Synthesis and Characterization of Mixed Oligoheterocycles Based on End-capped Oligothiophenes

Ullrich Mitschke, Elena Mena Osteritz, Tony Debaerdemaeker, Moritz Sokolowski, and Peter Bäuerle*

Abstract: A homologous series of mixed oligoheterocycles **2**–**6**, based on the end-capped quinquethiophene EC5T **1**, was synthesized by the introduction of electronegative heteroatoms, such as oxygen and nitrogen, into the conjugated π-system. This led to novel structures in which the central thiophene unit of the parent compound **1** is substituted by other heterocycles (thiazole, 1,3,4-thiadiazole, furan, oxazole, 1,3,4-oxadiazole) that have a more pronounced acceptor character. The characterization of the optical and electrochemical properties clearly reveal the influence of the heteroatoms on the electronic properties. The electron-withdrawing character of the central heterocycles renders the oxidation of the oligomer more difficult while reduction is facilitated. Moreover, in some cases a hypsochromic shift of the longest-wavelength absorption and emission is observed along with a significant enhancement of the fluorescence quantum yield in solution and in the solid state. The HOMO/LUMO energy difference, determined from optical and electrochemical measurements, corresponds qualitatively well with the values obtained from semiempirical calculations. An X-ray structural determination was performed on oligoheterocycle **6** and the experimental and calculated data are compared.

Keywords: conjugation · fluorescence spectroscopy · oligomers · oligothiophenes · organic light-emitting diodes · structure–property relationships

Introduction

The synthesis of well-defined conjugated oligomers is very useful in order to gain more insight into the structural and electronic peculiarities of the corresponding polydisperse polymers;[1] particular attention has been paid to the oligothiophenes in recent years.[2] On account of their controllable and rigorously defined structure, the physical properties can be followed and correlated with the chain and conjugation length. In this respect the synthesis and characterization of a complete series of end-capped oligothiophenes (EC*n*T) up to the heptamer clearly revealed the advantages of this approach. Excellent correlations of the optical and electrochemical data with the chain length were obtained.[3] Not only the model character of a series of oligomers plays an important role nowadays; defined oligomers represent novel materials with properties which, in some respects, surpass those of the corresponding polymers. Oligothiophenes have recently been used as active components in all-organic field-effect transistors,[4] and light-modulating[5] and light-emitting devices (LED).[6] In order to study the electroluminescent properties of conjugated systems systematically, a series of end-capped oligothiophenes (EC4T to EC7T) was used to prepare LEDs by vacuum sublimation of the active organic material.[6a,b] The devices emit light in the yellow/orange range of the visible spectrum at relatively low voltages and moderate current densities. Optical data from solid-state measurements also correlate well with the chain length of the oligomers. Since oligothiophenes are generally electron-rich compounds and are therefore easy to oxidize or to *p*-dope, further investigation on ITO/EC*n*T/metal LEDs showed that the corresponding current/voltage curves are a consequence of injection and transport of holes. In contrast, these materials are more difficult to *n*-dope on account of the LUMO energy level. Therefore, the mobility of the electrons is diminished and light emission arises directly from a zone close to the cathode.[6a]

In order to tailor the electronic properties of oligothiophenes and to investigate structure–property relationships,

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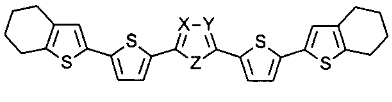
we synthesized and characterized a novel series of mixed oligoheterocycles based on end-capped oligothiophenes. By the introduction of a five-membered heterocycle with a more pronounced acceptor character (thiazole, 1,3,4-thiadiazole, furan, oxazole, 1,3,4-oxadiazole) the electronic structure and properties of the resulting mixed oligomers are expected to be altered, whereas the geometric structure remains practically constant. In a combined experimental and theoretical approach, we report on the synthesis and structure, on optical and electrochemical characterization, and on theoretical studies of the mixed oligoheterocycles **2**–**6** and compare the data obtained with the parent end-capped quinquethiophene EC5T **1**.



1 (X=CH, Y=CH, Z=S) **4** (X=CH, Y=CH, Z=O)
2 (X=N, Y=CH, Z=S) **5** (X=N, Y=CH, Z=O)
3 (X=N, Y=N, Z=S) **6** (X=N, Y=N, Z=O)

Results and Discussion

In general, the electronic properties of oligothiophenes can be altered to a certain extent by the attachment of either sterically[7] or electronically active substitutents at both the β[8] and the terminal α positions[9] of the conjugated π system. Another approach is the synthesis of mixed oligoheterocycles in which thiophene units are replaced by other heteroaromatic moieties. The latter case often includes the combination of thiophene units and other electron-rich heterocycles. Thus, mainly thiophene- and pyrrole-containing oligomers have been synthesized so far by means of transition-metal-catalyzed coupling reactions[10] or by ring-closure reactions of acyclic precursors.[11] For example, Meijer et al.[10] very recently prepared various series of mixed oligomers comprised of alternating unsubstituted, *N*-boc-protected, or *N*-dodecyl-substituted pyrrole and thiophene units by means of the Stille coupling reaction. Cava et al.[11d] reported on a systematic study of pentamers in which (*N*-alkylated) pyrrole moieties are connected to thiophene units. In comparison to the parent quinquethiophene, the longest wavelength absorptions of these mixed oligomers are blue-shifted and the redox transitions displaced to more negative potentials due to the decrease of both the HOMO and the LUMO energy levels. In several series of mixed thiophene/pyrrole oligomers the oxidation potential remained almost constant as the chain length was increased from two to seven heterocyclic units;[10, 11b] this is in contrast with the decrease in the oxidation potential generally observed with increasing chain length.

Abstract in German: *Auf der Basis des end-capped Quinquethiophens EC5T **1** wurde unter Einbeziehung elektronegativer Heteroatome wie Sauerstoff und/oder Stickstoff eine Serie von gemischten Oligoheterocyclen, **2**–**6**, synthetisiert. In diesen neuartigen Strukturen ist die zentrale Thiopheneinheit der Stammverbindung durch Heterocyclen höherer Elektronenaffinität (Thiazol, 1,3,4-Thiadiazol, Furan, Oxazol, 1,3,4-Oxadiazol) ersetzt. Wie die Untersuchung der optischen und elektrochemischen Eigenschaften dieser Verbindungen zeigt, werden die elektronischen Eigenschaften durch die Anwesenheit der Heteroatome deutlich beeinflußt. Während die Reduktion aufgrund des elektronenziehenden Charakters des zentralen Heterocyclus erleichtert wird, wird die Oxidation des Oligomers durch den Einbau mehrerer elektronegativer Heteroatome sukzessive erschwert. In einigen Fällen konnte eine hypsochrome Verschiebung der längstwelligen Absorption und Emission sowie eine signifikante Erhöhung der Fluoreszenzquantenausbeute sowohl in Lösung als auch im Festkörper beobachtet werden. Die aus den optischen und elektrochemischen Messungen erhaltenen HOMO/LUMO-Energiedifferenzen sind im Einklang mit den aus semiempirischen Rechnungen erhaltenen Werten. Die röntgenographische Kristallstrukturbestimmung des Oligoheterocyclus **6** ermöglicht schließlich den Vergleich von dessen Molekülstruktur mit den berechneten geometrischen Daten.*

There have been few reports on mixed thiophene oligomers, including electron-accepting five-membered heterocycles. Combinations of thiophene and furan rings were synthesized in good yields by the dehydration of 1,4-diketones[11d] and by nickel-catalyzed coupling reactions.[12] Kossmehl and Manecke synthesized an alternating thiophene/1,3,4-oxadiazole trimer and a pentamer as model compounds for the corresponding polymer.[13] Both compounds are included in a patent dealing with optical brighteners, dyes, and UV-protectors.[14] Trimeric and tetrameric combinations of thiophene and thiazole were synthesized for further polymerization.[15] On account of their low-lying LUMO levels, silacyclopentadiene moieties have recently been introduced into mixed oligoheterocycles as electron-deficient units and investigated with respect to their electroluminescence behavior.[16] Dimeric to tetrameric combinations of thiophenes and electron-accepting thiophene-1,1-dioxides have been synthesized very recently by means of palladium-catalyzed cross-coupling reactions and were investigated with respect to their electronic properties.[17]

Synthesis: The central building block for the synthesis of all five novel mixed oligoheterocycles **2**–**6** is 2-(4,5,6,7-tetrahydrobenzo[*b*]thien-2-yl)thiophene (**9**). Bithiophene **9** is available from the ring-closure reaction of 1,4-diketone **8**, which was synthesized from α-halogenoketone **7**[18] and 1-(*N*-pyrrolidino)cyclohexene in 43% yield. Reaction of 1,4-diketone **8** with either diphosphorus pentasulfide or Lawesson's reagent (L.R.) gave in both cases a mixture of the capped bithiophene **9** and the corresponding furyl derivative **10**, which can be separated by column chromatography. Whereas in the case of P_2S_5 only 20% of the bithiophene **9** could be isolated, L.R. gave an isolated yield of 86% (Scheme 1).

The synthesis of thiophene/thiazole oligomer **2** was achieved by a Stille-type palladium-catalyzed cross-coupling reaction of the corresponding 2,5-dibrominated thiazole **12**[19] with two equivalents of the stannylated capped bithiophene **11**. Bithiophene **11** was obtained in 97% yield by

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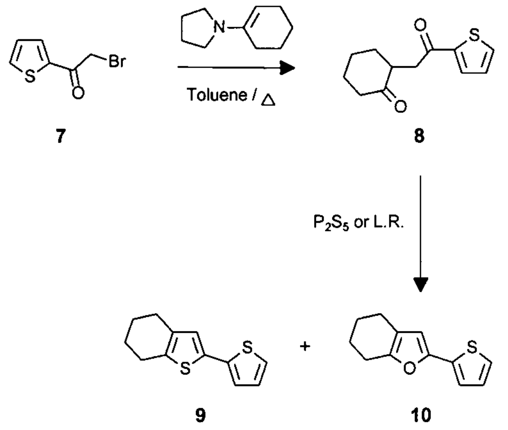


Scheme 1. Synthesis of the central building block end-capped bithiophene **9**.

selective metalation of the capped bithiophene **9** with *n*-BuLi and reaction with chlorotrimethylstannane (Scheme 2). The coupling reaction led to a mixture of pentamer **2**, homocoupling product EC4T **15**, and demetalated capped bithiophene **9**. As a consequence of its low solubility, the thiophene/thiazole oligomer **2** precipitated from the reaction mixture. Chromatography and subsequent fractionated sublimation gave pure oligomer **2** in 43% yield.

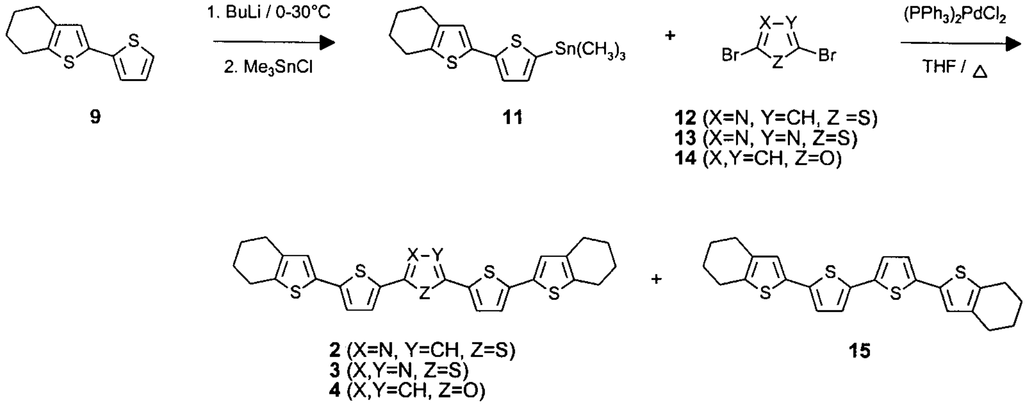
Thiophene/1,3,4-thiadiazole oligomer **3** was synthesized from the corresponding dibrominated 1,3,4-thiadiazole **13**[20] in 28% yield and purified in a similar manner. Also in this case, the homocoupling product EC4T **15** was isolated as the main byproduct. On account of its even lower solubility in nearly all common organic solvents, the chromatographic isolation of mixed oligomer **3** is more difficult than that of the thiophene/1,3,4-thiazole oligomer **2**. Consequently, the yield is diminished to 28% (Scheme 2).

The synthesis of pentamer thiophene/furan **4** was also accomplished by means of the palladium-catalyzed cross-coupling of capped stannyl-bithiophene **11** and 2,5-dibromofuran **14**.[21] In addition to the homocoupling product EC4T **15**, which was formed as a consequence of the lower stability of the dibromoheterocycle in distinctly larger amounts compared with the previous cases **2** and **3**, oligomer **4** was isolated analytically pure in 23% yield after repeated chromatography and fractionated sublimation (Scheme 2).

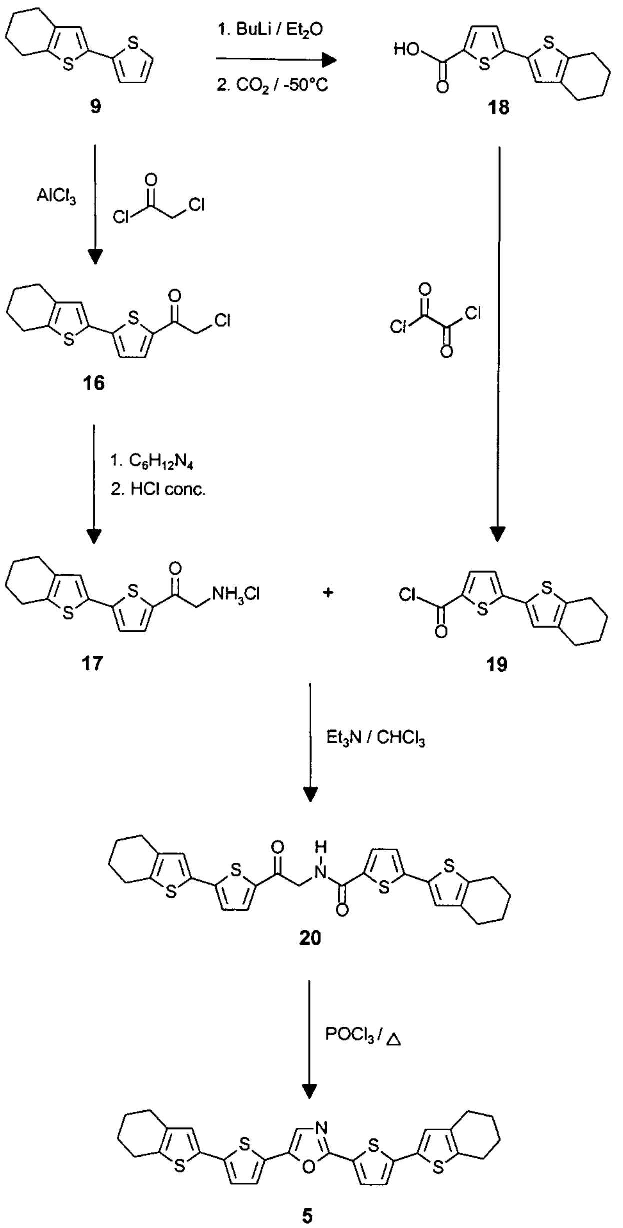
Because of the inherent low stability of 2,5-dimetalated or 2,5-dihalogenated oxazoles[22] and 1,3,4-oxadiazoles,[23] which would be required for the synthesis of the mixed pentamers thiophene/oxazole **5** and thiophene/1,3,4-oxadiazole **6** in aryl–aryl coupling reactions, a different synthetic route was used in which the central heterocycle is formed from acyclic precursors in the last step. The dehydration of 1,2-diacylhydrazines and 2-acylaminoketones is one of the most common methods to produce 1,3,4-oxadiazole and oxazole rings, respectively.[23] We started from bithiophene **9**: the first step was a Friedel–Crafts acylation with chloroacetic acid chloride and $AlCl_3$ to form capped bithiophene **16** in 51% yield along with at least five side-products that were separated by chromatography. Bithiophene **16** was converted in 61% yield to the corresponding amine **17** by a Delépine reaction that used urotropine as the nucleophile and subsequent release of the amino group with concentrated hydrochloric acid. For the synthesis of the second component, bithiophene **9** was first transformed into the carbonic acid **18** in 94% yield by lithiation with *n*-BuLi and quenching with carbon dioxide. Bithiophene carboxylic acid **18** was then quantitatively treated with oxalylchloride to give the corresponding acid chloride **19**, which was used without further purification. Both bithiophene components **17** and **19** were treated under basic conditions to form the precursor amide **20** in 22% yield, which was subsequently dehydrated and cyclized in boiling phosphorusoxitrichloride to afford the desired thiophene/oxazole pentamer **5** in 39% yield after chromatographic work-up and subsequent sublimation (Scheme 3).

The synthesis of thiophene/1,3,4-oxadiazole pentamer **6** was somewhat easier due to the symmetry of the 1,3,4-oxadiazole ring. Thus, two equivalents of capped bithiophene acid chloride **19** were treated with one equivalent hydrazine to form *N,N'*-diacylhydrazine **21** in 80% yield. Dehydration of the acyclic precursor **21** in boiling phosphoroxitrichloride finally led to the mixed oligoheterocycle thiophene/1,3,4-oxadiazole **6**, which was purified by sublimation to give 68% of a partially crystalline material (Scheme 4).

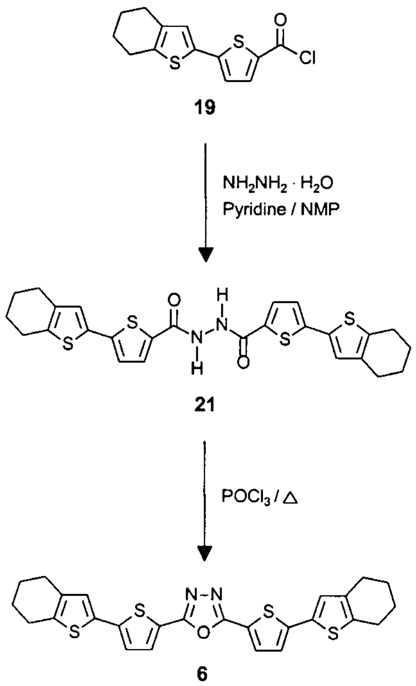
Optical properties: The optical properties of quinquethiophene EC5T **1** and the mixed oligoheterocycles **2**–**6** were studied. The absorption and emission maxima, fluorescence quantum yields, and the optical energy gaps are given in Table 1. The optical energy gaps correspond to the energy difference of the ground and excited states and therefore correlate to the HOMO/LUMO gap of the oligomers. Thus,



Scheme 2. Synthesis of the mixed pentamers **2**, **3**, and **4**.



Scheme 3. Synthesis of bithiophene components **17** and **19**, precursor amide **20**, and finally thiophene/oxazole pentamer **5**.



Scheme 4. Synthesis of mixed oligoheterocycle thiophene/1,3,4-oxadiazole **6**.

Table 1. Optical properties of the mixed oligoheterocycles **2**–**6** compared to the end-capped quinquethiophene EC5T **1**.

	λ_{max}^{abs} [a] [nm]	lg ε	λ_{max}^{em} [a] [nm]	Φ_{295K}^{em} [b] [%]	$\Delta E_{opt.}$ [c] [eV]	$\Delta\tilde{\nu}$ [d] [cm^{-1}]
1	431	4.71	497, 525[e]	19 (±5)	2.56	974
2	435	4.71	511, 530[e]	12 (±5)	2.53	1081
3	428	4.71	494, 520[e]	20 (±5)	2.61	958
4	427	4.66	481, 513	32 (±5)	2.64	891
5	414	4.68	479, 500[e]	30 (±5)	2.76	≈1120
6	402	4.71	453, 477	62 (±5)	2.81	828

[a] Solvent dichloromethane, $c = 5 \times 10^{-6}$ M for absorption measurements, $c = 1 \times 10^{-6}$ M for emission measurements. [b] The external standard was 9,10-diphenylanthracene. [c] The energy gap was determined by the difference in energy between the 0–0 transition in absorption and emission. [d] Stoke's shift, determined by deconvolution of the spectra. [e] Shoulder.

several effects can be investigated: firstly the influence of the introduction of more electronegative nitrogen atoms which replace one or two methine groups in compounds **2**, **3**, **5**, and **6** can be evaluated in two different series: one of these series is based on EC5T **1** and comprises oligoheterocycles **1**–**3** (thiophene series), the second is based on the furan analogue **4** and comprises compounds **4**–**6** (furan series). Secondly, the change in properties due to the replacement of the sulfur by oxygen in the central heterocyclic ring can be evaluated by cross-comparison of compounds **1** and **4**, **2** and **5**, as well as **3** and **6** between the two series.

The absorption spectra of compounds **1**–**6** were measured in dichloromethane at a concentration of 5×10^{-6} M. Typically, broad and unstructured bands due to the π–π* transition are observed which reflect the noncoplanarity and rotational freedom of the individual rings in the aromatic system. In the thiophene series the introduction of nitrogen atoms at the β-position of the central ring, a situation which is realized in oligothiophene/thiazole **2** and oligothiophene/1,3,4-thiadiazole **3**, in comparison with the pure oligothiophene EC5T **1** leads only to a marginal shift of the absorption maxima ($\Delta\lambda^{abs} = 3-4$ nm), with unaltered extinction coefficients (Table 1, Figure 1). In contrast, in the furan series the absorption maxima are distinctly blue-shifted on going from furan **4** to oxazole **5** and to 1,3,4-oxadiazole **6** ($\Delta\lambda_{4,5}^{abs} = 13$ nm, $\Delta\lambda_{4,6}^{abs} = 25$ nm), respectively. In the case of the nitrogen-containing oligoheterocycles **5** and **6**, a second weaker absorption band at about $\lambda = 355$ nm is uncovered (Figure 2). Cross-comparison in both series reveals that the replacement of sulfur by oxygen leads in the case of thiophene **1** and furan **4** only to a small blue-shift of the absorption ($\Delta\lambda_{1,4}^{abs} = 4$ nm) whereas for the couples **2**/**5** ($\Delta\lambda_{2,5}^{abs} = 21$ nm) and **3**/**6** ($\Delta\lambda_{3,6}^{abs} = 26$ nm) distinct displacements to higher energies are found. This result is consistent with the optical properties of some

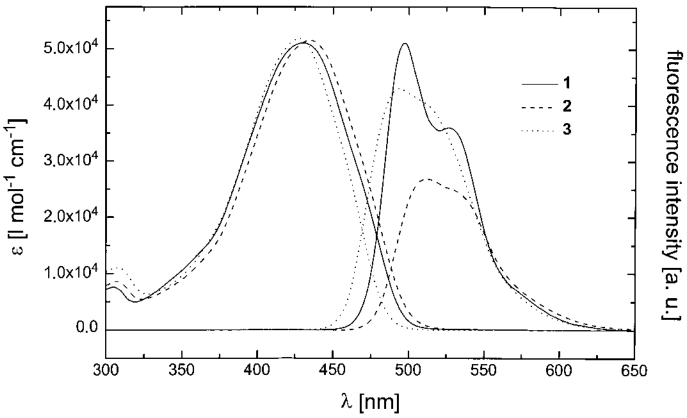


Figure 1. Absorption and emission spectra of oligoheterocycles **1**–**3** in dichloromethane (thiophene series).

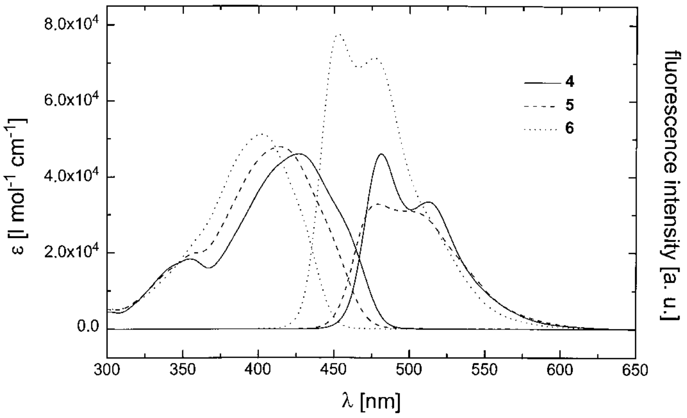


Figure 2. Absorption and emission spectra of oligoheterocycles **4**–**6** in dichloromethane (furan series).

similar pentameric mixed oligoheterocycles with thiophene/furan sequences (T-T-T-F-T and T-F-T-F-T) which are compared to α-quinquethiophene.[11d] In this series, the introduction of each furan ring leads to a successive hypsochromic shift of the absorption maximum of $\Delta\lambda^{abs} = 2$ nm.

The emission spectra of all oligomers **1**–**6** were measured in dichloromethane at a concentration of 1×10^{-6} M (Figures 1 and 2). On account of vibronic couplings, structured emission bands are found that indicate a more planarized and stiffer structure in the excited state. Deconvolution of the absorption and emission bands allowed the determination of the 0–0 transitions and the energy difference of the vibrational levels ($\Delta\nu \approx 1100-1300$ cm^{-1}), which typically corresponds in those systems to the symmetric stretch vibration of the C=C double bonds in the heteroaromatic moieties.[24] The Stoke's shifts of $\Delta\nu \approx 830-1120$ cm^{-1} indicate that, compared with the ground state, the geometric change in the excited state is relatively small. In analogy to the absorption data in the thiophene series, the emission maxima vary to a certain extent ($\Delta\lambda^{em} \leq 17$ nm). The optical energy gap, which corresponds to the energy of the 0–0 transition, exhibits the same trend as found for the absorption maxima and oligothiophene/thiazole **2** exhibits the smallest gap ($\Delta E_{opt.} = 2.53$ eV). In the furan series, the emission maxima are blue-shifted stepwise with each successive nitrogen atom present in the oligomer ($\Delta\lambda^{em}_{4,5} = 2$ nm, $\Delta\lambda^{em}_{4,6} = 28$ nm). 1,3,4-Oxadiazole **6** exhibits a bright blue-green emission ($\lambda^{em}_{max} = 455$ nm) and the most pronounced hypsochromic displacement. Cross-comparison in both series clearly reveals that the replacement of sulfur by the more electronegative oxygen leads to distinct blue-shifts of the emission maxima ($\Delta\lambda^{em} = 16-41$ nm).

Compounds **1**–**6** show a bright fluorescence and, with respect to the application of these oligomers in LEDs, the fluorescence quantum yields of the oligomers are of special interest. In order to quantify their fluorescence behavior in solution, the fluorescence quantum yields were determined in dichloromethane at ambient temperature by the optically diluted solution method[25] and with 9,10-diphenylanthracene as the standard.[26] Systematic errors of ±5% should be taken into account. Whereas in the thiophene series **1**–**3** the successive introduction of nitrogen atoms leads only to small changes of the emission efficiency ($\Phi_{295\,K} = 12-20\%$), the presence of oxygen atoms in furan oligomers **4**–**6** strongly enhances the fluorescence quantum yield. In comparison to the parent quinquethiophene EC5T **1** ($\Phi_{295\,K} = 19\%$), the values determined nearly than doubled for furan **4** ($\Phi_{295\,K} = 32\%$) and oxazole **5** ($\Phi_{295\,K} = 30\%$) and, surprisingly, more than threefold in the case of oxadiazole **6** ($\Phi_{295\,K} = 62\%$). The remarkable increase of the fluorescence quantum yield from the furan series to the thiophene series can be explained by the heavy atom effect.[26] The replacement of sulfur by oxygen seems to favor fluorescence emission of **4**–**6**, while other deactivation processes, especially intersystem crossing (ISC) to the triplet state, are rendered more difficult. Preliminary measurements on the photo- and electroluminescence properties of 1,3,4-oxadiazole **6** in the solid state clearly support these findings. In comparison to EC5T **1**, an enhancement of the emission intensity by a factor of 6–7 is found for thin layers of oligomer **6**.[27]

A solvatochromic study for oligoheterocycles **1**–**6** was performed in n-hexane ($\varepsilon = 1.9$), acetone ($\varepsilon = 20.7$), and DMF ($\varepsilon = 36.7$) as solvents with differing polarities. Compounds **1**, **2**, **4**, and **5** exhibit a small positive solvatochromism indicating that the dipole moment in the excited state is greater than that of the ground state. In contrast, we found that oligomers **3** and **6**, which contain two nitrogens in the central heterocyclic moiety, do not show any solvatochromic effects and therefore there is no change in the dipole moment during the optical transition.

Finally, it can be concluded that the optical properties of the oligoheterocycles do not change dramatically in the thiophene series (compounds **1**–**3**), whereas the effects are more pronounced in the furan-series (compounds **4**–**6**). Compared with the parent oligomer, oligothiophene/1,3,4-oxadiazole **6** exhibits the largest blue-shift in absorption and in emission and simultaneously the highest increase in the fluorescence efficiency. Thus, it is evident that the introduction of more electronegative heteroatoms in oligomers **2**, **3**, **5**, and **6** affects the energy level of the individual HOMO and LUMO in both series in different ways. This is discussed below, taking redox potentials and calculations on the electronic structure into account.

Electrochemical properties: Whereas optical measurements can be correlated to the energy difference of the frontier orbitals, the oxidation and reduction potentials provide additional information on the relative position of the energy levels of both HOMOs and LUMOs. This is important with respect to organic LEDs, since the charged species of the active organic material, created by oxidation and reduction at the electrodes, migrate into the film.[28] On account of the blocking of the reactive terminal positions in the end-capped oligothiophenes the precise determination of the redox potentials is possible, even for the shorter members.[3a] Thus, consistent with the general behavior of electron-rich oligothiophenes, investigations of pentamer EC5T **1** by cyclic voltammetry (CV) showed that it can be reversibly oxidized to stable radical cations and dications at relatively low potentials ($E^{\circ}_{\mathrm{Ox1}} = 0.25$ V, $E^{\circ}_{\mathrm{Ox2}} = 0.51$ V vs Fc/Fc$^+$). CVs in the oxidative potential regime were recorded in the electrolyte dichloromethane/tetrabutylammonium hexafluorophosphate (TBAHPF) (0.1 M) and potentials are given versus the ferrocene/ferricenium (Fc/Fc$^+$) couple at scan rates of 100 mV s^{-1} (Table 2, Figure 3). The reduction of oligomer EC5T **1** was performed in the electrolyte THF/TBAHPF (0.1 M) and did indeed lead to stable radical anions; however, it proceeded at a relatively negative potential ($E^{\circ}_{\mathrm{Red1}} = -2.33$ V vs Fc/Fc$^+$). The second reduction wave at $E^{\circ}_{\mathrm{Red2}} = -2.58$ V vs Fc/Fc$^+$, however, is quasireversible and less stable dianions are formed. The HOMO/LUMO gap of $\Delta E_{\mathrm{EC}} = 2.56$ eV is estimated from the onset of the first oxidation and reduction process, respectively. For EC5T **1** it is in excellent agreement with the optically determined gap ($\Delta E_{\mathrm{opt.}} = 2.56$ eV). The oxidation and reduction potentials and the HOMO/LUMO gaps of the oligoheterocycles **1**–**6** are listed in Table 2 and clearly show the influence of the heteroatoms. In both the thiophene and the furan series, the first reversible and the second quasi- or irreversible reduction is, as expected, facilitated stepwise with the successive introduction of electronegative nitrogen atoms into the oligomer ($\Delta E^{\circ}_{\mathrm{Red1}} = 0.21$ to 0.33 V, $\Delta E^{\circ}_{\mathrm{Red2}} = 0.05$ to 0.10 V). In a similar manner, the first and the second oxidation potentials are gradually shifted to more positive values ($\Delta E^{\circ}_{\mathrm{Ox1}} = 0.23$ to 0.61 V, $\Delta E^{\circ}_{\mathrm{Ox2}} = 0.13$ to 0.15 V) due to the greater electron-attracting properties of the central heterocyclic moieties in oligomers **2**, **3**, **5**, and **6**. Moreover, in the case of 1,3,4-thiadiazole **3** and 1,3,4-oxadiazole **6** the first oxidation process already leads to an irreversible wave in the CV, which indicates follow-up reactions of the radical cation formed (Figure 3). Cross-comparison between the two series shows that the oxidation potentials are practically identical for each couple; however, the reduction of the oligomers in the furan series generally occurs at more negative potentials ($\Delta E^{\circ}_{\mathrm{Red1}} = 0.17$ to 0.32 V). This leads simultaneously to a widening of the HOMO/LUMO gap in the latter series, which is indeed found experimentally ($\Delta[\Delta E_{\mathrm{EC}}] = 0.05$ to 0.43 V). This is in excellent agreement with the trend found in the optical measurements. The half-wave potentials determined for unsubstituted α-quinquethiophene ($E^{\circ}_{\mathrm{Ox1}} \approx 0.54$ V, $E^{\circ}_{\mathrm{Ox2}} \approx 0.89$ V vs Fc/Fc$^+$) and oligothiophene/furan (T-T-T-F-T) ($E^{\circ}_{\mathrm{Ox1}} \approx 0.45$ V, $E^{\circ}_{\mathrm{Ox2}} \approx 0.85$ V vs Fc/Fc$^+$)[11d] are about 250–400 mV more positive than those of EC5T **1** and furan **4**, respectively; this is due to the weak electron-donating effect of the cyclohexene end-caps in oligomers **1** and **4**.

Table 2. Electrochemical properties of the mixed oligoheterocycles **2**–**6** compared to the end-capped quinquethiophene EC5T **1**.

	$E^{\circ}_{\mathrm{Red2}}$[a] [V]	$E^{\circ}_{\mathrm{Red1}}$[a] [V]	E°_{Ox1}[b] [V]	E°_{Ox2}[b] [V]	ΔE_{EC}[c] [V]
1	−2.58[d]	−2.33	0.25	0.51	2.56
2	−2.56[d]	−2.20	0.48	0.64	2.62
3	−2.48[d]	−2.00	≈0.84[e]	–	2.56
4	−2.66[e]	−2.50	0.20	0.49	2.61
5	−2.61[e]	−2.39	0.48	0.64	2.77
6	−2.68[e]	−2.32	≈0.81[e]	–	2.99

[a] In THF/TBAHPF (0.1 M) vs Fc/Fc$^+$ at 100 mV s^{-1}. The solvent correction is 50–100 mV vs dichloromethane. [b] In dichloromethane/TBAHPF (0.1 M) vs Fc/Fc$^+$ at 100 mV s^{-1}. [c] Determined by $\Delta E_{\mathrm{CV}} = E'_{\mathrm{Ox1}} - E'_{\mathrm{Red1}}$ (E' is the potential at which the redox process starts) and solvent correction. [d] Quasireversible redox process. [e] Irreversible redox process, E° determined at $I^{\circ} = 0.855\ I_{\mathrm{p}}$.[29]

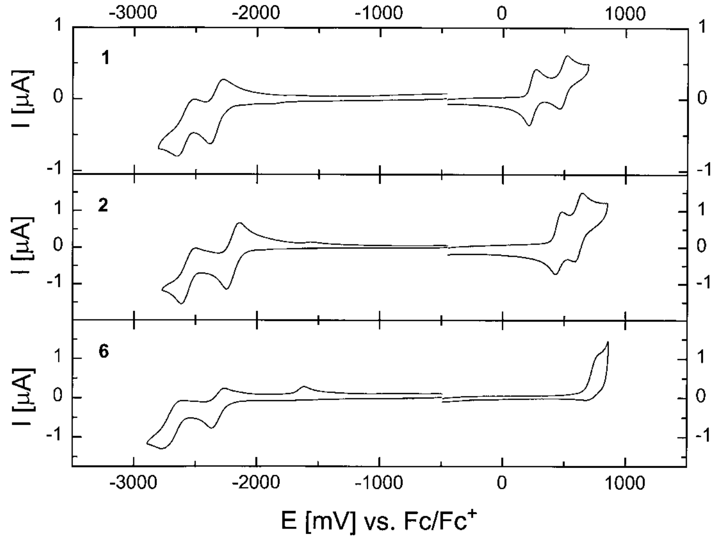


Figure 3. Electrochemical characterization of EC5T **1**, oligothiophene/thiazole **2**, and 1,3,4-oxadiazole **6**. Reduction in THF, TBAHPF (0.1 M), oxidation in CH_2Cl_2, TBAHPF (0.1 M), $c = 5 \times 10^{-4}$ mol l^{-1}; $v = 100$ mV s^{-1}).

With regard to the HOMO/LUMO gap, the determination of the redox potentials revealed the same trend as found in the optical measurements. The energy difference only marginally changed in the thiophene series **1**–**3**, whereas oligothiophene/1,3,4-oxadiazole **6** exhibited by far the largest gap and changes. The experimentally determined redox potentials can now be compared to the calculated HOMO/LUMO energies of the oligomers **1**–**6**.

Semiempirical calculations: From the observed spectroscopic and electrochemical behavior, the influence of the additional, more electronegative heteroatoms on the electronic properties becomes evident. The data and trends observed are well supported by semiempirical calculations. Semiempirical quantum chemical methods are able to describe the geometric and electronic structure of organic aromatic compounds in good agreement with experimental data. The quantum-chemical Austin Model 1 (AM1) method[30] was used to evaluate the electronic properties of the oligomers **1**–**6**. The determination of the energy levels of the exited states was realized with a full single-configuration interaction (CI). The performance

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of the available parameters from AM 1 in the case of our type of compounds was verified with other semiempirical calculations (PM 3, MNDO) as well as by ab initio methods.[31]

Table 3 gives the calculated HOMO and LUMO energies and the resulting energy gap for all members of the two series.

Table 3. HOMO/LUMO energies, gap energies, and dipole moments calculated by semi-empirical methods (AM 1) for the mixed oligoheterocycles **2**–**6** compared to the end-capped quinquethiophene EC5T **1**. The gap energies are compared with the optically and electrochemically determined gaps.

	HOMO [eV]	LUMO [eV]	$\Delta E_{\text{ber.}}$ [eV]	$\Delta E_{\text{corr.}}$ [eV][a]	$\Delta E_{\text{opt.}}$ [eV]	ΔE_{EC} [eV]	μ (μ'[b]) [D]
1	−8.00	−3.21	4.79	2.89	2.56	2.56	0.6 (0.9)
2	−8.10	−3.40	4.70	2.80	2.53	2.62	1.0 (1.44)
3	−8.22	−3.57	4.65	2.75	2.61	2.56	2.6 (3.42)
4	−7.87	−3.19	4.68	2.78	2.64	2.61	0.5 (0.77)
5	−8.08	−3.32	4.76	2.86	2.76	2.77	1.4 (1.58)
6	−8.31	−3.41	4.90	3.00	2.81	2.99	3.3 (3.35)

[a] Relaxation correction by −1.9 eV for solvent interaction.[32] [b] μ' of the central heterocyclic ring was calculated on an ab initio [6-31G(d′)] basis.[33]

The calculated energy gaps, which were determined for the gas phase, were additionally corrected by −1.9 eV for solvent interaction[32] and can now be compared with the experimentally determined values in solution. As expected, the introduction of electronegative heteroatoms generally leads to a stabilization and a decrease of both the HOMO and the LUMO energies. A more detailed examination of the data of the thiophene series reveals a successive decrease of about 0.1 eV in the HOMO energy for EC5T **1**, thiazole **2**, and 1,3,4-thiadiazole **3**, and a simultaneous decrease in the LUMO energy by about 0.2 eV. Consequently, this results in a decreasing energy separation of the frontier orbitals from $\Delta E_{\text{corr.}} = 2.89$ eV for oligomer **1**, to 2.80 eV for **2**, and to 2.75 eV for **3**. The reverse trend is found for the members of the furan series: the HOMO energy successively decreases by about 0.2 eV on going from furan **4**, to oxazole **5**, and to 1,3,4-oxadiazole **6**, whereas the LUMO energy decreases by about 0.1 eV. The consequence is an increase of the energy gap from $\Delta E_{\text{corr.}} = 2.78$ eV for oligomer **4**, to 2.86 eV for **5**, and to 3.00 eV for **6**. Compared with the optical and electrochemical gap, the theoretical values correspond very well and systematically lie only slightly higher ($\Delta E = 0.01$ to 0.33 eV). The calculated energy positions of the frontier orbitals and the resulting HOMO/LUMO gaps (gas phase) for oligoheterocycles **1**–**6** are depicted graphically (solid lines) in Figure 4. Additionally, the optical gaps determined in solution are given (dashed lines). However, with respect to the calculated levels, the absolute energetic positions were estimated by taking the solvatochromism of the individual molecules into account. If one compares the calculated and the optical gaps in the furan series, a perfect correlation of the trend is found for all compounds. The gap gradually increases on going from furan **4**, to oxazole **5**, and to 1,3,4-oxadiazole **6**. On the other hand, in the thiophene series, the calculated energy gaps gradually decrease from EC5T **1**, to thiazole **2**, and to 1,3,4-thiadiazole **3**. However, the experimental value for oligomer **3** was somewhat higher than that theoretically expected and the gap increases again. This effect can be rationalized by taking account of the solvatochromic behavior, which is positive for oligomers **1**, **2**, **4**, and **5**. This indicates a larger stabilization of the LUMO level in solution than of the HOMO level. For 1,3,4-oxadiazole **6** there is not much stabilization of the LUMO since no solvatochromism could be detected. Thus, this leads in the furan series to the expected increase of the gaps in solution. In contrast in the thiophene series, due to the lack of solvatochromism and the resulting increased gap for oligomer **3**, the trend observed for oligomers **1** and **2** is reversed and the relative gap increases instead of decreasing (Figure 4).

The dipole moments are also given in Table 3. Parent compounds **1** ($\mu = 0.6$ D) and **4** ($\mu = 0.5$ D) exhibit a small dipole moment. This is increased by the introduction of the more electronegative nitrogen atoms and is highest for oligothiophene/1,3,4-oxadiazole **6** ($\mu = 3.3$ D). On account of the symmetrical arrangment of the thiophene rings around the central unit, the contribution to the total dipole moment originates from the central heterocyclic ring. Calculations of the monomeric heterocycles on an ab initio level gave almost the same values and thus proved this explanation.

X-ray crystallography: X-ray data for oligothiophenes have been sparse, since the growth of single crystals is very difficult, and the crystals often exhibit intrinsic disorder and defects. Crystallographic structure determinations of several unsubstituted α-oligothiophenes have been reported.[34] Since the longer oligomers do not crystallize well from solutions, vapor growth methods or growth from the melt have very recently led to crystals suitable for X-ray analysis.[34d, 34e, 35] Typically, the molecules adopt a coplanar, all-*anti*-conformation and show the propensity to pack in a herringbone pattern due to favorable edge-to-face aromatic interactions. Occasionally, a

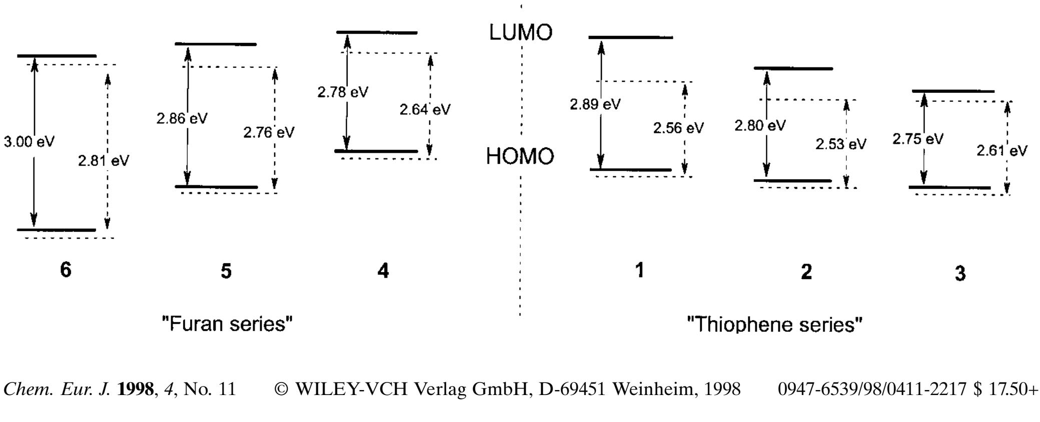


Figure 4. Energy level diagram of the frontier orbitals for oligoheterocycles **1**–**6**. Calculated HOMO/LUMO levels (—) and optically determined values (- - -).

certain percentage of the *syn*-conformation of the terminal thiophene ring with respect to its nearest neighbor is found. Substitution in oligothiophenes may lead to deviations from coplanarity resulting in twist and deformation of thiophene rings.[36] However, in these cases the molecules generally tend to stack in parallel layers.

To our knowledge, crystallographic data of mixed oligoheterocycles in general and of comparable quinquethiophenes are not yet known. We were able to grow single crystals of mixed pentamer thiophene/1,3,4-oxadiazole **6** suitable for X-ray analysis by repeated fractionated sublimation of a highly purified material in a gradient-tube furnace. At temperatures of 220 to 230°C ($p = 1 \times 10^{-3}$ mbar) the deposition of amorphous material in the colder part of the sublimation unit is observed. As soon as the organic material covers the glass surface, long yellow needles of up to 0.5 mm × 0.5 mm × 10 mm start to form. The crystal growth is not much influenced by the speed of sublimation, but it is favored by an enhanced amount, and especially by high purity, of the inserted starting material. This is in contrast to the observation reported by Laudise et al. when the physical vapor deposition is conducted in a stream of inert gas.[35] Crystals selected for X-ray analysis were typical of the bulk and there was no indication of polymorphism. Crystallographic data and refinement parameters are given in Table 4, and views of the unit cell and the structure along various axes are given in Figure 5. Atomic labeling and the side view of one molecule are presented in Figure 6, which also gives some selected, experimentally determined bond lengths and angles and the comparison with calculated parameters.

Table 4. Crystallographic data, data collection, and refinement parameters for oligothiophene/1,3,4-oxadiazole **6**.

	6
formula	$C_{26}H_{22}N_2OS_4$
M_r	506.70
T [K]	293(2)
wavelength [Å]	$\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$
crystal system	triclinic
space group	$P\bar{1}$
a [Å]	6.655(2)
b [Å]	14.221(5)
c [Å]	14.406(5)
α [°]	62.25(3)
β [°]	85.09(4)
γ [°]	76.59(4)
V [Å^3]	1173.2(7)
Z	2
ρ_{calcd} [g cm^{-3}]	1.434
μ ($\mathrm{Mo_{K\alpha}}$) [mm^{-1}]	0.428
F (000)	528
crystal size [mm]	0.20 × 0.20 × 0.15
θ range [°]	2.78–25.91
index ranges	$-8 \leq h \leq 8$, $-17 \leq k \leq 17$, $-17 \leq l \leq 17$
reflections collected	9970
unique reflections	4185
R_{int} (F^2)	0.0725
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	4185/0/302
GoF S	0.874
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0567$, $wR_2 = 0.1283$
R indices (all data)	$R_1 = 0.1242$, $wR_2 = 0.1496$
largest diff. peak/hole [e Å^{-3}]	0.455/−0.374

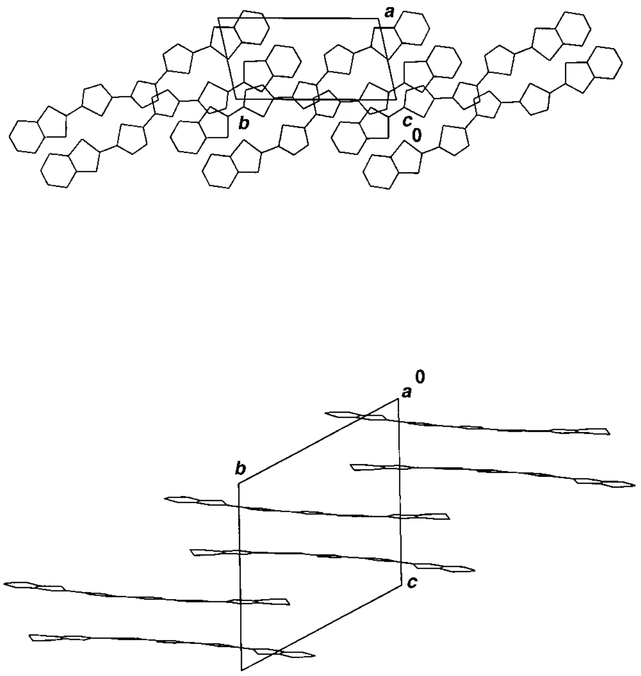


Figure 5. Packing views of oligomer **6** on the *a*/*b* plane (top) and the *b*/*c* plane (bottom).

The crystals of oligomer **6** belong to the triclinic space group $P\bar{1}$, with two molecules in the unit cell ($Z = 2$). The packing in the crystal and the conformation of the molecules in the solid state, however, show rather unique features not normally observed for conjugated oligomers. At first glance a ribbon-like dimer formation along the molecular plane is evident. The top-view projection, which corresponds to the *a*/*b*-plane of the unit cell, shows that the dimers are formed from two oligomers that face each other point-inverted and which are laterally displaced by about half a ring unit (Figure 5, top). Therefore, the dipole moments of the central oxadiazole rings operate in the opposite direction and are compensated, indicating a minimized electronic repulsion. The next dimer is laterally displaced by exactly half the length of a molecule to form a lamella-like structure. The side-view projection of the molecules, which corresponds to the *b*/*c*-plane, further clarifies the dimer arrangement into slipped π-stacks (Figure 5, bottom). The dimers form curved parallel layers that are oriented perpendicular to the *b*/*c* plane. If the bent structure of every single molecule is neglected, then the mean distance between two layers is 3.60 Å.

The packing motif of oligothiophene/1,3,4-oxadiazole **6** is different to that of unsubstituted oligothiophenes, which typically pack in a herringbone-like manner.[34] However, very recently, structures with different packing motifs were found for a low-temperature form of α-2T[34a] and for high-temperature polymorphs of α-4T[34c] and α-6T[34d]. Comparison of the structure of oligomer **6** can be made to the very recently published crystal data of α,ω-dicyano-oligothiophenes.[36k] The tetramer and the pentamer also form slipped π-stacks in which a lateral shifting of 0.5 molecule per layer is detected. An α,ω-disilylated sexithiophene crystallizes in the same triclinic space group $P\bar{1}$ and, on account of the bulky end groups, also forms slipped stacks. However, in this case, with

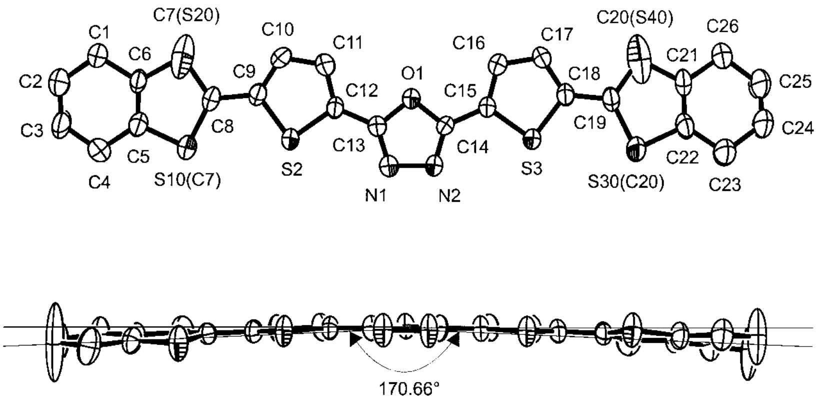


Figure 6. ORTEP front view of oligomer **6** showing the atomic labeling, 50 % thermal ellipsoids (top). Side view of oligomer **6** (bottom). Selected bond lengths [Å] (standard deviation)/ calculated values, PM3: O1–C13 1.369(6)/1.381, C13–N1 1.294(8)/1.338, N1–N2 1.416(7)/1.348, C12–C13 1.437(9)/1.440, S2–C9 1.729(6)/ 1.737, S2–C12 1.720(9)/1.739, C9–C10 1.358(8)/1.379, C10–C11 1.403(8)/1.424, C11–C12 1.360(9)/1.379, C8–C9 1.461(7)/1.440, S10/C7–C8 1.689(8)*/ 1.747, S10/C7–C5 1.730(0)*/1.734, C5–C6 1.359(9)/1.374, C6–C7/S20 1.594(7)*/1.433, C7/ S20–C8 1.580(5)*/1.375, C5–C4 1.495(0)/1.483, C4–C3 1.423(5)*/1.525, C3–C2 1.302(8)*/ 1.521, C2–C1 1.490(9)/1.524, C1–C6 1.495(7)/1.483. The values indicated by * are not reliable due to disordering and to the presence of two conformations (*syn*/*anti*).

respect to the conformation of the individual molecule, only the two middle thiophene rings are coplanar and have an *anti* arrangement, whereas relatively large gradual twists are found for the other rings.[36j]

The second unique feature of oligomer **6** concerns the conformation of the individual molecules. It is evident from the side view in Figures 5 and 6 that the molecules are slightly bent in a u-form and two bent oligomers form convexly oriented dimers. The curvature angle of the molecule respective to a completely coplanar form was determined to be 170.66°. Thus, the vertical deviation of each terminal tetrahydrobenzo[*b*]thiophene unit from the molecular plane is 4.67°. Interestingly, this intriguing behavior is confirmed theoretically; for oligomer **6** the curvature was calculated to be 174.8°. Moreover, this phenomenon seems to be a general trend, since calculations reveal an angle of 166° and 167° for end-capped quinquethiophene **1** and for unsubstituted α-5T, respectively.[37]

The inner three heterocyclic rings in oligomer **6** exhibit a coplanar all-*anti* conformation, the outer terminal tetrahydrobenzo[*b*]thienyl moieties are slightly twisted ($\Phi = 8^\circ$) and disordered to a certain extent. The terminal units show a preferred *syn* conformation (80 %; Figure 6, top). Thus, the determination of the bond lengths and angles in these units is not absolutely accurate and the atoms involved have been labeled C7(S20), S10(C7), C20(S40), S30(C20), reflecting the *syn(anti)* conformer ratio. Due to various possible conformations in the cyclohexene end-cap there is also some inaccuracy concerning the C2–C3 and C24–C25 bonds. Selected bond lengths are given in the legend to Figure 6. All heterocyclic rings show normal bond lengths and angles when compared with those from structural data of either a diphenyl-substituted 1,3,4-oxadiazole[38] or of α-oligothiophenes.[34c,e] Thus, the C–O bonds (1.36–1.37 Å), C–N bonds (1.29 Å), and the N–N bond (1.42 Å) in the 1,3,4-oxadiazole unit, the C–S bonds (1.72–1.73 Å), C=C double bonds (1.36–1.37 Å), and C–C single bonds (1.39–1.40 Å) in the thiophene units, and the C–C inter-ring bonds (1.44–1.46 Å) are in very good agreement with published data. The occurence of *syn* conformers was first discovered in β-substituted quater-,[36e] quinque-, and sexithiophenes.[36h] In contrast to the nearly coplanar oligomer **6**, and on account of conformational strain in these compounds, remarkable dihedral angles occur between adjacent *syn*-arranged thiophene rings (54.2°,[36e] 19–24°[36h]) causing deformations of bond lengths and bond angles.[36b, 36e]

The calculation of the geometry of oligothiophene/1,3,4-oxadiazole **6** reveals that the *syn/syn* rotamer (with respect to the thiophene rings) is energetically slightly more stable than the *anti/anti* rotamer by 0.8 kcal mol^{-1}. With respect to the central 1,3,4-oxadiazole ring, the inner thiophene rings are only marginally twisted by 1.2°, whereas the outer thiophene rings exhibit dihedral angles of 30.2°, which is markedly more than that determined for the molecules in the crystal. The calculated bond lengths ($\Delta d = \pm 0.03$ Å) are in excellent agreement with the experimental data. Only the length of the N–N single bond is somewhat underestimated.

Conclusions

The synthesis of a series of mixed oligoheterocycles **2**–**6**, based on quinquethiophene EC5T **1**, was developed: ring closure of acyclic precursors or transition-metal-catalyzed coupling reactions of suitable heterocyclic precursors were used to produce the novel oligomers **2**–**6**. In order to tune the electronic properties without greatly changing of the geometric parameters, successively more electronegative nitrogen atoms were incorporated in the central ring to give the oligoheterocycles **2** and **3** (thiophene series). The replacement of the central sulfur by the more electronegative oxygen leads to the oligomers **4**–**6** (furan series). All the compounds were obtained highly purified by repeated fractionated sublimation in order to allow investigation of precise structure–property relationships.

Detailed investigation of the optical and electrochemical properties clearly reveals that the changes in absorption, emission, and redox behavior are more pronounced in the furan series. Corroborated by semiempirical calculations, it becomes very evident that the introduction of more electronegative heteroatoms systematically affects the energy levels and the gap between the corresponding frontier orbitals. Thus, oligothiophene/1,3,4-oxadiazole **6** exhibited the most pronounced differences and, with respect to EC5T **1**, showed a remarkable increase in the fluorescence quantum yield—by a factor of 3 in solution and by a factor of 6–7 in the solid state. Preliminary attempts to produce organic LEDs based on 1,3,4-oxadiazole **6** showed that both the LED performance and the external quantum yield could be improved. This will be reported in a forthcoming publication.[39]

Detailed analyses of the structural parameters were possible for oligomer **6**, as crystals suitable for X-ray analysis could be grown by a sublimation technique. Two unique features, not yet observed in oligothiophenes, were found: in the oligomers, the two terminal thiophene rings are preferentially *syn* arranged and surprisingly show a u-type bending in the molecular plane; this was also confirmed theoretically. This leads to a novel packing motif in the crystal lattice in which two oligomers form a dimer. The dimers then are arranged in slipped π-stacks.

Current efforts in our laboratory are now directed towards the synthesis of (longer) mixed oligoheterocycles in which more than one thiophene ring is replaced by other electron-deficient heterocycles.

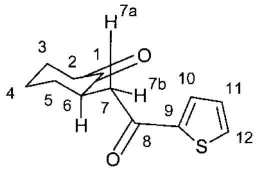
Experimental Section

General methods: Solvents and reagents were purified and dried by usual methods prior to use. Thin-layer chromatography (TLC) was carried out on plastic plates Polygram SIL and Polygram Alox from Macherey & Nagel. Developed plates were dried and examined under a UV lamp. Preparative column chromatography was performed on glass columns of different sizes packed with Kieselgel 60 (0.020–0.200 nm, Merck). Melting points were determined with an Electrothermal 9100 melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on Bruker DMX600 (600 MHz), AMX500 (500 MHz), and ACF250 (250 MHz) spectrometers (with deuterated solvent as the lock-in and tetramethylsilane as the internal reference). ^{13}C NMR spectra were recorded on Bruker DMX600 (151 MHz), AMX500 (126 MHz) and ACF250 (63 MHz) spectrometers. Elemental analyses were performed on a Carlo Erba Instrumentatione Elementar Analyser 1106. UV/Vis/NIR spectra were recorded on a Perkin–Elmer Lambda 19 in 1 cm cuvettes. Fluorescence spectra were recorded on a Perkin–Elmer LS50 in 1 cm cuvettes. Fluorescence quantum yields were determined with respect to 9,10-diphenylanthracene ($\Phi_R^{em} = 0.85$ in cyclohexane[26]). The cyclic voltammetry experiments were performed with a computer-controlled EG&G PAR273 potentiostat in a three-electrode single-compartment cell (5 mL). The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of $A = 0.785$ mm², which was polished down to 0.5 μm with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire; the reference was an Ag/AgCl secondary electrode. All potentials were internally referenced to the ferrocene/ferricenium couple. Argon 4.8 was used to purge all solutions before use. Routinely, a constant concentration of $2.5-5\times10^{-4}$ M of electroactive species was used. The electrolyte consisted of either dichloromethane (p.a., Riedel de Haën) which was refluxed and distilled over CaH_2 under N_2 or THF (which was refluxed and distilled first over $LiAlH_4$ and then over potassium under N_2). The solvents were directly transferred by syringe to the electrochemical cell. The supporting salt was 0.1 M TBAHPF from Fluka, which was recrystallized twice from ethanol/water and dried in a high vacuum.

X-ray crystal structure analysis: Single crystals of **6** suitable for X-ray crystallography were grown by sublimation. Diffraction data were collected on a STOE–IPDS image-plate diffractometer ($Mo_{K\alpha}$ radiation, graphite monochromator) in the φ-rotation scan mode. The structure was solved by direct methods with the XMY93 program system[40] and subjected to full-matrix refinement with SHELXL-93.[41] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added in calculated positions. The terminal 4,5,6,7-tetrahydrobenzo[*b*]thienyl rings are conformationally disordered. Two orientations, related by a 180° rotation about one ring–ring bond, are realized in the solid sate (80:20 *syn*/*anti*). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101488. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit @ccdc.cam.ac.uk).

Starting materials were prepared according to literature procedures: 1-(*N*-pyrrolidino)cyclohexene, [b.p. 112 °C/12 mbar; yield 75 %],[42] 2-(2-bromo-1-oxoethyl)thiophene (**7**) [b.p. 70–75 °C/5 × 10^{-3} mbar; yield 62 %],[18] 2,5-dibromothiazole (**12**) [m.p. 46–47 °C; yield 42 %][19], 2,5-dibromo-1,3,4-thiadiazole (**13**) [m.p. 111 °C; yield 49 %],[20] 2,5-dibromofuran (**14**) [b.p. 48–49 °C/12 mbar; yield 23 %],[21] bis(triphenylphosphino)palladiumdichloride [m.p. 269–273 °C; yield 97 %].[43]

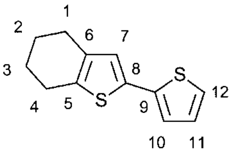
2-[2-Oxo-2-(2-thienyl)ethyl]cyclohexanone (**8**): A solution of **7** (27.9 g, 136 mmol) in toluene (25 mL) was added dropwise to a boiling solution of 1-(*N*-pyrrolidino)cyclohexene (20.6 g, 136 mmol) in toluene (75 mL). The resulting mixture was stirred for three hours. Water (100 mL) was added dropwise and the reaction mixture was stirred for an additional 2 h under reflux. After removal of the toluene by azeotropic distillation, the remaining aqueous phase was extracted with diethyl ether. The organic phase was washed with water, dried ($MgSO_4$), and evaporated to give **8** as a red oil, which can be purified and crystallized from hexane to yield **8** as colorless crystals (13.0 g, 43 %). M.p. 62 °C; ^1H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.71$ (dd, $^3J(H,H) = 3.7$ Hz, $^4J(H,H) = 1.2$ Hz, 1 H; H10), 7.57 (dd, $^3J(H,H) = 4.9$ Hz, $^4J(H,H) = 1.2$ Hz, 1 H; H12), 7.07 (dd, $^3J(H,H) =$ 4.0 Hz, $^3J(H,H) = 4.9$ Hz, 1 H; H11), 3.44 (dd, $^2J(H,H) = 17.1$ Hz, $^3J(H,H) =$ 6.7 Hz, 1 H; H7a), 3.07 (m, 1 H; H2), 2.61 (dd, $^2J(H,H) = 17.1$ Hz, $^3J(H,H) =$ 6.1 Hz, 1 H; H7b), 2.37 (m, 2 H; H6), 2.11 (m, 2 H; H3), 1.62 (m, 4 H; H4, H5); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta =$ 211.2 (C8), 191.5 (C1), 144.2 (C9), 133.3, 131.8, 127.9 (C10,11,12), 46.4, 41.8, 38.9, 34.1, 27.8, 25.2 (C2,3,4,5,6,7); $C_{12}H_{14}O_2S$ (222.3): calcd C 64.83, H 6.35, S 14.42; found C 64.97, H 6.40, S 14.13.



8

2-(4,5,6,7-Tetrahydrobenzo[*b*]thien-2-yl)thiophene (**9**)

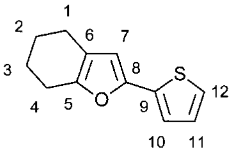
Ring closure with Lawesson's reagent: A stirred suspension of **8** (34.0 g, 153 mmol) and Lawesson's reagent (77.6 g, 192 mmol) in dry toluene (1.5 L) was heated at reflux for 5 h under nitrogen. The resulting mixture was extracted with water and saturated $NaHCO_3$ solution, and dried with $MgSO_4$. After evaporation of the solvent, the remaining oil, which was a mixture of **9** and **10**, was separated by chromatography (SiO_2/cyclohexane) to yield **9** as a colorless, amorphous solid (29.0 g, 86 %). M.p. 51 °C; ^1H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.15$ (dd, $^3J(H,H) = 4.9$ Hz, $^4J(H,H) =$ 1.1 Hz, 1 H; H12), 7.08 (dd, $^3J(H,H) = 3.6$ Hz, $^4J(H,H) = 1.1$ Hz, 1 H; H10), 6.98 (dd, $^3J(H,H) = 4.9$ Hz, $^3J(H,H) =$ 3.6 Hz, 1 H; H11), 6.84 (s, 1 H; H7), 2.74 (t, $^3J(H,H) = 5.8$ Hz, 2 H; H4), 2.59 (t, $^3J(H,H) = 5.8$ Hz, 2 H; H1), 1.82 (m, 4 H; H2,3); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 138.1$, 136.0, 135.1, 133.4 (C5,6,8,9), 127.6, 124.4, 123.6, 122.9 (C7,10,11,12), 25.5, 25.0, 23.5, 22.8 (C1,2,3,4); $C_{12}H_{12}S_2$ (220.4): calcd C 65.41, H 5.49, S 29.10; found C 65.70, H 5.38, S 29.22.



9

Ring closure with diphosphorouspentasulfide: A stirred suspension of **8** (12.5 g, 56.1 mmol) and P_2S_5 (13.7 g, 61.8 mmol) in dry toluene (250 mL) was heated at reflux for 2 h under nitrogen. The resulting mixture was extracted with water and saturated $NaHCO_3$ solution, and dried with Na_2SO_4. After evaporation of the solvent, the remaining oil, which was a mixture of **9** and **10**, was separated by chromatography (SiO_2/cyclohexane) to yield **9** as a colorless, amorphous solid in the first fraction (2.50 g, 20 %). M.p. 51 °C; ^1H and ^{13}C NMR spectra are identical to those obtained with Lawesson's reagent as the sulfur donor; $C_{12}H_{12}S_2$ (220.4): calcd C 65.41, H 5.49, S 29.10; found C 65.58, H 5.41, S 29.39.

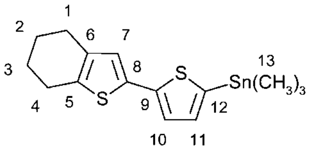
2-(4,5,6,7-Tetrahydrobenzo[*b*]fur-2-yl)thiophene (**10**): In the second fraction of the above chromatography, byproduct **10** was obtained as colorless, relatively unstable oil (1.60 g, 14 %). ^1H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.14$ (m, 2 H; H10, H12), 6.98 (dd, $^3J(H,H) = 5.2$ Hz, $^3J(H,H) = 3.7$ Hz, 1 H; H11), 6.31 (s, 1 H; H7), 2.62 (t, $^3J(H,H) = 6.1$ Hz, 2 H; H4), 2.42 (t, $^3J(H,H) = 6.1$ Hz, 2 H; H1), 1.82 (m, 4 H; H2,3); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 150.3$, 147.0, 134.7 (C5,6,8,9), 127.5, 123.1, 121.3 (C10,11,12), 118.9 (C5,6,8,9), 106.1 (C7), 26.9, 23.0, 22.9, 22.0 (C1,2,3,4);



10

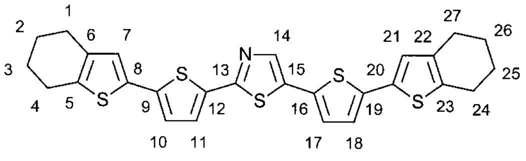
MS: m/z (%): 205 (16) [M^+], 204 (97) [M^+], 203 (14) [M^+], 177 (12), 176 (100) [M^+ – CO], 166 (15), 147 (26), 111 (10), 39 (8).

5-(4,5,6,7-Tetrahydrobenzo[*b*]thien-2-yl)-2-trimethylstannylthiophene (11): *n*-Butyllithium (7.76 mL, 12.4 mmol, 1.6 M in *n*-hexane) was added dropwise at 0 °C to a solution of **9** (2.50 g, 11.3 mmol) in dry diethyl ether (25 mL). The resulting mixture was stirred for 1 h and then cooled to –50 °C. Subsequently, a solution of trimethylchlorostannane (2.47 g, 12.4 mmol) in dry diethyl ether (20 mL) was added, and the mixture was stirred for an additional hour and allowed to warm up over night. The reaction mixture was hydrolyzed and extracted with diethyl ether. The organic phase was washed with saturated NaCl solution, dried ($MgSO_4$), and evaporated to yield **11** as a green oil (4.20 g, 97 %). ^1H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.18$ (d, $^3J(H,H) = 3.4$ Hz, 1 H; H10), 7.05 (d, $^3J(H,H) = 3.4$ Hz, 1 H; H11), 6.82 (s, 1 H; H7), 2.73 (t, $^3J(H,H) = 5.8$ Hz, 2 H; H4), 2.58 (t, $^3J(H,H) = 5.8$ Hz, 2 H; H1), 1.81 (m, 4 H; H2,3), 0.37 (s, d, $^2J(H,^{119}Sn) = 57.4$ Hz, 9 H; H13); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 143.6$, 136.4, 136.0 (C5,6,8,9,12), 135.7 (C7,10, 11), 134.9, 133.5 (C5,6,8,9,12), 124.3, 124.2 (C7,10,12), 25.5, 25.0, 23.5, 22.8 (C1,2,3,4), –8.3 (C13); $C_{15}H_{20}S_2Sn$ (383.0): calcd C 47.04, H 5.26, S 16.74; found C 47.32, H 5.23, S 16.67.



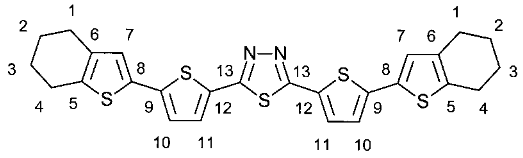
11

2,5-Bis[5-(4,5,6,7-tetrahydrobenzo[*b*]thien-2-yl)thien-2-yl]thiazole (2): Under the exclusion of light **12** (811 mg, 3.34 mmol) was added to a stirred suspension of bis(triphenylphosphino)palladiumdichloride (234 mg, 3.34 × 10^{-4} mol) in dry THF (40 mL) under nitrogen. Subsequently, a solution of **11** (2.81 g, 7.35 mmol) in THF (30 mL) was added and the resulting mixture was refluxed for 100 h. Due to its low solubility, the major portion of thiophene/thiazole pentamer **2** was separated as an almost pure compound by filtration and purified by sublimation. The organic phase was extracted with water and dried ($MgSO_4$). After evaporation of the solvent, the remaining mixture of **2** and homocoupling product EC4T **15** were separated by chromatography (SiO_2/toluene). Further sublimation finally yielded **2** as orange needles (632 mg, 36 %) and additionally as an amorphous orange powder (115 mg, 7 %). M.p. 276–277 °C; ^1H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.74$ (s, 1 H; H14), 7.34 (d, $^3J(H,H) = 4.0$ Hz, 1 H; H11), 7.04 (d, $^3J(H,H) = 3.7$ Hz, 1 H; H17), 7.02 (d, $^3J(H,H) = 3.7$ Hz, 1 H; H18), 6.98 (d, $^3J(H,H) = 4.0$ Hz, 1 H; H10), 6.89 (s, 1 H; H7), 6.84 (s, 1 H; H21), 2.73 (m, 4 H; H4,24), 2.58 (m, 4 H; H1,27), 1.80 (m, 8 H; H2,3,25,26); ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): $\delta = 159.7$ (C13), 140.6, 138.7 (C12,15), 138.3 (C14), 136.6, 136.5, 136.4, 136.0, 134.6, 132.7, 131.6, 130.9 (C5,6,8,9,16,19,20,22,23), 127.2, 126.2, 125.3, 124.8, 123.5, 123.4 (C7,10,11,17,18,21), 25.5, 25.1, 23.5, 22.8 (C1,2,3,4, 24,25,26,27); FT-IR (KBr): $\tilde{\nu} = 3060$ (w), 2927 (s), 2839 (m), 1500 (s), 1438 (m), 1141 (m), 834 (m), 802 (s), 625 (w), 474 (w) cm^{-1}; $C_{27}H_{23}NS_5$ (521.8): calcd C 62.15, H 4.44, N 2.68, S 30.73; found C 61.97, H 4.52, N 2.67, S 30.51.



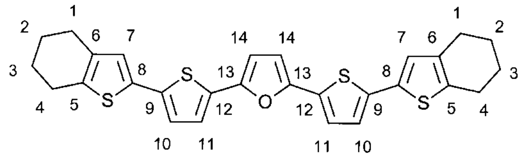
2

2,5-Bis[5-(4,5,6,7-tetrahydrobenzo[*b*]thien-2-yl)thien-2-yl]-1,3,4-thiadiazole (3): Under the exclusion of light **13** (989 mg, 4.05 mmol) was added to a stirred suspension of bis(triphenylphosphino)palladiumdichloride (284 mg, 4.05 x 10^{-4} mol) in dry THF (40 mL) under nitrogen. Subsequently, a solution of **11** (3.42 g, 8.92 mmol) in THF (20 mL) was added and the resulting mixture was refluxed for 100 h. After evaporation of the solvent, the dark brown residue was suspended in diethyl ether and extracted with water. Due to its low solubility, the major portion of 1,3,4-thiadiazole **3** was separated by filtration and purified by sublimation as an almost pure compound. After evaporation of the diethyl ether extract, a mixture of 1,3,4-thiadiazole **3** and end-capped quaterthiophene **15** remained. This was separated by chromatography (SiO_2/toluene). Subsequent sublimation of the product finally yielded **3** as an amorphous orange powder (594 mg, 28 %). M.p. 306–307 °C; ^1H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 7.39$ (d, $^3J(H,H) = 3.9$ Hz, 2 H; H11), 7.06 (d, $^3J(H,H) = 3.9$ Hz, 2 H; H10), 6.94 (s, 2 H; H7), 2.76 (m, 4 H; H4), 2.61 (m, 4 H; H1), 1.85 (m, 4 H; H3), 1.80 (m, 4 H; H2); ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): $\delta = 145.4$ (C13), 137.1, 136.6, 132.3, 130.2, 129.6, 126.0, 125.8, 123.3 (C5,6,7,8,9,10,11,12), 25.5, 25.1, 23.4, 22.7 (C1,2,3,4); FT-IR (KBr): $\tilde{\nu} = 3060$ (s), 2926 (m), 2837 (w), 1483 (s), 1420 (s), 1324 (w), 1236 (w), 1136 (w), 1052 (s), 808 (s), 602 (m) cm^{-1}; $C_{26}H_{22}N_2S_5$ (522.8): calcd C 59.73, H 4.24, N 5.36, S 30.67; found C 60.02, H 4.02, N 5.31, S 30.61.



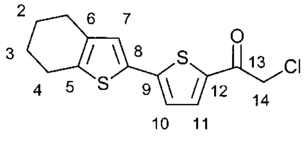
3

2,5-Bis[5-(4,5,6,7-tetrahydrobenzo[*b*]thien-2-yl)thien-2-yl]-furan (4): Under the exclusion of light **14** (986 mg, 4.36 mmol) was added to a stirred suspension of bis(triphenylphosphino)palladiumdichloride (306 mg, 4.36 × 10^{-4} mol) in dry THF (40 mL) under nitrogen. Subsequently, a solution of **11** (3.68 g, 9.60 mmol) in THF (25 mL) was added and the resulting mixture was refluxed for 100 h. After evaporation of the major portion of the solvent, the reaction mixture was poured into water and a yellow solid precipitated. The crude product, which was identified as a mixture of furan **4** and end-capped quaterthiophene **15**, was chromatographed on silica (petroleum ether/dichloromethane 9:1). Subsequent sublimation of the product finally yielded **4** as an amorphous yellow powder (500 mg, 23 %). M.p. 233 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 7.16$ (d, $^3J(H,H) = 3.8$ Hz, 2 H; H11), 7.01 (d, $^3J(H,H) = 3.8$ Hz, 2 H; H10), 6.85 (s, 2 H; H7), 6.52 (s, 2 H; H14), 2.76 (m, 4 H; H4), 2.60 (m, 4 H; H1), 1.86 (m, 4 H; H3), 1.81 (m, 4 H; H2); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): $\delta = 148.3$ (C13), 137.0, 136.3, 135.5 (C8,9,12), 133.2, 131.2, (C5,6), 124.4, 123.4, 123.2 (C7,10,11), 107.3 (C14), 25.5, 25.1, 23.5, 22.8 (C1,2,3,4); FT-IR (KBr): $\tilde{\nu} = 3070$ (w), 2928 (s), 2837 (m), 1517 (m), 1437 (m), 986 (m), 799 (s), 784 (m), 775 (m) cm^{-1}; $C_{28}H_{24}OS_4$ (504.76): calcd C 66.63, H 4.79, S 25.41; found C 66.57, H 4.80, S 25.65.



4

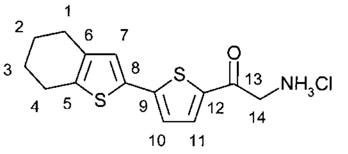
5-(4,5,6,7-Tetrahydrobenzo[*b*]thien-2-yl)-2-(chloroacetyl)thiophene (16): Compound **9** (10.0 g, 45.4 mmol) and chloroacetylchloride (5.12 g, 3.61 mL, 45.4 mmol) were dissolved in carbon disulfide (500 mL) and cooled to 0 °C. Aluminiumtrichloride (7.56 g, 56.7 mmol) was added and the resulting reaction mixture was allowed to warm to room temperature. The mixture was refluxed for 50 h, cooled, hydrolyzed, and dried ($MgSO_4$). After evaporation of the solvent, the remaining residue was purified by chromatography (SiO_2/toluene) to yield **16** as a yellow solid (6.88 g, 51 %). M.p. 167 °C; ^1H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.62$ (d, $^3J(H,H) = 4.0$ Hz, 1 H; H11), 7.06 (d, $^3J(H,H) = 4.0$ Hz, 1 H; H10), 6.99 (s, 1 H; H7), 4.52 (s, 2 H; H14), 2.74 (t, $^3J(H,H) = 5.8$ Hz, 2 H; H4), 2.58 (t, $^3J(H,H) = 5.8$ Hz, 2 H; H1), 1.79 (m, 4 H; H2,3); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 183.7$ (C13), 148.2 (C12), 138.6, 137.6, 136.9 (C5,8,9), 134.2 (C11), 131.8 (C6), 126.9 (C10), 123.3 (C7), 45.1 (C14),



16

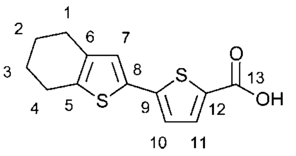
25.4, 25.2, 23.3, 22.6 (C1,2,3,4); $C_{14}H_{13}ClOS_2$ (296.8): calcd C 56.65, H 4.42, S 21.60; found C 56.84, H 4.18, S 21.42.

5-(4,5,6,7-Tetrahydrobenzo[*b*]thien-2-yl)-2-(aminoacetyl)thiophene hydrochloride (17): Compound **16** (2.32 g, 7.82 mmol), hexamethylenetetraamine (1.10 g, 7.82 mmol), and sodium iodide (1.17 g, 7.82 mmol) were suspended in ethanol and stirred for one week at room temperature. Concentrated hydrochloric acid (3 mL) was added and the mixture was warmed to 50 °C and then stirred for additional 5 h. The precipitated crude hydrochloride was isolated by filtration and recrystallized twice from ethanol to yield **17** as an ochre powder (1.50 g, 61 %). M.p. 264 °C (decomp); ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C): $\delta = 8.53$ (t, ^{3}J(H,H) = 5.8 Hz, 3H; NH$_3$Cl), 8.03 (d, ^{3}J(H,H) = 4.0 Hz, 1H; H11), 7.37 (d, ^{3}J(H,H) = 4.0 Hz, 1H; H10), 7.27 (s, 1H; H7), 4.45 (q, 2H; H14), 2.71 (t, ^{3}J(H,H) = 5.8 Hz, 2H; H4), 2.55 (t, ^{3}J(H,H) = 5.8 Hz, 2H; H1), 1.74 (m, 4H; H2,3); ^{13}C NMR (63 MHz, [D$_6$]DMSO, 25 °C): $\delta = 185.4$ (C13), 146.9 (C12), 138.4, 137.2, 137.1 (C5,8,9), 136.7 (C11), 131.3 (C6), 127.7 (C10), 124.6 (C7), 56.2 (C14), 25.2, 24.8, 23.1, 22.4 (C1,2,3,4); $C_{14}H_{16}ClNOS_2$ (313.87): calcd C 53.57, H 5.14, N 4.46, S 20.43; found C 53.44, H 5.18, N 4.44, S 20.48.



17

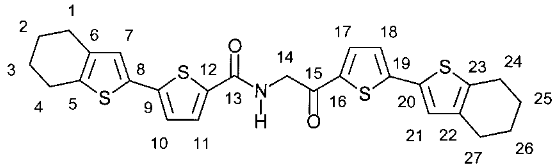
5-(4,5,6,7-Tetrahydrobenzo[*b*]thien-2-yl)thiophene-2-carbonic acid (18): *n*BuLi (2.86 mL of a 1.6 M solution in hexane, 4.58 mmol) was added to a stirred solution of **9** (1.00 g, 4.54 mmol) in dry diethyl ether (25 mL) was slowly added and the mixture then cooled to −50 °C. Gaseous carbon dioxide was bubbled through the mixture over a period of 1 h. The organic phase was hydrolyzed and extracted with additional water. After separation, the aqueous phase was acidified with a few drops of concentrated HCl. The bithiophene carbonic acid **18** precipitated as an amorphous, yellow solid which was filtered, washed, and dried over diphosphorouspentoxide to give **18** as an amorphous yellow powder (1.13 g, 94 %). M.p. 223–224 °C; ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C): $\delta = 7.61$ (d, ^{3}J(H,H) = 4.0 Hz, 1H; H11), 7.20 (d, ^{3}J(H,H) = 4.0 Hz, 1H; H10), 7.13 (s, 1H; H7), 2.70 (t, ^{3}J(H,H) = 5.5 Hz, 2H; H4), 2.54 (t, ^{3}J(H,H) = 5.5 Hz, 2H; H4), 1.74 (m, 4H; H2,3), COO*H* not resolved; ^{13}C NMR (63 MHz, [D$_6$]DMSO, 25 °C): $\delta = 162.9$ (C13), 143.7, 136.9, 136.8, 134.4, 132.0, 131.7, 126.5, 123.8 (C5,6,7,8,9, 10,11,12), 25.2, 24.7, 23.1, 22.4 (C1,2,3,4); $C_{13}H_{12}O_2S_2$ (264.4): calcd C 59.06, H 4.57, S 24.26; found C 58.96, H 4.67, S 24.46.



18

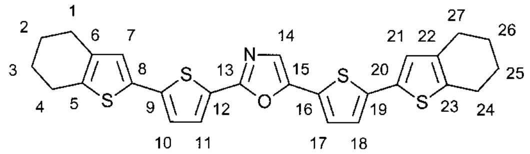
5-(4,5,6,7-Tetrahydrobenzo[*b*]thien-2-yl)thiophene-2-carbonic acid chloride (19): Oxalylchloride (1.06 g, 715 µL, 8.32 mmol,) in toluene (20 mL) was added to a suspension of **18** (265 mg, 0.1 mmol) in toluene (20 mL) at 0 °C was slowly added. The mixture was heated to 55 °C and stirred for 3 h. After evaporation of the solvent and the excess oxalylchloride, the remaining yellow solid residue was dissolved twice in chloroform and evaporated in order to remove last traces of oxalylchloride. The crude acid chloride **19** was dissolved in the desired solvent and used without further purification.

***N*-{2-[5-(4,5,6,7-tetrahydrobenzo[*b*]thien-2-yl)thien-2-yl]-2-oxoethyl}-5-(4,5,6,7-tetrahydrobenzo[*b*]thien-2-yl)thiophene-2-carbonic acid amide (20)**: Triethylamine (421 mg, 0.58 mL, 4.16 mmol) in chloroform (5 mL) and **19** (577 mg, 2.04 mmol) in chloroform (40 mL) were added to an icecold solution of **17** (650 mg, 2.07 mmol) in chloroform (20 mL). The resulting mixture was stirred for 1 h at 0 °C and was then allowed to warm up overnight. The obtained suspension was hydrolyzed, acidified with 2 N HCl and extracted with additional water, while the crude product remained suspended in the organic phase. After filtration, the crude amide was dried and recrystallized twice from DMF yielding **20** as an amorphous orange solid (240 mg, 22 %). M.p. 268–270 °C (decomp); ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): $\delta = 7.70$ (d, ^{3}J(H,H) = 4.0 Hz, 1H; H17), 7.46 (d, ^{3}J(H,H) = 3.9 Hz, 1H; H11), 7.11 (d, ^{3}J(H,H) = 4.0 Hz, 1H; H18), 7.03 (d, ^{3}J(H,H) = 3.9 Hz, 1H; H10), 7.01 (s, 1H; H21), 6.91 (s, 1H; H7), 4.80 (d, ^{3}J(H,H) = 4.3 Hz, 2H; H14), 2.75 (m, 4H; H4,24), 2.60 (m, 4H; H1,27), 1.85 (m, 4H; H3,25), 1.79 (m, 4H; H2,26), N*H* not resolved; ^{13}C NMR (151 MHz, CDCl$_3$, 25 °C): $\delta = 186.4$ (C15), 161.7 (C13), 148.0 (C16), 143.3 (C12), 138.6, 137.5, 137.0, 136.9, 136.5, 135.2 (C5,6,8,9,19,20,22,23), 133.7 (C17), 132.4, 131.9 (C5,6,8,9,19,20,22,23), 129.3 (C11), 126.9 (C18), 125.8 (C10), 123.5 (C21), 123.0 (C7), 46.4 (C14), 25.5 (C4,24), 25.2 (C27), 25.1 (C1), 23.5 (C25), 23.4 (C3), 22.7 (C2,26); $C_{27}H_{25}NO_2S_4$ (523.8): calcd C 61.92, H 4.81, N 2.67, S 24.49; found C 61.84, H 4.64, N 2.68, S 24.38.



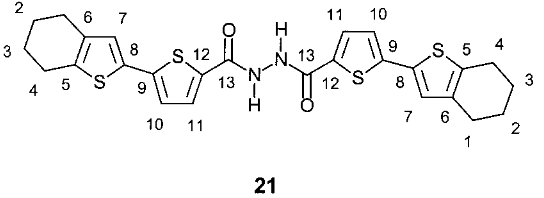
20

2,5-Bis[5-(4,5,6,7-tetrahydrobenzo[*b*]thien-2-yl)thien-2-yl]-oxazole (5): A suspension of amide **20** (618 mg, 1.18 mmol) in phosphorousoxitrichloride (50 mL) was refluxed for 20 h. From the reaction mixture 90 % of the solvent was removed by distillation and the remaining dark brown residue was added dropwise to lukewarm water in order to hydrolyze the POCl$_3$. The crude product precipitated during this procedure and was isolated by filtration. Chromatographic workup (SiO$_2$/toluene) and subsequent sublimation yielded **5** as amorphous bright yellow powder (233 mg, 39 %). M.p. 246–248 °C; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta = 7.59$ (d, ^{3}J(H,H) = 3.9 Hz, 1H; H11), 7.28 (s, 1H; H14), 7.23 (d, ^{3}J(H,H) = 3.8 Hz, 1H; H17), 7.10 (d, ^{3}J(H,H) = 3.9 Hz, 1H; H10), 7.06 (d, ^{3}J(H,H) = 3.8 Hz, 1H; H18), 6.95 (s, 1H; H7), 6.90 (s, 1H; H21), 2.78 (m, 4H; H4,24), 2.63 (m, 4H; H1,27), 1.89 (m, 4H; H3,25), 1.84 (m, 4H; H2,26); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C): $\delta = 157.4$ (C13), 156.6 (C15), 146.1, 141.3 (C12,14), 138.5, 136.7, 136.5, 136.4, 136.1, 132.7, 132.6, 128.4, 127.3, 127.0, 125.4, 124.9, 123.5, 123.4, 123.1 (C5,6,7,8,9,10,11,16,17,18,19,20,21,22,23), 25.5, 25.1, 23.5, 22.8 (C1,2,3,4,24,25,26,27); FT-IR (KBr): $\tilde{\nu} = 3071$ (w), 2930 (s), 2841 (m), 1599 (m), 1579 (w), 1517 (s), 1438 (m), 1347 (w), 1121 (w), 995 (w), 799 (s), 717 (m) cm^{-1}; $C_{27}H_{23}NOS_4$ (505.8): calcd C 64.12, H 4.58, N 2.77, S 25.36; found C 63.94, H 4.81, N 2.75, S 25.01.



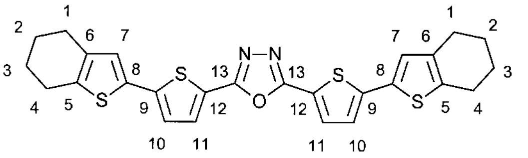
5

***N,N'*-bis[5-(4,5,6,7-tetrahydrobenzo[*b*]thien-2-yl)thien-2-oyl]hydrazine (21)**: A solution of **19** (1.58 g, 5.60 mmol) in *N*-methylpyrrolidone (15 mL) was added to a mixture of hydrazine (170 µL, 80 % hydrazinemonohydrate solution in water, 2.80 mmol), pyridine (4 mL), and *N*-methylpyrrolidone (15 mL). The resulting mixture was stirred overnight at room temperature. After evaporation of the solvent, the crude product was digested with water, filtered, and dried. Recrystallization from DMF yielded **21** as colorless needles (1.18 g, 80 %). M.p. 319–321 °C; ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C): $\delta = 10.54$ (s, 2H; NH), 7.78 (d, ^{3}J(H,H) = 4.0 Hz, 2H; H11), 7.25 (d, ^{3}J(H,H) = 4.0 Hz, 2H; H10), 7.12 (s, 2H; H7), 2.72 (t, ^{3}J(H,H) = 5.0 Hz, 4H; H4), 2.56 (t, ^{3}J(H,H) = 5.0 Hz, 4H; H1), 1.76 (m, 8H; H2,3); ^{13}C NMR (63 MHz, [D$_6$]DMSO, 25 °C): $\delta = 160.8$ (C13), 142.4, 136.7, 136.6, 134.7, 131.7, 130.3, 126.3, 123.9 (C5,6,7,8,9,10,11,12), 25.2, 24.7, 23.1, 22.4 (C1,2,3,4); $C_{26}H_{24}N_2O_2S_4$ (524.8): calcd C 59.51, H 4.61, N 5.34, S 24.44; found C 59.45, H 4.60, N 5.34, S 24.53.



21

2,5-Bis[5-(4,5,6,7-tetrahydrobenzo[*b*]thien-2-yl)thien-2-yl]-1,3,4-oxadiazole (6): A suspension of diacylhydrazine **21** (800 mg, 1.52 mmol) in $POCl_3$ (50 mL) was refluxed for 150 h. From the reaction mixture 90% of the solvent was removed by distillation and the remaining black residue then added dropwise to lukewarm water in order to hydrolyze the $POCl_3$. The crude product precipitated during this procedure and was isolated by filtration. Sublimation yielded **6** as bright yellow needles (133 mg, 17%) and a second fraction as an amorphous yellow powder (389 mg, 51%). M.p. 287–288 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.64$ (d, ^3J(H,H) = 4.0 Hz, 2H; H11), 7.09 (d, ^3J(H,H) = 4.0 Hz, 2H; H10), 6.95 (s, 2H; H7), 2.75 (t, ^3J(H,H) = 5.2 Hz, 4H; H4), 2.60 (t, ^3J(H,H) = 5.2 Hz, 4H; H1), 1.82 (m, 8H; H2,3); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 159.4$ (C13), 142.7, 136.8, 136.1, 131.5, 130.0, 125.5, 122.9, 121.4 (C5,6,7,8,9,10,11,12), 25.0, 24.6, 22.9, 22.2 (C1,2,3,4); FT–IR (KBr): $\tilde{\nu} = 3100$ (w), 2928 (m), 2845 (w), 1576 (s), 1498 (s), 1436 (w), 1068 (m), 1033 (m), 803 (m) 724 (m) cm^{-1}; $C_{26}H_{22}N_2OS_4$ (506.74): calcd C 61.63, H 4.38, N 5.53, S 25.31; found C 61.36, H 4.48, N 5.49, S 25.60.



6

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