (7.0)	**3e**[e]	0.50
b 0.71 (6.25)	4.2 (6.25)	0.85 (6.25)	0.1 (0.1)	60	**b** 1.19 (5.0)	**4b**[f]	0.78
d 1.27 (10.0)	6.3 (10.0)	1.36 (10.0)	1.0 (1.0)	70	**b** 2.14 (9.0)	**4d**[g]	0.18

		calcd, found			
3, 4	emp. form. (mol. mass)	C	H	N	S
3a	$C_8H_5NO_2S_2$ (211.3)	45.48, 45.44	2.39, 2.39	6.63, 6.52	30.35, 30.12
3b	$C_9H_7NO_3S_2$ (241.3)	44.80, 44.74	2.92, 2.97	5.81, 5.67	26.57, 26.46
3c	$C_9H_7NO_2S_3$ (257.3)	42.01, 41.76	2.74, 2.69	5.44, 5.43	37.37, 37.17
3d	$C_{10}H_{10}N_2O_2S_2$ (254.3)	47.23, 47.02	3.96, 4.05	11.01, 10.93	25.21, 25.48
3e	$C_{12}H_{12}N_2O_2S_2$ (280.4)	51.41, 51.25	4.31, 4.41	9.99, 9.87	22.87, 23.09
4b	$C_{10}H_8O_2S_2$ (224.3)	53.55, 53.81	3.60, 3.55		28.59, 28.69
4d	$C_{11}H_{11}NOS_2$ (237.3)	55.67, 55.53	4.67, 4.64	5.90, 5.61	27.02, 27.19

compd	^1H NMR (δ, $CDCl_3$)
3a	7.09 (d, J = 4.6 Hz, 1 H), 7.10 (d, J = 3.7 Hz, 1 H), 7.36 (d, J = 5.2 Hz, 1 H), 7.41 (d, J = 1.1 Hz, 1 H), 7.85 (d, 1 H)
3b	3.95 (s, 3 H), 6.20 (d, J = 4.1 Hz, 1 H), 6.88 (d, J = 4.4 Hz, 1 H), 7.06 (d, 1 H), 7.80 (d, 1 H)
3c	2.56 (s, 3 H), 6.99 (d, J = 3.8 Hz, 1 H), 7.01 (d, J = 4.4 Hz, 1 H), 7.21 (d, 1 H), 7.83 (d, 1 H)
3d	3.03 (s, 6 H), 5.83 (d, J = 4.2 Hz, 1 H), 6.75 (d, J = 4.4 Hz, 1 H), 7.16 (d, 1 H), 7.78 (d, 1 H)
3e	2.09, 3.34 (s, 8 H), 5.73 (d, J = 4.2 Hz, 1 H), 6.72 (d, J = 4.5 Hz, 1 H), 7.18 (d, 1 H), 7.77 (d, 1 H)
4b	3.94 (s, 3 H), 6.19 (d, J = 4.1 Hz, 1 H), 7.05 (d, 1 H), 7.06 (d, J = 4.0 Hz, 1 H), 7.62 (d, 1 H), 9.81 (s, 1 H)
4d	3.00 (s, 6 H), 5.82 (d, J = 4.1 Hz, 1 H), 6.95 (d, J = 4.0 Hz, 1 H), 7.13 (d, 1 H), 7.58 (d, 1 H), 9.76 (s, 1 H)

[a] 1.5 or 1.6 N solution. [b] 1.0 N solution in *n*-heptane. [c] Addition of BuLi at −45 °C and of $ZnCl_2$ at −20 °C, recrystallization from *n*-hexane. [d] Chromatography with *n*-hexane/dichloromethane (1:1), recrystallization from *n*-hexane. [e] Chromatography with dichloromethane (2×), recrystallization from *n*-hexane/toluene (2:1). [f] Chromatography with dichloromethane, recrystallization from *n*-hexane. [g] Chromatography with dichloromethane (2×), recrystallization from *n*-hexane

2-iodo-5-nitrothiophene (**2b**) according to ref 38, 2-iodothiophene (**2c**), 2-cyano-5-iodothiophene (**2d**), 2-(1,1-dicyanovinyl)-5-iodothiophene (**2e**), and 2-iodo-5-methylsulfonylthiophene (**2g**) according to ref 39, 5-bromo-2,2′-bithiophene (**10b**) according to ref 20, 5-iodo-2,2′-bithiophene according to ref 24, and $PdCl_2(PPh_3)_2$ according to ref 14.

Preparation of Bithiophenes 3 and 4 from 1 via Organozinc Compounds. General Procedure. A solution of *n*-BuLi in *n*-hexane was dropped under Ar at rt to a solution of **1** in THF. After being stirred for 20–30 min the mixture was cooled to 0 °C and a solution of zinc chloride (anhydrous, dried at 110 °C and weighed under Ar) in THF (10 mL/g $ZnCl_2$) was added dropwise to give the organozinc compound of **1**. To the suspension of $PdCl_2(PPh_3)_2$ in THF (mol % related to **1**, see Table 1) was added 2 equiv of DIBAL followed by a solution of **2** in THF and the solution of the organozinc compound. After being stirred for 2–4 h at rt the reaction mixture was hydrolyzed with ice-cold 0.5 N HCl and extracted with diethyl ether. The combined extracts were washed with 1 N sodium bicarbonate solution and H_2O, dried with Na_2SO_4, and concentrated. For purification (chromatography on silica gel and recrystallization) see Table 5.

2-(2,4-Dinitrophenyl)-5-pyrrolidinothiophene. As described above for **3** and **4** from **1e** (1.22 g, 8.0 mmol), 1.5 N *n*-BuLi (5.3 mL, 8.0 mmol), $ZnCl_2$ (1.08 g, 8.0 mmol), $PdCl_2(PPh_3)_2$ (0.28 g, 0.4 mmol), DIBAL (1.0 mL, 1.0 mmol), 2,4-dinitroiodobenzene[40] (1.91 g, 6.5 mmol), THF (60 mL), chromatography with dichloromethane/*n*-hexane (2:1), and recrystallization from methanol: yield 1.10 g (53%); mp 176–177 °C; ^1H NMR ($CDCl_3$) δ 2.09 (m, 4 H), 3.36 (m, 4 H), 5.81 (d, J = 4.4 Hz, 1 H), 7.11 (d, 1 H), 7.54 (d, J = 8.9 Hz, 1 H), 8.19 (dd, J = 8.9, 2.4 Hz, 1 H), 8.38 (d, 1 H). Anal. Calcd for $C_{14}H_{13}N_3O_4S$: C, 52.66; H, 4.10; N, 13.16; S, 10.04. Found: C, 52.84; H, 4.22; N, 12.88; S, 9.90.

2-Amino-Substituted 5-(Trimethylstannyl)thiophenes 5. Under Ar a solution of *n*-BuLi in *n*-hexane (1.6 M) was dropped within 10 min into a stirred solution of **1** in THF. After 1 h the mixture was cooled to −70 °C, and a solution of trimethyltin chloride in THF was slowly added. After being stirred for 4 h the reaction mixture was allowed to warm to rt (16 h) and poured into H_2O. The organic phase was separated and the aqueous phase was extracted three times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and concentrated, and the residue was distilled under Ar in vacuo.

2-(Dimethylamino)-5-(trimethylstannyl)thiophene (5d). From **1d** (5.05 g, 40.0 mmol), *n*-BuLi in *n*-hexane (27.5 mL, 44.0 mmol), Me_3SnCl (7.97 g, 40.0 mmol), and THF (78 mL): yield 9.63 g (83%); bp 80–81 °C/0.04 Torr; ^1H NMR(C_6D_6) δ 0.51 (s, 9 H), 2.79 (s, 6 H), 6.31 (d, J = 3.5 Hz, 1 H), 7.23 (d, 1 H). Anal. Calcd for $C_9H_{17}NSnS$: C, 37.28; H, 5.91; N, 4.83; S, 11.06. Found: C, 37.50; H, 5.97; N, 4.85; S, 10.93.

2-Pyrrolidino-5-(trimethylstannyl)thiophene (5e). From **1e** (12.3 g, 80.0 mmol), *n*-BuLi in *n*-hexane (51 mL, 82.0 mmol), Me_3SnCl (16.0 g, 80.0 mmol), and THF (180 mL): yield 20.9 g (83%); bp 98–99 °C/0.005 Torr; ^1H NMR (C_6D_6) δ 0.64 (s, 9 H), 1.80 (m, 4 H), 3.36 (m, 4 H), 6.31 (d, J = 3.5 Hz, 1 H), 7.40 (d, 1 H). Anal. Calcd for $C_{11}H_{19}NSnS$: C, 41.81; H, 6.06; N, 4.43; S, 10.14. Found: C, 42.08; H, 6.20; N, 4.47; S, 10.43.

Preparation of Bithiophenes 3d,e, 4d, 6d,e, and 8a-c via Organotin Compounds. General Procedure. Under Ar **2** was added to a solution of the palladium catalyst $PdCl_2(PPh_3)_2$ in THF followed by addition of **5** via syringe, and the reaction mixture was warmed to 60 °C. After the given reaction times (TLC control, Table 6) the solution was worked up. Method A. The reaction solution was concentrated, the residue was dissolved in dichloromethane or dichloromethane/*n*-hexane (4:1) and chromatographed on silica gel with dichloromethane or dichloromethane/*n*-hexane, and the product was recrystallized from *n*-hexane/toluene (2:1) and dried over paraffin in vacuo. Method B. The reaction mixture was poured into H_2O, and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried

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Table 6. Palladium-Catalyzed Preparation of Bithiophenes 3, 4, 6, and 8 as Well as Physical Data

2 (g) (mmol)	**5** (g) (mmol)	catalyst (g) (mmol)	THF (mL)	reactn time (h)	**3**, **4**, **6**, **8**	yield (g)	method
a 7.64 (30.0)	**d** 8.70 (30.0)	0.67 (0.9)	400	2	**3d**	5.16	B
a 0.47 (1.8)	**e** 0.66 (2.1)	0.064 (0.09)	30	0.75	**3e**	0.40	A
b 0.36 (1.5)	**d** 0.47 (1.6)	0.057 (0.08)	35	3.5	**4d**	0.23	A
c 8.20 (39.0)	**d** 11.7 (40.0)	1.4 (2.0)	200	16	**6d**	3.4	A[a,b]
c 4.20 (20.0)	**e** 6.0 (19.0)	0.7 (1.0)	300	16	**6e**	2.0	A[a,c]
d 0.59 (2.5)	**d** 0.72 (2.5)	0.089 (0.12)	35	3	**8a**	0.36	A
e 3.85 (13.5)	**d** 3.9 (13.5)	0.48 (0.7)	210	0.5	**8b**	2.69	B[d]
f 1.99 (6.9)	**d** 2.0 (6.9)	0.25 (0.36)	100	3.5	**8c**	1.15	A

8	emp form. (mol. mass)	calcd, found C	H	N	S
8a	$C_{11}H_{10}N_2S_2$ (234.3)	56.38, 56.26	4.30, 4.31	11.95, 11.77	27.36, 27.66
8b	$C_{14}H_{11}N_3S_2$ (285.4)	58.92, 58.97	3.89, 3.88	14.72, 14.58	22.47, 22.26
8c	$C_{11}H_{13}NO_2S_3$ (287.4)	45.97, 45.83	4.56, 4.51	4.87, 4.81	33.46, 33.41

compd	^{1}H NMR (δ, $CDCl_3$)
8a	2.98 (s, 6 H), 5.78 (d, 1 H), 6.81 (d, 1 H), 7.01 (d, J = 4.1 Hz, 1 H), 7.42 (d, J = 4.0 Hz, 1 H)
8b	3.06 (s, 6 H), 5.87 (d, J = 4.3 Hz, 1 H), 6.95 (d, 1 H), 7.26 (d, J = 4.2 Hz, 1 H), 7.43 (d, J = 4.2 Hz, 1 H), 7.61 (s, 1 H)
8c	2.98 (s, 6 H), 3.17 (s, 3 H), 5.79 (d, 1 H), 6.85 (d, J = 3.9 Hz, 1 H), 7.02 (d, J = 4.0 Hz, 1 H), 7.51 (d, J = 4.0 Hz, 1 H)

[a] Chromatography with *n*-hexane. [b] **6d/7d** (70:30), no separation. [c] Mixture of **6e/7e** (70:30), separation by chromatography after conversion with *n*-BuLi and subsequent formylation with DMF to give **4e** and **7e**. **7e:** mp 67–68 °C, yellow brown crystals; ^{1}H NMR ($CDCl_3$) δ 2.04 (m, 4 H, pyr-H), 3.31 (m, 4 H, pyr-H), 5.73 (d, J = 3.7 Hz, 1 H, H4), 7.05 (d, 1 H, H3), 7.08–7.16 (dd, 1 H, Ph), 7.25–7.32 (m, 2 H, Ph), 7.43–7.47 (m, 2 H, Ph); MS calcd for $C_{14}H_{15}NS$ 229.0925, found 229.0924. [d] The precipitate was dissolved in hot toluene (800 mL), silica gel was added (15 g), the mixture was refluxed and filtered off, and silica gel was washed with hot toluene (100 mL). The combined filtrates were concentrated to about 400 mL. The resulting precipitate was dissolved by heat, and the solution was cooled to rt. After 4 h **8b** was filtered off, washed with *n*-hexane, and dried in vacuo.

Table 7. Palladium-Catalyzed Preparation of Bi-, Ter-, and Quaterthiophenes 6, 12, 13, and 14 as Well as Physical Data

1, **6**, **12** (g) (mmol)	BuLi[a] (mL) (mmol)	$ZnCl_2$ (g) (mmol)	DIBAL[b] (mL) (mmol)	**2**, **10**	(g) (mmol)	**6**, **12**, **13**, **14**	yield (g)
1b 2.28 (20.0)	12.5 (20.0)	2.73 (20.0)	0.4 (0.4)	**10a**	2.93 (18.0)	**6b**[c]	1.50
1b 1.14 (10.0)	6.4 (10.2)	1.36 (10.0)	1.0 (1.0)	**10b**	2.21 (9.0)	**12**[d]	1.32
6b 0.59 (3.0)	2.0 (3.0)	0.41 (3.0)	0.1 (0.1)	**2a**	0.64 (2.5)	**13b**[e]	0.59
12 0.28 (1.0)	0.7 (1.0)	0.17 (1.2)	0.03 (0.03)	**2a**	0.26 (1.0)	**14b**[e,f]	0.30
6e 0.51 (2.17)	1.4 (2.2)	0.28 (2.1)	0.23 (0.23)	**2a**	0.45 (1.76)	**13e**[g]	0.30
6e 0.47 (2.0)	1.37 (2.0)	0.27 (2.0)	0.2 (0.2)	**2h**	0.54 (1.6)	**14e**[h]	0.39, 0.21

compd	emp form. (mol mass)	calcd, found C	H	N	S
6b	$C_9H_8OS_2$ (196.3)	55.07, 55.08	4.11, 4.19		32.67, 32.50
12	$C_{13}H_{10}OS_3$ (278.4)	56.09, 56.05	3.62, 3.60		34.55, 34.69
13b	$C_{13}H_9NO_3S_3$ (323.4)	48.28, 48.40	2.81, 2.83	4.33, 4.26	29.74, 29.50
14b	$C_{17}H_{11}NO_3S_4$ (405.5)	50.35, 50.24	2.73, 2.72	3.45, 3.35	31.62, 31.78
13e	$C_{16}H_{14}N_2O_2S_3$ (362.5)	53.02, 52.87	3.89, 3.91	7.73, 7.60	26.53, 26.43
14e	$C_{20}H_{16}N_2O_2S_4$ (444.6)	54.03, 54.26	3.63, 3.75	6.30, 6.10	28.84, 28.86

compd	^{1}H NMR (δ, $CDCl_3$)
6b	3.91 (s, 3 H), 6.13 (d, J = 3.9 Hz, 1 H), 6.82 (d, 1 H), 6.98–7.02 (m, 2 H), 7.14 (dd, J =1.4, 4.9 Hz, 1 H)[i]
12	3.91 (s, 3 H), 6.13 (d, J = 4.0 Hz, 1 H), 6.80 (d, 1 H), 6.90 (d, J = 3.8 Hz, 1 H), 7.01 (dd, J = 3.6, 5.1 Hz, 1 H), 7.03 (d, 1 H), 7.14 (dd, 1 H), 7.20 (dd, J = 5.1, 1.2 Hz, 1 H)
13b	3.93 (s, 3 H), 6.16 (d, J = 4.0 Hz, 1 H), 6.90 (d, 1 H), 6.95 (d, J = 3.9 Hz, 1 H), 7.03 (d, J = 4.4 Hz, 1 H), 7.23 (d, 1 H), 7.84 (d, 1 H)
14b	3.93 (s, 3 H), 6.15 (d, J = 4.0 Hz, 1 H), 6.85 (d, 1 H), 6.93 (d, J = 3.8 Hz, 1 H), 7.01 (d, J = 3.9 Hz, 1 H), 7.06 (d, J = 4.4 Hz, 1 H), 7.11 (d, 1 H), 7.27 (d, 1 H), 7.85 (d, 1 H)
13e	2.05, 3.31 (m, 8 H), 5.69 (d, J = 4.0 Hz, 1 H), 6.85 (d, J = 3.9 Hz, 1 H), 7.01 (d, J = 4.4 Hz, 1 H), 7.02 (d, 1 H), 7.26 (d, 1 H), 7.83 (d, 1 H)

[a] 1.5 or 1.6 N solution. [b] 1.0 N solution in *n*-heptane. [c] Chromatography with *n*-hexane/dichloromethane (4:1): fractions 1,3, **11b**,**11a**; fraction 2, **6b**. [d] Extraction with dichloromethane, extraction with toluene (80 mL), filtration of **11c**, chromatography with toluene and recrystallization from *n*-hexane/toluene (2:1). [e] Extraction with dichloromethane, uptake in hot toluene (200 mL), filtration through a silica gel column, recrystallization from toluene. [f] Addition of the solutions of **2a** and activated catalyst to the poor soluble organozinc compound of **12**. [g] Extraction with dichloromethane (400 mL), chromatography with *n*-hexane/dichloromethane, recrystallization from toluene. [h] The precipitate was filtered off, washed with methanol, and recrystallized twice from boiling toluene (650 mL), addition of silica gel (10 g) and subsequent filtration at the first recrystallization; characterization by MS *m/z* 444.0 (100). [i] ABM system.

($MgSO_4$), $MgSO_4$ was filtered off and washed with dichloromethane, and the combined filtrates were concentrated. The residue was taken up in *n*-hexane and treated with ultrasound, and the remaining solid was filtered off, washed with *n*-hexane, and recrystallized from *n*-hexane/toluene (2:1).

5-Mercapto-2,2′-bithiophene (9). At −30 °C under Ar a 1.5 N solution of *n*-BuLi in *n*-hexane (116 mL, 0.18 mol) was dropped to a stirred solution of 2,2′-bithiophene (30.8 g, 0.18 mol) in THF (170 mL). After being for 1 h the mixture was cooled to −60 °C, sulfur (5.95 g, 0.18 mol) was added under Ar, and the suspension was stirred for 30 min, warmed to 0 °C, and poured into ice-cold H_2O. *n*-Hexane (50 mL) was added, the phases were separated, and the organic phase was extracted with H_2O. The combined extracts were acidified with 4 N H_2SO_4 and extracted with diethyl ether. The extracts were washed with H_2O, dried with Na_2SO_4, and concentrated. The residue was distilled in vacuo: yield 14.1 g (40%); bp 95 °C/0.1 Torr; mp 20 °C; ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 1 H), 7.00

(broad s, 2 H), 7.01 (dd, J = 3.6, 5.1 Hz, 1 H), 7.13 (dd, J = 3.6, 1.1 Hz, 1 H), 7.22 (dd, J = 1.1, 5.1 Hz, 1 H). Anal. Calcd for $C_8H_6S_3$: C, 48.45; H, 3.05; S, 48.50. Found: C, 48.56; H, 3.11; S, 48.59.

5-Pyrrolidino-2,2′-bithiophene (6e). Under N_2 **9** (3.11 g, 15.7 mmol) and pyrrolidine (1.23 g, 17.3 mmol) were added to xylene (16 mL) via syringe. The reaction mixture was refluxed for 6 h, and then xylene was removed under N_2. The residue was dissolved in dichloromethane and chromatographed on silica gel with *n*-hexane/dichloromethane (4:1), and the product was recrystallized from *n*-hexane: yield 1.35 g (37%); mp 88 °C; ^1H NMR ($CDCl_3$) δ 2.03, 3.28 (m, 8 H), 5.64 (d, J = 3.9 Hz, 1 H), 6.89 (d, 1 H), 6.92 (m, AB system, 2 H), 7.03 (m, 1 H). Anal. Calcd for $C_{12}H_{13}NS_2$: C, 61.24; H, 5.57; N, 5.95; S, 27.24. Found: C, 61.38; H, 5.69; N, 5.72; S, 27.20.

In toluene, bis(2,2′-bithienyl-5-yl) disulfide (0.61 g, 10%) was isolated: mp 123 °C; ^1H NMR ($CDCl_3$) δ 7.03 (dd, J = 3.7, 5.2 Hz, 1 H), 7.06 (d, J = 3.7 Hz, 1 H), 7.08 (d, 1 H), 7.21 (dd, J = 3.7, 1.1 Hz, 1 H), 7.27 (dd, J = 1.1, 5.2 Hz, 1 H). Anal. Calcd for $C_{16}H_{10}S_6$: C, 48.70; H, 2.55; S, 48.75. Found: C, 48.72; H, 2.70; S, 48.63.

5-Formyl-5′-pyrrolidino-2,2′-bithiophene (4e). A 1.6 N solution of *n*-BuLi in *n*-hexane (2.5 mL, 4.0 mmol) was dropped under Ar at rt to a stirred solution of **6e** (0.9 g, 3.8 mmol) in THF (30 mL). The reaction mixture was cooled to −40 °C, DMF (0.35 g, 4.8 mmol) was slowly added, and after 2 h the solution was warmed to rt, poured into ice-cold 2 N HCl (50 mL), neutralized with saturated sodium bicarbonate solution to pH 6, and extracted with dichloromethane (200 mL). The combined extracts were washed with H_2O, dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel with dichloromethane, and the product was recrystallized from *n*-hexane/dichloromethane (10:1): yield 0.63 g (62%) violet crystals: mp 142 °C; ^1H NMR ($CDCl_3$) δ 2.07 and 3.33 (m, 8 H), 5.70 (d, J = 4.1 Hz, 1 H), 6.92 (d, J = 4.1 Hz, 1 H), 7.15 (d, 1 H), 7.57 (d, 1 H), 9.75 (s, 1 H).

5-Iodo-5′-nitro-2,2′-bithiophene (2g). To a stirred solution of **3a** (2.11 g, 10.0 mmol) in acetic acid (150 mL) finely powdered iodine (2.6 g, 10.2 mmol) and HgO (2.2 g, 10.2 mmol) were added portionwise at rt. After treatment with ultrasound for 15 min and stirring for 3 h the resulting precipitate was filtered off, washed with potassium iodide solution (50%) to remove HgI_2, dried, and recrystallized from toluene (200 mL): yield 2.6 g (77%); mp 234 °C; ^1H NMR (CD_2Cl_2) δ 7.06 (d, J = 3.9 Hz, 1 H), 7.07 (d, J = 4.3 Hz, 1 H), 7.28 (d, 1 H), 7.84 (d, 1 H). Anal. Calcd for $C_8H_4INO_2S_2$: C, 28.50; H, 1.20; N, 4.15; I, 37.64; S, 19.02. Found: C, 28.52; H, 1.25; N, 4.13; I, 37.61; S, 19.12.

5-Methoxy-2,2′-bithiophene (6b). To a solution of sodium methanolate (1.38 g (0.06 mol) of sodium in methanol (20 mL)) were added 5-iodo-2,2′-bithiophene (5.84 g, 0.02 mol) and CuO (0.80 g, 0.01 mol) and the resulting mixture refluxed for 24 h. The solid was filtered off and washed with methanol. The filtrates were poured into H_2O (100 mL) and extracted with diethyl ether. The combined extracts were washed with H_2O, dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel with dichloromethane, and the product was distilled in vacuo: yield 2.54 g (65%); for physical data see Tables 2 and 7.

Preparation of Bi-, Ter-, and Quaterthiophenes 6, 11, 13, and 14 via Organozinc Compounds. General Procedure. As described above for bithiophenes **3** and **4**; for purification (chromatography on silica gel or extraction for the poor soluble compounds and recrystallization) data see Table 7.

Acknowledgment. This work was generously supported by the Deutsche Forschungsgemeinschaft (SFB 329). We thank Prof. W. Liptay for his program SOLVDEPE and F.-M. Kiess and F. Zocher for their contribution to the experimental work.

JO9417683