Band-Gap Engineering of Donor–Acceptor-Substituted π-Conjugated Polymers

H. A. M. van Mullekom, J. A. J. M. Vekemans, and E. W. Meijer*

Abstract: Three series of alternating donor–acceptor-substituted co-oligomers (with different chain lengths) have been prepared by application of the Pd-catalyzed Stille coupling methodology. They contain pyrrole or thiophene as the electron-rich unit and quinoxaline or 2,1,3-benzothiadiazole as the electron-deficient unit. The trimethylstannyl group is always located on the electron-rich unit, whereas the bromo substituent is always located on the electron-deficient one. The *t*Boc-protecting group is used in the synthesis of the pyrrole-containing oligomers. The incremental bathochromic shift of λ_{max} upon chain elongation of the three series of oligomers is less than that of the homo-oligomers of thiophene and pyrrole; this decrease is caused by a diminished dispersion of the LUMO level upon chain elongation. This conclusion was drawn after comparing the oxidation and reduction behavior of the thiophene/benzothiadiazole co-oligomers with that of thiophene oligomers. The incremental bathochromic shift is similar for all three series of oligomers and is used as a tool in the band-gap engineering of donor–acceptor-substituted π-conjugated polymers.

Keywords: conducting materials · conjugation · donor–acceptor systems · oligomers · cross-coupling reactions

Introduction

Since π-conjugated polymers allow virtually endless manipulation of their chemical structure, control of the band gap of these semiconductors is a research issue of ongoing interest. This band-gap engineering gives the polymer its desired electrical and optical properties; reduction of the band gap to approximately zero is expected to give an intrinsically conducting polymer.[1] One of the most successful approaches to these low-band-gap polymers is the application of an alternating sequence of donor–acceptor (D–A) units in the π-conjugated polymer chain.[2] Since the semiconducting behavior of π-conjugated polymers originates from the dispersion of the HOMO and LUMO levels of the monomer into a valence and a conduction band upon chain elongation, a narrow band gap can indeed be obtained by starting from a monomer that already has a narrow HOMO–LUMO energy separation, for example, the D–A compounds mentioned above. However, it is not known whether the narrowing of the band gap upon chain elongation of these systems is comparable with that of polymers like polythiophene and polypyrrole. The question is relevant not only for the understanding of band-gap engineering, but also with respect to theoretical considerations that have revealed the unique electronic properties of the D–A type systems.[3]

Numerous examples of polymers belonging to the class of π-conjugated D–A systems are known that do not show a lower band gap than that of the traditional low-band-gap polymer polyisothianaphthene (1 eV).[4] However, Tanaka et al. have shown that the application of the electron-releasing thiophene unit in combination with benzo[1,2-c:4,5c′]-bis[1,2,5]thiadiazole- or thieno[3,4-*b*]pyrazine-derived electron-withdrawing units yields conjugated copolymers that have the lowest optical absorption gaps reported so far.[5]

In our search for a low-band-gap conjugated copolymer consisting of electron-rich pyrrole and electron-deficient 2,1,3-benzothiadiazole units,[6] we noticed that the incremental red shift in the absorption spectra upon chain elongation was smaller than that of polythiophene, although both systems are completely coplanar. In a recent paper of Meier et al. the dependence of chain length and absorption maximum for a large series of homopolymers and their oligomers has been evaluated systematically.[7] In this paper, we report on the synthesis of three series of D–A oligomers **1**–**11** (Figure 1), the investigations of the dependence of the absorption maximum on chain length, and the formulation of the consequences for the design of low-band-gap D–A conjugated polymers.

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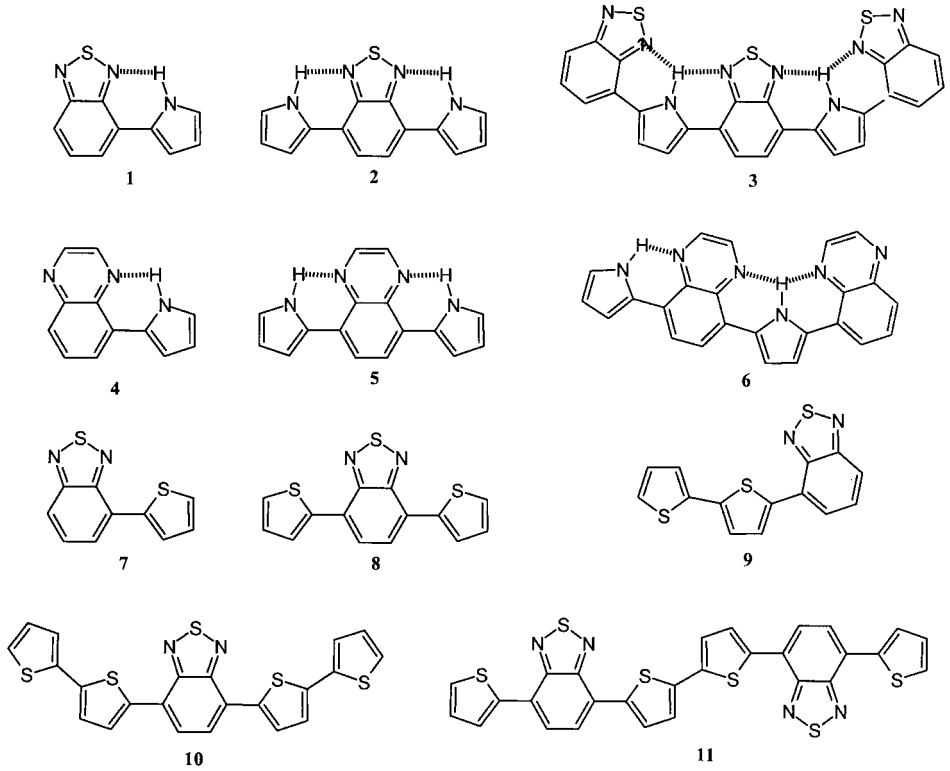
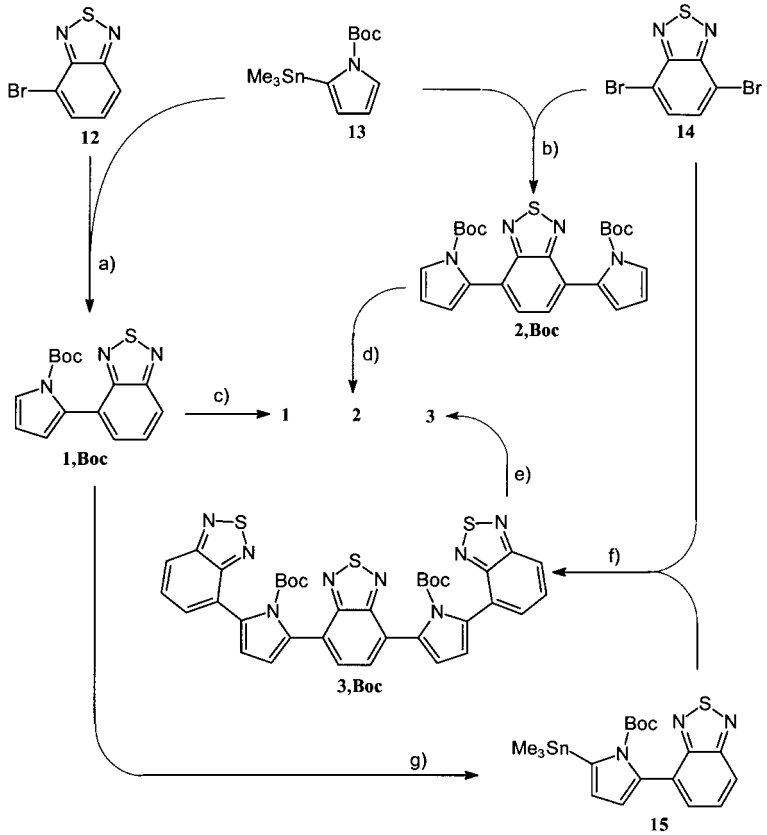


Figure 1. Donor–acceptor oligomers investigated in this study.

Results

Synthesis of pyrrole/2,1,3-benzothiadiazole co-oligomers: The syntheses of oligomers **1**–**3** are outlined in Scheme 1. Stille coupling gives access to the appropriate oligomers.[8] The combination of the solvent system toluene/1M Na_2CO_3 and the catalyst $[Pd^0(PPh_3)_4]$ has previously proven effective in the coupling of *N*-*t*Boc-2-trimethylstannylpyrroles with aryl bromides[9] and is used here in the synthesis of pyrrole-containing oligomers **1**–**6**. Thus, the bromide **12**[10] was treated with *N*-*t*Boc-2-trimethylstannylpyrrole (**13**)[11] in a boiling two-phase system of toluene/1M Na_2CO_3 (1:1) under catalysis of $[Pd^0(PPh_3)_4]$ for 48 hours, to give the Boc-protected precursor **1-Boc** in 78% yield. This precursor was deprotected by heating the solid briefly at 200 °C to give **1**.[12]

Analogously, **2-Boc** was synthesized in 42% yield from the dibromide **14** and trimethylstannylpyrrole **13**, and was subsequently deprotected to afford **2**. The synthesis of **3** requires the intermediate stannyl compound **15** that was prepared in 57% yield from **1-Boc** by deprotonation with Li-tetramethylpiperidide (LTMP) in THF at −80 °C, and subsequent quenching with $SnMe_3Cl$. Compound **15** was then treated under the stand-



Scheme 1. Synthesis of pyrrole/2,1,3-benzothiadiazole co-oligomers. Reagents and conditions: a) $[Pd(PPh_3)_4]$, toluene, 1M Na_2CO_3, reflux 48 h, 78%; b) $[Pd(PPh_3)_4]$, toluene, 1M Na_2CO_3, reflux 48 h, 42%; c) heat, 200 °C, 30 min, 95%; d) heat, 200 °C, 30 min, 96%; e) heat, 0.1 mm Hg, 200 °C, 30 min, 100%; f) $[Pd(PPh_3)_4]$, toluene, 1M Na_2CO_3, reflux 72 h, 11%; g) LTMP, then $SnMe_3Cl$, THF, −80 °C, 57%.

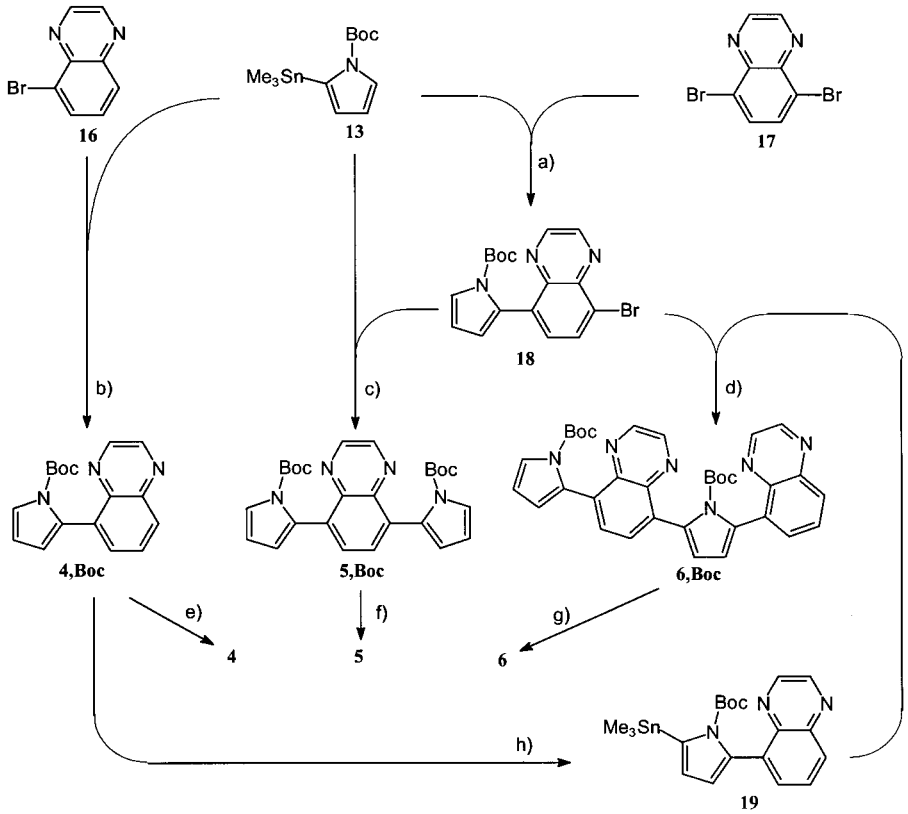
Abstract in Dutch: *Drie reeksen co-oligomeren van verschillende lengtes, met alternerende elektronendonor (pyrrool of thiofeen) en -acceptor (chinoxaline of 2,1,3-benzothiadiazool) eenheden in de hoofdketen, zijn gesynthetiseerd met behulp van de Pd-gekatalyseerde Stille koppeling. De waargenomen bathochrome verschuiving van λ_{max} bij toenemende ketenlengte in de drie genoemde reeksen is geringer dan die bij overeenkomstige homo-oligomeren van thiofeen of pyrrool. Dit kan—zoals de vergelijking van het oxidatie– en reductiegedrag van de thiofeen/benzothiadiazool co-oligomeren met die van overeenkomstige thiofeen homo-oligomeren suggereert—veroorzaakt worden door een kleinere dispersie van de LUMO band bij ketenverlenging. De bathochrome verschuivingen voor de drie reeksen D–A oligomeren zijn onderling nagenoeg gelijk. Dit fenomeen kan worden gebruikt als een hulpmiddel bij de band-gap engineering van D–A gesubstitueerde π-geconjugeerde polymeren.*

0947-6539/98/0407-1236 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 7

ard conditions with dibromide **14** to give **3-Boc** in 11% yield, which upon deprotection gave **3**. A general trend in the Stille couplings used here is that with increasing oligomer size the reaction yields drop; this is presumably as a result of the more difficult ligand exchange with larger molecules.[13]

Synthesis of pyrrole/quinoxaline co-oligomers: The syntheses of oligomers **4**–**6** are outlined in Scheme 2. The $[Pd^0(PPh_3)_4]$-catalyzed Stille reactions are again performed in the boiling two-phase system toluene/1M Na_2CO_3 (1:1).

The bromide **16**[14] was treated with **13** to give **4-Boc** in 36% yield. Thermal deprotection of this compound then gave **4**. The synthesis of compound **5** differed from that of its analogue **2**. In view of the longer reaction times needed to complete the Stille coupling with bromoquinoxalines compared with that for bromobenzothiadiazoles (and hence the greater probability of by-product formation), the intermediate compound **18** was first isolated (23% yield) and thereafter treated again with an additional equivalent of **13** to give the desired **5-Boc** in 75% yield. Thermal deprotection then gave **5**. For the synthesis of **6**, the trimethylstannyl compound **19** was prepared first from **4-Boc** (analogously to the synthesis of **15** from **1-Boc**) in 32% yield. Subsequent reaction with **18** gave **6-Boc** in 85% yield and thermal deprotection then gave crude **6**. During the deprotection process an unidentified by-product was formed, hence **6** had to be purified by precipitation from THF in hexane.



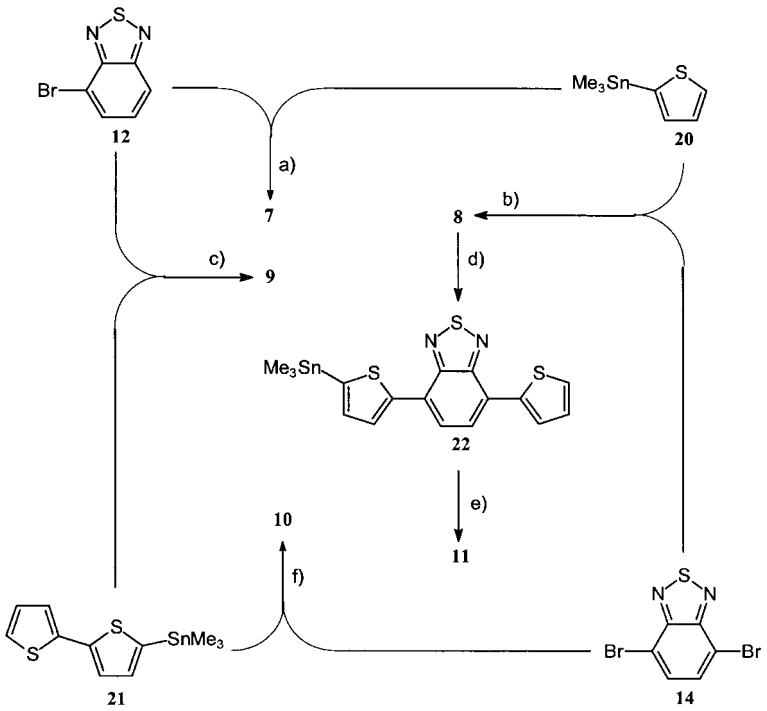
Scheme 2. Synthesis of pyrrole/quinoxaline co-oligomers. Reagents and conditions: a) $[Pd(PPh_3)_4]$, toluene, 1M Na_2CO_3, reflux 72 h, 23%; b) $[Pd(PPh_3)_4]$, toluene, 1M Na_2CO_3, reflux 72 h, 36%; c) $[Pd(PPh_3)_4]$, toluene, 1M Na_2CO_3, reflux 72 h, 75%; d) $[Pd(PPh_3)_4]$, toluene, 1M Na_2CO_3, reflux 72 h, 85%; e) heat, 200 °C, 30 min, 95%; f) Heat, 200 °C, 30 min, 95%; g) heat, 0.1 mmHg, 200 °C, 30 min, 90%; h) LTMP, then $SnMe_3Cl$, THF, −80 °C, 32%.

As already mentioned, the Stille coupling of bromoquinoxalines with trimethylstannylpyrroles proceeds more slowly than that of bromobenzothiadiazoles. Presumably, the lower electron-withdrawing power of quinoxaline leads to lower activation of this substrate compared with benzothiadiazole. In this context, it is strange that the yields in the synthesis of **5-Boc** and **6-Boc** are quite high, since the bromide here is expected to be even less activated. A lower yield would also be expected in light of the oligomer size. It seems therefore that the introduction of the first substituent is more difficult than the introduction of the second one.

Synthesis of thiophene/benzothiadiazole co-oligomers: The Stille coupling of 2-tributylstannylthiophene with 4,7-dibromo-2,1,3-benzothiadiazole has previously been described, with THF as the solvent and $[Pd^{II}(PPh_3)_2Cl_2]$ as the catalyst.[15] However, we found that reaction of 2-trimethylstannylthiophene with 4,7-dibromo-2,1,3-benzothiadiazole in dry DMF at 75 °C with the $[Pd^{II}(PPh_3)_2Cl_2]$ catalyst gave a cleaner reaction with comparable yields. The synthesis is outlined in Scheme 3. Thus, **7** was synthesized in 89% yield from bromobenzothiadiazole **12** and trimethylstannylthiophene **20**, whereas **8** was synthesized from two equivalents of **20** and dibromobenzothiadiazole **14** in 56% yield.

In order to investigate the effect of bithiophene as the electron-releasing unit, compounds **9** and **10** were synthesized from 2-trimethylstannylbithiophene **21** and (di)bromobenzothiadiazoles **12** and **14** in 75% and 15% yield, respectively. Especially notable is the low yield of **10**, probably connected with the size of the oligomer and its low solubility. Finally, oligomer **11** was synthesized by a $[Pd^{II}(PPh_3)_2Cl_2]$-catalysed oxidative coupling of the trimethylstannyl compound **22** in the presence of air. This reaction is often encountered as a side reaction during a Stille coupling if the reaction mixture is not adequately deaerated. Other examples in which this homocoupling is utilized have recently been described.[16]

Compound **8** was monostannylated to **22** in 99% yield, in the same way as compounds **1-Boc** and **4-Boc**, with LTMP and $SnMe_3Cl$ in THF at −80 °C. Subsequently, compound **22** was heated under reflux in toluene in the presence of air and $[Pd^{II}(PPh_3)_2Cl_2]$ to give **11** in 14% yield. The ESI-MS spectrum showed minor amounts of methyl- and dimethyl-substituted derivatives of **11**, the origin of which is not yet clarified. Compound **11** is insoluble in most organic solvents, and is very slightly soluble in solvents like $CHCl_3$ and DMSO.



Scheme 3. Synthesis of thiophene/2,1,3-benzothiadiazole co-oligomers. Reagents and conditions: a) $[Pd(PPh_3)_2Cl_2]$, DMF, 75 °C, 1 h, 89 %; b) $[Pd(PPh_3)_2Cl_2]$, DMF, 75 °C, 1.5 h, 56 %; c) $[Pd(PPh_3)_2Cl_2]$, DMF, 75 °C, 1 h, 75 %; d) LTMP, then $SnMe_3Cl$, THF, −80 °C, 99 %; e) air, $[Pd(PPh_3)_2Cl_2]$, toluene, reflux, 18 h, 15 %; f) $[Pd(PPh_3)_2Cl_2]$, DMF, 75 °C, 2 h, 14 %.

UV/Vis spectroscopy: The D – A character of the oligomers is manifested in the UV/Vis spectra (Table 1). The oligomers are divided into three classes: P – B for the pyrrole- and 2,1,3-benzothiadiazole-containing oligomers **1** – **3**, P – Q for the pyrrole- and quinoxaline-containing oligomers **4** – **6**, and T – B for the thiophene- and 2,1,3-benzothiadiazole-containing oligomers **7** – **11**. When the absorption maximum energies are plotted as a function of the reciprocal number of aryl units $1/n$, a deviation in behavior is found for the D – A oligomers compared with homo-oligomers such as oligothiophene[17] and oligopyrrole.[9, 18]

Table 1. Optical properties of compounds **1** – **11**.

Class	Compound	λ_{max} [nm]	E_{max} [eV]
P – B	**1**	442	2.81
	2	532	2.33
	3	599	2.07
P – Q	**4**	421	2.95
	5	502	2.47
	6	535	2.32
T – B	**7**	390	3.18
	8	447	2.77
	9	429	2.89
	10	502	2.47
	11	521	2.38

Although the λ_{max} of short D – A oligomers is at much higher wavelength than the corresponding homo-oligomers, the incremental red shift upon chain elongation is less pronounced, as seen by the slope of the lines for oligopyrroles (3.19 eV on going from $1/n = 0$ to $1/n = 1$) and oligothiophenes (3.77 eV) versus the D – A oligomers in Figure 2 (P – B: 2.48 eV; P – Q: 2.57 eV; T – B: 2.44 eV). This behavior is usually found in conjugated oligomers in which the consecutive aryl units are not coplanar. This is exemplified in Figure 3 for the P – B oligomers, oligopyrroles, and *tert*-butoxycarbonyl-protected oligopyrroles.[18] The latter possess significant steric hindrance, and hence the slope of the curve for these oligomers is only 1.21 eV.

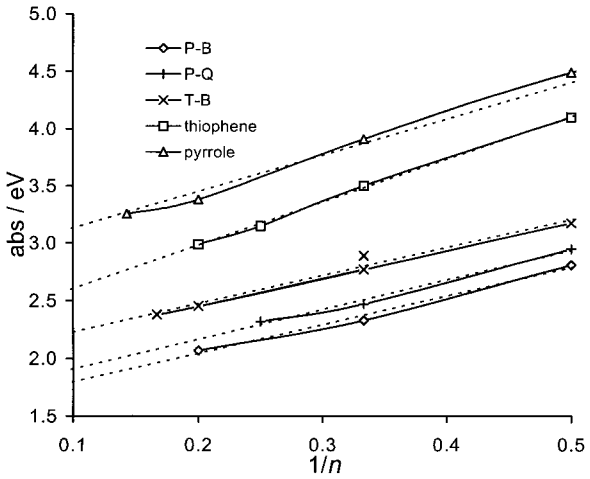


Figure 2. Chain-length dependence of the absorption maxima of co-oligomers **1** – **11** compared with the homo-oligomers of pyrrole and thiophene, with n = number of aryl units.

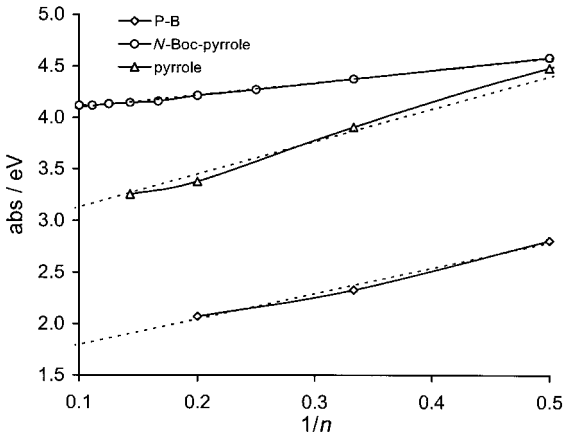


Figure 3. Chain-length dependence of the absorption maxima of compounds **1** – **3** (P – B series) compared with the homo-oligomers of pyrrole and *N*-Boc-pyrrole. n = Number of aryl units.

The P – B as well as the P – Q oligomers are expected to be completely coplanar by virtue of hydrogen bonding (depicted in Figure 1 by the dashed lines). In the proton NMR spectra of compounds **1** – **6** ($CDCl_3$), the pyrrole N – H signal is found at low field (Table 2). Moreover, this signal showed no concentration dependence and only a very small temperature

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Table 2. Position of the pyrrole N–H absorption in the ^{1}H NMR spectrum ($CDCl_3$) of compounds **1** – **6**.

Compound	δ_{N-H} in $CDCl_3$
1	10.9
2	10.9
3	12.1
4	11.9
5	11.9
6	14.2/11.9

dependence; this is an additional indication for strong intramolecular hydrogen bonding.[19] Therefore, the smaller slope of the D–A oligomers in Figure 2 is not caused by conformational factors, but rather by electronic factors.

Cyclic voltammetry: The bathochromic shift in the absorption maximum upon extension of a conjugated π-system originates from the dispersion of the HOMO and LUMO levels of the monomeric units into new bands until, in the case of conjugated polymers, broad valence and conduction bands have emerged, which give these polymers their semiconducting properties. The less-pronounced bathochromic shift for the D–A oligomers should therefore be caused by a diminished dispersion of the HOMO and/or LUMO level(s) upon extension of these systems. In order to confirm this hypothesis, the cyclic voltammograms of compounds **7**, **9**, and **10** were measured in a 0.1M Bu_4NPF_6 solution in CH_2Cl_2 versus a standard calomel electrode (SCE). The data are summarized in Table 3.

Table 3. Cyclic voltammetry data for compounds **7**, **9** and **10** vs. SCE in 0.1M Bu_4NPF_6 in CH_2Cl_2.

Compound	Oxidation E_1^0 [V]	Reduction E_1^0 [V]
7	1.62	– 1.60
9	1.30	– 1.40
10	0.98	– 1.32

Meerholz et al.[20] have investigated the oxidation and reduction potentials (vs. Ag/AgCl) of oligothiophenes versus the inverse chain length $1/n$. They report Equations (1) and (2) for the reduction and oxidation, respectively, of thiophenes.

$$E_1^0(N) = \left(\frac{-1.95}{n}\right) - 1.42 \quad (1)$$

$$E_1^0(N) = \left(\frac{+1.80}{n}\right) + 0.35 \quad (2)$$

In Figure 4, Equations (1) and (2) are plotted together with the oxidation and reduction data of the T–B oligomers. Linear regression of the data for the T–B oligomers give Equations (3) and (4) for their reduction and oxidation, respectively.

$$E_1^0(N) = \left(\frac{-0.95}{n}\right) - 1.11 \quad (3)$$

$$E_1^0(N) = \left(\frac{+2.11}{n}\right) + 0.57 \quad (4)$$

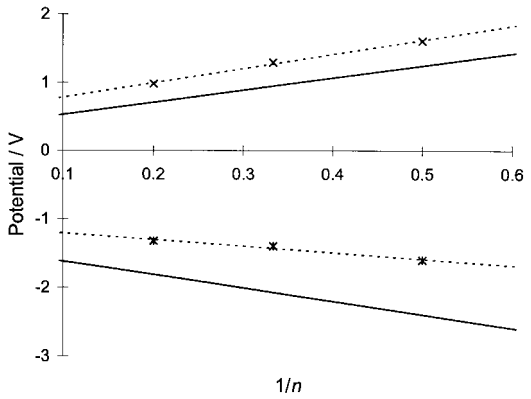

Figure 4. Chain-length dependence of oxidation and reduction potentials for oligothiophenes (—) vs. Ag/AgCl and for T–B oligomer oxidation (- - × - -) and reduction (- - * - -) vs. SCE. n = Number of aryl units.

Whereas the dispersion of the HOMO level for the T–B oligomers upon chain elongation is comparable with that of oligothiophenes [as concluded from the slopes of Equations (2) and (4)], the dispersion of the LUMO level for the T–B oligomers is significantly lower [Eq. (1) and (3)]. The smaller slope for the D–A oligomers in Figure 2 is therefore mainly caused by the smaller dispersion of the LUMO level upon chain elongation compared with homo-oligomers such as oligothiophenes and oligopyrroles.

Discussion

The degree of dispersion of the HOMO and LUMO levels depends on the size of the atomic orbital (AO) coefficients on the coupling positions of the monomers. Preliminary semiempirical PMO/MNDO calculations[21] on bithiophene and T–B oligomer **7** reveal that the LUMO AO coefficients of the latter are indeed smaller, as expected on the basis of the cyclic voltammetry (CV) results. In the LUMO, the largest electron density is found in the electron-poor part of the D–A systems. When this part is located outside the polymer backbone, the dispersion of the LUMO level is diminished.

Therefore, it must be kept in mind that when designing low band-gap D–A conjugated polymers of this type the initial reduction of the energy separation between HOMO and LUMO levels cannot be scaled to homopolymers such as polythiophene, in order to prevent a too optimistic estimation of the band gap. Preferably, the acceptor unit must have its electron-accepting part incorporated in the conjugated backbone.

When we reconsider Figure 2, it is remarkable that the slope for all three D–A oligomers is more or less equal at about 2.5 eV on going from $1/n = 0$ to $1/n = 1$. If we assume that this slope is found for all D–A oligomers, it gives us a quantitative guideline for the design of D–A-conjugated polymers with the desired (optical) properties. This is exemplified in Figure 5 in which the low-band-gap area is supposed to start with polymers that have an absorption maximum of < 1 eV.

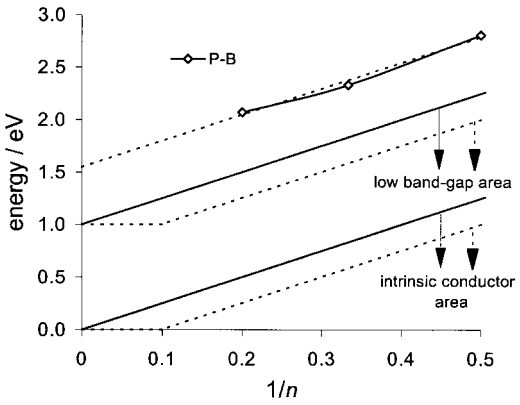

Figure 5. Application of the universal slope of 2.5 eV on low band-gap D–A copolymers (for which $E_{abs}(n=\infty)=1$ eV is taken) and (possibly intrinsically conducting) zero band-gap D–A copolymers (for which $E_{gap}(n=\infty)=0$ is estimated from $E_{abs}(n=\infty)=0$).

Of course, a few limitations hold:

1) The prediction is only valid for alternating D–A-conjugated copolymers that are completely planar.

2) Figure 5 is based on absorption maxima, not on band gaps. The intrinsic conductor area in the graph corresponds to polymers with an absorption maximum of 0 eV. Since the band gap is always lower in energy than the absorption maximum, this area may start at higher energy.

3) No experimental data is available to check the assumption that in the low-energy region of Figure 5 the slope of the curve is still 2.5 eV.

4) For large values of n, it has been found that the linear relationship between E_{max} and $1/n$ does not hold anymore.[7] Beyond a certain number of repeat units (referred to as the effective conjugation length, n_{ECL}) the absorption maximum is no longer shifted to higher wavelengths, indicating that some kind of saturation is reached. To account for this effect, the dotted lines beneath the low band gap and intrinsic conductor areas are introduced in Figure 5. An effective conjugation length $n_{ECL}=10$ is assumed, which may seem rather low for these completely planar systems, yet it serves merely to indicate the boundary case since a conjugation length of 10 repeat units is the minimum for sterically nonhindered conjugated polymers.

Bearing these limitations in mind, we can now predict that if a D–A-conjugated copolymer is to be obtained with an absorption maximum of 1 eV (upper edge of the low-band-gap area in Figure 5), the corresponding D–A dimer must show a λ_{max} of >550 nm (>620 nm with $n_{ECL}=10$). A polymer with an absorption maximum of 0 eV must have a corresponding D–A dimer with an absorption maximum of >990 nm (>1240 nm with $n_{ECL}=10$).

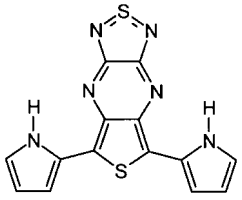

Figure 6. Donor–acceptor cotrimer with $\lambda_{max}=1345$ nm, prepared by Tanaka et al.

Tanaka et al. recently reported a D–A cotrimer that exhibits an absorption maximum of 1345 nm[22] (Figure 6). This value approaches the value of 1488 nm that is predicted by the intrinsic conductor line in Figure 5 for a trimer, and, taking into account the many assumptions, it may therefore indeed be a monomer candidate for an intrinsically conducting polymer.

Conclusions

Various push–pull conjugated oligomers with varying chain length, consisting of pyrrole or thiophene as the electron-rich subunit and 2,1,3-benzothiadiazole or quinoxaline as the electron-deficient subunit, can be synthesized in moderate yields by means of Stille cross-coupling. The incremental bathochromic shift in the absorption spectra upon chain elongation of the investigated oligomers—typically ≈ 2.5 eV on going from $1/n=0$ to $1/n=1$—is not as large as in homopolymers such as polythiophene (3.77 eV) and polypyrrole (3.19 eV). Cyclic voltammetry measurements show that this is mainly due to the diminished dispersion of the LUMO level upon chain elongation, which is supported by semi-empirical calculations that predict small LUMO AO coefficients on the coupling sites of the D–A monomers. The incremental bathochromic shift appears to be ≈ 2.5 eV for all three classes of D–A oligomers. Based on this equity, we can predict—if some assumptions are made—which requirements the monomers must meet to yield low-band-gap or even intrinsically conducting conjugated polymers. For a polymer with an absorption maximum below 1 eV, the corresponding D–A codimer must show an absorption maximum >550 nm, whereas a polymer with an absorption maximum of 0 eV requires a codimer with an absorption maximum of at least 990 nm. With these guidelines in mind, we are currently investigating new push–pull oligomers and polymers featuring low band gaps.

Experimental Section

General techniques: All solvents and reagents were reagent grade and used as received. Tetrahydrofuran (THF) was distilled over Na/benzophenone prior to use. For column chromatography, Merck silica gel 60 (particle size 0.063–0.200 mm) or Merck aluminum oxide 90 (neutral; activity I deactivated with 7 wt% of water) were used. Melting points are uncorrected and determined with a Büchi melting point apparatus (Dr. Tottoli). NMR spectra were recorded on a Bruker AM400 spectrometer at frequencies of 400.1 and 100.6 MHz for ^{1}H and ^{13}C nuclei, respectively, or on a Varian Gemini spectrometer at frequencies of 300.1 and 75.0 MHz for ^{1}H and ^{13}C nuclei, respectively. Tetramethylsilane (TMS) was used as an internal standard for ^{1}H NMR and $CDCl_3$ or [D_6]DMSO for ^{13}C NMR. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 3B UV/Vis or Lambda 900 UV/Vis/NIR spectrometer. Infrared (FT-IR) spectra were recorded on a Perkin–Elmer 1605 FT-IR spetrophotometer with wavenumbers between 4400 and 450 cm^{-1}. Elemental analyses were performed on a Perkin–Elmer 2400 Series II CHN Analyzer. GC/MS measurements were performed on a Shimadzu GCMS-QP5000. Electrospray-MS (ESI/MS) measurements were performed on a Perkin–Elmer/Sciex API300 mass spectrometer. Cyclic voltammetry was performed in CH_2Cl_2/Bu_4NPF_6 (0.1 mol L^{-1}) at 295 K, scan rate 100 mV s^{-1}, potential vs. SCE calibrated with Fc/Fc^+ (0.470 V).

4-(*N*-*tert*-Butoxycarbonylpyrrol-2-yl)-2,1,3-benzothiadiazole (1-Boc): In a 50 mL flask, *N*-*tert*-butoxycarbonyl-2-trimethylstannylpyrrole (**13**, 1.04 g, 3.10 mmol) and 4-bromo-2,1,3-benzothiadiazole (**12**, 0.65 g, 3.00 mmol) were dissolved in a mixture of toluene and 1M Na_2CO_3 (1:1, 20 mL). This mixture was deaerated and brought under an argon atmosphere. Then,

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tetrakis(triphenylphosphine)palladium() (2 mol %) was added and the resulting mixture was heated under reflux for 48 h. Subsequently, the reaction mixture was allowed to cool to room temperature, and the organic layer was separated. The aqueous layer was extracted three times with ether, and the combined organic layers were dried ($MgSO_4$), filtered, and evaporated to give crude **1-Boc** as a brown oil (1.25 g). This oil was subjected to column chromatography on Al_2O_3 (hexane/dichloromethane 5:1 as the eluent) to give pure **1-Boc** (0.49 g, 0.00163 mol, 77.8 %) as a fluorescent green-yellow solid. M.p. 71 °C, decomp 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.95$ (dd, J = 8.7, 1.1 Hz, 1H; H7 benzothiadiazole (btd)), 7.60 (dd, $J = 8.7$, 6.8 Hz, 1H; H6 btd), 7.54 (dd, $J = 6.8$, 1.1 Hz, 1H; H5 btd), 7.50 (m, 1H; H5 pyrrole (pyr)), 6.40 (dd, J = 3.3, 1.77 Hz, 1H; H3 pyr), 6.33 (m, 1H; H4 pyr), 1.10 (s, 9H; CH_3 Boc); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.7$, 154.5, 149.0, 130.0, 129.4, 128.5, 127.5, 123.4, 120.5, 115.6, 110.7, 83.18, 27.29; UV/Vis ($CHCl_3$): $\lambda_{max} = 369$ nm; IR (KBr): $\tilde{\nu} = 2975$, 1737, 1312, 1149, 848–448 cm^{-1}; $C_{15}H_{15}N_3O_2S$ (301.368): calcd C 59.78, H 5.02, N 13.94; found C 60.13, H 5.09, N 13.97.

4-(Pyrrol-2-yl)-2,1,3-benzothiadiazole (**1**): **1-Boc** (6 mg, 0.2 mmol) was put in a 10 mL flask and heated on an oil bath at 200 °C. Evolution of CO_2 and isobutene, and a rapid color change of the solid were observed. After 30 min the flask was allowed to cool to room temperature, in which pure **1** (4 mg, 0.19 mmol, 95 %) was found as a dark yellow solid. M.p. > 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.9$ (s, 1H; NH), 7.78 (dd, J = 7.2, 0.7 Hz, 1H; H7 btd), 7.74 (dd, J = 8.8, 0.7 Hz, 1H; H6 btd), 7.55 (dd, J = 8.8, 7.2 Hz, 1H; H5 btd), 7.02 (m, 1H; H3 pyr), 6.89 (m, 1H; H4 pyr), 6.35 (m, 1H; H5 pyr); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.5$, 151.5, 130.2, 129.2, 124.8, 121.9, 120.3, 117.7, 109.9, 107. 5; UV/Vis ($CHCl_3$): $\lambda_{max} = 442$ nm; IR (KBr): $\tilde{\nu} = 3395$, 1481, 1091, 880–450 cm^{-1}; MS (70 eV, EI): m/z (%): 200.85 (100) [M^+]; $C_{10}H_7N_3S$ (201.251): calcd C 59.68, H 3.51, N 20.88; found C 59.13, H 3.63, N 20.61.

4,7-Bis(*N*-Butoxycarbonylpyrrol-2-yl)-2,1,3-benzothiadiazole (**2-Boc**): This compound was prepared with the procedure described for **1-Boc** by means of a Stille coupling between dibromo-2,1,3-benzothiadiazole (**14**, 2.0 g, 6.8 mmol) and **13** (4.5 g, 14 mmol) in a mixture of toluene and 1M Na_2CO_3 (1:1, 100 mL), and a reaction time of 48 h. Column chromatography of the crude product (3.53 g) over Al_2O_3 with hexane/dichloromethane (5:1) yielded pure **2-Boc** (1.32 g, 2.83 mmol, 41.6 %) as a fluorescent orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.58$ (s, 2H; H5,6 btd), 7.49 (dd, J = 3.3, 1.8 Hz, 2H; H2 pyr), 6.41 (dd, J = 3.3, 1.8 Hz, 2H; H4 pyr), 6.34 (t, J = 3.3 Hz, 2H; H3 pyr), 1.19 (s, 9H; CH_3 Boc); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.8$, 149.1, 130.2, 127.4, 125.9, 123.4, 115.6, 110.8, 83.4, 27.4; UV/Vis ($CHCl_3$): $\lambda_{max} = 401$ nm; IR (KBr): $\tilde{\nu} = 2976$, 1743, 1318, 1138, 846–400 cm^{-1}; $C_{24}H_{26}N_4O_4S$ (466.560): calcd C 61.78, H 5.61, N 12.00; found C 61.17, H 6.05, N 11.82.

4,7-Bis(pyrrol-2-yl)-2,1,3-benzothiadiazole (**2**): This compound was prepared by the procedure described for **1** from **2-Boc** (0.196 g, 0.43 mmol) to give **2** (0.1084 g, 0.407 mmol, 95.5 %) as a deep purple solid. M.p. > 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.9$ (s, 1H; NH), 7.84 (s, 1H; H btd), 7.03 (m, 1H; H3 pyr), 6.88 (m, 1H; H4 pyr), 6.37 (m, 1H; H5 pyr); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.5$, 129.5, 123.2, 121.4, 120.0, 110.0, 107.0; UV/Vis ($CHCl_3$): $\lambda_{max} = 532$ nm; IR (KBr): $\tilde{\nu} = 3415$, 1481, 1113, 888–450 cm^{-1}; GC/MS: 265.95 (100 %) [M^+]; $C_{14}H_{10}N_4S$ (266.326): C 63.61, H 3.05, N 21.20; found C 63.92, H 3.47, N 21.18.

4-(*N*-*tert*-Butoxycarbonyl-2-trimethylstannylpyrrol-5-yl)-2,1,3-benzothiadiazole (**15**): In a 50 mL flask, a solution of 2,2,6,6-tetramethylpiperidine (TMP, 0.1 g, 0.7 mmol) in dry THF (20 mL) was cooled to −80 °C and subsequently treated with a solution of *n*-butyllithium in hexane (1.6 M, 0.44 mL, 0.7 mmol). This mixture was stirred for 15 min at −80 °C, warmed to room temperature, stirred for another 15 min and recooled to −80 °C. A solution of **1-Boc** (0.191 g, 0.63 mmol) in THF (5 mL) was added and the reaction mixture was stirred at −80 °C for 30 min. The reaction mixture was then quenched with a solution of $SnMe_3Cl$ (0.14 g, 0.7 mmol) in THF (5 mL) and subsequently warmed to room temperature. The THF was evaporated and the residue was dissolved in ether/water. The layers were separated and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, dried ($MgSO_4$), and evaporated to give the crude stannyl compound **15** as a dark oil. This oil was dissolved in hexane and filtered over Al_2O_3 and, after evaporation, gave the pure stannyl compound **15** (0.169 g, 0.36 mmol, 57 %) as a fluorescent yellow-green oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.93$ (dd, J = 8.8, 1.1 Hz, 1H; H7 btd), 7.59 (dd, J = 8.8, 6.7 Hz, 1H; H6 btd), 7.49 (dd, J = 6.7, 1.1 Hz, 1H; H5 btd), 6.49 (d, J = 3.2 Hz, 1H; pyr), 6.46 (d, J = 3.1 Hz, 1H; pyr), 0.79 (s, 9H; CH_3 Boc), 0.32 (s, 9H; $SnMe_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.9$, 154.7, 151.0, 139.0, 133.2, 129.7, 129.4, 127.2, 121.3, 120.2, 116.8, 82.75, 26.93, −8.0; $C_{18}H_{23}N_3O_2SnS$ (464.174): calcd C 46.58, H 4.99, N 9.05; found C 46.90, H 5.31, N 8.66.

4,7-Bis[5-(2,1,3-benzothiadiazol-4-yl)-*N*-*tert*-butoxycarbonylpyrrol-2-yl]-2,1,3-benzothiadiazole (**3-Boc**): This compound was prepared with the procedure described for **1-Boc** by means of a Stille coupling between **15** (0.169 g, 0.36 mmol) and **14** (0.051 g, 0.17 mmol) in a mixture of toluene and 1M Na_2CO_3 (1:1, 10 mL), reaction time 72 h. The crude reaction product (0.22 g) was subjected to column chromatography over Al_2O_3 with hexane/dichloromethane (3:1) as the eluent to give pure **3-Boc** (30 mg, 0.031 mmol, 11.3 %) as a fluorescent yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.00$ (dd, J = 8.7, 1.4 Hz, 2H; H7 btd′), 7.79 (s, 2H; H5 btd), 7.72 (dd, J = 6.9, 1.4 Hz, 2H; H5 btd′), 7.67 (dd, J = 8.6, 6.8 Hz, 2H; H6 btd′), 6.55 (d, J = 3.4 Hz, 2H; pyr), 6.52 (d, $J = 3.5$ Hz, 2H; pyr), 0.74 (s, 9H; CH_3 Boc); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.8$, 154.4, 154.2, 149.1, 132.4, 132.3, 129.6, 128.5, 128.1, 127.5, 120.7, 114.3, 114.1, 83.26, 26.94; UV/Vis ($CHCl_3$): $\lambda_{max} = 412$ nm; IR (KBr): $\tilde{\nu} = 2976$, 1751, 1304, 1146, 872–400 cm^{-1}; $C_{36}H_{30}N_8O_4S_3$ (734.882): calcd C 58.84, H 4.11, N 15.24; found C 58.79, H 3.96, N 15.25.

4,7-Bis[5-(2,1,3-benzothiadiazol-4-yl)-pyrrol-2-yl]-2,1,3-benzothiadiazole (**3**): This compound was prepared by the procedure described for **1**. However, the deprotection was performed under vacuum for 45 min. Thus **3-Boc** (22.9 mg, 0.031 mmol) was deprotected to yield **3** (16.5 mg, 0.031 mmol, 100 %) as a deep blue powder. M.p. > 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 12.1$ (s, 2H; NH), 7.94 (s, 2H; H btd), 7.89 (dd, J = 8.0, 0.8 Hz, 2H; H7 btd′), 7.83 (dd, J = 8.8, 0.9 Hz, 2H; H5 btd′), 7.66 (dd, J = 8.8, 8.1 Hz, 2H; H6 btd′), 7.1 (m, 2H; H3,4 pyr); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 130.1$, 123.5, 122.3, 118.2, 110.0, 109.6 (owing to the poor solubility of this compound in $CDCl_3$, only the peaks corresponding to carbon nuclei bearing a proton could be detected); UV/Vis ($CHCl_3$): λ_{max} = 599 nm; IR (KBr): $\tilde{\nu} = 3308$ (broad), 1475, 1120, 875–450 cm^{-1}; ESI/MS: m/z: 533.9 [M^++H]; $C_{26}H_{14}N_8S_3$ (534.648):calcd C 58.41, H 2.64, N 20.96; found C 58.26, H 2.70, N 20.34.

5-(*N*-*tert*-Butoxycarbonylpyrrol-2-yl)quinoxaline (**4-Boc**): This compound was prepared with the procedure described for **1-Boc** by means of a Stille coupling between 5-bromoquinoxaline (**16**; 0.30 g, 1.44 mmol) and **13** (0.57 g, 1.7 mmol) in a mixture of toluene and 1M Na_2CO_3 (1:1, 20 mL) with a reaction time of 72 h. Chromatography of the crude product (0.8 g) on Al_2O_3 with hexane/dichloromethane (3:1) as the eluent gave **4-Boc** as a fluorescent yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.81$ (dd, $J = 4.9$, 1.8 Hz, 2H; H2,3 qui), 8.10 (t, $J = 5.1$ Hz, 1H; H7 qui), 7.77 (dd, $J = 4.7$, 0.4 Hz, 2H; H6,7 qui), 7.52 (d, $J = 2.8$ Hz, 1H; H4 pyr), 6.35 (d, $J = 2.8$ Hz, 2H; H3,5 pyr), 1.02 (s, 9H; CH_3 Boc); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 144.5, 144.3, 142.7, 142.5, 134.8, 130.6, 129.8, 129.5, 129.1, 122.7, 115.2, 110.6, 82.72, 27.21; $C_{17}H_{17}N_3O_2$ (295.340): calcd C 69.14, H 5.80, N 14.23; found C 69.13, H 5.89, N 14.09.

5-(Pyrrol-2-yl)quinoxaline (**4**): This compound was prepared by the procedure described for **1** from **4-Boc** (0.15 g, 0.51 mmol) to give **4** (0.11 g, 0.41 mmol, 95.2 %) as a dark yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 11.98$ (s, 1H; NH), 8.89 (d, $J = 1.7$ Hz, 1H; H2,3 qui), 8.83 (d, $J = 1.8$ Hz, 1H; H2,3 qui), 8.15 (dd, J = 7.5, 1.3 Hz, 1H; H5 qui), 7.89 (dd, $J = 8.4$, 1.3 Hz, 1H; H7 qui), 7.78 (t, $J = 3.8$ Hz, 1H; H6 qui), 7.03 (m, 1H; H3,4 pyr), 6.93 (m, 1H; H3,4 pyr), 6.35 (m, 1H; H5 pyr); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.7$, 143.8, 142.6, 139.4, 129.8, 130.5, 126.3, 125.3, 119.9, 100.3, 100.0; UV/Vis ($CHCl_3$): $\lambda_{max} = 421$ nm; IR (KBr): $\tilde{\nu} = 3332$, 1493, 1465, 1088, 760, 734 cm^{-1}; MS (70 eV, EI): m/z (%): 195 (100) [M^+].

8-Bromo-5-(*N*-*tert*-butoxycarbonylpyrrol-2-yl)quinoxaline (**18**): This compound was prepared with the procedure described for **1-Boc** by means of a Stille coupling between 5,8-dibromoquinoxaline **17** (1.40 g, 4.7 mmol) and **13** (1.7 g, 5.2 mmol) in a mixture of toluene and 1M Na_2CO_3 (1:1, 40 mL) with a reaction time of 72 h. Chromatagraphy of the crude product (1.0 g) over Al_2O_3 with hexane/dichloromethane (2:1) as the eluent gave **18** as a fluorescent yellow solid (0.40 g, 1.08 mmol, 23 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.84$ (d, J = 1.8 Hz, 1H; H2 qui), 8.75 (d, $J = 1.7$ Hz, 1H; H3 qui), 8.01 (d, $J = 7.8$ Hz, 1H; H7 qui), 7.56 (d, $J = 7.7$ Hz, 1H; H6 qui), 7.41 (m, 1H; H5 pyr), 6.26 (m, 2H; H3,4 pyr), 1.00 (s, 9H; CH_3 Boc); ^{13}C NMR

(75 MHz, $CDCl_3$): $\delta = 148.9$, 146.0, 144.9, 144.8, 143.3, 134.7, 133.6, 133.0, 129.9, 123.3, 122.9, 115.4, 110.7, 83.00, 27.25.

5,8-Bis(*N*-*tert*-butoxycarbonylpyrrol-2-yl)quinoxaline (**5-Boc**): This compound was prepared with the procedure described for **1-Boc** by means of a Stille coupling between **18** (0.10 g, 0.27 mmol) and **13** (0.10 g, 0.22 mmol) in a mixture of toluene and 1M Na_2CO_3 (1:1, 20 mL) with a reaction time of 72 h. Chromatography of the crude product (0.6 g) over Al_2O_3 with hexane/dichloromethane (1:1) as the eluent gave **5-Boc** as a fluorescent yellow oil (0.17 g, 0.17 mmol, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.78$ (s, 2H; H2,3 qui), 7.80 (s, 2H; H5,6 qui), 7.52 (m, 2H; H2 pyr), 6.38 (m, 4H; H3,4 pyr), 1.12 (CH_3 Boc); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.8$, 144.1, 142.2, 136.4, 131.8, 129.7, 123.4, 115.7, 111.8, 27. 9.

5,8-Bis(pyrrol-2-yl)quinoxaline (**5**): This compound was prepared by the procedure described for **1** from **5-Boc** (0.10 g, 0.20 mmol) to give **5** as a dark red solid (0.047 g, 0.18 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 11.9 (s, 2H; NH), 8.87 (s, 2H; H2,3 qui), 8.12 (s, 2H; H6,7 qui), 7.01 (m, 2H; H3 pyr), 6.90 (m, 2H; H4 pyr), 6.35 (m, 2H; H5 pyr); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 142.4$, 142.3, 130.6, 126.5, 125.9, 119.6, 109.3, 107.6; UV/Vis ($CHCl_3$): $\lambda_{max} = 505$ nm; IR (KBr): $\tilde{\nu} = 3362$, 1469, 1107, 1083, 794, 725 cm^{-1}; ESI/MS: m/z: 261.2 [M^++H].

5-(*N*-*tert*-Butoxycarbonyl-2-trimethylstannylpyrrol-5-yl)quinoxaline (**19**): This compound was prepared by the procedure described for **15** in dry THF (20 mL) with TMP (0.11 g, 0.75 mmol), *n*-BuLi (0.47 mL of a 1.6M solution in hexane, 0.75 mmol), **4-Boc** (0.20 g, 0.68 mmol), and $SnMe_3Cl$ (0.11 g, 0.75 mmol). The crude product was subjected to column chromatography over Al_2O_3 with hexane/dichloromethane (2:1) as the eluent to give **19** as a yellow oil (0.10 g, 0.22 mmol, 32%), which was used in the next step without further purification. The proton spectrum of **19** is qualitatively equal to that of **4-Boc**, except for the absence of the α-proton of pyrrole and the appearance of the $SnMe_3$ peak at $\delta = 0.3$.

5-[5-(*N*-*tert*-Butoxycarbonylpyrrol-2-yl)quinoxalin-8-yl]-2-(quinoxalin-5-yl)-*N*-*tert*-butoxycarbonylpyrrole (**6-Boc**): This compound was prepared with the procedure described for **1-Boc** by means of a Stille coupling between **18** (0.09 g, 0.24 mmol) and **19** (0.10 g, 0.22 mmol) in a mixture of toluene and 1M Na_2CO_3 (1:1, 20 mL) with a reaction time of 72 h. Chromatography of the crude product (0.8 g) over Al_2O_3 with hexane/dichloromethane (1:1) as the eluent gave **6-Boc** as a fluorescent yellow solid (0.12 g, 0.20 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.81$ (d, $J = 1.8$ Hz, 1H; H2 qui), 8.79 (d, $J = 1.8$ Hz, 2H; H3 qui), 8.74 (d, $J = 1.8$ Hz, 1H; H2 qui′), 8.71 (d, $J = 1.8$ Hz, 1H; H3 qui′), 8.13 (dd, $J = 8.5$, 1.4 Hz, 1H; H8 qui), 8.00 (m, 2H; H6,7 qui), 7.85 (m, 2H; H6,7 qui′), 7.51 (m, 1H; H5 pyr′), 6.49 (s, 2H; H3,4 pyr), 6.37 (m, 2H; H3,4 pyr′), 1.10 (CH_3 Boc), 0.59 (CH_3 Boc′); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.1$, 149.0, 142.3, 142.2, 142.0, 141.9, 141.4, 141.3, 141.2, 141.2, 131.2, 131.1, 131.0, 130.9, 130.8, 130.5, 130.1, 130.0, 129.9, 129.8, 129.7, 122.0, 112.2, 111.5, 110, 81.3, 81.0, 28.8, 28.5.

5-[5-(Pyrrol-2-yl)quinoxalin-8-yl]-2-(quinoxalin-5-yl)pyrrole (**6**): This compound was prepared by the procedure described for **1** from **5-Boc** (0.10 g, 0.17 mmol) to give crude **5** as a purple solid. This solid was dissolved in THF and precipitated in hexane to give pure **5** as purple needles (0.058 g, 0.15 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 14.2$ (s, 1H; NH pyr), 11.9 (s, 1H; NH pyr′), 9.01 (d, $J = 1.7$ Hz, 1H; H3 qui), 8.98 (d, $J = 1.7$ Hz, 1H; H2 qui′), 8.92 (d, $J = 1.7$ Hz, 1H; H2 qui), 8.89 (d, $J =$ 1.6 Hz, 1H; H3 qui′), 8.16 (m, 3H; H6,7 qui′, H6 qui), 7.90 (dd, $J = 8.3$, 1.1 Hz, 1H; H6 qui), 7.78 (t, $J = 7.9$ Hz, 1H; H7 qui), 7.00 (m, 3H; H pyr′, H4 pyr), 6.37 (m, 1H; H5 pyr′); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 144.7$, 143.8, 142.7, 142.5, 142.3, 139.9, 132.2, 131.8, 130.7, 130.4, 130.0, 126.6, 126.4, 126.1, 125.8, 125.5, 119.7, 109.7, 109.4, 109.3, 107.8; UV/Vis ($CHCl_3$): $\lambda_{max} =$ 535 nm; IR (KBr): $\tilde{\nu} = 2959$ (very broad), 1692, 1657, 1589, 1529, 1255, 771.8 cm^{-1}; ESI/MS: m/z: 389.2 [M^++H].

4-(Thien-2-yl)-2,1,3-benzothiadiazole (**7**): Compound **12** (1.00 g, 0.00463 mol) and 2-trimethylstannylthiophene (**20**, 1.14 g, 0.00463 mol) were dissolved in dry DMF (25 mL). The solution was degassed by evacuation of the flask with a single-stage vacuum pump (until effervescence of air ceased) followed by the introduction of dry argon gas. After this cycle was repeated three times, [$Pd^{II}(PPh_3)_2Cl_2$] catalyst (0.03 g, 0.043 mmol) was added and the reaction mixture stirred at 75 °C for 60 min. The resulting orange solution was diluted with ether and extracted five times with ice water to remove DMF. The ether layer was dried ($MgSO_4$) and evaporated to give crude **7** (1.06 g), which was purified by sublimation of the solid in a kugelrohr apparatus at approximately 100 °C to give **7** (0.90 g, 0.0041 mol, 89%) as a yellow-green solid. M.p. 46 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 MHz): $\delta = 8.11$ (dd, $J = 3.8$, 1.3 Hz, 1H; H5 thienyl (th)), 7.9 (dd, $J = 8.8$, 1.1 Hz, 1H; H4 btd), 7.85 (dd, $J = 7.1$, 1.1 Hz, 1H; H6 btd), 7.6 (dd, $J = 7.2$, 8.8 Hz, 1H; H5 btd), 7.5 (dd, $J = 5.0$, 1.1 Hz, 1H; H3 th), 7.21 (dd, $J = 3.8$, 5.0 Hz, 1H; H4 th); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 155.4, 152.1, 139.2, 132.1, 129.5, 127.9, 127.7, 126.7, 125.4, 120.0; UV/Vis ($CHCl_3$) $\lambda_{max} = 390$ nm; IR (KBr): $\tilde{\nu} = 1589$, 1541, 1484, 1427, 1210, 1166, 1046, 852, 820, 804, 753, 688, 504 cm^{-1}; $C_{10}H_6N_2S_2$ (218.302): calcd C 55.02, H 2.77, N 12.83; found C 55.46, H 2.75, N 12.66.

Bis-4,7-(thien-2-yl)-2,1,3-benzothiadiazole (**8**): Compound **8** was prepared by the procedure described for **7** from **14** (1.13 g, 0.00384 mol) and **20** (1.90 g, 0.00769 mol) in dry DMF (25 mL) with [$Pd^{II}(PPh_3)_2Cl_2$] catalyst (0.108 g) with a reaction time of 90 min. The crude product was crystallized from $CHCl_3$/hexane after treatment with active carbon to give **8** as highly fluorescent orange needles (0.64 g, 0.00213 mol, 55.5%). M.p. 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.07$ (dd, $J = 3.8$, 1.2 Hz, 2H; H5 th), 7.80 (s, 2H; H5,6 btd), 7.42 (dd, $J = 5.1$, 1.1 Hz, 2H; H3 th), 7.18 (dd, $J = 3.8$, 5.1 Hz, 2H; H4 th); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.6$, 139.3, 128.0, 126.0, 127.5, 126.8, 125.8; UV/Vis ($CHCl_3$) $\lambda_{max} = 447$ nm; IR (KBr): $\tilde{\nu} = 1526$, 1481, 1422, 1379, 1216, 1073, 1042, 881, 825, 710, 700, 690, 508 cm^{-1}; $C_{14}H_8N_2S_3$ (300.428): calcd C 55.97, H 2.68, N 9.32; found C 55.63, H 2.56, N 9.10.

4-(2,2′-Bithien-5-yl)-2,1,3-benzothiadiazole (**9**): Compound **9** was prepared by the procedure described for **7** from **12** (0.50 g, 0.00232 mol) and 2-thieno-5-trimethylstannylthiophene (**21**; 0.76 g, 0.00232 mol) in dry DMF (15 mL) with [$Pd^{II}(PPh_3)_2Cl_2$] catalyst (0.032 g), and a reaction time of 60 min. The crude product was chromatographed on silica gel with a gradient of dichloromethane/hexane (1:5 → 1:1) as eluent to give, after evaporation of the solvent, **9** as fluorescent, orange plates (0.52 g, 0.00173 mol, 74.8%). M.p. 156 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.04$ (dd, $J = 3.9$, 1.1 Hz, 1H; H5 th), 7.9 (dd, $J = 8.8$, 1.1 Hz, 1H; H7 btd), 7.83 (dd, $J = 7.1$, 1.1 Hz, 1H; H5 btd), 7.63 (dd, $J = 7.1$, 8.6 Hz, 1H; H6 btd), 7.3 (m, 3H; H4 th H4′,5′ th′), 7.07 (dd, $J = 3.9$, 4.9 Hz, 1H; H3 th); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 155.1$, 152.1, 139.0, 138.5, 137.4, 129.6, 128.5, 128.0, 125.0, 124.6, 124.5, 124.1, 120.0; UV/Vis ($CHCl_3$) $\lambda_{max} = 429$ nm; IR (KBr): $\tilde{\nu} = 1527$, 1479, 1445, 1039, 828, 800, 745, 715, 524, 491 cm^{-1}; $C_{14}H_8N_2S_3$ (300.428): calcd C 55.97, H 2.68, N 9.32; found C 56.09, H 2.74, N 9.23.

Bis-4,7-(2,2′-bithien-5-yl)-2,1,3-benzothiadiazole (**10**): Compound **10** was prepared by the procedure described for **7** from **12** (0.22 g, 0.75 mmol) and **21** (0.50 g, 1.5 mmol) in dry DMF (15 mL) with [$Pd^{II}(PPh_3)_2Cl_2$] catalyst (0.042 g), and a reaction time of 120 min. The crude product was crystallized from $CHCl_3$ to give **10** as lustrous, copper-like plates (50 mg, 0.108 mmol, 14.4%). M.p. 188 °C; ^{1}H NMR (400 MHz, [D_6]DMSO): $\delta =$ 8.17 (s, 2H; H5,6 btd), 8.15 (dd, $J = 3.9$, 1.1 Hz, 2H; H5 th), 7.59 (dd, $J = 5.1$, 1.1 Hz, 2H; H3 th), 7.47 (m, 4H; H3,4 th), 7.16 (dd, $J = 3.6$, 5.1 Hz, 2H; H4′ th′); UV/Vis ($CHCl_3$) $\lambda_{max} = 505$ nm; IR (KBr): $\tilde{\nu} = 1480$, 1226, 1064, 840, 796, 698, 683, 527 cm^{-1}; $C_{22}H_{12}N_2S_5$ (464.680): calcd C 56.86, H 2.60, N 6.03; found C 56.90, H 2.60, N 5.69.

4-(Thien-2-yl)-7-(2-trimethylstannylthien-5-yl)-2,1,3-benzothiadiazole (**22**): TMP (0.265 g, 0.0017 mol) was dissolved in dry THF (25 mL) under an argon atmosphere. The solution was cooled to −78 °C on a dry-ice/acetone bath and *n*-butyllithium (1.06 mL of a 1.6M solution in hexane, 0.0017 mol) was added rapidly. The resulting solution was allowed to warm to room temperature, was kept at this temperature for 10 min, and subsequently recooled to −78 °C. At this temperature, a solution of **8** (0.40 g, 0.0013 mol) in dry THF (5 mL) was added dropwise. The resulting deeply colored solution was kept at −78 °C for 30 min at which temperature a solution of $SnMe_3Cl$ (0.338 g, 0.0017 mol) in dry THF (5 mL) was added. The reaction mixture was then allowed to warm to room temperature, and mixed with ether. The organic phase was extracted three times with dilute hydrochloric acid to remove TMP, dried ($MgSO_4$), and evaporated to give a brown oil. This oil was filtered over aluminum oxide with hexane as the eluent. Evaporation of the orange hexane filtrate gave **22** as fluorescent orange plates (0.55 g, 0.00128 mol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.17$ (dd, $J = 3.5$, 2.0 Hz, 1H; H5 th), 8.10 (dd, $J =$ 4.8, 2.0 Hz, 1H; H4 th), 7.84 (s, 2H; H5,6 btd), 7.44 (dd, $J = 4.7$, 3.6 Hz, 1H; H3 th), 7.29 (dd, $J = 3.6$, 1.5 Hz, 1H; H3 thSn), 7.20 (dd, $J = 3.7$, 1.5 Hz, 1H; H4 thSn), 0.43 (s, 9H; $HSnMe_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.6$, 145.0, 140.2, 139.3, 136.1, 128.5, 128.4, 128.0, 127.5, 127.3, 126.8, 126.6, 125.7, −8.17; $C_{17}H_{16}N_2S_3Sn$ (463.235): calcd C 44.07, H 3.48, N 6.04; found C 43.67, H 3.84, N 5.45.

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Bis-5,5′-(4-thieno-2,1,3-benzothiadiazol-7-yl)-2,2′-bithiophene (**11**): $[Pd^{II}(PPh_3)_2Cl_2]$ catalyst (0.02 g) was added to a solution of **22** (0.12 g, 0.28 mmol) in of toluene (25 mL), without exclusion of air. The reaction mixture was then refluxed for 18 h and allowed to cool down to room temperature, and the black precipitate filtered off. The precipitate ($\approx$ 0.07 g) was extracted in a soxhlet apparatus with hexane and chloroform. The intensely red chloroform fraction was evaporated to give 0.06 g of a black powder. This powder was crystallized from chloroform at $-20\,^{\circ}C$ to give **11** as a black powder (12.5 mg, 0.021 mmol, 14.8 %). M. p. $> 300\,^{\circ}C$; UV/Vis ($CHCl_3$) $\lambda_{max} = 521$ nm; IR (KBr): $\tilde{\nu} = 1479, 1434, 1205, 1046, 881.2, 829.0, 796.1, 695.8, 513.2\ cm^{-1}$; ES/MS: m/z: 598.1 (612.1, 626.2) amu; $C_{28}H_{14}N_4S_6$ (598.841): calcd C 56.16, H 2.36, N 9.36; found C 55.59, H 2.55, N 8.88.

Acknowledgements: The authors wish to thank R. A. S. Scholtes for his efforts with the synthesis, J. J. Apperloo for cyclic voltammetry measurements and Dr. R. A. J. Jansen and Dr. E. E. Havinga for stimulating discussions. One of the referees is acknowledged for suggesting the use of cyclic voltammetry and semiempirical calculations. Philips and PTN are acknowledged for unrestricted research grants.

Received: November 14, 1997 [F889]

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