Structure–Property Relationships in Mixed Oligoheterocycles Based on End-Capped Oligothiophenes

Ullrich Mitschke,[a] Tony Debaerdemaeker,[b] and Peter Bäuerle*[a]

Keywords: Cyclic voltammetry / Fluorescence spectroscopy / Mixed oligomers / Structure–property relationships / Organic light-emitting diodes / Oligothiophenes

Novel mixed oligoheterocycles **1**–**5**, containing thiophene/thiazole, thiophene/1,3,4-thiadiazole, thiophene/oxazole, or thiophene/1,3,4-oxadiazole moieties, were synthesized. The introduction of electronegative heteroatoms such as oxygen and nitrogen into the conjugated π-system leads to a more pronounced acceptor character than that found in the analogous oligothiophenes. Characterization of the redox properties reveals that the reduction of the mixed oligomers is facilitated while oxidation is shifted to higher potentials. For this series, clear structure–property relationships could be found by comparing optical properties, in particular absorptions, emissions and fluorescence quantum yields in solution. The X-ray structural determination of mixed thiophene/1,3,4-oxadiazole heptamer **5** indicates that the replacement of thiophene units by 1,3,4-oxadiazoles has a strong influence on the molecular arrangement and intermolecular interactions in the solid state.

Introduction

Their chemical stability and ease of functionalization make thiophene-based oligomers a subject of intense research activity with regard to their controllable and defined structure and the resulting model character for the corresponding polymers.[1] Moreover, in view of their technological applications in electrooptical devices, they have been applied successfully as active components in all-organic field-effect transistors,[2] light-modulating,[3] and light-emitting devices.[4] The performance of such devices is strictly related to the electronic structure of the organic material and is in particular related to the energy levels of its frontier orbitals. The electronic properties of oligothiophenes can be "tailored" by the attachment of either sterically[1] and/or electronically active substituents at both the β-[5] and the terminal α-positions[6] of the conjugated π-system. Recently, it was shown that the coordination of transition metals to an oligothiophene core also leads to pronounced alterations of the (electronic) properties.[7] Other approaches aimed at the incorporation of non-aromatic moieties[8] and other heterocycles into the oligothiophene core, to enhance the donor or acceptor character. By combining thiophenes with either electron-rich or electron-poor heterocycles, mixed oligoheterocycles were synthesized.[9−19]

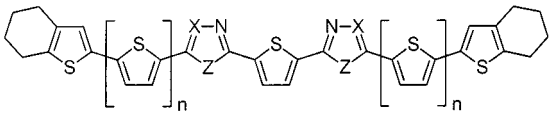
In this respect, the incorporation of furan[9][10] and pyrrole[10b−10d,11] moieties usually led to more electron-rich systems, indicated by the easier oxidation and the reduction at more negative potentials than in the corresponding oligothiophenes. Other combinations were pursued, but the optical and redox properties, in particular, were often not reported. More electron-deficient systems, represented by trimeric to pentameric combinations of thiophene/thiazole,[12] thiophene/1,3,4-thiadiazole,[13] and thiophene/1,3,4-oxadiazole[14][15] were synthesized as optical brighteners, (laser) dyes, UV protectors, and as model compounds for corresponding polymers. The hypervalent nature of sulfur was taken advantage of, and thiophene and thiophene 1,1-dioxide units were combined to synthesize a series of electron-deficient oligothiophene *S*,*S*-dioxides.[16] Their reduction potentials were remarkably lower than those of the corresponding oligothiophenes. An analogous effect was demonstrated for *p*-oligophenoquinones with a central dihydrothiophenediylidene structure.[17] Incorporation of electron-poor aromatic moieties resulted in electron-deficient conjugated oligomers that could be applied as electron-transporting materials in electrooptical devices. Different approaches were the combination of 1,3,4-oxadiazole and 1,3,4-thiadiazole units[18] and the inclusion of silacylopentadiene or cyclopentadienone rings into an oligothiophene backbone.[19]

In view of technological applications it is certainly of great value to know the specific influence of the various heterocyclic moieties and the resulting structure−property relationships in mixed oligoheterocycles. Following this approach, we recently reported a series of mixed oligoheterocycles **6−11** based on an end-capped quinquethiophene, in which the central thiophene ring is systematically replaced by other five-membered heterocycles (thiazole, 1,3,4-thiadiazole, furan, oxazole, and 1,3,4-oxadiazole).[9] Detailed investigations of the electrooptical properties, supported by theoretical studies, clearly elucidated the influence of the additional heteroatoms.

To generalize and to confirm the structure−property relationships obtained from this study, we further elaborated and extended our concept to mixed oligoheterocycles based on end-capped oligothiophenes, in which more than one thiophene ring is replaced by electron-deficient thiazoles,

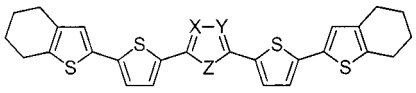
[a] Universität Ulm, Abteilung Organische Chemie II, Albert-Einstein-Allee 11, D-89081 Ulm, Germany
Fax: (internat.) + 49-731/502-2840
E-mail: peter.baeuerle@chemie.uni-ulm.de
Internet: http://www.uni-ulm.de/uni/fak/natwis/oc2
[b] Universität Ulm, Sektion Röntgen- und Elektronenbeugung, Albert-Einstein-Allee 11, D-89081 Ulm, Germany

  1434−193X/00/0203−0425 $ 17.50+.50/0



1 (X=CH, Z=S; n=0)
2 (X=N, Z=S; n=0)

3 (X=CH, Z=O; n=0)
4 (X=N, Z=O; n=0)
5 (X=N, Z=O; n=1)



6 (X=CH, Y=CH, Z=S)
7 (X=N, Y=CH, Z=S)
8 (X=N, Y=N, Z=S)

9 (X=CH, Y=CH, Z=O)
10 (X=N, Y=CH, Z=O)
11 (X=N, Y=N, Z=O)

1,3,4-thiadiazoles, oxazoles, and 1,3,4-oxadiazoles. We report here on the synthesis and structure, as well as the optical and electrochemical characterization of the mixed oligoheterocycles **1**−**5,** compared to previous results.

Results and Discussion

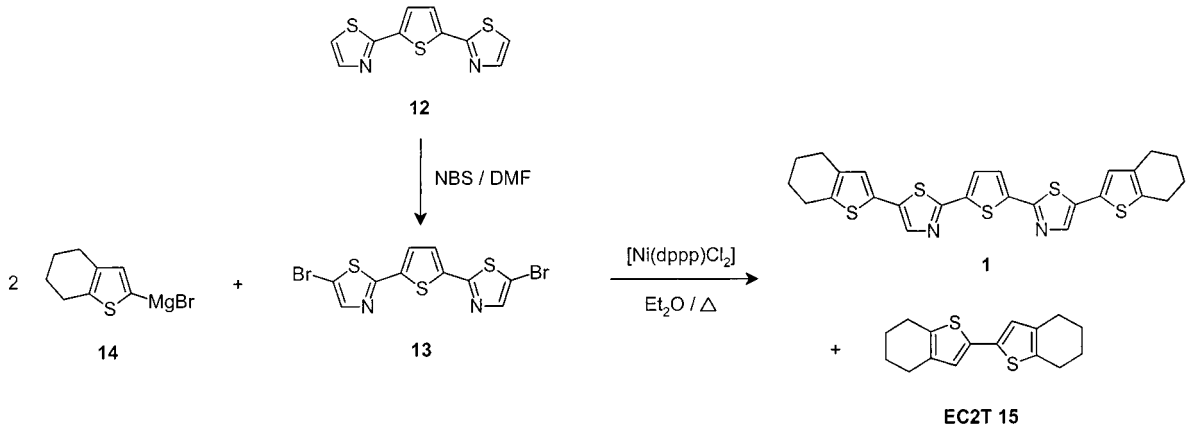
Synthesis

Two different synthetic routes were investigated to build up the mixed oligoheterocycles **1**−**5**. In the case of thiophene/thiazole oligomer **1**, a strategy based on transition-metal-catalyzed coupling reactions of thiazole-containing precursor molecules was elaborated, whereas the 1,3,4-thiadiazole, oxazole, and 1,3,4-oxadiazole units of the other oligomers **2**−**5** were formed from acyclic precursors in a final cyclization step.

In the synthesis of thiophene/thiazole oligomer **1**, the central terheterocycle 2,5-bis(5-bromo-2-thiazolyl)thiophene **13** was readily available in 92% yield by reaction of 2,5-bis(2-thiazolyl)thiophene (**12**)[20] with two equiv. of *N*-bromosuccinimide (NBS) in DMF. Terheterocycle **13** was then cross-coupled with two equiv. of Grignard reagent of 2-bromo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (**14**)[21] and a nickel catalyst, yielding pentamer **1** and homocoupling product EC2T **15** as the main side product (Scheme 1). As a consequence of its low solubility, pentamer **1** precipitated in almost pure form from the reaction mixture. A subsequent fractionated sublimation of the crude product gave analytically pure thiophene/thiazole oligomer **1** in 25% yield.

Thiophene/1,3,4-thiadiazole **2** and thiophene/1,3,4-oxadiazole **4** were built up in a four-step synthesis via the acyclic precursor **16** (Scheme 2). 4,5,6,7-Tetrahydrobenzo[*b*]thiophene (**17**)[22] was first transformed into the corresponding carboxylic acid **18**, in 89% yield, by lithiation with *n*BuLi and quenching with carbon dioxide; acid chloride **19** was quantitatively available by treating carboxylic acid **18** with oxalyl chloride, and was used without further purification. The reaction of two equiv. of acid chloride **19** with thiophene-2,5-dicarboxylic acid dihydrazide **20**[14a] under basic conditions gave the precursor bis(1,2-diacylhydrazine) **16** in 92% yield. In a final cyclization step, reaction of **16** with diphosphorus pentasulfide gave thiophene/1,3,4-thiadiazole **2** which, due to its extremely low solubility, precipitated from the reaction mixture. As in previously reported analogous reactions to build up 1,3,4-thiadiazoles,[23] we also observed the formation of side products containing 1,3,4-oxadiazole units, which were formed in a competitive dehydration reaction. Nevertheless, their removal was quantitatively achieved by fractionated sublimation, even though the yield of pentamer **2** was diminished to 26%.

Intentional dehydration of the acylic precursor **16** in boiling phosphoryl chloride led to thiophene/1,3,4-oxadiazole pentamer **4** which was purified by sublimation to give 70% of analytically pure material (Scheme 2). By applying the same concept, thiophene/1,3,4-oxadiazole heptamer **5** was synthesized. Thus, acylation of thiophene-2,5-dicarboxylic acid dihydrazide (**20**)[14a] with two equiv. of the corresponding bithienyl acid chloride **23**[9a] which was formed from capped bithiophene **21** and bithiophene carboxylic acid **22**, smoothly resulted in precursor molecule **24** in 85% yield. Dehydration and cyclization of **24** in boiling phosphoryl chloride gave thiophene/1,3,4-oxadiazole heptamer **5** in 25% yield after sublimative purification (Scheme 2).



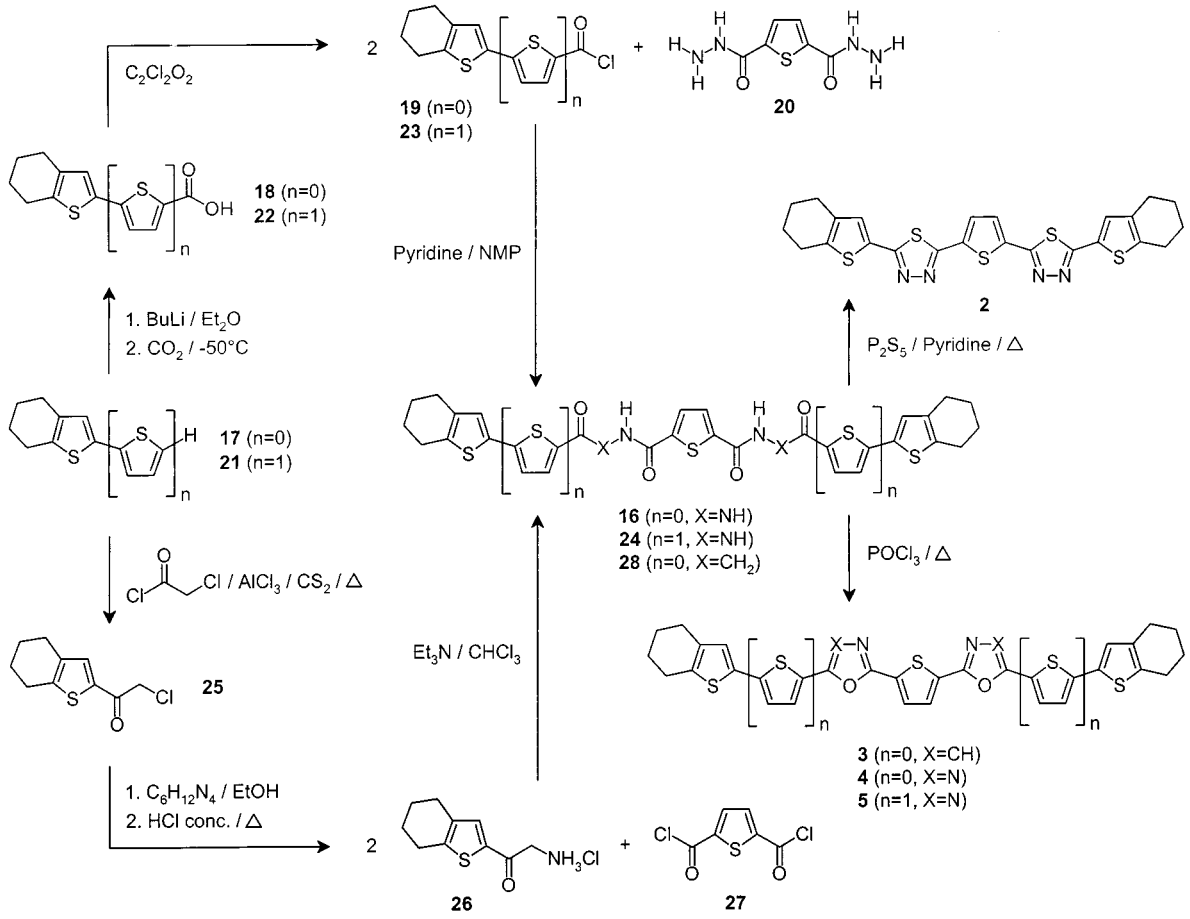
Scheme 1. Synthesis of thiophene/thiazole oligomer **1**

For the synthesis of the acylic precursor amide **28**, firstly, 4,5,6,7-tetrahydrobenzo[*b*]thiophene (**17**)[22] was acylated with chloroacetyl chloride and $AlCl_3$ to form chloroacetylthiophene **25** in 88% yield. Subsequent transformation of **25** with urotropine gave the hydrochloride of aminoacetylthiophene **26** (66% yield), which was subsequently reacted with thiophene-2,5-dicarboxylic acid dichloride (**27**)[24] to form amide **28** in 49% yield. Finally, dehydration and cyclization of the precursor amide **28** in boiling phosphoryl chloride occurred, much faster than in the 1,2-diacylhydrazines **16** and **24**, to yield 71% of thiophene/oxazole pentamer **3** after sublimative purification (Scheme 2).

Solubilities of Oligoheterocycles 1−11

Extended π-systems often exhibit low solubility due to π−π interactions of the molecules in the solid state. However, the incorporation of organic materials as active components into electrooptical devices often requires preparation techniques such as spin- or dip-coating, which demand good solubility of the materials. Several approaches have been taken to overcome this problem, including the generation of soluble precursors,[25] the introduction of alkyl or alkoxy substituents,[1][25] or spiro cores.[9b,26] To deduce structure−solubility relationships for oligomers **1**−**11**, we compared their saturation concentrations in dichloromethane, given in mol/L at ambient temperature (Table 1).

The obtained saturation concentrations cover a wide range, from excellent solubility for **3** and **4** (c_{sat} = 2.9 × 10^{-2} mol/L), to nearly insoluble for **5** (c_{sat} = 5.7 × 10^{-6} mol/L). A clear trend is seen with respect to structural features: The highest concentrations were attained for the oligoheterocycles containing two oxazole or 1,3,4-oxadiazole units. In contrast, thiadiazole-modified oligomers **2** and **8** revealed stronger intermolecular interactions in the solid state, and were therefore the least soluble of the series of pentamers. Thiophene/1,3,4-oxadiazole heptamer **5**, however, has the lowest solubility, in spite of the presence of two 1,3,4-oxadiazole units. Evidently, the solubilizing effect of the 1,3,4-oxadiazole units is overruled by the elongation of the conjugated π-system, which enhances the π−π interactions and therefore significantly decreases the saturation concentration. In the series of pentamers **6**−**11**, the solubilizing effect of the individual heterocyclic units can be evaluated as furan > oxazole > oxadiazole ≥ thiazole > thiophene > thiadiazole. In the series of pentamers **1**−**4** and **6** the approximately same order is recognized: oxazole ≈ oxadiazole >> thiophene > thiazole > thiadiazole. Although we did not find significantly altered trends in other solvents, these results are only valid for dichloromethane as solvent.



Scheme 2. Synthesis of mixed oligoheterocycles **2**−**5**

Table 1. Saturation concentrations c_{sat} and solubilities of the mixed oligoheterocycles **1**−**11** in dichloromethane at ambient temperature

Oligomer	c_{sat} [mol/L]	(solubility) [g/L]	Oligomer	c_{sat} [mol/L]	(solubility) [g/L]
1	1.1×10^{-4}	(5.5×10^{-2})	**6**	4.0×10^{-4}	(0.21)
2	5.0×10^{-5}	(2.6×10^{-2})	**7**	6.8×10^{-4}	(0.35)
3	2.9×10^{-2}	(14)	**8**	1.2×10^{-4}	(6.3×10^{-2})
4	2.9×10^{-2}	(14)	**9**	1.4×10^{-2}	(7.1)
5	5.7×10^{-6}	(3.7×10^{-3})	**10**	4.3×10^{-3}	(2.2)
			11	7.0×10^{-4}	(0.36)

Optical Characterization

The absorption and fluorescence spectra of the mixed oligoheterocycles **1**−**5** were studied and compared to the data previously obtained for oligomers **6**−**11**. The absorption and emission maxima, fluorescence quantum yields, and the optical energy gaps are given in Table 2. The energy gaps were determined from the average of the 0−0 transitions in absorption and emission, and therefore correlate to the HOMO/LUMO gap of the oligomers.

The absorption spectra of mixed oligomers **1**−**5** were measured in dichloromethane at a concentration of 5×10^{-6} mol/L. Reflecting the non-coplanarity and rotational freedom of individual rings, broad and rather nonstructured π−π* transition bands were obtained (Figures 1, 2). Compared to parent end-capped quinquethiophene **6** ($\lambda_{max}^{abs} = 431$ nm), the replacement of two thiophene by two thiazole rings, as realized for thiophene/thiazole oligomer **1**, led to a bathochromic shift of the absorption maximum ($\Delta\lambda_{\mathbf{6,1}}^{abs} = +9$ nm). However, two thiadiazole rings, as in pentamer **2** caused an opposite hypsochromic shift ($\Delta\lambda_{\mathbf{6,2}}^{abs} = -20$ nm). The nearly unaltered shape of the absorption bands excludes the possibility that this effect is caused by different contributions of vibronic states. The same trends were observed for the corresponding pentamers **7** and **8**.[9a] When the sulfur atoms in the thiazole moieties of oligomer **1** and the thiadiazole moieties of **2** were replaced by oxygen atoms, as represented in thiophene/oxazole **3** and in thiophene/oxadiazole **4**, distinct blue shifts of the absorption maxima ($\Delta\lambda_{\mathbf{1,3}}^{abs} = -27$ nm; $\Delta\lambda_{\mathbf{2,4}}^{abs} = -35$ nm) occurred. Compared to related pentamers **10** and **11**, in which only one thiophene ring was replaced by an oxazole or an 1,3,4-oxadiazole moiety, only the introduction of a second 1,3,4-oxadiazole unit led to a further significant hypsochromic shift ($\Delta\lambda_{\mathbf{11,4}}^{abs} = -26$ nm), while in the oxazole case the maximum absorption was maintained ($\Delta\lambda_{\mathbf{10,3}}^{abs} = -1$ nm). The effect of extending the conjugated π-system is seen when thiophene/1,3,4-oxadiazole pentamer **4** and heptamer **5** are compared: The expected bathochromic shift occurs ($\Delta\lambda_{\mathbf{4,5}}^{abs} = +31$ nm). This is in agreement with a theoretically calculated convergence of the frontier orbitals. Differences in the extinction coefficients of the π−π* transitions of the oligoheterocycles **1**−**4** are small. Nevertheless, the sulfur-containing heterocycles **1** and **2** seem to guarantee slightly higher transition probabilities than their oxygen analogs **3** and **4**. On account of two additional thiophene units, the extinction coefficient of thiophene/1,3,4-oxadiazole heptamer **5** is significantly larger than the values obtained for the pentamers **1**−**4**. Due to the electron-donating effect of the cyclohexane caps in thiophene/1,3,4-oxadiazole pentamer **4**, the absorption maximum ($\lambda_{max}^{abs} = 376$ nm, $\lg \varepsilon = 4.67$) is slightly displaced to lower energies than that of the analogous noncapped system ($\lambda_{max}^{abs} = 365$ nm (toluene), $\lg \varepsilon = 4.66$).[15a] However, the transition probability represented by the extinction coefficient remains identical.

Corrected emission spectra of mixed oligoheterocycles **1**−**5** were measured in dichloromethane at a concentration of 1×10^{-6} mol/L. The emission bands of each compound are more structured than the corresponding absorption bands, indicating more planar and stiffer excited-state structures (Figure 1, 2). Since the shapes of the emission spectra of this series of oligomers vary, and the absolute maxima sometimes do not correspond to the same vibronic state, the first vibronic level of all compounds was determined to make them comparable. Deconvolution of the absorption and emission bands gave the corresponding 0−0 transitions

Table 2. Optical properties of the mixed oligoheterocycles **1**−**5** and end-capped quinquethiophene **6**

Oligomer	λ_{max}^{abs} [a] [nm]	lg ε	λ_{max}^{em} [a] [nm]	Φ_{295K}^{sm} [%]	$\Delta E_{opt.}$ [d] [eV]	$\Delta\tilde{\nu}$ [e] [cm^{-1}]
1	440	4.69	512, 536	28 (±5)[b]	2.53	1136
2	411	4.72	468[f], 489	30 (±5)[c]	2.75	923
3	413	4.66	475, 497	48 (±5)[c]	2.73	1155
4	376	4.67	424[f], 444	52 (±5)[c]	3.03	923
5	407	4.85	497[f], 511	53 (±5)[c]	2.76	1191
6	431	4.71	499, 533	40 (±5)[b,c]	2.56	997

[a] Solvent dichloromethane, $c = 5 \times 10^{-6}$ mol/L for absorption measurements, $c = 1 \times 10^{-6}$ mol/L for emission measurements. − [b] External standard was fluorescein. − [c] External standard was 9,10-diphenylanthracene. − [d] The energy gap was determined from the average of the 0−0 transitions in absorption and emission. − [e] Stoke's shift determined by deconvolution of the spectra. − [f] Shoulder.

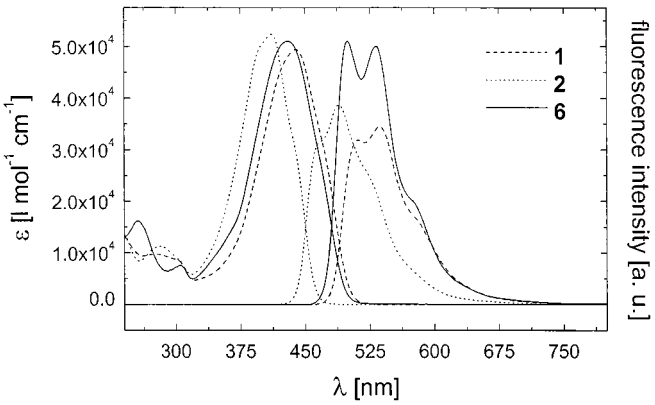


Figure 1. Absorption and corrected emission spectra of end-capped quinquethiophene **6** and oligoheterocycles **1** and **2** in dichloromethane, $c = 5 \times 10^{-6}$ mol/L (abs.) and 1×10^{-6} mol/L (em.)

and the energy difference of the vibrational levels ($\Delta\nu \approx 1100-1300$ cm^{-1}) which typically corresponds to the symmetric stretch vibration of the C=C double bonds in the heteroaromatic moieties.[27] As indicated by the Stoke′s shifts ($\Delta\tilde{\nu} = 923-1191$ cm^{-1}), the geometric change between ground and excited state is relatively small. In general, the displacements of the corresponding fluorescence bands caused by electronic reasons followed the same trends as found for the absorption spectra.

The determination of the 0−0 transitions for both absorption and emission bands allowed the evaluation of the optical energy gaps, which correspond to the energy difference of the frontier orbitals. Thiophene/thiazole oligomer **1** showed a slightly smaller gap ($\Delta E_{opt.} = 2.53$ eV) than the parent pentamer **6** ($\Delta E_{opt.} = 2.56$ eV), followed by thiophene/oxazole and thiophene/1,3,4-thiadiazole pentamers **3** ($\Delta E_{opt.} = 2.73$ eV) and **2** ($\Delta E_{opt.} = 2.75$ eV). The highest energetically separated frontier orbitals were found for thiophene/1,3,4-oxadiazole **4** ($\Delta E_{opt.} = 3.03$ eV), a value which expectedly decreased again for heptamer **5** ($\Delta E_{opt.} = 2.76$ eV).

With respect to the application of oligothiophenes and related compounds in electrooptical devices, the fluorescence quantum yields of the oligomers are of special interest. All oligoheterocycles investigated in this study show a bright fluorescence in solution, which was quantified in dichloromethane at ambient temperature by the optically diluted solution method.[28] 9,10-Diphenylanthracene in cyclohexane[29] and fluorescein in 0.1 M NaOH[30] were used as standards. Systematic errors of ±5% should be taken into account. The introduction of nitrogen atoms, by replacing thiophene units by thiazoles or 1,3,4-thiadiazoles, only slightly affected the fluorescence quantum yield. The values obtained for thiophene/thiazole and thiophene/1,3,4-thiadiazole oligomers **1** ($\Phi_{295K} = 28\%$) and **2** ($\Phi_{295K} = 30\%$), are therefore in agreement with the series **6**−**8**, in which the fluorescence intensity of the corresponding pentamers remained nearly unaltered ($\Phi_{295K} = 26-40\%$).[31] In the oxygen-containing systems **3** and **4**, the quantum yield increased to $\Phi_{295K} = 48$ and 52%, respectively. The latter value for oligomer **4** is somewhat higher than the value published for the analogous non-capped pentamer ($\Phi_{295K} = 30\%$).[15a] The increase in fluorescence intensity going from oxazole **3** to 1,3,4-oxadiazole **4** was smaller than expected, since corresponding pentamers **10** and **11** showed an analogously directed but more pronounced structure/fluorescence relationship ($\Phi_{295K} = 59$ and 85%).[31] Interestingly, the introduction of a second 1,3,4-oxadiazole unit did not improve the value obtained for thiophene/1,3,4-oxadiazole **11**, although 1,3,4-oxadiazole moieties are reported to be strong fluorophor.[32] The relative position and sequence of different heterocyclic units in an extended conjugated chain is therefore of great importance, since the probability of nonradiative deactivation processes is promoted by the presence of heavy atoms in specific positions. This agrees with a previous optical study on heteroanalogs of the well-known laser dye 1,4-bis(5-phenyl-2-oxazolyl)benzene with combinations of *p*-phenylene, furan, oxazole, 1,3,4-oxadiazole, and thiophene units: A decrease in fluorescence intensity was found especially in the systems in which a thiophene unit was incorporated into the center of a pentameric system.[15] Theoretical calculations showed that 80% of the $S_0 \rightarrow S_1$* transition is located on the three central rings, and, accordingly, the presence of a thiophene ring in the central position causes a decrease in fluorescence quantum yield as a consequence of the heavy-atom effect.[29] These findings confirm the distinctly higher fluorescence quantum efficiency of oxadiazole pentamer **11** compared to that of the corresponding oligomer **4**. As a consequence of the identical terheterocyclic core, the quantum efficiencies of thiophene/1,3,4-oxadiazole pentamer **4** and heptamer **5** are nearly the same.

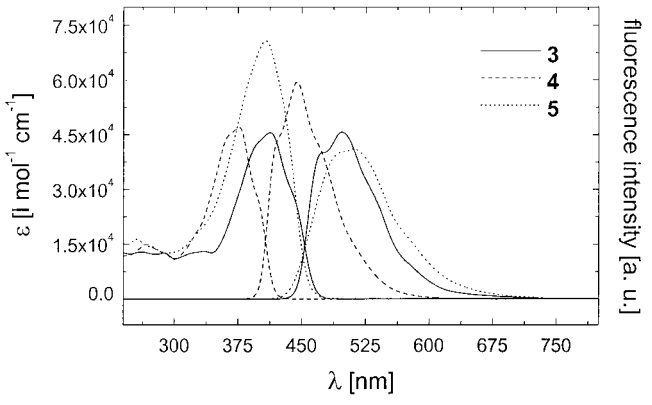


Figure 2. Absorption and corrected emission spectra of oligoheterocycles **3**−**5** in dichloromethane, $c = 5 \times 10^{-6}$ mol/L (abs.) and 1×10^{-6} mol/L (em.)

In summary, it can be concluded that the replacement of thiophene by different heterocyclic units in oligoheterocycles affects the spectral range of absorption and emission in a significant way. In contrast to 1,3,4-thiadiazole, oxazole, and in particular 1,3,4-oxadiazole moieties, which cause shifts to higher energies, the incorporation of thiazole leads to a bathochromic displacement of absorption and emission. As a consequence, the optical energy gaps were found to be increased in the same way. In contrast to the

Table 3. Electrochemical properties of the mixed oligoheterocycles **1**−**5** and end-capped quinquethiophene **6**

Oligomer	$E°_{Red2}$[a] [V]	$E°_{Red1}$[a] [V]	$E°_{Ox1}$[b] [V]	$E°_{Ox2}$[b] [V]	ΔE_{EC}[b,d] [V]
1	−2.33	−2.03	0.66	0.74	2.49
2	−2.18	−1.84	ca. 1.16[c,f]	−	2.73[c]
3	−2.64[f]	−2.23	0.66[e]	0.78[e]	2.74
4	−2.48[f]	−2.02	ca. 1.27[c,f]	−	3.03[c]
5	−2.20[c]	−1.94[c]	ca. 0.90[f]	−	2.65
6	−2.58[e]	−2.33	0.25	0.51	2.44

[a] In THF/nBu$_4$NPF$_6$ (0.1 M) vs. Fc/Fc$^+$ at 100 mV/s. − [b] In dichloromethane/nBu$_4$NPF$_6$ (0.1 M) vs. Fc/Fc$^+$ at 100 mV/s. − [c] In benzonitrile/nBu$_4$NPF$_6$ (0.1 M) vs. Fc/Fc$^+$ at 100 mV/s. − [d] Determined by $\Delta E_{CV} = E'_{Ox1} - E'_{Red1}$ (E' is the potential at which the redox process starts) and solvent correction. − [e] Quasireversible redox process. − [f] Irreversible redox process, $E°$ determined at $I° = 0.855 \times I_p$.[34]

transition probability, which is not dramatically influenced by the presence of nitrogen and/or oxygen atoms, the fluorescence quantum yield is strongly affected by the position of different heterocycles in the oligomer, and is distinctly increased by the incorporation of oxazole and, in particular, 1,3,4-oxadiazole units.

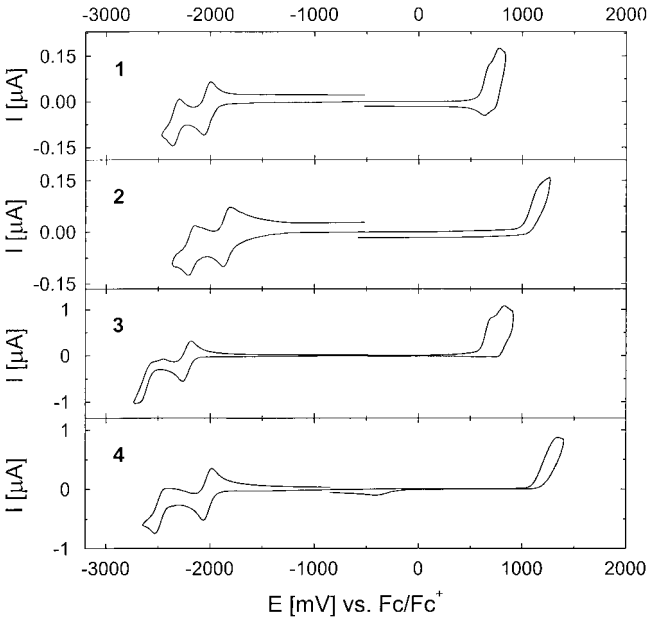


Figure 3. Electrochemical characterization of oligoheterocycles **1**−**4**; reduction in THF, nBu$_4$NPF$_6$ (0.1 M), $c = 7 \times 10^{-5}$ (**1**,**2**) and 3.5×10^{-4} mol/L (**3**,**4**); oxidation in CH_2Cl_2 (**1**,**3**) and benzonitrile (**2**,**4**), nBu$_4$NPF$_6$ (0.1 M), $c = 5 \times 10^{-5}$ (**1**,**2**) and 2.5×10^{-4} mol/L (**3**,**4**); $v = 100$ mV/s

Cyclic Voltammetry

Optical measurements provide information concerning the energy difference of the frontier orbitals in oligoheterocycles **1**−**5**. Nevertheless, in particular with respect to applications in electrooptical devices, it is of great value to ascertain the relative positions of the frontier orbitals. The fundamental processes in organic light-emitting diodes, charge creation, migration, and recombination are decisively determined by charged states in the active, organic layer.[33] Despite the model character of the MO concept, information on the relative positions of both HOMOs and LUMOs are helpful with regard to the manufacture of devices, and can be approximately derived from the oxidation and reduction potentials. Oxidation and reduction of oligoheterocycles **1**−**5** were performed by cyclic voltammetry in dichloromethane, benzonitrile, or THF (Figure 3). Reduction and oxidation potentials as well as the electrochemically determined energy gaps are listed in Table 3.

All oligoheterocycles investigated in this study had reversible first reductions that led to stable radical anions. The dianions, however, were sufficiently stable only in the case of thiazole **1,** thiadiazole **2**, and oxadiazole **5**, whereas the second reduction of thiophene/oxazole **3** and thiophene/1,3,4-oxadiazole oligomer **4** were quasireversible. Compared to EC5T **6** ($E°_{Red1} = -2.33$ V), the first reduction of thiophene/thiazole **1** ($E°_{Red1} = -2.03$ V) and thiophene/1,3,4-thiadiazole pentamer **2** ($E°_{Red1} = -1.84$ V) was stepwise facilitated by the introduction of two and four electronegative nitrogen atoms. Accordingly, the first reduction is shifted to more positive values if thiophene/oxazole **3** ($E°_{Red1} = -2.23$ V) and thiophene/1,3,4-oxadiazole pentamer **4** ($E°_{Red1} = -2.02$ V) are compared. Due to the extended delocalization as a consequence of the incorporation of two additional thiophene units, the reduction potential of thiophene/1,3,4-oxadiazole heptamer **5** ($E°_{Red1} = -1.98$ V) is slightly shifted to values more positive than those of pentamer **4**. Cross-comparison between the oligomer couples **1/3** ($\Delta E°_{Red1/(1,3)} = -0.20$ V) and **2/4** ($\Delta E°_{Red1/(2,4)} = -0.18$ V) reveals that the oxygen-containing systems are harder to reduce, not according to electronegativity, which is higher in oxygen than in sulfur, but in accordance with the higher aromaticity of thiaheterocycles, which supercedes the former effect. These findings were confirmed by the second reduction processes. In both groups of compounds, an increasing number of nitrogen atoms facilitated the reduction to the dianions ($\Delta E°_{Red2/(1,2)} = +0.15$ V, $\Delta E°_{Red2/(3,4)} = +0.16$ V). Compared to the analogous pentamers **7**, **8**, **10**, and **11**, the introduction of a second nonthiophenic heterocyclic unit, represented in **1**−**4,** shifted both reductions to more positive values.

In contrast to the reduction processes, full reversibility of the first and second oxidation is only reached in the case of thiophene/thiazole **1**. While the oxidation waves of thiophene/oxazole pentamer **3** partly indicate reversibility, the oxidation to the cation radical is fully irreversible in the case of thiophene/1,3,4-thiadiazole **2** and thiophene/1,3,4-oxadiazole oligomer **4**. Evidently, two adjacent nitrogen atoms in a heterocyclic unit seem to favor follow-up reactions and decomposition of the cation radical. The irreversibility of the oxidation of conjugated systems containing 1,3,4-oxadiazole units was mentioned before in several publications.[9][35] The oxidation potentials are, similar to reduction, gradually shifted to higher values due to the electron-withdrawing character of incorporated nitrogen (and

oxygen) atoms. The first oxidation of thiophene/thiazole **1** (E°_{Ox1} = 0.66 V) and thiophene/1,3,4-thiadiazole oligomer **2** ($E^{\circ}_{Ox1} \approx$ 1.16 V) are strongly shifted to higher potentials than in quinquethiophene EC5T **6** (E°_{Ox1} = 0.25 V) . In the oxygen-containing systems **3** (E°_{Ox1} = 0.66 V) and **4** ($E^{\circ}_{Ox1} \approx$ 1.27 V), this effect is even larger. The extension of the π-conjugation, as in thiophene/1,3,4-oxadiazole heptamer **5** ($E^{\circ}_{Ox1} \approx$ 0.90 V), decreases the oxidation potential relative to pentamer **4**, although irreversibility is maintained. Cross-comparison of thiophene/thiazole **1** and thiophene/oxazole oligomers **3** shows that their first oxidation potentials coincide. In contrast, oxidation is more difficult if sulfur is replaced by oxygen, when thiophene/1,3,4-thiadiazole **2** and thiophene/1,3,4-oxadiazole **4** are compared ($\Delta E^{\circ}_{Ox1/(2,4)} \approx +0.11$ V). The introduction of a second non-thiophenic heterocyclic unit in **1**−**4** shifts the oxidation processes to values higher than those found for their pentameric analogs **7**, **8**, **10**, and **11**.

The electrochemically determined energy differences ΔE_{EC}, which approximately correspond to HOMO/LUMO gaps, are in excellent agreement with the trends found from the optical measurements (Table 2). The above-mentioned more difficult reduction of oxygen-containing systems consequently leads to a widening of the HOMO/LUMO gap. Within the series of oligoheterocycles **1**−**5**, thiophene/1,3,4-oxadiazole **4** (ΔE_{EC} = 3.03 V) has the highest value and thiophene/thiazole **1** (ΔE_{EC} = 2.49 V) has the lowest value.

Finally, it can be concluded that the introduction of electronegative nitrogen atoms significantly affects the redox potentials. Reduction is facilitated with the increasing number of nitrogen atoms, while oxidation becomes gradually more difficult. The transfer of electrons to thiophene/thiaheterocycle oligomers occurs at lower potentials than in their oxygen-containing analogs. Adjacent nitrogen atoms in one heterocycle lead to irreversible oxidation. Both optical and electrochemical measurements gave the same trend within the series for the energy gap between the frontier orbitals. Because both its HOMO and LUMO are low-lying, oligomer **4** can be used as a hole-blocking, electron-transporting material in electrooptical devices.

X-ray Crystallography

Whereas several publications in the near past dealt with X-ray single-crystal analyses of, particularly, longer oligothiophenes,[1d,36,37] structure determinations of mixed oligoheterocycles are rather scarce. In a previous publication[9a] we reported on the crystal structure of thiophene/1,3,4-oxadiazole pentamer **11** and observed interesting structural features, different from those reported on related oligothiophenes. The presence of a 1,3,4-oxadiazole unit in the center of the conjugated backbone led to formation of dimers and to parallel orientation of the molecules in the solid state. In contrast to this packing motif, unsubstituted oligothiophenes usually prefer favorable edge-to-face aromatic interactions, and tend to pack in a "herringbone" pattern.[1d] Furthermore, the molecules of pentamer **11** exhibited a particular U-type bending, and, in addition, two terminal thiophene rings were preferentially *syn*-arranged. Oligothiophenes typically only occasionally have a certain percentage of *syn* orientations relative to terminal neighboring thiophene rings.[36] In this study, we will report on the X-ray crystal analysis of thiophene/1,3,4-oxadiazole heptamer **5**.

We were able to grow single crystals of heptamer **5** suitable for X-ray analysis by repeated fractionated sublimation of a highly purified material in a gradient-tube furnace (270−300 °C/$p = 1 \times 10^{-3}$ mbar). In agreement with a previously reported observation,[9a] crystal growth in the colder part of the glass tube only started when amorphous material already covered the glass surface. Crystalline material was obtained as bright yellow needles with sizes up to 0.25 × 0.25 × 13 mm. Crystal growth did not depend strongly on the speed of sublimation. 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, views of the unit cell and the structure along the axes are given in Figure 4. Atomic labeling and the side view of one molecule are presented together with selected bond lengths in Figure 5.

Table 4. Crystallographic data, data collection, and refinement parameters for thiophene/1,3,4-oxadiazole oligomer **5**

	5
Formula	$C_{32}H_{24}N_4O_2S_5$
M_r	656.85
T (K)	293(2)
Wavelength [Å]	λ(Mo-K_α) = 0.71073
Crystal system	monoclinic
Space group	$P2_1/c$ (IT no. 14)
a [Å]	10.7534(8)
b [Å]	12.7028(7)
c [Å]	21.707(2)
β [°]	96.248(10)
V [Å^3]	2947.5(4)
Z	4
$\rho_{calcd.}$ [g cm^{-3}]	1.480
μ (Mo-K_α) [mm^{-1}]	0.432
F(000)	1360
Crystal size [mm]	0.11 × 0.19 × 0.58
θ range [°]	1.89−25.89
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 15$, $-26 \le l \le 26$
Reflections collected	36355
Unique reflections	5626
R_{int} (F^2)	0.1422
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	5626/0/392
GoF S	0.897
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0498, wR_2 = 0.1180
R indices (all data)	R_1 = 0.0839, wR_2 = 0.1277
Largest diff. peak/hole [e Å^{-3}]	0.460/−0.318

The crystals of thiophene/1,3,4-oxadiazole oligomer **5** belong to the monoclinic space group $P2_1/c$, with four molecules in the unit cell (Z = 4). The top-view projection which corresponds to a view along the c axis of the unit cell, shows that the single molecules are oriented parallel to each other and form slipped layers (Figure 4, left). Adjacent

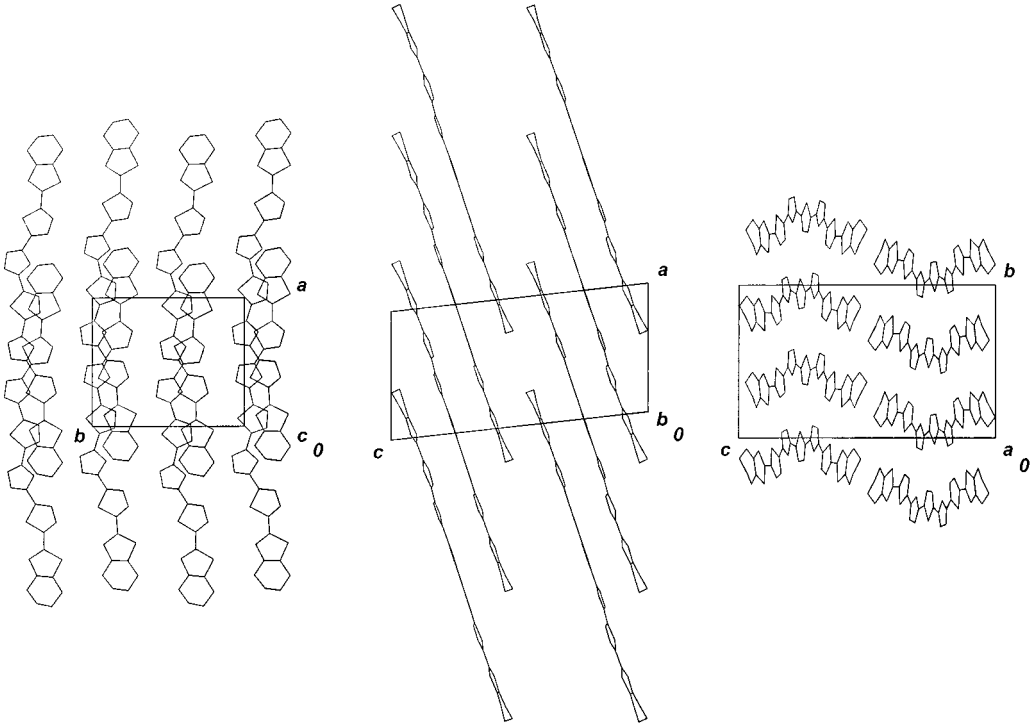


Figure 4. Packing views of oligomer **5** along the *c* axis (left), along the *b* axis (center) and along the *a* axis (right)

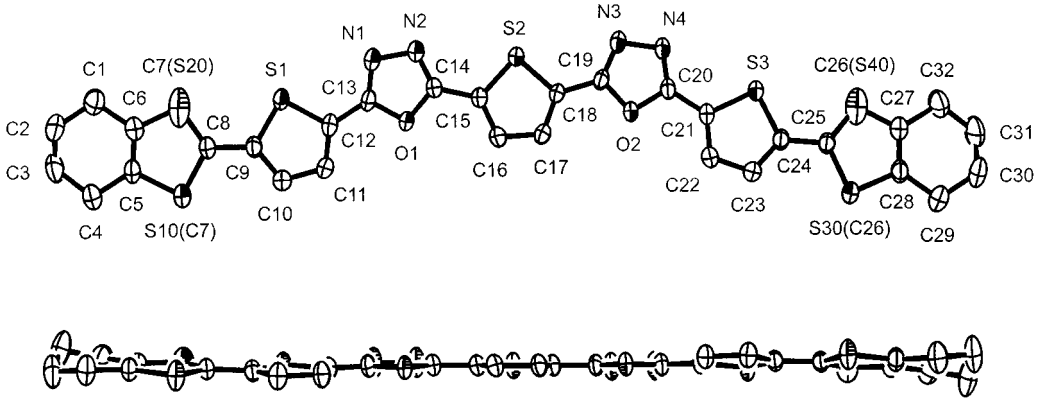


Figure 5. ORTEP front view of oligomer **5** showing the atomic labeling, 50% thermal ellipsoids (top); side view of oligomer **5** (bottom); Selected bond lengths [Å] (standard deviation): S1−C12 1.726(2), S1−C9 1.728 (3), S2−C15 1.720 (2), S10(C7)−C5 1.707 (3)*, S10(C7)−C8 1.720 (3)*, O1−C14 1.361 (3), O1−C13 1.370 (3), C9−C10 1.361 (4), C9−C8 1.456 (3), C14−N2 1.287 (4), C14−C15 1.449 (3), C13−N1 1.281 (4), C13−C12 1.447 (3), N2−N1 1.416 (3), C11−C12 1.355 (4), C11−C10 1.402 (3), C7(S20)−C8 1.504 (4)*, C7(S20)−C6 1.506 (3)*, C15−C16 1.349 (4), C4−C3 1.477 (5)*, C4−C5 1.492 (4), C6−C5 1.351 (4), C6−C1 1.496 (4), C16−C17 1.400 (3), C1−C2 1.476 (5)*, C3−C2 1.451 (6)*; the *-indicated values are not absolutely reliable due to disorder and two conformations (*syn*/*anti*)

molecules are laterally displaced by the length of three heterocyclic units, resulting in an overlap of four heterocyclic moieties. In contrast to the related thiophene/1,3,4-oxadiazole pentamer **11**,[9a] the molecules do not form dimers, as can clearly been seen in the side-view projection, which corresponds to the *a*/*c* plane (Figure 4, center). Rather, individual molecules are practically planar, not bent, and form parallel layers that are oriented perpendicular to the *a*/*c* plane. The mean distance between adjacent layers is 3.60 Å. The view along the *a* axis (Figure 4, right) reveals that the molecules are U- or bow-shaped, and form parallel stacks of alternating concavely and convexly bent molecules.

The packing motif of thiophene/1,3,4-oxadiazole heptamer **5** is different to that of unsubstituted oligothiophenes, which typically pack in a "herringbone" structure,[1d] but it is rather comparable to the molecular arrangement of α,ω-dicyanooligothiophenes.[37] In the latter series, the tetramer and the pentamer also form slipped π-stacks. Interestingly, the hexamer already favors the "herringbone"-like arrangement, thereby indicating that there is only a small energy difference between the alternative packing motifs.

The inner three heterocyclic rings in thiophene/1,3,4-oxadiazole oligomer **5** exhibit a nearly coplanar all-*anti* confor-

mation; the terminal tetrahydrobenzo[*b*]thiophenyl moieties are slightly twisted (Φ = 9°) with respect to the central thiophene ring (Figure 5).

The second and the sixth heterocycle are coplanar with the terminal thiophene units (Φ = 1°), but the structure is disordered with respect to the relative orientation of the terminal thiophene rings. Although the *anti* conformation prevails, 35% of the molecules are *syn*-oriented in the crystals. The atoms involved in the disordered rings were therefore labeled C7(S20), S10(C7), C26(S40), and S30(C26), reflecting the *anti*(*syn*) conformer ratio. Selected bond lengths are given in the caption to Figure 5. Due to various possible conformations in the cyclohexene end-cap, there is also some inaccuracy concerning the C2−C3 and C30−C31 bonds. All heterocyclic rings have normal bond lengths and angles, close to those found for related α-oligothiophenes[1d] and the previously reported corresponding thiophene/1,3,4-oxadiazole pentamer.[9a] The C−O (1.36−1.37 Å), C−N (1.28−1.29 Å), and N−N bonds (1.42 Å) in the oxadiazole units, the C−S (1.72−1.73 Å), C=C double (1.35−1.36 Å), and C−C single bonds (1.40 Å) in the thiophene units, as well as the C−C interring bonds (1.45−1.46 Å) agree very well with published data.

So far *syn* conformers in the solid state have been reported for an α,ω-substituted quaterthiophene[36a] and partly disordered β-substituted quater-,[36b,36c] quinque-,[36d] and sexithiophenes.[36d,36e] Occasionally, the coplanarity between adjacent, *syn*-oriented rings is remarkably infringed upon, due to conformational strain provoked by bulky β-alkyl substitution.[36c,36d] However, the outer rings in 3′,4′′-didecylquaterthiophene are only tilted by 3.6(5)°, despite the presence of β-substituents.[36b] In systems without any β-substituents close to the interring carbon−carbon single bond, the *syn*-oriented units were found to be coplanar. The value of 1° found for thiophene/1,3,4-oxadiazole **5** agrees well with the reported dihedral angles of 3.9°,[36c] 5°[36a] and 11°.[36e]

Conclusions

We systematically incorporated different heterocyclic units into a conjugated system based on oligothiophenes. The mixed oligoheterocyles **1−5** were synthesized by either transition-metal-catalyzed cross-coupling reactions of suitable heterocyclic components, or by ring-closure reactions of acyclic precursors. All compounds were purified to a high level of purity by repeated fractionated sublimation.

Detailed investigations of the electronic properties of mixed oligoheterocycles **1−5** and previously reported compounds **6−11** clearly revealed that, depending on the corresponding molecular structure, there is a systematic change in the spectral range of absorption and emission, the fluorescence quantum yield in solution, redox potentials, energy gaps, and solubilities. Clear structure−property relationships within this series of conjugated oligomers provide a data set for the evaluation of properties of related compounds.

Crystals suitable for X-ray analysis could be grown, by sublimation, for thiophene/1,3,4-oxadiazole heptamer **5**. In contrast to unsubstituted oligothiophenes, the oligomers do not pack in a "herringbone" pattern, but prefer an arrangement in slipped π-stacks. The individual molecules realize a nearly coplanar conformation. Statistically distributed *syn* orientations of terminal bithienyl units were found.

Experimental Section

General Remarks: 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 silica gel 60 (0.040−0.063 mm and 0.063−0.200 mm, Merck) or aluminum oxide 90 (activity II-III, 0.063−0.200 mm, Merck). Melting points were determined with a Büchi B-545 melting point apparatus and are corrected. FT-IR spectroscopy was performed on a Perkin−Elmer Spectrometer 2000. ^{1}H NMR spectra were recorded on Bruker AMX 500 (500 MHz), and AC 200 (200 MHz) spectrometers (with deuterated solvent as lock-in and tetramethylsilane as internal reference). ^{13}C NMR spectra were recorded with Bruker AMX 500 (126 MHz) and AC 200 (50 MHz) spectrometers. Solid-state ^{13}C NMR spectra were recorded with a Bruker DSX 400 (100 MHz) spectrometer equipped with a 4-mm CPMAS sample head. Mass spectra were recorded with a Varian MAT 711. Ions were generated by electron impact (EI) or fast-atom bombardment (FAB). Elemental analyses were performed on a Elementar vario EL. Saturation concentrations and solubilities were determined by mixing a precise amount of substance (1−25 mg) with dichloromethane at ambient temperature until complete solution occurred. Without heating the sample, the dissolution was promoted by ultrasound and stirring. Additional solvent was added in time periods of ten minutes to warrant thermodynamic equilibrium. UV/VIS/NIR spectra were recorded on a Perkin−Elmer Lambda 19 in 1-cm cuvettes. Fluorescence spectra were recorded with a Perkin−Elmer LS 50 in 1-cm cuvettes. Fluorescence quantum yields were determined with respect to 9,10-diphenylanthracene (Φ_R^{em} = 0.85 in cyclohexane[29]) or fluorescein (Φ_R^{em} = 0.90 in 0.1 M NaOH[30]). The cyclic voltammetry experiments were performed with a computer-controlled EG & G PAR 273 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 mm^2, 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 0.5−3.5 × 10^{-4} mol/L of electroactive species was used. The electrolyte consisted of either dichloromethane (p. a., SDS), which was refluxed and distilled in the presence of sulfuric acid under argon and subsequently filtered over aluminum oxide (ICN Alumina B − Activity grade Super I), THF (anhydrous, Aldrich), which was refluxed and distilled from potassium under argon, or benzonitrile (HPLC grade, Aldrich), which was distilled under argon and filtered through aluminum oxide (ICN Alumina B − Activity grade Super I). The solvents were directly transferred through syringes to the electrochemical cell. The supporting salt was 0.1 M nBu$_4$NPF$_6$ from Fluka which was

twice recrystallized from ethanol/water and dried in a high vacuum. − Starting materials were prepared according to literature procedures: 2,5-bis(2-thiazolyl)thiophene (**12**) [m. p. 145−147 °C, yield 58%],[20] 2-bromo-4,5,6,7-tetrahydrobenzo[*b*]thiophene [b. p. 56−58 °C/5 × 10^{-2} mbar, yield 93%],[21] 4,5,6,7-tetrahydrobenzo[*b*]thiophene (**17**) [b. p. 87−88 °C/18 mbar, yield 88%],[22] thiophene-2,5-dicarboxylic acid dihydrazide (**20**) [m. p. 258−260 °C, yield 53%],[14a] 2-(4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)thiophene (**21**) [m. p. 51 °C, yield 86%],[9a] 5-(4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)thiophene-2-carboxylic acid (**22**) [m. p. 223−224 °C, yield 94%],[9a] 5-(4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)thiophene-2-carboxylic acid chloride (**23**),[9a] thiophene-2,5-dicarboxylic acid dichloride (**27**) [m. p. 45−46 °C, yield 48%].[24]

X-ray Crystal Structure Analysis: Single crystals of **5** suitable for X-ray crystallography were grown by sublimation. Diffraction data were collected on a STOE-IPDS image-plate diffractometer (Mo-K_α radiation, graphite monochromator) in the φ-rotation scan mode. The structure was solved by direct methods with the XMY93 program system[38] and subjected to full-matrix refinement with SHELXL-93.[39] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added in calculated positions. The terminal 4,5,6,7-tetrahydrobenzo[*b*]thiophenyl rings are conformationally disordered. Two orientations related by a 180° rotation about one ring−ring bond are realized in the solid sate (35:65 *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-114943. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

2,5-Bis(5-bromo-2-thiazolyl)thiophene (13): A solution of *N*-bromosuccinimide (601 mg, 3.38 mmol) in DMF (25 mL) was added dropwise to a solution of 2,5-bis(2-thiazolyl)thiophene (**13**) (339 mg, 1.35 mmol) in DMF (25 mL) at 0 °C. The resulting mixture was kept for 1 h at 0 °C and was then allowed to warm to room temperature. After 100 h the reaction mixture was poured in water and extracted with dichloromethane. The organic phase was washed with saturated $NaHCO_3$ solution and water and was dried ($MgSO_4$). After evaporation of the solvent, the remaining yellow solid was purified by chromatography (SiO_2/toluene) to yield **13** (505 mg, 92%) as bright yellow flakes, m. p. 194 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3053 w, 1477 s, 1420 m, 1264 w, 1129 w, 1000 s, 880 s, 842 m, 655 w, 627 m, 464 w cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.68 (s, 2 H, H4′), 7.38 (s, 2 H, H3,4). − ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 162.0 (C2′), 144.9 (C4′), 138.5 (C2,5), 127.0 (C3,4), 108.7 (C5′). − MS (EI); *m*/*z* (%): 410 (59), 408 (100) [M^+], 406 (49), 329 (57) [M^+ − Br], 327 (51) [M^+ − Br], 272 (23) [329 − C_2HS], 270 (21) [327 − C_2HS], 191 (44) [272/270 − Br], 69 (10), 57 (64) [C_2HS^+]. − $C_{10}H_4Br_2N_2S_3$ (408.2): calcd. C 29.43, H 0.99, N 6.86, S 23.57; found C 29.64, H 1.29, N 6.82, S 23.40.

2,5-Bis[5-(4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-2-thiazolyl]thiophene (1): A solution of 2-bromo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (1.90 g, 8.75 mmol) in diethyl ether (10 mL) was added dropwise to magnesium chips (266 mg, 10.9 mmol) in boiling diethyl ether (10 mL). The resulting mixture was heated reflux for 5 h, allowed to cool to room temperature, and transferred by use of a syringe to the dropping funnel of a second apparatus. The Grignard solution was added dropwise to a suspension of 2,5-bis(5-bromo-2-thiazolyl)thiophene (**13**, 715 mg, 1.75 mmol) and 1,3-bis(diphenylphosphanyl)propane nickel(II) chloride (14.2 mg, 2.63 × 10^{-5} mol) in diethyl ether/toluene (2:1, 60 mL). The resulting mixture was refluxed for 20 h. Due to its low solubility, the major portion of thiophene/thiazole pentamer **1** was separated as an almost pure compound by filtration, suspended in toluene to remove soluble impurities and purified by sublimation, yielding **1** (200 mg, 25%) as an amorphous orange powder, m. p. 298 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3057 w, 2927 s, 2833 w, 1547 w, 1512 s, 1416 m, 1274 m, 1242 m, 1148 w, 879 m, 812 s, 630 m, 477 w cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.75 (s, 2 H, H4′), 7.43 (s, 2 H, H3,4), 6.88 (s, 2 H, H3′′), 2.77 (t, $^3J_{H6'',H7''}$ = 6.0 Hz, 4 H, H7′′), 2.61 (t, $^3J_{H4'',H5''}$ = 6.0 Hz, 4 H, H4′′), 1.84−1.89 (m, 4 H, H6′′), 1.79−1.84 (m, 4 H, H5′′). − SS-^{13}C NMR (100 MHz, 25 °C): δ = 157.4 (C2′), 138.6, 137.3, 135.3, 133.1, 130.1, 127.5, 125.4 (C2,2′′,3,3′′,3a′′,4,4′,5,5′,7a′′), 25.6 (C4′′,7′′), 22.9 (C5′′,6′′). − MS (EI); *m*/*z* (%): 524 (22), 523 (29), 522 (100) [M^+], 518 (5) [M^+ − $2H_2$], 494 (10) [M^+ − C_2H_4], 466 (5) [494 − C_2H_4], 300 (5), 261 (5) [M^{2+}], 233 (8), 166 (8). − $C_{26}H_{22}N_2S_5$ (522.8): calcd. C 59.73, H 4.24, N 5.36, S 30.67; found C 59.58, H 4.20, N 5.27, S 30.78. [In order to regain unchanged starting material, 2 N HCl (50 mL) was added to the organic phase followed by an extraction with toluene. The combined organic layers were washed with water and $NaHCO_3$ solution and dried ($MgSO_4$). After evaporation of the solvent, the remaining mixture consisting of homocoupling product EC2T **15**, 2,5-bis(5-bromo-2-thiazolyl)thiophene (**13**), and only traces of **1** was separated by chromatography (SiO_2/dichloromethane), yielding **13** (100 mg, 14%) as bright yellow flakes.]

4,5,6,7-Tetrahydrobenzo[*b*]thiophene-2-carboxylic Acid (18): *n*BuLi (33.9 mL of a 1.6 M solution in hexane, 54.3 mmol) was slowly added to a stirred solution of 4,5,6,7-tetrahydrobenzo[*b*]thiophene (**17**) (7.50 g, 54.3 mmol) in diethyl ether (100 mL). After the resulting mixture was cooled to −50 °C, gaseous carbon dioxide was bubbled through the mixture over a period of 4 h. The organic phase was hydrolyzed and extracted with additional water. After separation, the aqueous phase was heated to 50 °C and acidified with a few drops of concentrated HCl. The thiophene carboxylic acid **18** precipitated as an amorphous, colorless solid which was filtered, washed, and dried over diphosphorus pentoxide to give **18** (8.76 g, 89%) as an amorphous, colorless powder, m. p. 195 °C. − FT-IR (KBr): $\tilde{\nu}$ = 2933 s, 2855 m, 2579 br, 1670 s, 1464 s, 1314 s, 1276 m, 1181 m, 1142 m, 1071 w, 937 w, 756 m, 509 m cm^{-1}. − ^{1}H NMR (200 MHz, [D_6]DMSO, 25 °C): δ = 9.01 (s, br, 1 H, COO*H*), 7.37 (s, 1 H, H3), 2.72 (t, $^3J_{H6,H7}$ = 5.2 Hz, 2 H, H7), 2.55 (t, $^3J_{H4,H5}$ = 5.2 Hz, 2 H, H4), 1.62−1.82 (m, 4 H, H5,6). − ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 168.0 (*C*OOH), 146.2 (C2), 136.8 (C7a), 135.8 (C3), 128.3 (C3a), 25.56 (C4), 25.29 (C7), 23.08 (C6), 22.51 (C5). − MS (EI); *m*/*z* (%): 183 (9), 182 (76) [M^+], 181 (11) [M^+ − H], 155 (8), 154 (100) [M^+ − C_2H_4], 141 (5), 138 (6), 137 (59) [M^+ − COOH], 135 (6), 97 (5), 91 (6), 77 (5), 45 (7) [$COOH^+$]. − $C_9H_{10}O_2S$ (182.3): calcd. C 59.31, H 5.53, S 17.59; found C 59.28, H 5.39, S 17.65.

4,5,6,7-Tetrahydrobenzo[*b*]thiophene-2-carboxylic Acid Chloride (19): Oxalyl chloride (12.5 g, 8.50 mL, 98.8 mmol) in toluene (20 mL) was slowly added to a suspension of thiophenecarboxylic acid **18** (4.50 g, 24.7 mmol) in toluene (20 mL) at 0 °C. The mixture was heated to 55 °C and stirred for 3 h. After evaporation of the solvent and the excess oxalyl chloride, the remaining orange oil was dissolved twice in chloroform and evaporated in order to remove last traces of oxalyl chloride. The crude acid chloride **19** was dissolved in the desired solvent and used without further purification.

Thiophene-2,5-dicarboxylic Acid Bis[2-(4,5,6,7-tetrahydrobenzo[*b*]-thiophene-2-carbonyl)hydrazide] (16): Acid chloride **19** (4.93 g, 24.6 mmol), dissolved in NMP (50 mL), was added dropwise to a

suspension of thiophene-2,5-dicarboxylic acid dihydrazide **20** (2.46 g, 12.3 mmol) in NMP/pyridine (4:1, 100 mL). The resulting mixture was stirred overnight at room temperature. After evaporation of the solvent, the crude product was suspended in water, filtered, and dried. Recrystallization from EtOH yielded **16** (5.96 g, 92%) as an amorphous, colorless powder, m. p. 311−312 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3246 br, 3015 w, 2935 m, 2858 w, 1677 s, 1650 s, 1533 s, 1504 s, 1457 m, 1275 s, 1065 w, 820 w cm^{-1}. − ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 10.68 (s, br, 2 H, N*H*), 10.42 (s, br, 2 H, N′*H*), 7.85 (s, 2 H, H3,4), 7.53 (s, 2 H, H3′), 2.69−2.79 (m, 4 H, H7′), 2.53−2.63 (m, 4 H, H4′), 1.66−1.86 (m, 8 H, H5′,6′). − ^{13}C NMR (126 MHz, [D$_6$]DMSO, 25 °C): δ = 160.97 (*C*O), 160.23 (*C*O′), 141.54 (C2,5), 141.14 (C2′), 136.1, 132.6, 129.74, 129.30 (C3,3′,3a′,4,7a′), 24.90 (C4′), 24.62 (C7′), 22.73 (C6′), 22.10 (C5′). − MS (FAB); *m*/*z* (%): 573 (19) [(M − H + 2Na)$^+$], 553 (21), 552 (35), 551 (100) [(M + Na)$^+$], 550 (30) [(M − H + Na)$^+$], 549 (11), 529 (19) [(M + H)$^+$]. − $C_{24}H_{24}N_4O_4S_3$ (528.7): calcd. C 54.53, H 4.58, N 10.60, S 18.20; found C 54.25, H 4.52, N 10.44, S 17.97.

2,5-Bis[5-(4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-1,3,4-thiadiazol-2-yl]thiophene (2): Bishydrazide **16** (2.00 g, 3.78 mmol) was added to a suspension of diphosphorus pentasulfide (2.52 g, 11.3 mmol) in pyridine (100 mL). The resulting mixture was heated at reflux for 20 h. After evaporation of the solvent, the remaining orange solid was suspended in water, filtered, and dried. The crude product is a mixture of **2** as the major component and side products containing one or two 1,3,4-oxadiazole instead of 1,3,4-thiadiazole units. Subsequent fractionated sublimation of the raw material finally yielded **2** (515 mg, 26%) as an amorphous, bright orange powder, m. p. 383−384 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3069 w, 2926 m, 2837 w, 1548 w, 1482 s, 1416 s, 1364 w, 1065 w, 888 m, 810 m, 759 m, 607 w cm^{-1}. − ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 7.54 (s, 2 H, H3,4), 7.24 (s, 2 H, H3′′), 2.82 (t, $^3J_{H6'',H7''}$ = 6.0 Hz, 4 H, H7′′), 2.65 (t, $^3J_{H4'',H5''}$ = 6.0 Hz, 4 H, H4′′), 1.86−1.91 (m, 4 H, H6′′), 1.80−1.85 (m, 4 H, H5′′). − SS-^{13}C NMR (100 MHz, 25 °C): δ = 160.4 (C2′,5′), 139.5, 136.4, 133.0, 130.6, 128.2 (C2,2′′,3,3′′,3a′′,4,5,7a′′), 25.5 (C4′′,7′′), 22.3 (C5′′,6′′). − MS (EI); *m*/*z* (%): 526 (22), 525 (27), 524 (100) [M$^+$], 496 (10) [M$^+$ − C_2H_4], 329 (31), 301 (20), 181 (20), 135 (39). − $C_{24}H_{20}N_4S_5$ (524.8): calcd. C 54.93, H 3.84, N 10.68, S 30.55; found C 54.89, H 3.71, N 10.69, S 30.24.

2,5-Bis[5-(4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-1,3,4-oxadiazol-2-yl]thiophene (4): A suspension of bishydrazide **16** (1.00 g, 1.89 mmol) in POCl$_3$ (100 mL) was heated of reflux for 21 d. 90% of the solvent was removed from the reaction mixture by distillation and the remaining olive-colored residue was added dropwise to lukewarm water in order to hydrolyze the POCl$_3$. The crude product precipitates during this procedure and was isolated by filtration, washed with water, and dried. Sublimation yielded **4** (650 mg, 70%) as an amorphous, pale yellow powder, m. p. 255−256 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3069 w, 2931 m, 2851 w, 1583 s, 1530 s, 1478 m, 1446 m, 1346 w, 1183 w, 1143 w, 1030 m, 929 w, 814 w, 722 m, 512 w cm^{-1}. − ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 7.81 (s, 2 H, H3,4), 7.50 (s, 2 H, H3′′), 2.84 (t, $^3J_{H6'',H7''}$ = 6.1 Hz, 4 H, H7′′), 2.68 (t, $^3J_{H4'',H5''}$ = 6.1 Hz, 4 H, H4′′), 1.87−1.92 (m, 4 H, H6′′), 1.81−1.86 (m, 4 H, H5′′). − ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C): δ = 161.2, 159.0 (C2′,5′), 142.6, 137.0 (C2,2′′,5), 131.1, 129.8 (C3,3′′,4), 128.6, 120.2 (C3a′′,7a′′), 25.38, 25.32 (C4′′,7′′), 23.15 (C6′′), 22.48 (C5′′). − MS (EI); *m*/*z* (%): 494 (18), 493 (30), 492 (100) [M$^+$], 488 (8) [M$^+$ − 2 H$_2$], 315 (5), 231 (6), 166 (8), 165 (78) [$C_9H_9OS^+$], 137 (6), 135 (5), 96 (5), 69 (6). − $C_{24}H_{20}N_4O_2S_3$ (492.7): calcd. C 58.51, H 4.09, N 11.37, S 19.53; found C 58.21, H 4.11, N 11.38, S 19.55.

Thiophene-2,5-dicarboxylic Acid Bis{2-[5-(4,5,6,7-tetrahydrobenzo-[*b*]thiophen-2-yl)-2-thenoyl]hydrazide} (24): Bisthiophene acid chloride **23** (550 mg, 1.94 mmol), dissolved in NMP (10 mL), was added dropwise to a suspension of thiophene-2,5-dicarboxylic acid dihydrazide (**20**) (195 mg, 9.72 × 10^{-4} mol) in NMP/pyridine (4:1, 15 mL). The resulting mixture was stirred overnight at room temperature. After evaporation of the solvent, the crude product was suspended in water, filtered, and dried. Recrystallization from EtOH yielded **24** (570 mg, 85%) as an amorphous, pale yellow powder, m. p. 307−308 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3262 br, 3092 w, 2930 m, 2851 w, 1645 s, 1535 m, 1478 s, 1441 m, 1270 s, 1085 w, 806 w, 730 w cm^{-1}. − ^{1}H NMR (200 MHz, [D$_6$]DMSO, 25 °C): δ = 10.78 (s, br, 2 H, N*H*), 10.63 (s, br, 2 H, N′*H*), 7.89 (s, 2 H, H3,4), 7.79 (d, $^3J_{H3',H4'}$ = 3.6 Hz, 2 H, H3′), 7.26 (d, $^3J_{H3',H4'}$ = 3.6 Hz, 2 H, H4′), 7.12 (s, 2 H, H3′′), 2.66−2.76 (m, 4 H, H7′′), 2.50−2.60 (m, 4 H, H4′′), 1.66−1.86 (m, 8 H, H5′′,6′′). − ^{13}C NMR (126 MHz, [D$_6$]DMSO, 25 °C): δ = 160.65 (*C*O), 160.38 (*C*O′), 142.4 (C2,5), 141.2 (C2′), 136.64, 136.60, 134.5, 131.6, 130.31, 129.55, 126.2, 123.7 (C2′′,3,3′,3′′,3a′′,4,4′,5′,7a′′), 25.07 (C4′′), 24.57 (C7′′), 23.01 (C6′′), 22.28 (C5′′). − MS (FAB); *m*/*z* (%): 737 (28) [(M − H + 2 Na)$^+$], 717 (39), 716 (49), 715 (100) [(M + Na)$^+$], 714 (34) [(M − H + Na)$^+$], 693 (10) [(M + H)$^+$]. − $C_{32}H_{28}N_4O_4S_5$ (692.9): calcd. C 55.47, H 4.07, N 8.09, S 23.14; found C 55.21, H 3.99, N 7.90, S 22.88.

2,5-Bis{5-[5-(4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-2-thienyl]-1,3,4-oxadiazol-2-yl}thiophene (5): A suspension of bishydrazide **24** (1.94 g, 2.80 mmol) in POCl$_3$ (250 mL) was heated at reflux for 21 d. 90% of the solvent was removed from the reaction mixture by distillation and the remaining brown residue was added dropwise to lukewarm water to hydrolyze the POCl$_3$. The crude product precipitates during this procedure and was isolated by filtration, washed with water, and dried. Sublimation yielded **5** (465 mg, 25%) sporadically as bright yellow needles and mainly as bright yellow flakes, m. p. 365 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3069 w, 2925 m, 2838 w, 1578 s, 1509 s, 1504 s, 1478 s, 1444 m, 1078 w, 1034 m, 804 m, 725 m, 480 w cm^{-1}. − ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 7.87 (s, 2 H, H3,4), 7.71 (d, $^3J_{H3'',H4''}$ = 4.0 Hz, 2 H, H3′′), 7.14 (d, $^3J_{H3'',H4''}$ = 4.0 Hz, 2 H, H4′′), 6.99 (s, 2 H, H3′′′), 2.76−2.80 (m, 4 H, H7′′′), 2.61−2.65 (m, 4 H, H4′′′), 1.86−1.90 (m, 4 H, H6′′′), 1.81−1.85 (m, 4 H, H5′′′). − SS-^{13}C NMR (100 MHz, 25 °C): δ = 159.4 (C2′,5′), 142.1, 136.2, 132.8, 128.1, 122.9, 118.0 (C2,2′′,2′′′,3,3′′,3′′′,3a′′′,4,4′′,5,5′′,7a′′′), 25.7 (C4′′′,7′′′), 22.1 (C5′′′,6′′′). − MS (EI); *m*/*z* (%): 658 (26), 657 (35), 656 (100) [M$^+$], 653 (8), 652 (24) [M$^+$ − 2 H$_2$], 648 (11) [652 − 2 H$_2$], 314 (7), 248 (8), 247 (48) [$C_{13}H_{11}OS^+$], 243 (9), 219 (9), 175 (15), 69 (13). − $C_{32}H_{24}N_4O_2S_5$ (656.9): calcd. C 58.51, H 3.68, N 8.53, S 24.41; found C 58.56, H 3.55, N 8.53, S 24.63.

2-Chloroacetyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene (25): 4,5,6,7-Tetrahydrobenzo[*b*]thiophene (**17**) (10.2 g, 73.7 mmol) and chloroacetyl chloride (8.32 g, 5.87 mL, 73.7 mmol) were dissolved in carbon disulfide (200 mL) and cooled to 0 °C. Aluminum trichloride (12.0 g, 90.4 mmol) was subsequently added and the resulting reaction mixture was allowed to warm to room temperature. The mixture was refluxed for 20 h, cooled, hydrolyzed, and dried (MgSO$_4$). After evaporation of the solvent, the remaining crude product was purified by recrystallization (EtOH/H$_2$O, 1:1) to yield **25** (14.0 g, 88%) as colorless flakes, m. p. 94 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3058 w, 2929 m, 2856 w, 1670 s, 1452 s, 1393 s, 1228 s, 1186 m, 1168 m, 862 m, 790 m, 717 m, 573 w cm^{-1}. − ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 7.46 (s, 1 H, H3), 4.50 (s, 2 H, C*H*$_2$Cl), 2.76−2.88 (m, 2 H, H7), 2.58−2.70 (m, 2 H, H4), 1.74−1.94 (m, 4 H, H5,6). − ^{13}C NMR (50 MHz, CDCl$_3$, 25 °C): δ = 183.8 (*C*O), 147.8 (C2), 137.20, 136.47 (C3a,7a), 134.0 (C3),

45.2 (CH_2Cl), 25.64 (C4), 25.22 (C7), 22.90 (C6), 22.34 (C5). − MS (EI) *m/z* (%): 216 (8), 215 (3), 214 (22) [M^+], 167 (5), 166 (11), 165 (100) [$M^+ - CH_2Cl$], 137 (6) [165 − CO], 91 (4), 77 (4), 65 (3). − $C_{10}H_{11}ClOS$ (214.7): calcd. C 55.94, H 5.16, S 14.93; found C 55.76, H 5.03, S 15.19.

2-Aminoacetyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene Hydrochloride (26): Chloroacetylthiophene (**25**) (4.29 g, 20.0 mmol), hexamethylenetetraamine (2.80 g, 20.0 mmol) and sodium iodide (3.00 g, 20.0 mmol) were suspended in ethanol (200 mL) and stirred for 70 h at room temperature. Concentrated hydrochloric acid (15 mL) was added and the mixture was heated at reflux for 3 h. The reaction mixture was allowed to cool to room temperature. During this process the major part of the side products precipitates and can be removed by filtration. Their quantitative removal is possible by repeating this procedure with a stepwise decreased amount of solvent. Neat **26** (3.05 g, 66%) can be obtained by recrystallization from a small amount of ethanol as an amorphous, pale yellow solid, m. p. 219−220 °C (decomp.). − FT-IR (KBr): $\tilde{\nu}$ = 3140 m, 3042 s, 2939 s, 2858 m, 1665 s, 1452 s, 1405 s, 1262 m, 1189 w, 906 w cm^{-1}. − ^1H NMR (200 MHz, [D$_6$]DMSO, 25 °C): δ = 8.55 (s, br, 3 H, NH_3Cl), 7.82 (s, 1 H, H3), 4.39 (s, 2 H, COCH_2), 2.74−2.86 (m, 2 H, H7), 2.54−2.66 (m, 2 H, H4), 1.65−1.85 (m, 4 H, H5,6). − ^{13}C NMR (50 MHz, [D$_6$]DMSO, 25 °C): δ = 185.3 (*C*O), 147.3 (C2), 137.6, 135.9 (C3,3a,7a), 44.1 (CO*C*H$_2$), 25.31 (C4), 25.07 (C7), 22.74 (C6), 22.15 (C5). − MS (EI); *m/z* (%): 195 (21) [base, M^+], 166 (13), 165 (100) [$M^+ - CH_2NH_2$], 137 (3) [165 − CO], 77 (3), 38 (10), 36 (32). − $C_{10}H_{14}ClNOS$ (231.8): calcd. C 51.83, H 6.09, N 6.04, S 13.84; found C 51.53, H 6.06, N 6.04, S 13.44.

***N*,*N*′-Bis[2-(4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-2-oxoethyl]thiophene-2,5-dicarboxamide (28):** Triethylamine (3.62 g, 4.99 mL, 35.8 mmol) and thiophene-2,5-dicarboxylic acid dichloride **27** (1.87 g, 8.97 mmol) in chloroform (75 mL) were successively added to an ice-cold solution of aminoacetylthiophene **26** (4.16 g, 17.9 mmol) in chloroform (75 mL). The resulting suspension was stirred for 1 h at 0 °C, allowed to warm up overnight, hydrolyzed, and filtered. The crude amide was washed with water dried, and recrystallized twice from EtOH yielding **28** (2.34 g, 49%) as an amorphous, colorless solid, m. p. 282−283 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3362 br, 3059 w, 2935 m, 2853 w, 1650 s, 1544 s, 1516 m, 1452 m, 1239 m, 1188 w, 1022 w, 976 w, 905 w, 737 w, 576 w cm^{-1}. − ^1H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 9.15 (t, $^3J_{CH_2,NH}$ = 5.6 Hz, 2 H, N*H*), 7.85 (s, 2 H, H3,4), 7.80 (s, 2 H, H3′), 4.60 (d, $^3J_{HCH_2,NH}$ = 5.6 Hz, 4 H, CH_2CO), 2.76 (t, $^3J_{H6',H7'}$ = 5.4 Hz, 4 H, H7′), 2.60 (t, $^3J_{H4',H5'}$ = 5.5 Hz, 4 H, H4′), 1.71−1.81 (m, 8 H, H5′,6′). − ^{13}C NMR (126 MHz, [D$_6$]DMSO, 25 °C): δ = 187.8 (*C*O), 161.2 (*C*O′), 145.8 (C2,5), 142.9 (C2′), 137.35, 137.18, 134.3, 129.0 (C3,3′,3a′,4,7a′), 45.9 (*C*H$_2$CO), 25.18 (C4′), 25.05 (C7′), 22.79 (C6′), 22.19 (C5′). − MS (EI); *m/z* (%): 527 (4), 526 (14) [M^+], 332 (6) [$M^+ - C_{10}H_{12}NOS$], 167 (5), 166 (12), 165 (100) [$C_9H_9OS^+$], 137 (4) [165 − CO], 111 (4). − $C_{26}H_{26}N_2O_4S_3$ (526.7): calcd. C 59.29, H 4.98, N 5.32, S 18.26; found C 59.02, H 4.97, N 5.32, S 18.05.

2,5-Bis[5-(4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-2-oxazolyl]-thiophene (3): A suspension of diamide **28** (705 mg, 1.34 mmol) in $POCl_3$ (150 mL) was heated at reflux for 15 h. 90% of the solvent was removed from the reaction mixture by distillation and the remaining orange residue was added dropwise to lukewarm water to hydrolyze the $POCl_3$. The crude product precipitates during this procedure and was isolated by filtration, washed with water, and dried. Chromatographic workup (aluminum oxide/dichloromethane) and subsequent sublimation yielded **3** (465 mg, 71%) as an amorphous, bright yellow powder, m. p. 223−224 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3069 w, 2935 s, 2839 w, 1602 s, 1544 s, 1441 m, 1348 m, 1123 w, 1034 w, 991 w, 905 m, 823 s, 717 s, 513 w cm^{-1}. − ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.64 (s, 2 H, H4′), 7.17 (s, 2 H, H3,4), 7.02 (s, 2 H, H3′′), 2.78 (t, $^3J_{H6'',H7''}$ = 5.9 Hz, 4 H, H7′′), 2.63 (t, $^3J_{H4'',H5''}$ = 5.9 Hz, 4 H, H4′′), 1.84−1.90 (m, 4 H, H6′′), 1.79−1.84 (m, 4 H, H5′′). − ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 155.6 (C2′), 147.3 (C5′), 137.17, 136.29, 131.6, 125.24 (C2,2′′,3a′′,5,7a′′), 127.8, 125.37, 122.5 (C3,3′′,4,4′), 25.46 (C4′′), 25.05 (C7′′), 23.38 (C6′′), 22.65 (C5′′). − MS (EI); *m/z* (%): 493 (4), 492 (18), 491 (31), 490 (100) [M^+], 462 (3) [$M^+ - C_2H_4$], 245 (8) [M^{2+}], 231 (9), 217 (8), 165 (11) [$C_9H_9OS^+$]. − $C_{26}H_{22}N_2O_2S_3$ (490.7): calcd. C 63.64, H 4.52, N 5.71, S 19.61; found C 63.63, H 4.54, N 5.67, S 19.70.

Acknowledgments

We would like to thank Dr. E. Mena-Osteritz for encouraging discussions and her aid concerning fluorescence spectroscopy.

[1] [1a] P. Bäuerle, *Oligothiophenes* in *Electronic Materials: The Oligomer Approach* (Eds.: G. Wegner, K. Müllen), Wiley-VCH, Weinheim, **1998**, pp. 105−197. − [1b] J. M. Tour, *Chem. Rev.* **1996**, *96*, 537−553. − [1c] J. Roncali, *Chem. Rev.* **1997**, *97*, 173−205. − [1d] D. Fichou, *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, Weinheim, **1999**.

[2] [2a] G. Horowitz, *Adv. Mater.* **1998**, *10*, 365−377. − [2b] W. Li, H. E. Katz, A. J. Lovinger, J. G. Laquindanum, *Chem. Mater.* **1999**, *11*, 458−465. − [2c] G. Horowitz, R. Hajlaoui, D. Fichou, A. El Kassmi, *J. Appl. Phys.* **1999**, *85*, 3202−3206. − [2d] F. Garnier, R. Hajlaoui, A. El Kassmi, G. Horowitz, L. Laigre, W. Porzio, M. Armanini, F. Provasoli, *Chem. Mater.* **1998**, *10*, 3334−3339. − [2e] C. D. Dimitrakopoulos, B. K. Furmann, T. Graham, S. Hegde, S. Purushothaman, *Synth. Met.* **1998**, *92*, 47−52. − [2f] G. Barbarella, P. Ostoja, P. Maccagnani, O. Pudova, L. Antolini, D. Casarini, A. Bongini, *Chem. Mater.* **1998**, *10*, 3683−3689.

[3] D. Fichou, J.-M. Nunzi, F. Charra, N. Pfeffer, *Adv. Mater.* **1994**, *6*, 64−67.

[4] [4a] F. Geiger, M. Stoldt, P. Bäuerle, H. Schweizer, E. Umbach, *Adv. Mater.* **1993**, *5*, 922−925. − [4b] M. G. Harrison, R. H. Friend, *Optical Applications* in *Electronic Materials: The Oligomer Approach* (Eds.: G. Wegner, K. Müllen), Wiley-VCH, Weinheim, **1998**, pp. 515−558. − [4c] K. Kawate, K.-I. Ohkura, M. Yamazaki, M. Kuroda, O. Nabeta, *Proc. SPIE Int. Soc. Opt. Eng.* **1994**, *2174*, 200−211. − [4d] Y. Kunugi, I. Tabakovic, A. Canavesi, L. L. Miller, *Synth. Met.* **1997**, *89*, 227−229. − [4e] T. Noda, H. Ogawa, N. Noma, Y. Shirota, *Adv. Mater.* **1997**, *9*, 720−722.

[5] [5a] G. Zotti, M. C. Gallazzi, G. Zerbi, S. V. Meille, *Synth. Met.* **1995**, *73*, 217−225. − [5b] L. L. Miller, Y. Yu, *J. Org. Chem.* **1995**, *60*, 6813−6819. − [5c] P. Bäuerle, G. Götz, A. Synowczyk, J. Heinze, *Liebigs Ann.* **1996**, 279−284. − [5d] G. Barbarella, M. Zambianchi, R. DiToro, M. Colonna, L. Antolini, M. Bongini, *Adv. Mater.* **1996**, *8*, 327−331. − [5e] A. Smie, A. Synowczyk, J. Heinze, R. Alle, P. Tschuncky, G. Götz, P. Bäuerle, *J. Electroanal. Chem.* **1998**, *452*, 87−95. − [5f] P. Hapiot, F. Demanze, A. Yassar, F. Garnier, *J. Phys. Chem.* **1996**, *100*, 8397−8401. − [5g] F. Demanze, J. Cornil, F. Garnier, G. Horowitz, P. Valat, A. Yassar, R. Lazzaroni, J.-L. Brédas, *J. Phys. Chem. B* **1997**, *101*, 4553−4558.

[6] [6a] J. Roncali, M. Giffard, P. Frère, M. Jubault, A. Gorgues, *J. Chem. Soc., Chem. Commun.* **1993**, 689−691. − [6b] F. Effenberger, F. Würthner, *Angew. Chem.* **1993**, *105*, 742−744; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 719−721. − [6c] F. Würthner, M. S. Vollmer, F. Effenberger, P. Emele, D. U. Meyer, H. Port, H. C. Wolf, *J. Am. Chem. Soc.* **1995**, *117*, 8090−8099. − [6d] H. Higuchi, Y. Uraki, H. Yokota, H. Koyama, J. Ojima, T. Wada, H. Sasabe, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 483−495. − [6e] J. Lewis, N. J. Long, P. R. Raithby, G. P. Shields, W.-Y. Wong, M. Younus, *J. Chem. Soc., Dalton Trans.* **1997**, 4283−4288. − [6f] T. Olinga, S. Destri, W. Porzio, A. Selva, *Macromol. Chem.*

Phys. **1997**, *198*, 1091−1107. − [6g] Y. Wie, Y. Yang, J.-M. Yeh, *Chem. Mater.* **1996**, *8*, 2659−2666.
[7] [7a] D. D. Graf, N. C. Day, K. R. Mann, *Inorg. Chem.* **1995**, *34*, 1562−1575. − [7b] D. D. Graf, K. R. Mann, *Inorg. Chem.* **1997**, *36*, 141−149. − [7c] D. D. Graf, K. R. Mann, *Inorg. Chem.* **1997**, *36*, 150−157. − [7d] M.-G. Choi, D.-J. Jeong, M. Lee, *Mol. Cryst. Liq. Cryst.* **1997**, *295*, 121−124. − [7e] D. H. Kim, B. S. Kang, S. M. Lim, K.-M. Bark, B. G. Kim, M. Shiro, Y.-B. Shimand, S. C. Shin, *J. Chem. Soc., Dalton Trans.* **1998**, 1893−1898. − [7f] G. Grüner, T. Debaerdemaeker, P. Bäuerle, *Chem. Commun.*, **1999**, 1097−1098.
[8] [8a] T. Sato, H. Ino, M. Fujitsuka, K. Tanaka, *Tetrahedron Lett.* **1997**, *38*, 6039−6042. − [8b] Y. Hong, L. L. Miller, D. D. Graf, K. R. Mann, B. Zinger, *Synth. Met.* **1996**, *82*, 189−191. − [8c] Y. Kunugi, L. L. Miller, T. Maki, A. Canavesi, *Chem. Mater.* **1997**, *9*, 1061−1062. − [8d] A. Donat-Bouillud, L. Mazerolle, M. Leclerc, *Synth. Met.* **1997**, *84*, 235−236. − [8e] A. Donat-Bouillud, L. Mazerolle, P. Gagnon, L. Goldenberg, M. C. Petty, M. Leclerc, *Chem. Mater.* **1997**, *9*, 2815−2821. − [8f] T. S. Novikova, N. N. Barashkov, A. Yassar, M. Hmyene, J. P. Ferraris, *Synth. Met.* **1997**, *84*, 247−248.
[9] [9a] U. Mitschke, E. Mena Osteritz, T. Debaerdemaeker, M. Sokolowski, P. Bäuerle, *Chem. Eur. J.* **1998**, *4*, 2211−2224. − [9b] P. Bäuerle, U. Mitschke, E. Mena-Osteritz, M. Sokolwski, D. Müller, M. Groß, K. Meerholz, *Proc. SPIE Int. Soc. Opt. Eng.* **1998**, *3476*, 32−39.
[10] [10a] H. Zimmer, R. Shabana, A. Galal, H. B. Mark, Jr., S. Gronowitz, A.-B. Hörnfeldt, *Phosphorus Sulfur Silicon* **1989**, *42*, 171−176. − [10b] L.-H. Chen, C.-Y. Wang, T.-M. H. Luo, *Heterocycles* **1994**, *38*, 1393−1398. − [10c] J. P. Parakka, M. P. Cava, *Synth. Met.* **1995**, *68*, 275−279. − [10d] M. V. Joshi, C. Hemler, M. P. Cava, J. L. Cain, M. G. Bakker, A. J. McKinley, R. M. Metzger, *J. Chem. Soc., Perkin Trans. 2* **1993**, 1081−1086. − [10e] A. Hucke, M. P. Cava, *J. Org. Chem.* **1998**, *63*, 7413−7417.
[11] [11a] H. Wynberg, J. Metselaar, *Synth. Commun.* **1984**, *14*, 1−9. − [11b] R. E. Nizurski-Mann, M. P. Cava, *Adv. Mater.* **1993**, *5*, 547−551. − [11c] J. P. Parakka, J. A. Jeevarajan, A. S. Jeevarajan, L. D. Kispert, M. P. Cava, *Adv. Mater.* **1996**, *8*, 54−59. − [11d] M. Kozaki, J. P. Parakka, M. P. Cava, *J. Org. Chem.* **1996**, *61*, 3657−3661. − [11e] U. Geissler, M. L. Hallensleben, N. Rohde, *Synth. Met.* **1997**, *84*, 173−174. − [11f] M. Kozaki, J. P. Parakka, M. P. Cava, *Tetrahedron Lett.* **1995**, *36*, 6835−6838. − [11g] L. Groenendaal, H. W. I. Peerlings, E. E. Havinga, J. A. J. M. Vekemans, E. W. Meijer, *Synth. Met.* **1995**, *69*, 467−470.
[12] [12a] A. Dondoni, M. Fogagnolo, A. Medici, E. Negrini, *Synthesis* **1987**, 185−186. − [12b] M. O. Wolf, M. S. Wrighton, *Chem. Mater.* **1994**, *6*, 1526−1533. − [12c] S. Gronowitz, D. Peters, *Heterocycles* **1990**, *30*, 645−658.
[13] [13a] Patent, CIBA Ltd. GB 900815, **1960**; *Chem. Abstr.* **1964**, *60*, 4287b−4289a. − [13b] Patent, CIBA Ltd. CH 411906, **1966**; *Chem. Abstr.* **1966**, *67*, 64406c.
[14] [14a] G. Kossmehl, G. Manecke, *Makromol. Chem.* **1969**, *123*, 233−244. − [14b] F. Newton Hayes, B. S. Rogers, D. G. Ott, *J. Am. Chem. Soc.* **1955**, *77*, 1850−1852.
[15] [15a] L. D. Patsenker, L. Sh. Afanasiadi, V. M. Shershukov, *Chem. Heterocycl. Compd.* **1991**, *27*, 642−645. − [15b] A. E. Obukhov, L. Sh. Afanasiadi, L. D. Patsenker, V. M. Shershukov, *Chem. Heterocycl. Compd.* **1989**, *25*, 1185−1189.
[16] [16a] G. Barbarella, O. Pudova, C. Arbizzani, M. Mastragostino, A. Bongini, *J. Org. Chem.* **1998**, *63*, 1742−1745. − [16b] G. Barbarella, L. Favaretto, M. Zambianchi, O. Pudova, C. Arbizzani, A. Bongini, M. Mastragostino, *Adv. Mater.* **1998**, *10*, 551−554. − [16c] G. Barbarella, L. Favaretto, G. Sotgiu, M. Zambianchi, L. Antolini, O. Pudova, A. Bongini, *J. Org. Chem.* **1998**, *63*, 5497−5506. − [16d] C. Arbizzani, G. Barbarella, A. Bongini, L. Favaretto, M. Mastragostino, P. Ostoja, O. Pudova, M. Zambianchi, *Opt. Mater.* **1998**, *9*, 43−45.
[17] [17a] K. Takahashi, T. Suzuki, *J. Am. Chem. Soc.* **1989**, *111*, 5483−5485. − [17b] K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami, Y. Fukazawa, *J. Am. Chem. Soc.* **1991**, *113*, 4576−4583.
[18] K. H. Chmil, D. M. de Leeuw, M. M. J. Simenon, A. J. W. Tol, *Synth. Met.* **1997**, *84*, 387−388.
[19] [19a] K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, S. Yamaguchi, *J. Am. Chem. Soc.* **1996**, *118*, 11974−11975. − [19b] S. Yamaguchi, K. Tamao, *J. Chem. Soc., Dalton Trans.* **1998**, 3693−3702. − [19c] K. Tamao, S. Yamaguchi, Y. Ito, *J. Chem. Soc., Chem. Commun.* **1994**, 229−230.
[20] S. Gronowitz, D. Peters, *Heterocycles* **1990**, *30*, 645−658.
[21] P. Cagniant, D. Cagniant, *Bull. Soc. Chim. Fr.* **1955**, 1252−1257.
[22] P. Cagniant, D. Cagniant, *Bull. Soc. Chim. Fr.* **1953**, 62−69.
[23] J. Reubke, *1,3,4-Thiadiazole, 1,3,4-Thiadiazolium-Verbindungen* in *Houben-Weyl: Methoden der Organischen Chemie, Band E 8 d, Hetarene III/Teil 4* (Ed.: E. Schaumann), Thieme, Stuttgart, New York, **1994**, pp. 189−304.
[24] L. I. Belen′kii, M. A. Cheskis, V. P. Zvolinskii, A. E. Obukhov, *Chem. Heterocycl. Compd.* **1986**, *22*, 654−663.
[25] [25a] W. J. Feast, J. Tsibouklis, K. L. Pouwer, L. Groenendaal, E. W. Meijer, *Polymer* **1996**, *37*, 5017−5047. − [25b] H. S. Nalwa, *Handbook of Organic Conducting Molecules and Polymers, Volume 2, Conductive Polymers: Synthesis and Electrical Properties*, Wiley, Chichester, **1997**.
[26] [26a] J. Salbeck, F. Weissörtel, J. Bauer, *Macromol. Symp.* **1997**, *125*, 121−132. − [26b] K.-H. Weinfurtner, F. Weissörtel, G. Harmgarth, J. Salbeck, *Proc. SPIE Int. Soc. Opt. Eng.* **1998**, *3476*, 40−48. − [26c] J. Salbeck, N. Yu, J. Bauer, F. Weissörtel, H. Bestgen, *Synth. Met.* **1997**, *91*, 209−215. − [26d] M. Thelakkat, H.-W. Schmidt, *Polym. Adv. Technol.* **1998**, *9*, 429−442. − [26e] R. Wu, J. S. Schumm, D. L. Pearson, J. M. Tour, *J. Org. Chem.* **1996**, *61*, 6906−6921.
[27] [27a] C. Ehrendörfer, H. Neugebauer, A. Neckel, P. Bäuerle, *Synth. Met.* **1993**, *55*, 493−498. − [27b] C. Ehrendörfer, A. Karpfen, P. Bäuerle, H. Neugebauer, A. Neckel, *J. Mol. Struct.* **1993**, *298*, 65−86.
[28] C. A. Parker, W. T. Rees, *Analyst (London)* **1960**, *85*, 587−599.
[29] H. G. O. Becker, H. Böttcher, F. Dietz, A. V. El′cov, D. Rehorek, G. Roewer, K. Schiller, O. P. Studzinskij, H.-J. Timpe, *Einführung in die Photochemie*, 2nd ed., Thieme, Stuttgart, New York, **1983**.
[30] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991−1024.
[31] Fluorescence quantum yields of oligoheterocycles **6**−**11** in ref.[9] originate from uncorrected fluorescence spectra. The corrected values (external standard: 9,10-diphenylanthracene), which are directly comparable to oligoheterocycles **1**−**5** reported in this study, were determined as: Φ_{295K}^{em} (±5%) corr. (uncorr.): **6**: 40 (19)%, **7**: 26 (12)%, **8**: 39 (20)%, **9**: 65 (32)%, **10**: 59 (30)%, **11**: 85 (62)%.
[32] [32a] B. M. Krasovitskii, B. M. Bolotin, *Organic Luminescent Materials*, Wiley-VCH, Weinheim, **1988**. − [32b] A. Hetzheim, *1,3,4-Oxadiazole*, in *Houben-Weyl: Methoden der Organischen Chemie, Band E 8 c, Hetarene III/Teil 3* (Ed.: E. Schaumann), Thieme, Stuttgart, New York, **1994**, pp. 526−647.
[33] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem.* **1998**, *110*, 416−443; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 402−428.
[34] R. N. Adams, *Electrochemistry at Solid Electrodes*, Marcel Dekker, New York, **1969**, p. 146.
[35] [35a] S. Janietz, B. Schulz, *Eur. Polym. J.* **1996**, *32*, 465−474. − [35b] B. Schulz, M. Bruma, L. Brehmer, *Adv. Mater.* **1997**, *9*, 601−613. − [35c] A. Freydank, S. Janietz, B. Schulz, *J. Electroanal. Chem.* **1998**, *456*, 61−69. − [35d] W.-L- Yu, H. Meng, J. Pei, W. Huang, *J. Am. Chem. Soc.* **1998**, *120*, 11808−11809. − [35e] W. Huang, W.-L. Yu, H. Meng, J. Pei, S. F. Y. Li, *Chem. Mater.* **1998**, *10*, 3340−3345.
[36] [36a] H. Muguruma, K. Kobiro, S. Hotta, *Chem. Mater.* **1998**, *10*, 1459−1467. − [36b] S. Wang, F. Brisse, F. Bélanger-Gariépy, A. Donat-Bouillud, M. Leclerc, *Acta Crystallogr.* **1998**, *C54*, 533−555. − [36c] G. Barbarella, M. Zambianchi, A. Bongini, L. Antolini, *Adv. Mater.* **1993**, *5*, 834−838. − [36d] J.-H. Liao, M. Benz, E. LeGoff, M. G. Kanatzidis, *Adv. Mater.* **1994**, *6*, 135−138. − [36e] J. K. Herrema, J. Wildeman, F. van Bolhuis, G. Hadziioannou, *Synth. Met.* **1993**, *60*, 239−248.
[37] T. M. Barclay, A. W. Cordes, C. D. MacKinnon, R. T. Oakley, R. W. Reed, *Chem. Mater.* **1997**, *9*, 981−990.
[38] T. Debaerdemaeker, *Z. Kristallogr.* **1993**, *206*, 173−182.
[39] G. M. Sheldrick, *SHELXL-93*, University of Göttingen, **1993**.

Received July 2, 1999
[O99395]