The chemistry of oligopyrroles : design, synthesis and characterization of well-defined and fuctional alpha,alpha-linked oligomers

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L. Groenendaal

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PROEFSCHRIFT

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Aan mijn ouders.

Voor Bianca.

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Chapter 1

INTRODUCTION

1.1 *Pyrrole...oligopyrroles...polypyrrole*

For decades scientists have been attempting to design new molecules with functional properties in the quest for new materials. One class of compounds that created an enormous interest during this period are π-conjugated polymers. Due to the substantial π-electron delocalization along their backbones, these polymers show appealing (nonlinear) optical properties and become good electronic conductors when oxidized or reduced. Hence, a prominent and active role is foreseen for these compounds in a variety of practical applications such as information storage, optical signal processing, electromagnetic interference (EMI) shielding and solar energy conversion, as well as rechargeable batteries, light emitting diodes (LED's), field effect transistors (FET's), printed circuit boards (PCB's) and antistatic materials.

Despite the overwhelming effort that has been put in the development of these polymers, only very few compounds are actively being applied in devices at this moment; the vast majority still remain 'materials of the future'. The main reason for this lack of application is the fact that the performance of π-conjugated polymers is still not optimal. This delay is related to the low stability under atmospheric conditions, the lack of processability and/or the undefined structure of the existing polymers.

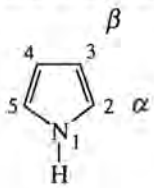
Polypyrrole is one of the numerous π-conjugated polymers that has been studied in this field. In contrast to most other polymers, it is extremely stable in its oxidized form; the latter makes it very interesting for applications as a conducting polymer. However, as a result of the synthetic strategies applied, its structure contains many defects that reduce the effective conjugation length and, therefore, diminish its useful properties. The preparation of a well-defined α,α-linked polypyrrole that can be used in several of the aforementioned applications, necessitates the development of a more controlled polymerization route. Therefore, several organometallic aryl-aryl coupling reactions have been investigated. However, instead of applying these coupling reactions for the synthesis of perfectly α,α-linked polypyrrole, we decided to study the synthesis of well-defined α,α-linked *oligo*pyrroles first. Well-defined oligomers can be used to obtain a detailed insight into the behavior of their corresponding polymeric analogs, while the synthetic methodology can be applied to prepare structurally perfect and directly applicable polymers.

Although our strategy "from pyrrole *via* oligopyrroles toward polypyrrole" seems quite straightforward, a number of problems are expected to cross our road. First of all, only little is known about the chemistry of oligopyrroles, especially if one compares the latter with the knowledge on the closely related oligothiophenes. This lack of knowledge is mainly due to the unilateral research that has been carried out on pyrrole derivatives in the past. Since pyrrole occupies an important position in many naturally occurring compounds such as vitamin B_{12}, prodigiosin, pigments and porphyrins, most of the research effort has been devoted to the synthesis of these systems and not to models for π-conjugated systems. Secondly, the notorious air-sensitivity of neutral oligopyrroles makes the handling of these systems extremely difficult. This urge to oxidize is observed in the few oligopyrrole systems that have been prepared up to now, and originates from the high electron-density on these systems due to accumulation of electron-rich pyrrole units.

In this thesis several synthetic strategies toward well-defined and functional oligopyrroles have been developed. The resulting oligomers were subsequently subjected to extensive characterization. Therefore, several techniques have been applied to obtain a detailed insight into their physical characteristics and structure-property relationships. Furthermore, a number of functional oligomers has been studied for their potential role in materials science. Therefore, these studies might be considered as the first steps toward future applications of pyrrole derivatives, being the development of *The Chemistry of Oligopyrroles*.

1.2 *Pyrrole: A historical overview*[1,2]

In May 1834 Friedlieb Ferdinand Runge[3], at that time working as a chemist at the Chemische Produktenfabrik in Oranienburg, discovered that coal tar contains several interesting compounds. One of these gave a beautiful bright red color on contact with hydrochloric acid. He called it *pyrrole* after the Greek word for 'fiery red oil'.[4] However, despite many attempts, Runge was not able to separate pyrrole from other products.

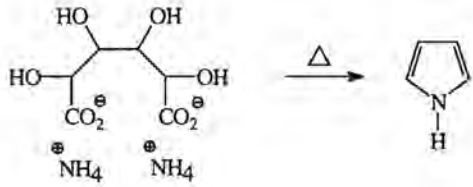


Pyrrole

In 1857 Thomas Anderson, Professor of Chemistry at Glasgow, was able to isolate pyrrole. Starting with 250 gallons of ivory oil weighing over a ton, he was finally able to transform pyrrole into its potassium salt.[5] Subsequent hydrolysis and distillation gave pure pyrrole as a colorless liquid with a boiling point of about 133°C, and an odor resembling that

of chloroform. Combustion analysis gave C_8H_5N, and considering that he used 6, instead of 12, as the atomic weight of carbon, this gives the modern formula C_4H_5N. However, it took another decade before the structure of pyrrole was resolved; in 1870 Baeyer and Emmerling suggested the correct structure while investigating indole.[6]

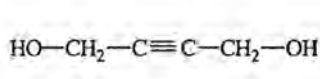
For a long time pyrrole was prepared by thermal decomposition of ammonium mucate **1** (scheme 1.1).[7,8]



1

Scheme 1.1: *Synthesis of pyrrole by thermal decomposition of ammonium mucate.*[7,8]

In 1941 Walter Reppe of I.G. Farbenindustrie discovered that pyrrole can also be prepared from 1,4-butyndiol (**2**) by passing an aqueous solution of this diol, saturated with ammonia, over a 5% thoria/alumina bed at 260-340°C.[9,10] In 1953 Charles Bordner of du Pont patented a method in which furan (**3**), ammonia and a large excess of steam are passed through an iron pipe with an alumina catalyst at 480-490°C.[11] In this way, allowing for the recovery of furan, the conversion went up to 63% of pyrrole. Nowadays, several other routes are known.[12]



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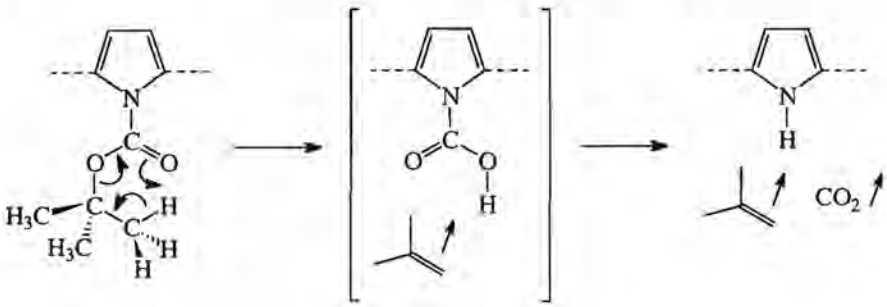
3

1.3 *Protecting groups at nitrogen*

The pyrrole unit contains three different hydrogen atoms from which the one at nitrogen is the most acidic ($pK_a = 17.5$)[13]. In order to functionalize pyrrole at the 2- and/or 3-position, protection at nitrogen is a prerequisite. In this study several protecting groups have been investigated, but the *tert*-butoxycarbonyl (*t*-BOC) group[14,15] appeared to be most suitable for a number of reasons:

1) Its *electron-withdrawing* character; this stabilizes the electron-rich pyrrole unit and increases the oxidation potential sufficiently to confer air stability.

2) Its *solubilizing* character; the *tert*-butyl moiety increases the solubility, which is an important property in the preparation of oligomeric and polymeric systems.
3) Its *facile removal*; from peptide chemistry it is well-known that the *t*-BOC group can be removed under acidic conditions.[16] However, earlier work performed on pyrrole shows that the *t*-BOC group can also easily be removed by thermolysis (T ≥ 190°C), without the requirement of any acid, base, or solvent.[17] During this process carbon dioxide, isobutene and the unprotected pyrrole derivative are formed *via* a concerted mechanism as is shown in scheme 1.2.
4) Its *stability toward carbanions*; in order to functionalize a pyrrole unit at the α-position, the formation of a carbanion is often required. The presence of a *t*-BOC group is compatible with the use of carbanions, and directs electrophilic substitution to the α-position.

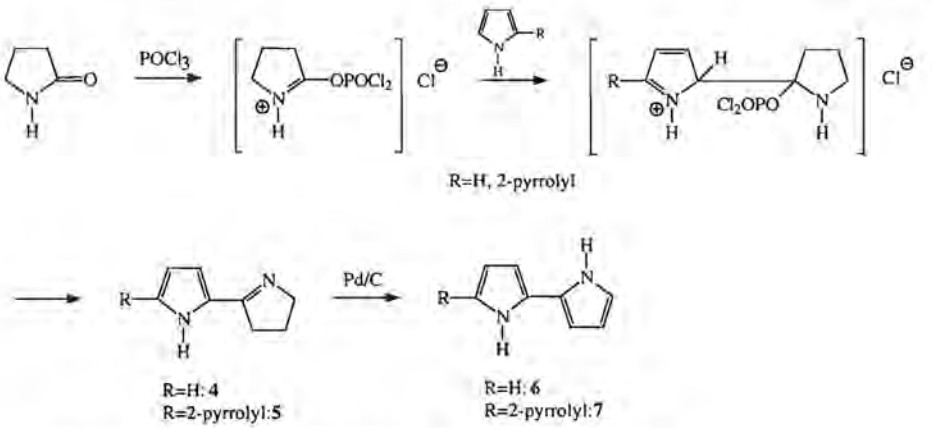


Scheme 1.2: *Thermal deprotection of the t-BOC group via a concerted mechanism.*

1.4 *Well-defined oligopyrroles*

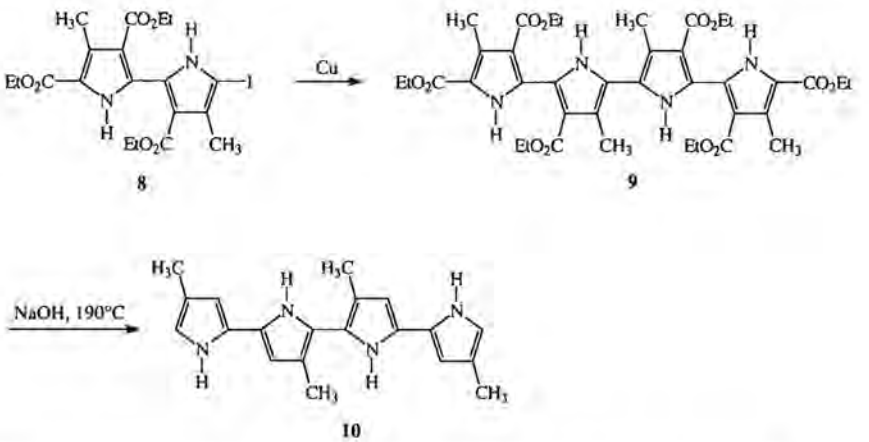
Oligopyrroles, as reported up to now, can be divided into two groups: N-unsubstituted and N-substituted oligomers. In this section an overview is given of the different coupling methods available to prepare both types of oligomers.

The number of papers dealing with N-unsubstituted oligopyrroles is limited. The first reports date from the beginning of the 1960's when Rapoport *et al.* reported on the synthesis of 2,2′-bipyrrole and 2,2′:5′,2″-terpyrrole, being interesting intermediates in the synthesis of vitamin B_{12}, pigments and prodigiosin.[18-22] Starting from pyrrole, phosphorus oxychloride and 2-pyrrolidinone, and performing a Vilsmeier condensation and subsequent dehydrogenation of the intermediate 2,2′-(1′-pyrrolinyl)pyrrole (**4**), 2,2′-bipyrrole (**6**) could be obtained as a white solid. Repetition of this sequence with **6** as starting material, yielded 2,2′:5′,2″-terpyrrole (**7**) (scheme 1.3).



Scheme 1.3: *Synthesis of 2,2'-bipyrrole and 2,2':5',2''-terpyrrole.*[18-22]

The air-sensitivity of N-unsubstituted oligopyrroles is already evident from **6** and **7**; these white compounds easily turn into brown materials upon exposure to air. Therefore, this approach is not appropriate to prepare larger systems. N-Unsubstituted oligomers that are substituted at the α- and/or β-positions with electron-withdrawing groups, exhibit a much higher stability. In porphyrin chemistry this strategy has often been used to prepare substituted bipyrrole units from α-monoiodo ester substituted pyrrole derivatives by performing an Ullmann reaction with copper bronze in DMF.[23-26] Also worth mentioning in this respect is the preparation of an α-linked quaterpyrrole by Sessler *et al.* (scheme 1.4).[26]

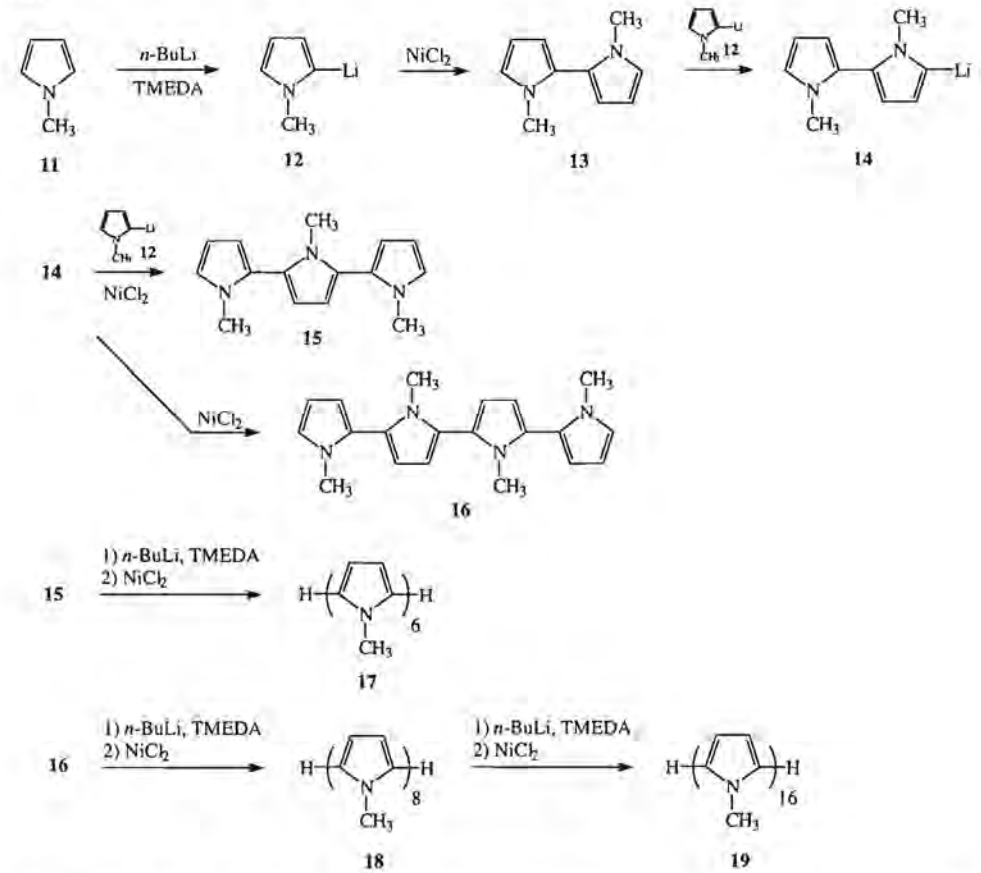


Scheme 1.4: *Synthesis of an α,α-linked quaterpyrrole by the Ullmann reaction.*[26]

Starting material α-monoiodo-2,2'-bipyrrole **8** was coupled to furnish the hexaester-substituted quaterpyrrole **9**, which appeared to be remarkably stable under normal conditions.

Subsequent removal of the stabilizing ester groups in a saponification-decarboxylation step (NaOH in ethylene glycol at 190°C), however, yielded product **10**, which decomposed within a few hours. Hence, in order to prepare longer oligomers without substitution at the α- or β-positions, it is a prerequisite to protect the pyrrole unit at nitrogen with an electron-withdrawing group.

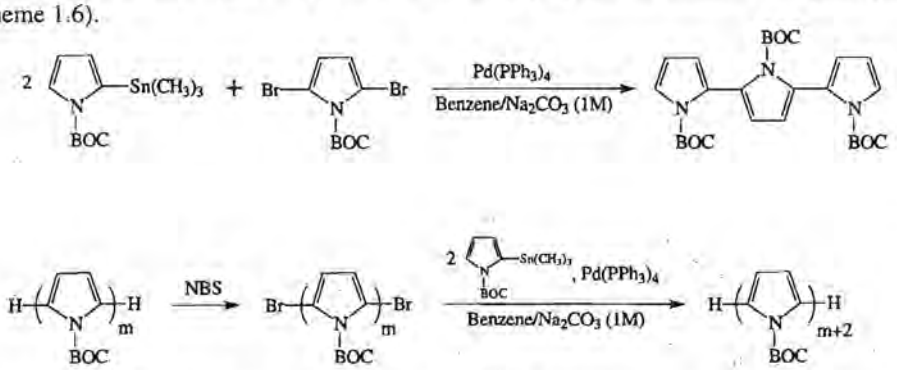
The first examples of N-substituted oligopyrroles are the oligo(N-methylpyrrole-2,5-diyl)s prepared by Kauffmann *et al.* in 1981.[27] Starting from N-methylpyrrole and performing a repetitive sequence of α-lithiation (*n*-BuLi, TMEDA) and oxidative coupling ($NiCl_2$), they were able to synthesize oligomers containing up to sixteen repeating pyrrole units (scheme 1.5).



Scheme 1.5: *Oligo(N-methylpyrrole-2,5-diyl)s by a lithiation/oxidative coupling sequence.*[27]

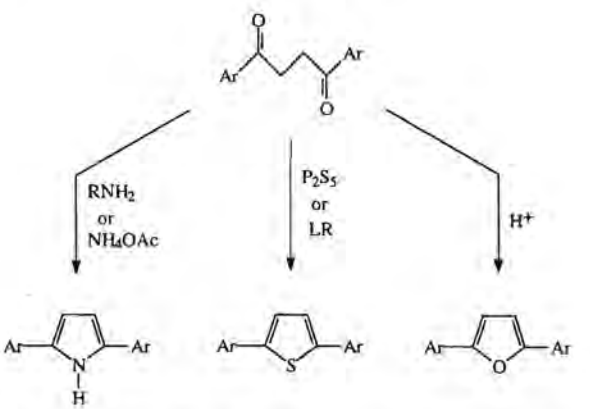
Although these oligomers represent the first series of oligopyrroles ever prepared, they are not useful as models for polypyrrole or as conducting materials since the methyl groups are detrimental for properties such as conductivity[28], and cannot be removed.

Therefore, the thermally labile *tert*-butoxycarbonyl (*t*-BOC) group was introduced into oligopyrrole chemistry as is demonstrated in the pioneering work of Martina, Schlüter and Wegner.[29-39] They investigated both the Pd-catalyzed Suzuki[40] and Stille[41] reaction. Although the results of the Suzuki coupling were not very promising[29-32], they were able to develop a good method based on the Stille reaction[29,30,34]. By performing a reaction between an α,α-dibrominated oligopyrrole and two equivalents of N-*t*-BOC-2-trimethylstannylpyrrole in a two-phase system of benzene and aqueous Na_2CO_3 (1 M), catalyzed by $Pd(PPh_3)_4$, oligomers containing up to nine repeating pyrrole units were prepared in moderate to good yields (scheme 1.6).



Scheme 1.6: *N-t-BOC protected oligo(pyrrole-2,5-diyl)s by the Stille reaction (m = 1, 3, 5, 7).*[29,30,34]

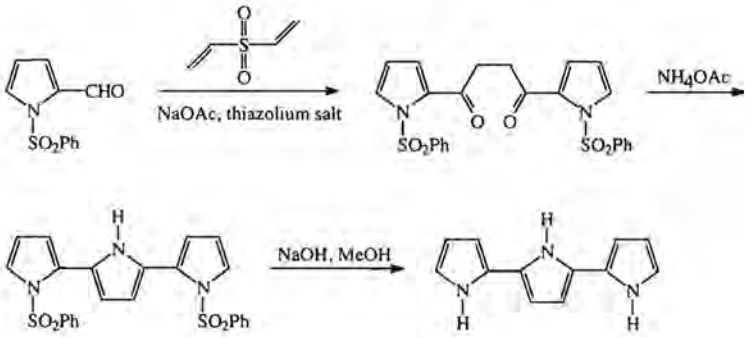
These N-*t*-BOC protected oligopyrroles could also be transformed into the parent N-unsubstituted derivatives by thermolysis at 190°C, resulting in oxidation sensitive species, which had to be handled under inert conditions.



Scheme 1.7: *Synthesis of oligomers by the ring closure of 1,4-diketones.*[42-50]

Another route to oligopyrroles makes use of a totally different strategy, namely the ring closure of 1,4-diketones (scheme 1.7).[42-44] This method is of special interest since it allows for the synthesis of oligomers with mixed configurations. Cyclization of 1,4-diketones with ammonia[45], ammonium salts[46,47] or primary amines[48] affords pyrroles, while treatment with P_2S_5[45-47] or Lawesson's reagent (LR)[49,50] gives thiophenes and acid catalyzed dehydration leads to furans.[45]

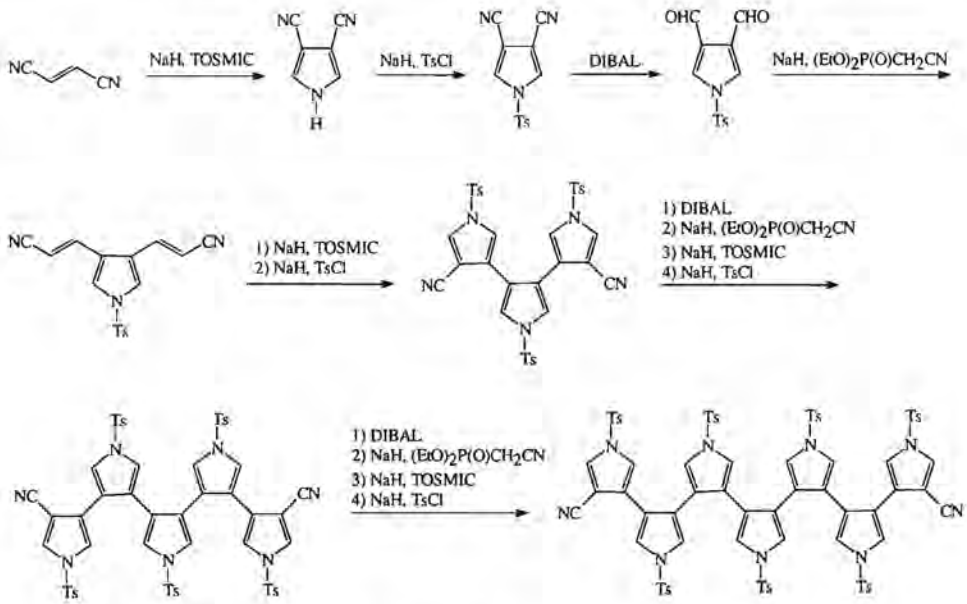
A number of oligopyrrole systems, both homo and mixed, have been prepared in this way.[49,51-57] An illustrative example is the synthesis of 2,2':5',2''-terpyrrole (scheme 1.8).[57] In the first step N-phenylsulfonyl-2-formylpyrrole is transformed into a 1,4-diketone by a so-called Stetter[42-44] reaction using divinyl sulfone and NaOAc in the presence of a thiazolium salt. In the next step this diketone is cyclized with NH_4OAc to afford the terpyrrole skeleton. Final removal of the protecting groups under basic conditions yields 2,2':5',2''-terpyrrole.



Scheme 1.8: *Synthesis of 2,2':5',2''-terpyrrole via a ring closure reaction.*[57]

Another interesting contribution is the synthesis of a series of β,β-linked oligopyrroles.[58] Although these oligomers are not of interest as models for conducting polypyrrole, the elegant synthetic approach makes them worth mentioning. Starting from fumaronitrile and performing a repetitive sequence of TOSMIC (tosylmethyl isocyanide) treatment, N-tosylation and a Wittig-Horner reaction, results in oligomers up to the heptamer (scheme 1.9).

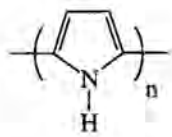
A final example of N-substituted oligopyrroles is the oxidative dimerization of N-aroylpyrroles with $Pd(OAc)_2$ published by Itahara *et al.*[59-61] However, in our hands, these results appeared to be irreproducible.



Scheme 1.9: *Synthesis of β,β-linked oligopyrroles.*[58]

1.5 *Polypyrrole*

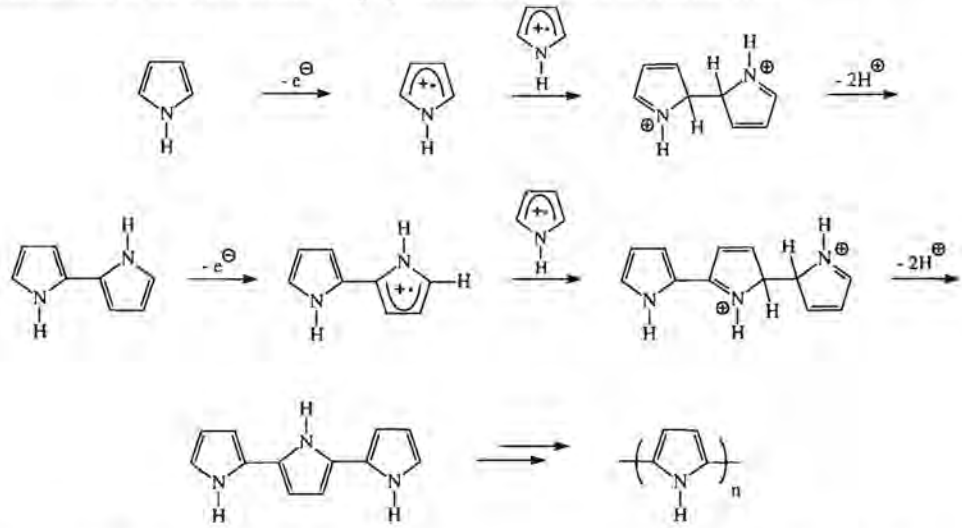
Polypyrrole is a well-known organic conductor with potential for industrial applications because of its high stability in the doped state, and its interesting physical, chemical and electrochemical properties.[28,62,63] Due to its extreme susceptibility to oxidation (-0.02 eV vs. saturated calomel electrode (SCE)), the neutral form of polypyrrole can only be prepared and characterized under inert conditions.



Polypyrrole

Oxidized polypyrrole can be prepared from pyrrole both by chemical and electrochemical polymerization.[64-67] In 1916 the first chemical synthesis of polypyrrole was reported by Angeli and Alessandri.[68] Using pyrrole and hydrogen peroxide in acetic acid, an insoluble brittle material was obtained, designated as pyrrole black. The first paper on the electrochemical preparation of polypyrrole, which included a description of the conducting properties of the product, was published in 1968.[69] The electrochemical oxidation of pyrrole in 0.1 N sulfuric acid yielded a black, brittle film with a conductivity of 8 Scm^{-1}. Improve-

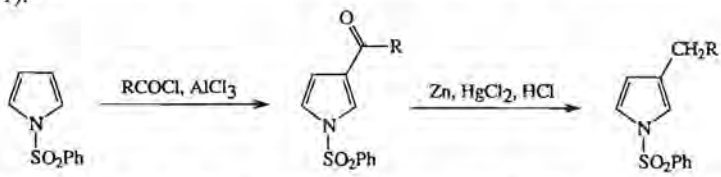
ments such as using organic solvents and different electrolytes have made the electrochemical method the most commonly employed polymerization technique. The proposed mechanism of the electrochemical polymerization is shown in scheme 1.10.[70]



Scheme 1.10: *Proposed mechanism of the electrochemical polymerization of pyrrole.*[70]

The electrochemical route to polypyrrole provides good quality films.[71] The counter ion has a considerable influence on the conductivity and the mechanical properties[72], while the stability of these films under ambient conditions is extremely good. The decrease in conductivity of commercially available polypyrrole films, exhibiting an initial conductivity of 15 Scm^{-1}, is less than 15% per year.[73]

Introduction of flexible side chains increases the processability of polypyrroles drastically.[74-77] Introduction of side chains at the β-positions is most frequently performed by a Friedel-Crafts acylation of N-protected pyrrole, followed by a Clemmensen reduction (scheme 1.11).[78-80]

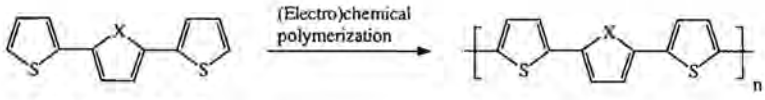


Scheme 1.11: *Synthesis of 3-alkylpyrroles via a Friedel-Crafts acylation/Clemmensen reduction sequence.*[78-80]

Polymers with substituents at nitrogen have also been prepared[81]; however, the conductivity of these polymers is low, due to steric interactions.[28]

The introduction of sulfonic acid groups in the alkyl side chain affords water-soluble self-doped polypyrroles.[82,83] When the sodium salt of a pyrrole-3-alkanesulfonic acid is used as a monomer, it also acts as an electrolyte for the electrochemical synthesis. Furthermore, Langmuir-Blodgett techniques have been applied to improve the ordering in polypyrrole films.[84,85]

Besides the homopolymerization of pyrrole (N-H, N-R), a variety of monomers consisting of mixtures of pyrrole, thiophene, benzene and/or furan units, have been copolymerized (electro)chemically.[86-92] An interesting contribution to this field comes from Ferraris *et al.*, who prepared copolymers and subsequently investigated them by cyclic voltammetry, spectroelectrochemistry, FT-IR and UV-Vis spectroscopy, and conductivity measurements (scheme 1.12).[89-92]



X = S, O, NH, N-alkyl

Scheme 1.12: *(Electro)chemical polymerization of mixed monomers.*[86-92]

Although both the electrochemical and the chemical route toward polypyrroles result in conducting polymers with interesting properties, these properties have most probably not yet reached their optimal values. Due to 'mislinkages' in the polymer backbone (figure 1.1; hydrogenated pyrrole units (a), α,β- (b) and β,β-couplings (c)), the effective conjugation length is limited.[93,94] In order to overcome this problem, organometallic coupling reactions have been developed. In the next section the most important contributions on this topic will be discussed.

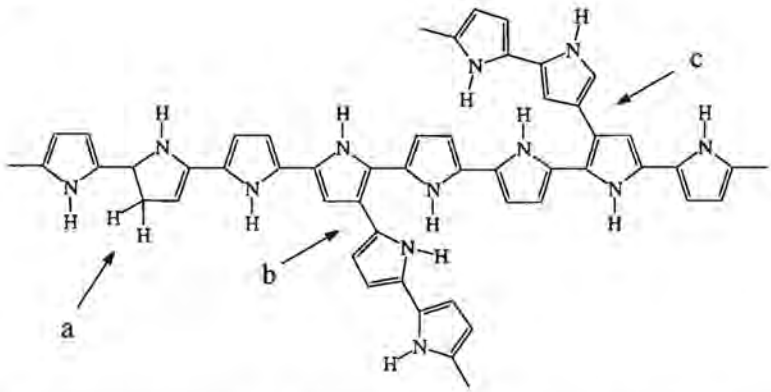


Figure 1.1: *Possible mislinkages in (electro)chemically prepared polypyrrole (hydrogenated pyrrole unit (a), α,β-coupling (b), β,β-coupling (c)).*

1.6 *Organometallic aryl-aryl coupling reactions*

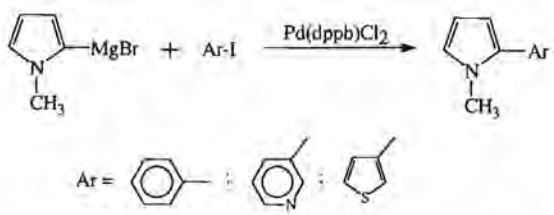
Over the past three decades a number of organometallic aryl-aryl coupling reactions has been developed.[95,96] Most of these reactions make use of catalysts consisting of Pd, Ni or Cu as the active metal, and a number of ligands. In this section we will discuss the Kumada, Suzuki, Negishi and Semmelhack/Yamamoto couplings, which had and still have a great impact on the synthesis of conducting polymers in general, and on that of (poly)pyrrole derivatives in particular. For details on the Pd-catalyzed cross coupling reaction involving organostannanes (Stille reaction) and the Ullmann reaction, the reader is referred to Chapter 2 and Chapter 6, respectively.

1.6.1 *Kumada coupling*

The Kumada coupling is a cross coupling reaction between a Grignard reagent (R-MgX) and an organohalide (R'-X).[97-101] The reaction is catalyzed by a group VIII metal (Ni, Pd), that forms a complex with a number of ligands (L). Well-known catalysts are $Ni(dppe)Cl_2$, $Ni(dppp)Cl_2$, $Pd(dppb)Cl_2$ and $Ni(acac)_2$ (dppe, dppp, dppb = 1,3-bis(diphenyl-phosphino)ethane, -propane, -butane; acac = acetylacetonate).

$$\text{R-MgX} + \text{R'-X} \xrightarrow{\text{cat.}} \text{R-R'} + \text{MgX}_2$$

A disadvantage of the Kumada coupling, whose mechanism is considered to proceed *via* a multistep catalytic cycle[102], is that it does not tolerate a wide variety of functional groups due to the reactivity of the Grignard reagent. Despite this, it has been applied to numerous cross couplings including benzene, pyridine, quinoline, thiophene, furan and pyrrole derivatives.[100-102] Two illustrative examples of Kumada couplings in which pyrroles are involved, are the $Pd(dppb)Cl_2$-catalyzed arylation of N-methyl-2-magnesiobromopyrrole with several aryl iodides (scheme 1.13)[103], and the $Ni(acac)_2$-catalyzed polymerization of N-methyl-2,5-dimagnesiobromopyrrole[104].



Scheme 1.13: *Synthesis of pyrrole derivatives by the Kumada coupling.*[103]

Another well-known application of the Kumada coupling is the Ni(dppp)Cl_2-catalyzed synthesis of regioregular poly(3-alkylthiophene)s developed by McCullough *et al.*, that will be discussed in Chapter 4.

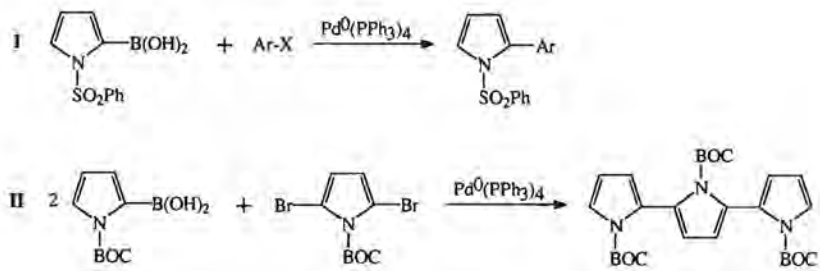
1.6.2 *Suzuki coupling*

The Suzuki coupling is a cross coupling reaction between an organoboron reagent (R-B(OR')$_2$; R' = H, alkyl)), and an unsaturated halide, triflate or sulfonate (R''-X).[105-109] In general it is catalyzed by tetrakis(triphenylphosphine)palladium(0) and performed in a two-phase system consisting of an organic solvent (benzene, toluene) and aqueous Na_2CO_3. Recently, also some examples of Ni-catalyzed Suzuki-type cross coupling reactions have become available.[109]

$$\text{R-B(OR')}_2 \;+\; \text{R''-X} \xrightarrow{\text{cat.}} \text{R-R''} \;+\; \text{X-B(OR')}_2$$

Despite the popularity of this condensation reaction, relatively little is known about the mechanistic details of the Suzuki coupling.[109,110] It is generally believed that this coupling reaction proceeds *via* a comparable multistep cyclic mechanism as depicted for the Stille coupling (Chapter 2). After activation of the Pd-catalyst, the rate-determining oxidative addition takes place, which is followed by the faster transmetallation and, finally, by a very rapid reductive elimination step. Furthermore, the presence of water and base is essential to activate the boronic acid, while LiCl is often used to prevent the catalyst from decomposing.

In literature there are numerous examples of Suzuki couplings. Besides the Pd-catalyzed (poly)condensation reactions of benzene derivatives[33,109,111-114], there are also a few examples of couplings in which pyrrole derivatives are involved (scheme 1.14). One such is the $Pd^0(PPh_3)_4$-catalyzed arylation of (N-phenylsulfonyl-2-pyrrolyl)boronic acid with Ar-X (**I**; Ar = phenyl, 1-naphthyl, 4-nitro- and 4-methoxyphenyl; X = Br, I)[115]; another describes the formation of N-*t*-BOC protected terpyrrole from (N-*t*-BOC-2-pyrrolyl)boronic acid and N-*t*-BOC-2,5-dibromopyrrole (**II**).[29,30]



Scheme 1.14: *Oligopyrroles by the Pd-catalyzed Suzuki coupling.*[29,30,115]

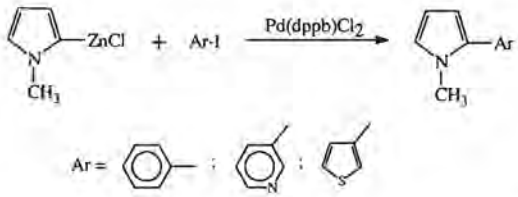
However, deboronification appears to be a major obstacle in Pd-catalyzed Suzuki couplings of N-*t*-BOC protected pyrrole derivatives, which makes this coupling reaction unattractive for polymerizations.

1.6.3 *Negishi coupling*

The Negishi coupling is a cross coupling reaction between an organozinc intermediate (R-ZnX) and an unsaturated halide (R'-X).[100,116-118] The reaction employs a Pd- or Ni-catalyst and is performed under mild conditions.

$$\text{R-ZnX} + \text{R'-X} \xrightarrow{\text{cat.}} \text{R-R'} + \text{ZnX}_2$$

In literature there are numerous examples of Negishi couplings. One worth mentioning is the regioregular synthesis of poly(3-alkylthiophene)s as developed by Rieke *et al.*[119,120]; using Ni(dppe)Cl_2 as catalyst, they were able to polymerize 2-bromo-5-(bromozincio)-3-hexylthiophene (for more details, the reader is referred to Chapter 4). The only example in which pyrrole derivatives are involved, is the Pd(dppb)Cl_2-catalyzed arylation of N-methyl-2-(chlorozincio)pyrrole with several aryl iodides (scheme 1.15).[103]



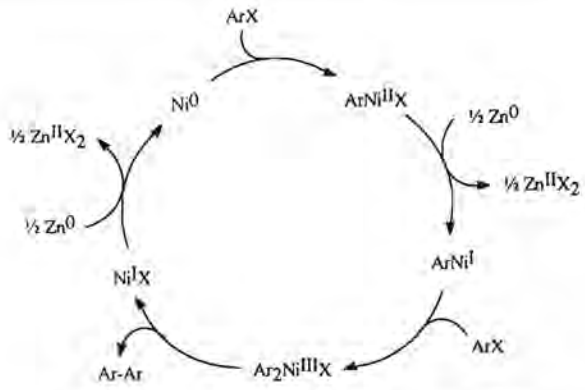
Scheme 1.15: *Synthesis of pyrrole derivatives by the Negishi coupling.*[103]

1.6.4 *Semmelhack/Yamamoto coupling*

The Semmelhack/Yamamoto coupling is a reductive homo-coupling of an arylhalide (R-X) using a Ni^0-complex. This coupling was initially studied by Semmelhack *et al.*[121-123], whereas Yamamoto *et al.*[123-125] applied it for various (hetero)aryl polymerization reactions. Well-known Ni^0-complexes are Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) and Ni(PPh$_3$)$_4$; the latter is prepared *in situ* from Ni(PPh$_3$)$_2$Cl$_2$, PPh$_3$ and Zn.

$$2\ \text{R-X} + \text{Ni}^0 \longrightarrow \text{R-R} + \text{NiX}_2$$

The Semmelhack/Yamamoto coupling is believed to proceed through a multistep cyclic mechanism including a zinc-mediated reduction of $ArNi^{II}X$ to $ArNi^{I}$, an oxidative addition of $ArNi^{I}$ to the arylhalide and a reductive elimination (scheme 1.16).[126-128]



Scheme 1.16: *Mechanism of the organozinc-mediated Semmelhack/Yamamoto coupling.*[126-128]

It has been applied for various aryl derivatives. Well-known are the studies on monofunctional benzene, pyridine and quinoline derivatives; additionally, polymers such as polyphenylenes, polythiophenes, polyfurans and polypyridines have been prepared in this way.[125,126,129,130] Concerning pyrrole derivatives, the only examples known are Yamamoto's polymerization of N-methyl-2,5-dibromopyrrole and 2,5-dibromopyrrole with the $Ni(cod)_2$-catalyst.[131]

1.7 *Aim of the research*

The aim of the research presented in this thesis, is two-fold. First of all, we like to develop the sparsely populated area of well-defined oligomers based on pyrrole and other (hetero)aromatics. Applying organometallic aryl-aryl coupling reactions in order to prepare these compounds, and subsequently studying their structural and physical characteristics by means of scanning tunnelling microscopy, cyclic voltammetry and various types of spectroscopy, gives a good insight into the structure-property relationship of these compounds. Subsequent extrapolation of these data to infinite chain length reveals important information about the corresponding well-defined polymers. Secondly, we like to apply this knowledge to prepare new and functional materials based on pyrrole and other (hetero)aromatics. The latter are expected to display interesting properties, which might be of use in future applications. For instance, introduction of electron-donating and -withdrawing substituents supplies derivatives which can be used to study nonlinear optical properties. Furthermore, we want to combine pyrrole and sulfur in order to prepare intrinsically conducting polymers analogous to polysulfur nitride, and develop a regioregular polymerization route toward poly(3-alkylpyrrole)s, which might improve the processability and properties of conventional polypyrroles.

1.8 *Scope of the thesis*

After a brief introduction on the chemistry of pyrrole, oligopyrroles and polypyrroles in *chapter 1*[132], several aspects of oligopyrrole chemistry will be discussed in the following five chapters. In *chapter 2* the Pd-catalyzed cross coupling reaction involving organostannanes, also known as the Stille reaction, is applied to the synthesis of a large number of phenyl-blocked oligomers consisting of pyrrole, thiophene, and/or benzene units. By first performing a number of model reactions, crucial information is obtained on mechanistical aspects of this coupling reaction. Subsequent utilization of this knowledge, results in the synthesis of numerous oligomers that are fully characterized.[133-135]

The properties of several series of oligomers, also prepared by Stille reactions, are studied more extensively in *chapter 3*. First of all, a series of donor-π-acceptor substituted oligopyrroles is prepared and studied for their optical and nonlinear optical properties. Furthermore, a N-dodecyl substituted oligomer is prepared and investigated by scanning tunnelling microscopy. Finally, two series of phenyl-blocked oligomers are studied for their redox properties.[134,136]

In *chapter 4* the synthesis and characterization of functionalized 3-alkylpyrroles are discussed in detail. Besides halogenation and stannylation experiments, a new stannyl-bromo exchange reaction is described, which opens the way to α-monobrominated pyrrole derivatives, that were almost inaccessible up to now. Furthermore, the first attempts toward regioregular oligo- and polypyrroles are revealed, applying the Stille coupling methodology once more.[137]

In *chapter 5* the synthesis of pyrrole-sulfur compounds is described. Adaptation of the only procedure known in literature to couple pyrrole and sulfur, gives access to both oligomers and polymers. Although these compounds are most probably not of use as intrinsically conducting polymers, useful information is obtained on structural and physical characteristics of pyrrole-sulfur compounds.[138,139]

Finally, in *chapter 6* the Ullmann reaction is applied to the synthesis of well-defined oligopyrroles. Polymerization of N-*t*-BOC protected α,α-dibrominated oligopyrroles gives rise to mixtures of oligomers. Subsequent separation by means of preparative HPLC results in the isolation of the first twenty oligomers. The latter are investigated by different techniques, while some of them are studied for their properties.[140,141]

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Chapter 2

OLIGOPYRROLES BY THE STILLE REACTION: A METHODOLOGICAL STUDY

Abstract: *The Pd-catalyzed cross coupling reaction involving organostannanes, also known as the Stille reaction, is applied to the synthesis of well-defined oligopyrrole systems. First, mechanistic aspects of this coupling reaction are investigated. Therefore, a number of halogenated and stannylated (hetero)aromatic compounds is prepared; halogenation reactions are performed with N-chloro- or N-bromosuccinimide in THF at -70°C, whereas stannylated compounds are obtained by a lithiation/stannylation sequence. Model reactions performed with these functionalized compounds, reveal that the kind of solvent, the type of halide and the electron-releasing/-withdrawing character of the substituents all strongly influence the course of these reactions. With this knowledge in mind, a large number of well-defined oligomers based on pyrrole, thiophene and/or benzene units are prepared. These Stille reactions between aryl halides and arylstannanes are performed in a two-phase system of toluene and aqueous Na_2CO_3 (1 M) with $Pd(PPh_3)_4$ as catalyst. After 2-3 days under reflux conditions, the reaction mixtures are subjected to work-up and extensive purification. Tedious isolation by a sequence of column chromatography and recrystallization, finally yields the desired oligomers, which are fully characterized.*

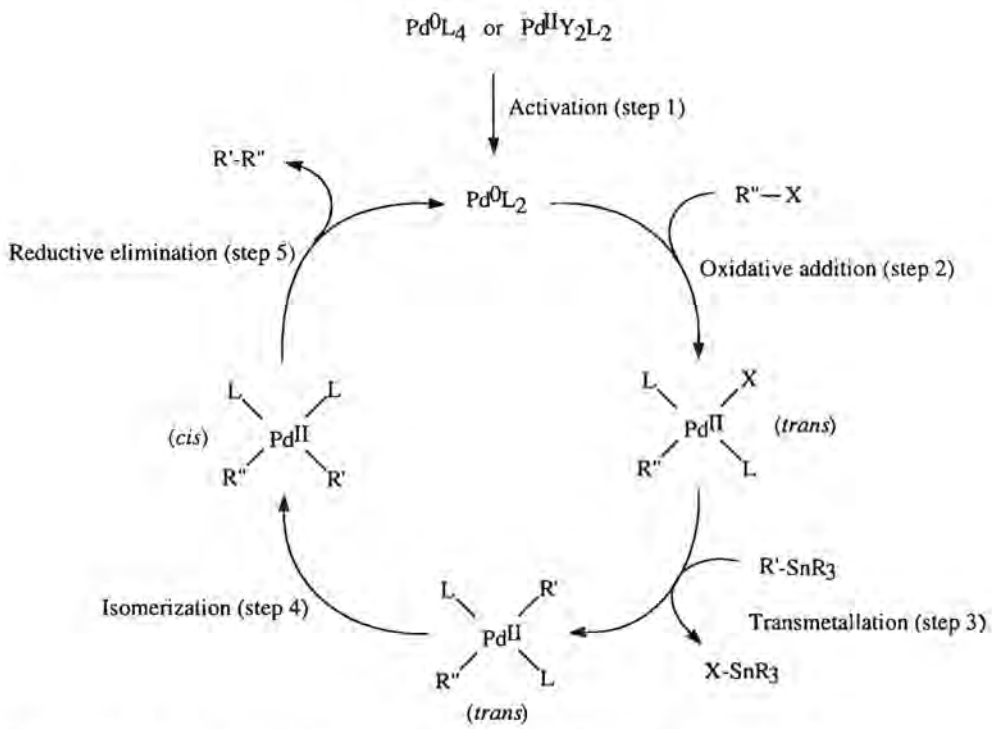
2.1 *Introduction*

Transition metal-mediated cross coupling reactions[1], such as those developed by Kumada[2], Negishi[3] and Heck[4], have become important tools in organic chemistry to facilitate the formation of carbon-carbon bonds between aryl or alkenyl halide substrates and a variety of alkyl, aryl and vinyl organometallic reagents. In the middle of the 1980's, the late John K. Stille[5] reported on palladium-catalyzed cross coupling reactions involving organostannanes.[6] As he can justly be considered as the pioneer in this field, this coupling reaction is now often referred to as the *Stille reaction*.

A Stille reaction is a substitution reaction between an organostannane (R_3Sn-R'), and an aryl or alkenyl substituted halide, triflate, fluorosulfonate or carbonyl chloride (R''-X).[6-9]

$$R_3Sn\text{-}R' + R''\text{-}X \xrightarrow{PdL_n} R'\text{-}R'' + R_3Sn\text{-}X$$

Although the mechanism of this coupling reaction is far from elucidated, it is generally accepted to proceed *via* a catalytic chain cycle (scheme 2.1).[10]

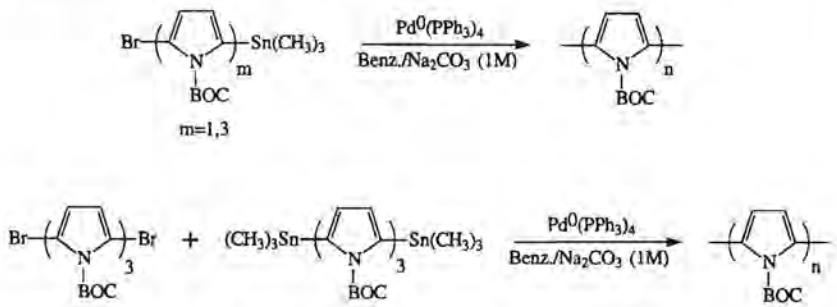


Scheme 2.1: *Multistep cyclic mechanism as proposed for the Stille reaction.*[10]

In the first step an activated doubly ligated zerovalent palladium-complex, Pd^0L_2, is formed *in situ* by spontaneous deligation of stable zerovalent complex precursors such as $Pd^0(PPh_3)_4$ or $Pd^0(dba)L_2$, generated from mixtures of $Pd^0(dba)_2$ (dba = dibenzylidene acetone) and phosphines (L), or by reduction of a stable divalent palladium-complex, $Pd^{II}Y_2L_2$; the reducing agent in the latter case is most generally the organostannane itself. This activated palladium(0)-complex then undergoes an oxidative addition with an organic halide or triflate (R''-X), which results in a planar *trans* palladium(II)-complex, $Pd^{II}R''L_2X$ (step 2). In the next step nucleophilic substitution occurs, resulting in the *trans* palladium(II)-complex, $Pd^{II}R'R''L_2$ (transmetallation; step 3), and finally reductive elimination gives rise to the formation of the coupling product (R'-R''), and regenerates the activated palladium intermediate (step 5). However, since reductive elimination may only proceed from *cis* complexes, the thermodynamically more stable *trans* derivative, formed upon nucleophilic substitution, must first isomerize (step 4) before step 5 may occur.

Besides the work that has been performed to gather more knowledge on the mechanism of the Pd-catalyzed cross coupling reaction (e.g. the role and effects of halide ions[11,12], the effects of CuI[13-16] or Ag_2O[17]), considerable effort has been put in developing new and better palladium-catalysts. Worth mentioning in this respect is the work of Farina *et al.* who investigated a whole array of new ligands, and were able to show that large rate enhancements can be obtained by replacing the 'traditional' triphenylphosphine ligand by tri(2-furyl)phosphine or triphenylarsine ligands.[18-20]

Although the Stille reaction has been applied to a large number of couplings between vinyl triflates, allyl halides and aryl halides on the one hand, and various organostannyl (alkyl, vinyl, alkynyl, allyl, aryl) compounds on the other hand[6-9,21-23], the number of papers dealing with heteroaryl systems is limited. Besides some work performed on thiophenes[24-27], furans[28,29] and pyridines[28], only one example of a Stille reaction involving pyrrole was known up to 1991.[30] However, in that year Martina, Schlüter and Wegner applied this type of coupling reaction to the synthesis of oligo(pyrrole-2,5-diyl)s.[31-41] Performing a $Pd^0(PPh_3)_4$-catalyzed cross coupling reaction between two equivalents of N-*t*-BOC-2-trimethylstannyl-pyrrole and one equivalent of an α,α-dibrominated oligopyrrole in a two-phase system of benzene and aqueous Na_2CO_3 (1 M), furnished oligomers containing up to nine repeating pyrrole units (Chapter 1, scheme 1.6). Similarly, they also prepared polymers starting from different monomers (scheme 2.2).



Scheme 2.2: *Well-defined N-t-BOC protected poly(pyrrole-2,5-diyl)s prepared by the Stille reaction.*[31-41]

One other paper dealing with the combination of pyrroles and Stille chemistry was published by Muchowski *et al.*[42] They investigated the synthesis of N-tri-*i*-propylsilyl substituted 3-aryl, 3-alkynyl and 3,4-dialkynyl pyrroles following the strategy as reported by Martina *et al.*

Two final remarks: from the extensive work performed by Stille *et al.* it has appeared that many functional groups are compatible with the Stille reaction: nitro, cyano, alkoxy, carbonyl, carboxyl and amino functionalized substrates are all tolerated.[6] Furthermore, they

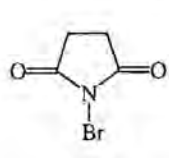
observed that aryl bromides containing electron-withdrawing substituents react very rapidly and go to completion with 2 mol% of catalyst, whereas aryl bromides bearing electron-releasing groups react more sluggishly and require the incremental addition of catalyst.[43-46]

Since it is our goal to prepare well-defined and functional oligomers based on pyrrole and other (hetero)aromatics, the use of an asymmetrical coupling reaction is a prerequisite. Therefore, the Stille reaction seems the method of choice. However, since the knowledge on the combination of Stille chemistry and pyrroles is limited, we first investigated some mechanistic aspects of this coupling reaction. Applying the acquired knowledge to the synthesis of oligomeric structures, resulted in a variety of well-defined oligomers and series of oligomers, which constituted the beginning of further studies.

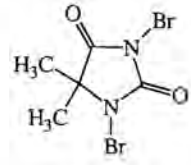
2.2 *Synthesis of Stille coupling reagents*

2.2.1 *Introduction*

In order to perform Stille reactions between pyrroles and/or other (hetero)aromatics, the coupling units have to be functionalized with halogen or trialkylstannyl substituents. In the early days of pyrrole chemistry a number of groups investigated the α-halogenation of N-unsubstituted pyrroles. Although some methods indeed resulted in the formation of 2-halo- and 2,5-dihalopyrroles, these compounds were only stable in solutions stabilized by a base (tributylamine).[47-49] The stability improved with the introduction of substituents at nitrogen, which replaced the most acidic proton. Using N-chlorosuccinimide (NCS) and N-bromo-succinimide (NBS), Gilow and Burton were able to isolate several α-halogenated N-benzyl- and N-phenylpyrroles.[50] At the end of the 1980's Chen and Cava reported on the synthesis of mono- and dibrominated N-*t*-BOC protected pyrroles.[51,52] Starting from pyrrole, they first brominated the α-positions with 1,3-dibromo-5,5-dimethylhydantoin (NBH), after which they protected the pyrrole unit with a *t*-BOC group.



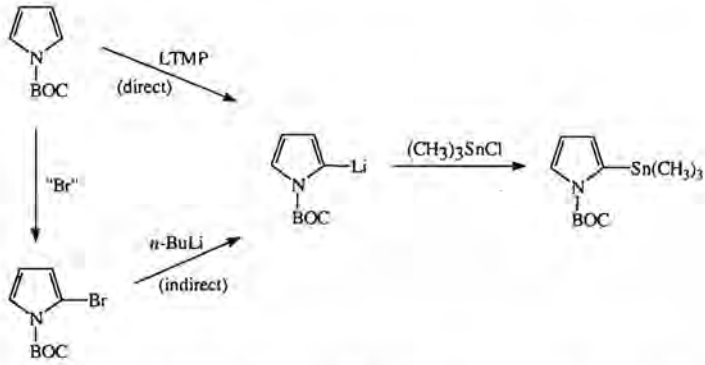
NBS



NBH

Eventually, it was found that the NBS procedure, as developed by Gilow and Burton for N-alkyl and N-aryl substituted pyrroles, could also be applied to the halogenation of N-*t*-BOC protected pyrrole derivatives. The latter was demonstrated by Martina *et al.* who used this method for the bromination of several pyrrole derivatives.[31-38]

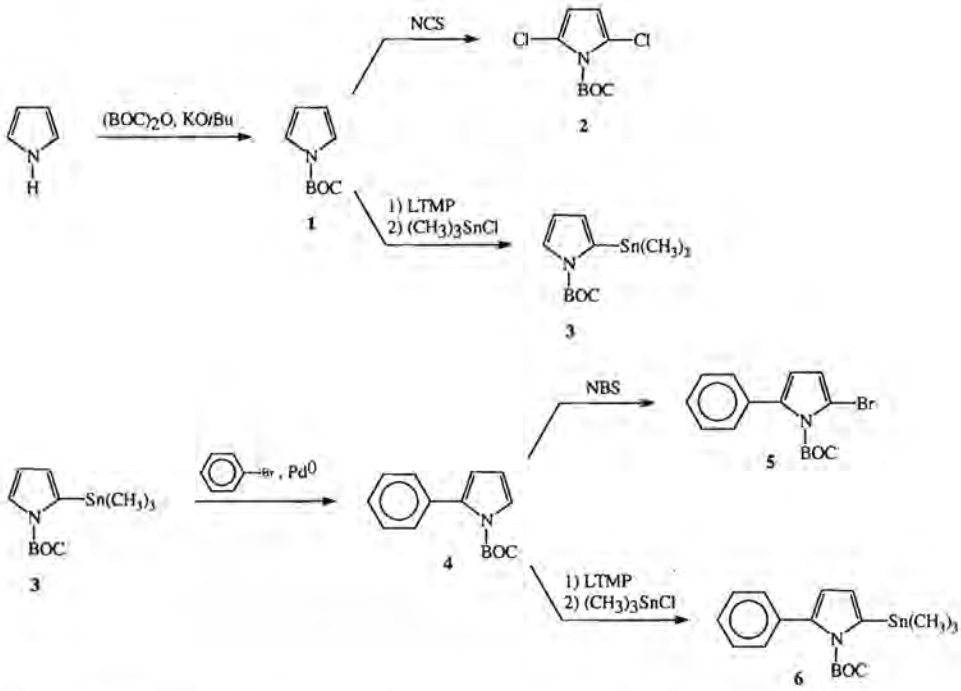
The number of reports on stannylated pyrrole derivatives is also very limited.[31,53-56] Again Martina *et al.* developed a procedure that could be applied to the synthesis of N-*t*-BOC protected pyrrolyl-2-boronic acid and pyrrolyl-2-trimethylstannane derivatives.[31,34] It consists in the formation of an α-pyrrolyl anion[57], using *t*-BuLi, lithium di-*i*-propylamide (LDA) or lithium 2,2,6,6-tetramethylpiperidide (LTMP) in case of direct lithiation, or *n*-BuLi in case of indirect lithiation, followed by the addition of trimethylstannyl chloride (scheme 2.3).



Scheme 2.3: *Stannylation of N-t-BOC-pyrrole via direct or indirect lithiation.*

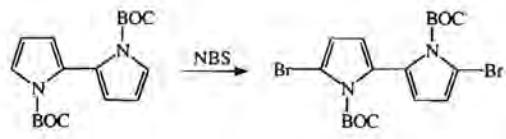
2.2.2 *Results and discussion*

For the synthesis of numerous oligopyrroles, N-*t*-BOC-2-phenyl-5-trimethylstannyl-pyrrole **6** was used as the organostannane. The synthesis of this compound is outlined in scheme 2.4. Pyrrole was first protected with the *t*-BOC group using di-*tert*-butyl dicarbonate and a catalytic amount of KO*t*Bu in refluxing THF[58]. After distillation (yield 85%), N-*t*-BOC-pyrrole **1** was directly stannylated using LTMP and trimethylstannyl chloride in THF at -70°C (**3**, yield 84%). Then, a Stille reaction between **3** and bromobenzene was performed in order to prepare N-*t*-BOC-2-phenylpyrrole **4**. For this coupling a two-phase system consisting of toluene and aqueous Na_2CO_3 (1 M) was used in combination with a catalytic amount of $Pd^0(PPh_3)_4$ (2 mol%). After refluxing for two days under inert atmosphere, **4** was finally isolated in 80% yield. This compound was then selectively brominated at the free α-pyrrolyl position using NBS in THF at -70°C, yielding N-*t*-BOC-2-bromo-5-phenylpyrrole **5** in quantitative yield. Compound **4** could also be stannylated directly using LTMP and trimethylstannyl chloride in THF at -70°C, affording N-*t*-BOC-2-phenyl-5-trimethylstannyl-pyrrole **6** (yield 97%).



Scheme 2.4: *Synthesis of halogenated and stannylated pyrrole derivatives.*

Besides organostannane **6**, several mono- and dihalogenated compounds were prepared. N-*t*-BOC-2,5-dichloropyrrole **2** was prepared from N-*t*-BOC-pyrrole **1** using NCS; after tedious purification, **2** could finally be isolated in 42% yield (scheme 2.4). Other halogenated compounds that were prepared are N,N'-di-*t*-BOC-5,5'-dibromo-2,2'-bipyrrole **7** from N,N'-di-*t*-BOC-2,2'-bipyrrole using NBS (yield 99%, total synthesis will be discussed in chapter 6)[58], 2,5-dibromothiophene **8** from thiophene using Br_2/HBr (yield 92%)[59], 5,5'-dibromo-2,2'-bithiophene **9** and 5,5''-dibromo-2,2':5',2''-terthiophene **10** from 2,2'-bithiophene and 2,2':5',2''-terthiophene, respectively, using NBS in DMF (yields 76% and 93%, respectively)[60], N-*t*-BOC-2,5-di(5-bromo-2-thienyl)pyrrole **11** by distannylation of N-*t*-BOC-2,5-di(2-thienyl)pyrrole[61] (LTMP, $(CH_3)_3SnCl$) followed by dibromination (NBS; overall yield 91%)[62], and 2-bromo-5-methylthiophene **12** from 2-methylthiophene using HBr/H_2O_2 (yield 69%) (scheme 2.5).



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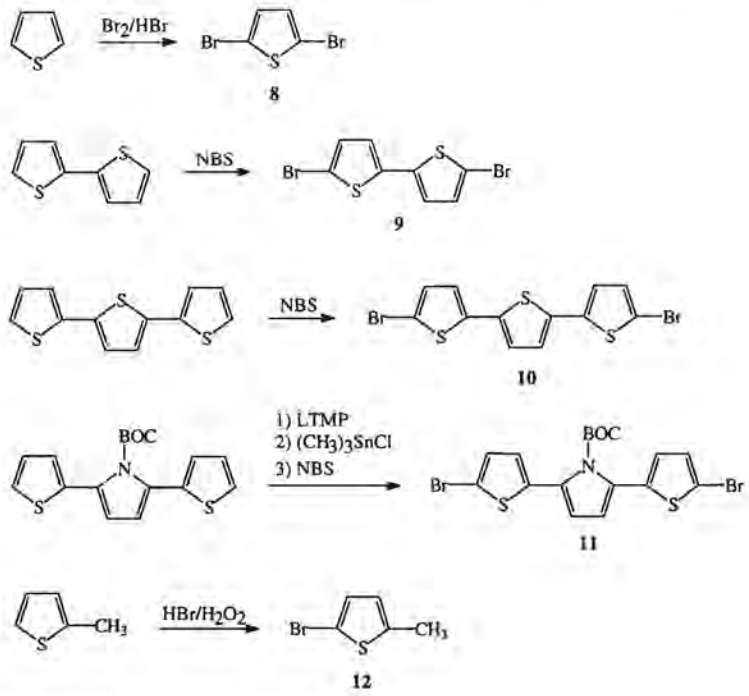


Scheme 2.5: *Synthesis of various aryl halides.*

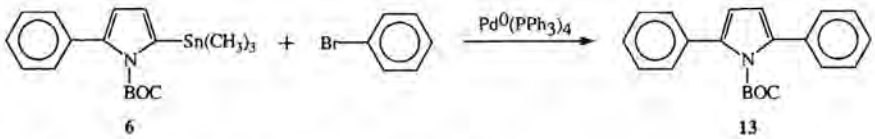
2.3 *Mechanistic studies*

In order to obtain more insight into mechanistic aspects of the Stille reaction in oligopyrrole synthesis, a number of parameters have been investigated. In the next sections the influence of different solvents, halides and electron-releasing or -withdrawing substituents is discussed.

2.3.1 *Influence of solvent on the Stille reaction*

The solvent is an important parameter in Stille reactions.[18,46,63] Therefore, a variety of solvents has been studied over the past decade. Commonly used are toluene[45,64] and THF[24,26], but also benzene[31], dioxane[15] , DMF[21] and NMP[16] have been applied. The only solvent described in pyrrole-Stille chemistry is the two-phase system of benzene and aqueous Na_2CO_3; the latter was adapted from the Suzuki polymerization of *p*-phenylenes[65]. The role of the aqueous Na_2CO_3 solution in this system is elimination of traces of acid, which originate from the hydrolysis of trimethylstannyl halide. These traces can be disastrous since they can cleave the *t*-BOC group.

In order to gather more knowledge on the influence of solvents on pyrrole-Stille reactions, several solvents and combinations of solvents were investigated using the $Pd^0(PPh_3)_4$-catalyzed coupling reaction between **6** and bromobenzene as a model reaction (scheme 2.6).



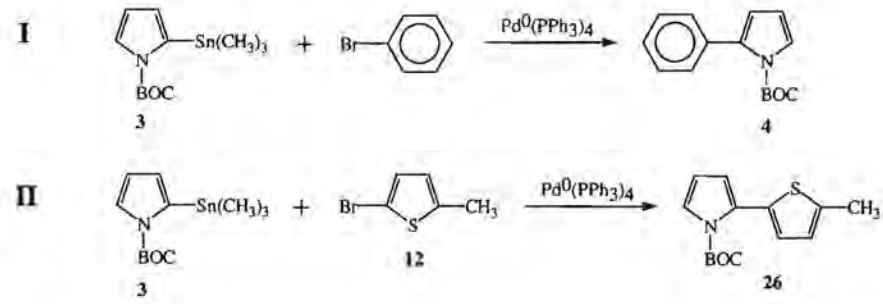
6 **13**

Scheme 2.6: *Model reaction to study solvent effects.*

Besides the abovementioned two-phase system (with toluene instead of benzene), this model reaction was also performed in toluene, xylene, and aqueous Na_2CO_3 (1 M). After two days under reflux conditions, the reaction mixtures were analyzed by ^{1}H-NMR. The two-phase system gave N-*t*-BOC-2,5-diphenylpyrrole as the main product (85-90%), besides some N-*t*-BOC-2-phenylpyrrole (10-15%, destannylation product). In case of toluene, the formation of N-*t*-BOC-2,5-diphenylpyrrole was suppressed significantly (40-50%); the main by-products were N-*t*-BOC-2-phenylpyrrole and a N-unsubstituted product (deprotection of the *t*-BOC group), while there was also some stannylated starting material left. In case of xylene the results were even worse; besides the formation of N-*t*-BOC-2,5-diphenylpyrrole and a N-unsubstituted derivative, a considerable amount of destannylated product and starting materials was observed in the reaction mixture. Surprising results were obtained in aqueous Na_2CO_3 (1 M); here the yield of N-*t*-BOC-2,5-diphenylpyrrole was over 95%.

In order to rationalize this surprising result, similar coupling reactions were performed in water, water/ethanol (1:1) and aqueous Na_2CO_3 (1 M)/ethanol (1:1). In all three cases only N-unsubstituted products were obtained. In case of water pure 2,5-diphenylpyrrole was formed, while the procedure in aqueous Na_2CO_3 (1 M)/ethanol (1:1) gave 2,5-diphenylpyrrole (95%) and 2-phenylpyrrole (5%, destannylation in combination with deprotection). The reaction in water/ethanol gave the same products but in different ratios (30 and 70%, respectively).

In order to verify the high yield in case of aqueous Na_2CO_3 (1 M), two other model reactions, being the synthesis of N-*t*-BOC-2-phenylpyrrole **4** (**I**, from N-*t*-BOC-2-trimethylstannylpyrrole (**3**) and bromobenzene) and N-*t*-BOC-2-(5-methyl-2-thienyl)pyrrole **26** (**II**, from N-*t*-BOC-2-trimethylstannylpyrrole (**3**) and 2-bromo-5-methylthiophene (**12**)), were investigated (scheme 2.7). After two days in aqueous Na_2CO_3 (1 M), the results were quite clear; in both cases starting materials, indicative of a lower reaction rate, as well as several deprotected products were found. However, in case of the two-phase system, the main product was the desired N-protected coupling product.



Scheme 2.7: *Two model reactions in order to study solvent effects.*

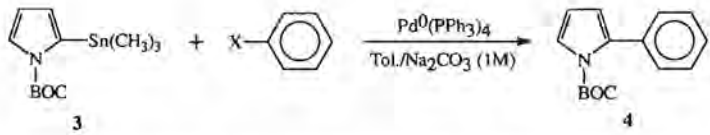
From the experiments described above it can be concluded that the solvent indeed strongly influences the course of Stille reactions in which pyrroles are involved. The standard two-phase system gives good results for both organostannanes **3** and **6**. In the absence of organic solvents, however, the Stille reaction has to take place in the concentrated melt of the reagents. In case of aqueous Na_2CO_3 (1 M) this is only beneficial for organostannane **6**, whereas in case of organostannane **3** undesired deprotection occurs, presumably due to its higher solubility in water. In pure water total deprotection of the desired product is observed. The latter is most probably due to the acidity of this solvent, which is even enhanced by the formation of HBr, formed upon hydrolysis of $(CH_3)_3SnBr$. In such acidic conditions the *t*-BOC groups do not survive. Ethanol, in which both the reagents and the liberated HBr dissolve, is equally unfavorable due to comparable deprotection. Since the *t*-BOC group is an important tool to guarantee solubility and stability for further functionalization steps, the use of these solvents is out of the question.

The big question that still remains is: what is the source for hydrogen atoms that are required for destannylation and deprotection? At first thought, one might think of water. However, in pure toluene we observed far more destannylation and deprotection than in the two-phase system. Another possibility might be that these hydrogen atoms are cleaved from $(CH_3)_3SnBr$. In order to prove this, more studies are required to get a deeper insight into these solvent effects. Until that time, the abovementioned two-phase system has been adopted.

2.3.2 *Influence of halide on the Stille reaction*

The oxidative addition of the aryl halide (R-X) to the activated Pd-complex (scheme 2.1, step 2) is an important step in the Stille reaction. The nucleophilic halides (X = Cl, Br, I) are most frequently used, although the non-nucleophilic sulfonates (triflate, fluorosulfonate, mesylate)[6-9] have also been applied. The reactivity of different halides is known to increase

from chloro to iodo (Cl << Br < I).[6] In order to investigate the influence of different halides in pyrrole-Stille chemistry, a competitive coupling reaction was performed (scheme 2.8).



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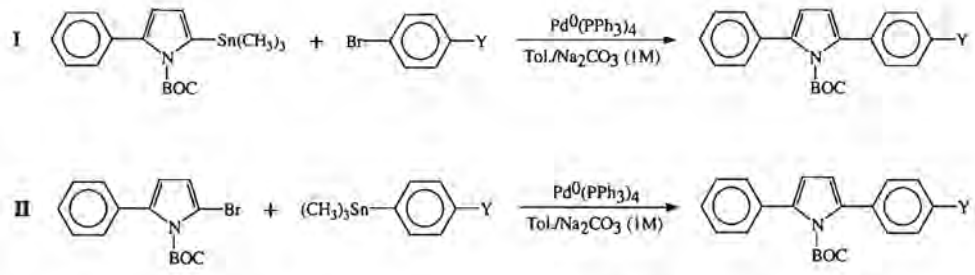
Scheme 2.8: *Competitive coupling reaction to study the influence of halide (X = Cl, Br, I).*

Starting from one equivalent of N-*t*-BOC-2-trimethylstannylpyrrole (**3**) and one equivalent of each halobenzene (X = Cl, Br, I), and performing a Stille reaction for two days in the presence of $Pd^0(PPh_3)_4$ in the two-phase system of toluene and aqueous Na_2CO_3 (1 M), the following product : starting compound ratio was obtained in the crude mixture: **4** : Ph-Cl : Ph-Br : Ph-I = 1 : 1 : 0.65 : 0.35. From this the reaction rate ratio of the three halobenzenes appears to be: Ph-Cl : Ph-Br : Ph-I = 0 : 0.35 : 0.65. This ratio is in agreement with the abovementioned order, and can be explained by the different bond strengths of C-X; the C-I bond is the longest and weakest bond of the three (~ 223 kJ/mol), followed by the C-Br (~ 273 kJ/mol) and finally the C-Cl bond (~ 336 kJ/mol). And the weaker the bond, the faster the oxidative addition to the activated Pd-complex takes place, the faster the reaction proceeds. However, in case of 2-pyrrolyl halides we have always applied bromo as substituent since the corresponding iodo derivatives are extremely unstable.

2.3.3 *Influence of electron-releasing/-withdrawing substituents on the Stille reaction*

As already mentioned in the introduction of this chapter, aryl bromides containing electron-withdrawing substituents react much faster in a Stille reaction than their analogs with electron-releasing groups[43-46]. In order to investigate the influence of electron-releasing and -withdrawing groups on Stille reactions in which pyrroles are involved, two competitive reactions were performed (scheme 2.9). In the first reaction (**I**) N-*t*-BOC-2-phenyl-5-trimethylstannylpyrrole was coupled with equimolar amounts of bromobenzene, 4-bromo-nitrobenzene and 4-bromoanisole. The reaction was performed in a two-phase system of toluene and aqueous Na_2CO_3 (1 M), catalyzed by $Pd^0(PPh_3)_4$. After two days the reaction mixture was analyzed by ^{1}H-NMR. Besides the formation of some destannylated product (20%), the product ratio appeared to be 5% of N-*t*-BOC-2,5-diphenylpyrrole, 75% of the corresponding nitro derivative and 0% of the corresponding methoxy derivative. However,

when a similar experiment was conducted in which the bromo and stannyl substituents were switched (**II**), the former three products were obtained in comparable yields.



Scheme 2.9: *Competitive coupling reactions to study the influence of electron-releasing/ -withdrawing substituents (Y = H, NO_2, OCH_3).*

From the abovementioned observations, two important statements can be distilled. First of all, it appears that the more electron-deficient the aryl halide is, the faster it reacts. This effect of the nitro substituent on the reaction rate, which is in agreement with observations made by Stille and others[43-46], can be explained by the lower electron density on the *ipso*-phenyl carbon atom. The latter facilitates the insertion of Pd^0L_2, which results in a faster reaction. A second statement which, at first glance, seems legitimate to make, concerns the rate-determining step in these Stille reactions. Since the electron-withdrawing substituent only influences the reaction in case it is connected to the aryl halide, the oxidative addition of the aryl halide to the activated Pd^0-complex seems to be the rate-determining step. This is in contradiction with earlier reports, which state that the addition of the aryl halide (step 2) is fast compared to the transmetallation step (step 3).[10,19] However, in case of the closely related Suzuki coupling, oxidative addition of the aryl halide is also the rate-determining step. One can also think of a second explanation for this deviant behavior. Since the oxidative addition and the transmetallation are two totally different kind of steps within the mechanism, it might be that the electron-releasing/-withdrawing substituents do have an influence on the oxidative addition step, whereas they do not have any influence on the transmetallation step. If this is the case, the transmetallation step might also be the rate-determining step here. In order to prove this, more studies are required. In the meantime we have applied the rate-increasing effect of an electron-withdrawing substituent to the synthesis of a number of donor-π-acceptor oligopyrroles, as shown in Chapter 3.

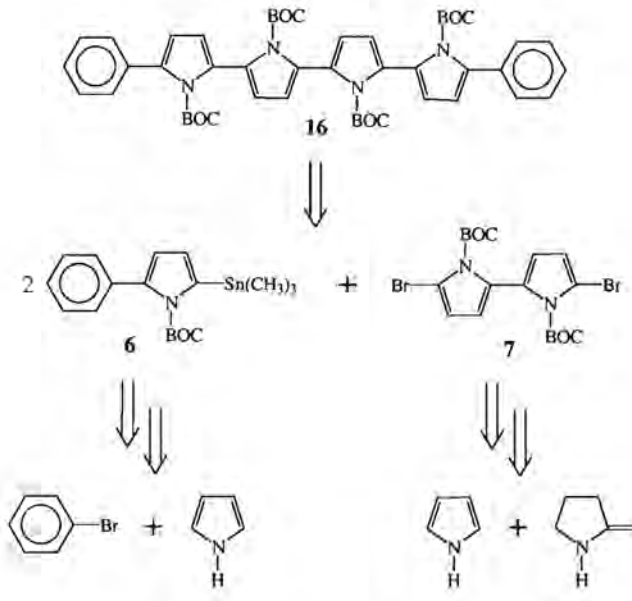
2.3.4 *Overall conclusions on the mechanistic studies*

From the mechanistic studies presented above, the conclusion can be drawn that Stille reactions, in which pyrroles are involved, show on some points deviant behavior. Since other systems, which have been used for mechanistic studies, are quite unilateral, the present study shows that it is difficult to make general statements about the optimal conditions to perform a particular Stille reaction. All parameters, e.g. solvent, catalyst, temperature and reaction time, have to be adjusted in order to find the optimal conditions. Although it seems that there are some trends within the class of pyrrole-Stille reactions, we are still not able to predict the outcome of a new coupling experiment for certain. Therefore, further studies are required. Until that time, it is this indistinctness, which makes the Stille reaction both loved and hated.

2.4 *Well-defined oligopyrroles by the Stille reaction*

2.4.1 *Synthesis*

The knowledge gathered during the mechanistic studies has been applied to the synthesis of a variety of well-defined oligomers consisting of pyrrole, thiophene and/or benzene units. A typical example is the synthesis of N,N′,N″,N‴-tetra-*t*-BOC-5,5‴-diphenyl-2,2′:5′,2″:5″,2‴-quaterpyrrole (**16**). The nine-step synthesis of this compound is retrosynthetically shown in scheme 2.10.

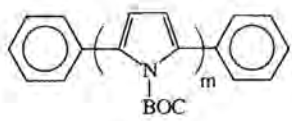


Scheme 2.10: *Retrosynthesis of oligomer* ***16****.*

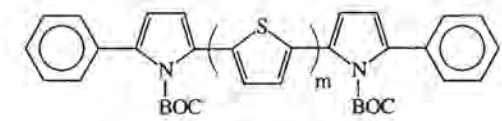
Organostannane N-*t*-BOC-2-phenyl-5-trimethylstannylpyrrole (**6**) is prepared from pyrrole by a sequence of *t*-BOC protection, selective α-stannylation, a Stille reaction with bromobenzene and, again, selective α-stannylation (for details, the reader is referred to 2.2.2). Aryl halide N,N'-di-*t*-BOC-5,5'-dibromo-2,2'-bipyrrole (**7**) is prepared from pyrrole and 2-pyrrolidinone by a sequence of a Vilsmeier condensation, dehydrogenation, *t*-BOC protection and selective α-bromination (for details, the reader is referred to Chapter 6). The final step consists of a Stille reaction between **6** and **7**. Since the mechanistic studies have shown that α-pyrrolylstannanes are liable to destannylation, an excess of **6** was used. Therefore, 2.15 eq of **6** and 1 eq of **7** were dissolved in the two-phase system of toluene and aqueous Na_2CO_3. The solution was deaerated several times, after which 2 mol% of $Pd^0(PPh_3)_4$ was added. The mixture was heated under reflux for two days, during which period the course of the reaction was followed by TLC and ^{1}H-NMR spectroscopy. After 2 days, when all organostannane had disappeared, the dark, troubled mixture was subjected to work-up (Et_2O/water extraction). ^{1}H-NMR analysis of the resulting dark oil revealed several products: besides the desired coupling product, small amounts of catalyst, starting compound **6**, N-*t*-BOC-2-phenylpyrrole (destannylation product) and a few unknown by-products were detected. In order to isolate compound **16**, purification by column chromatography was carried out, which finally yielded pure **16** in 39%.

Besides **16**, a variety of other oligomers and series of oligomers were prepared analogously (scheme 2.11; table 2.1). In all cases the Stille reactions went to completion within 2-3 days. Due to often tedious purification, the yields ranged from 14% in case of heptamer **25**, to 79% in case of trimer **13**.

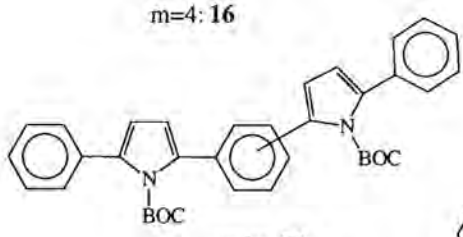
Most of the oligomers **13-27** were also transformed into their deprotected (N-H) form by thermolysis.[66] This was done by heating the neat oligomers for 20-30 minutes at 190°C under inert atmosphere, yielding their deprotected analogs in quantitative yields as was checked with ^{1}H-NMR, UV-Vis and IR spectroscopy.



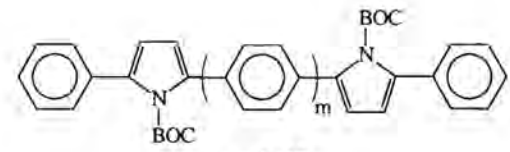
m=1: **13**
m=2: **14**
m=3: **15**
m=4: **16**



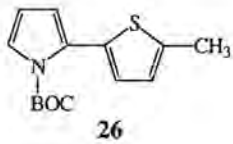
m=1: **17**
m=2: **18**
m=3: **19**



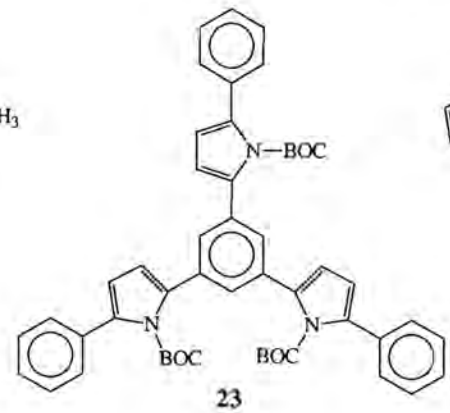
ortho: **20**
meta: **21**



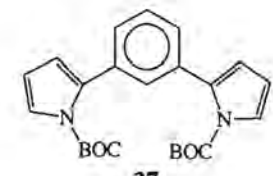
m=1: **22**
m=2: **24**



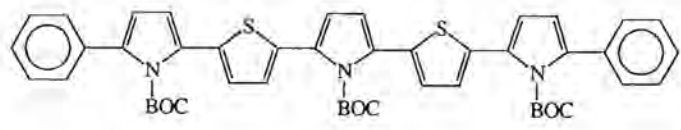
26



23



27



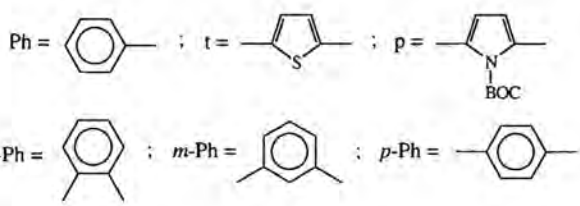
25

Scheme 2.11: *Survey of oligomers prepared by the Stille reaction.*

Table 2.1: *Oligomers prepared by the Stille reaction.*

$$(CH_3)_3Sn\text{-}R + R'\text{-}X \xrightarrow[Tol./Na_2CO_3\ (1M)]{Pd^0(PPh_3)_4} R\text{-}R' + (CH_3)_3Sn\text{-}X$$

Stannane $(CH_3)_3Sn$-R	Halide R′-X	Product R-R′	Yield (%)
6	bromobenzene	Ph-p-Ph (**13**)	79
6	**5**	Ph-p-p-Ph (**14**)	54
6	**2**	Ph-p-p-p-Ph (**15**)	43
6	**7**	Ph-p-p-p-p-Ph (**16**)	39
6	**8**	Ph-p-t-p-Ph (**17**)	20
6	**9**	Ph-p-t-t-p-Ph (**18**)	24
6	**10**	Ph-p-t-t-t-p-Ph (**19**)	21
6	1,2-dibromobenzene	Ph-p-*o*Ph-p-Ph (**20**)	35
6	1,3-dibromobenzene	Ph-p-*m*Ph-p-Ph (**21**)	54
6	1,4-dibromobenzene	Ph-p-*p*Ph-p-Ph (**22**)	15
6	1,3,5-tribromobenzene	1,3,5-(Ph-p)$_3$-benzene (**23**)	27
6	4,4′-dibromo-1,1′-biphenyl	Ph-p-Ph-Ph-p-Ph (**24**)	21
6	**11**	Ph-p-t-p-t-p-Ph (**25**)[64]	14
3	**12**	p-t-CH_3 (**26**)	42
3	1,3-dibromobenzene	p-*m*Ph-p (**27**)	51



2.4.2 *Characterization*

Both the protected (N-*t*-BOC) and deprotected (N-H) oligomers were characterized by several techniques. However, despite many attempts, it appeared very difficult to characterize these oligomers and their precursors by elemental analysis. The latter is due to the fact that (partial) oxidation of these compounds easily occurs, and that their appearance, mostly oils, hampers the removal of traces of solvents. Therefore, characterization is mainly based on a combination of NMR (^{1}H and ^{13}C), IR, UV-Vis and/or mass spectroscopy. The most striking results are summarized here. The ^{1}H-NMR data of the *t*-BOC-protected oligomers, which are all highly soluble due to the presence of the bulky *tert*-butoxycarbonyl groups, show some general trends. The proton signals of the blocking phenyl group give a broad multiplet between 7.5 and 7.2 ppm, β-pyrrolyl protons show a signal between 6.4 and 6.1 ppm, whereas the β-thienyl protons are situated between 7.2 and 7.0 ppm. The chemical shifts of the *t*-BOC groups can be found within the range of 1.5 and 1.1 ppm. After thermal removal of the *t*-BOC groups, the resultant oligomers are only soluble in THF-d_8; the protons of the phenyl group become well-separated: *ortho* protons at ~7.6, *meta* protons at ~7.3, and *para* protons at ~7.1 ppm. This difference in splitting pattern is most probably due to a lack of rotational freedom for the phenyl group in *t*-BOC-protected oligomers. Furthermore, the N-H resonances in THF-d_8 show broad singlets situated between 10.6 and 10.0 ppm, whereas β-pyrrolyl protons show a reasonably down-field shift (+ 0.1-0.3 ppm) and β-thienyl protons a small downfield shift (+ 0.1 ppm) compared to their N-protected analogs. The latter is due to enhanced anisotropic deshielding, which compensates for the enhanced electron density. FT-IR spectroscopy is an ideal technique to verify whether thermal deprotection of the *t*-BOC groups has gone to completion, since the C=O absorption at ~1750 cm^{-1} disappears upon heating.

UV-Vis data of N-*t*-BOC-protected oligopyrroles reveal a bathochromic shift of the π-π^* transition when the π-system is extended (figure 2.1). After thermal deprotection of the *t*-BOC groups, a large bathochromic shift is observed: this is the result of a higher degree of coplanarity, and thus, of conjugation of the aromatic units that is achieved upon replacement of the bulky *t*-BOC groups by the sterically less demanding hydrogen atoms. Surprising are the two identical absorption maxima of the oligomers with a mono- and a biphenylene spacer. Apparently, the conjugation length does not increase upon extension of the chain length with another phenylene unit; the latter is most probably due to steric hindrance between the two phenylene units.

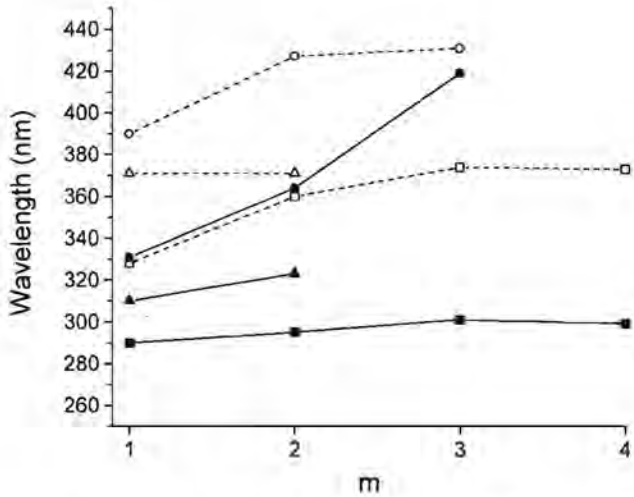


Figure 2.1: *UV-Vis data of phenyl-blocked oligomers in CH_3CN (Ph-p_m-Ph (■); Ph-p-t_m-p-Ph (●); Ph-p-Ph_m-p-Ph (▲). Closed markers refer to the N-t-BOC protected oligomers, whereas the open markers refer to the deprotected species).*

2.4.3 *Discussion*

The Stille reactions in table 2.1 show a number of characteristics. Analyzing the yields of the phenyl-blocked oligopyrrole series (**13-16**), one can observe a drastic decrease when increasing the number of pyrrole units. The latter can be rationalized by the fact that these four compounds are prepared using different aryl halides. For example, the synthesis of **15** requires the use of N-*t*-BOC-2,5-dichloropyrrole since, as was already noticed by Martina *et al.*[31], the corresponding dibrominated species is known for its inherent instability. However, the reactivity of aryl chloro derivatives is much lower, which opens the way to by-products *via* competitive side-reactions. If one compares these yields with those obtained from the phenyl-blocked oligopyrrole-thiophene series (**17-19**), the latter appear to be almost the same. This results from the fact that the required aryl halides, α,α-dibrominated mono-, bi- and terthiophene, are more or less similar. Concerning the oligomers with phenylene spacers (**20-24**), it is very difficult to see a trend. This is mainly due to the isolation by column chromatography: *meta* derivative **21** was relatively easily obtained, whereas **22-24** were very difficult to isolate.

Besides problems concerning work-up procedures, there is another reason for the moderate yields of these Stille reactions: lack of high selectivity. A survey of the main side-reactions that have been observed, is listed here. Although the origin of the by-products is not

always clear, it is our main purpose to give an overview of the side-reactions that have to be emphasized:

1. Destannylation of organostannanes

In contrast to other (hetero)arylstannanes, N-*t*-BOC protected pyrrolylstannanes are very sensitive toward protolysis. This phenomenon, called destannylation, is rationalized by the high electron density of the pyrrole nucleus. Therefore, protic conditions have to be avoided. However, since aqueous basic conditions are required to neutralize HBr, which is formed upon hydrolysis of $(CH_3)_3SnX$, a slight excess of organostannane is used as a compromise. In case of other, less electron-rich, arylstannanes, destannylation is seldomly observed.

2. Deprotection of N-t-BOC-pyrrole derivatives

As mentioned in 2.3.1, the *t*-BOC group on pyrrole is sensitive to acidic conditions. In addition, prolonged heating as generally applied to these coupling reactions, also causes partial deprotection. Even in optimized reaction conditions, some deprotection is unavoidable due to thermolysis. However, regarding the large difference in polarity and solubility between N-*t*-BOC and N-H derivatives, these by-products are easily removed by column chromatography.

3. Methyl shift

During some of the coupling reactions mentioned in table 2.1, a so-called methyl shift was observed. This methyl group, which originates from a trimethylstannyl substituent on pyrrole, always replaces the bromo substituent of the aryl bromide. Especially in case of the double Stille reaction toward **27**, the formation of the monomethyl derivative N-*t*-BOC-2-(3-tolyl)pyrrole is pronounced. Martina *et al.*, who observed analogous methyl shifts during his pyrrole-Stille reactions, investigated this phenomenon more closely[31]; they found that replacement by a tributylstannyl substituent circumvents this problem. Other studies, however, have shown that butyl groups can also be cleaved.[67]

4. Homo-coupling of organostannanes

During these Stille reactions, substantial homo-coupling of arylstannanes was observed. Especially the more electron-rich pyrrolylstannanes are prone to this side-reaction: while organostannane **6** does not suffer from this undesired reaction, the more electron-rich organostannane **3** does undergo homo-coupling. Recently, we also found an almost exclusive homo-coupling for bi- and terthienylstannanes, while the less electron-rich monothienylstannanes only undergo a Stille coupling.[68] The competition between the Stille coupling and homo-coupling of arylstannanes seems to be governed by the electron density on the aromatic

nucleus. The unanswered question remains whether this homo-coupling is accompanied by the formation of hexamethyldistannane.

A final reason for the moderate yields is related to the small scale at which these Stille reaction were performed (0.25-2.0 mmol). The latter was done since only small amounts of the oligomers were required for characterization and further investigation. However, especially during recrystallization, this resulted in quite some loss of material.

2.5 *Conclusions*

In order to investigate mechanistic aspects of the Pd-catalyzed cross coupling reaction, a number of model reactions has been performed. Therefore, several halogenated and stannylated (hetero)aromatics had to be prepared first; halogenation reactions were mostly performed with N-chloro- or N-bromosuccinimide in THF at -70°C, whereas stannylated derivatives were prepared by a lithiation/stannylation sequence under similar conditions. With the various functionalized halides and organostannanes in hand, a number of model reactions was performed. From these experiments it appeared that the solvent has a crucial influence on the course of these reactions. In general, the best results were obtained in a two-phase system of toluene and aqueous Na_2CO_3 (1 M). In one case, however, a reaction performed in aqueous Na_2CO_3 (1 M) gave a very high yield.

The influence of different halides was investigated by performing a competitive Stille reaction. From this it was observed that the iodo-substituted derivative reacts fastest, followed by the bromo- and finally the chloro-substituted compound. This order can be explained by taking the bond strength of each carbon-halide bond (C-X) into account: the weaker this bond, the faster the reaction.

Finally, the influence of electron-releasing and electron-withdrawing substituents was investigated. These studies revealed that when an electron-withdrawing substituent is attached to the aryl halide, the reaction rate is strongly and positively influenced. However, when these groups are attached to the organostannane, no difference in reaction rate is observed. The latter might indicate that oxidative addition of the aryl halide to the activated Pd^0-complex is the rate-determining step in these pyrrole-Stille reactions.

With this knowledge in mind, several oligomers consisting of pyrrole, thiophene and/or benzene units were prepared. All reactions were performed in the two-phase system of toluene and aqueous Na_2CO_3 (1 M) with $Pd^0(PPh_3)_4$ as catalyst. Work-up, after 2-3 days under reflux conditions and inert atmosphere, and subsequent column chromatography, gave the desired oligomers. Final purification by recrystallization yielded pure oligomers on a 0.05-0.5 g scale, which were fully characterized. Unfortunately, a number of side-reactions took

place; especially destannylation, deprotection of *t*-BOC groups, methyl shifts and homo-coupling of organostannanes often prevented these coupling reactions to occur in high yields.

Although the Stille reaction is a very interesting method to prepare both homo- and mixed oligomers, it is difficult to predict the outcome of a specific coupling reaction. In fact, one has to adjust a great number of parameters to obtain the optimal conditions for each coupling reaction. Therefore, more methodological studies are required in the near future in order to get a better understanding on the scope and limitations of this cross coupling reaction.

2.6 *Experimental section*

All materials and solvents were of p.a. quality and used as received. THF was distilled from sodium/benzophenone. For column chromatography Merck silica gel 60 (particle size 0.063-0.200 mm) and Merck aluminum oxide 90 (neutral; activity I) were used. The latter was deactivated before use by adding 7%(w) of distilled water. NMR spectra were run on a Bruker AM-400 spectrometer at frequencies of 400.1 and 100.6 MHz for ^{1}H and ^{13}C nuclei, respectively, with tetramethylsilane (TMS) as an internal standard. UV-Vis spectra were taken on a Perkin Elmer Lambda 3B UV-Vis spectrophotometer with wavelengths between 190 and 900 nm. IR spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer with wavenumbers between 4400 and 450 cm^{-1}. Mass measurements were performed on a HP 5970 A GC-MS (column: OV-1, l = 25 m, d = 200 µm), or by Field Desorption Mass Spectroscopy (FD-MS; performed at the Max Planck Institute for Polymer Research in Mainz). All deprotected oligomers were stored under inert conditions.

N-*tert*-Butoxycarbonylpyrrole (1)[18,19] A vigorously stirred mixture of pyrrole (13.95 g, 208 mmol), di-*tert*-butyl dicarbonate (52.56 g, 241 mmol), THF (1000 ml) and potassium *tert*-butoxide (2.0 g, 18 mmol) was heated under reflux, blanketed by argon. After 18 h the mixture was cooled to RT and 2-dimethylaminoethylamine (5.25 g, 60 mmol) was added. Stirring was continued for another 30 min, after which the solvent was evaporated. The residue was dissolved in Et_2O (600 ml) and washed with dilute HCl (3 x 200 ml, 0.1 M) and H_2O (3 x 200 ml). Evaporation of the solvent resulted in a brown liquid from which, after distillation, a colorless liquid was obtained (29.55 g, 177 mmol, 85%). Bp.: 80°C (18 mm Hg).
^{1}H-NMR ($CDCl_3$): δ 7.23 (t, J = 2.2 Hz, 2H, H-2,5), 6.20 (t, J = 2.2 Hz, 2H, H-3,4), 1.58 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.8 (C=O), 119.9 (C-2,5), 111.7 (C-3,4), 83.4 (C-q (BOC)), 27.9 (C-methyl (BOC)) ppm. IR (KBr): 2980, 1744, 1473, 1400, 1371, 1342, 1318, 1254, 1155, 1079, 1032, 952, 852, 774, 740 cm^{-1}. GC-MS: 167 (M'), 94, 67, 57.

N-*tert*-Butoxycarbonyl-2,5-dichloropyrrole (2) A solution of N-*tert*-butoxycarbonylpyrrole (**1**, 1.67 g, 10.0 mmol) in THF (50 ml) was cooled to -70°C, blanketed by argon. N-Chlorosuccinimide

(2.94 g, 22.0 mmol) was added in portions, after which the mixture was stirred for 1 h at -70°C. Then it was allowed to warm to RT. After stirring for 12 h at RT, Na_2SO_3 (0.5 g, 4.0 mmol) was added to the mixture and the solvent was evaporated. CCl_4 (50 ml) was added and the mixture was stirred for another 15 min. After filtration, the filtrate was concentrated to afford an orange liquid. Column chromatography (50 g SiO_2, CH_2Cl_2 : hexane (1:3), R_f = 0.30) gave a colorless liquid (0.98 g, 4.2 mmol, 42%). (N.B. **2** can also be purified by distillation (76-80°C, 0.35 mm Hg)).
^{1}H-NMR ($CDCl_3$): δ 6.08 (s, 2H, H-3,4), 1.63 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 146.7 (C=O), 115.9 (C-2,5), 110.6 (C-3,4), 86.1 (C-q (BOC)), 27.8 (C-methyl (BOC)) ppm.

N-*tert*-Butoxycarbonyl-2-trimethylstannylpyrrole (3)[34] 2,2,6,6-Tetramethylpiperidine (14.13 g, 100.0 mmol) and THF (250 ml) were added to a three-necked flask (1000 ml) and cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in *n*-hexane, 68 ml, 109 mmol) was added dropwise and the solution was stirred for 10 min at -70°C. The slightly yellow solution was allowed to warm to 0°C, at which temperature it was kept for 10 min. Then it was again cooled to -70°C and a solution of N-*tert*-butoxycarbonylpyrrole (**1**, 15.05 g, 90.0 mmol) in THF (60 ml) was added over a 20 min period. After additional stirring for another 45 min at -70°C, a solution of trimethylstannyl chloride (18.93 g, 95 mmol) in THF (60 ml) was added. The mixture was stirred for 3 h at -70°C and was then allowed to reach RT overnight. THF was evaporated and Et_2O (200 ml) and water (200 ml) were added. The aqueous phase was separated and extracted with Et_2O (3 x 100 ml). The combined organic fractions were washed with water (2 x 100 ml), dried ($MgSO_4$), filtered and concentrated. The dark liquid was finally distilled under vacuum resulting in a slightly yellow oil, which slowly crystallized when stored at 3°C (24.95 g, 75.60 mmol, 84%). Bp.: 68-69°C (0.01-0.02 mm Hg)
^{1}H-NMR ($CDCl_3$): δ 7.30 (dd, J = 3.0 and 1.3 Hz, 1H, H-5), 6.27 (dd, J = 3.0 and 1.4 Hz, 1H, H-3), 6.19 (t, J = 3.0 Hz, 1H, H-4), 1.48 (s, 9H, H-methyl (BOC)), 0.16 (s, 9H, H-methyl (stannyl)) ppm. ^{13}C-NMR ($CDCl_3$): δ 150.4 (C=O), 134.4 (C-2), 123.2/122.2 (C-3/C-5), 112.6 (C-4), 83.2 (C-q (BOC)), 27.8 (C-methyl (BOC)), -7.8 (C-methyl (stannyl)) ppm. IR (KBr): 2979, 2916, 1728, 1531, 1478, 1458, 1387, 1339, 1259, 1156, 1087, 1046, 980, 775, 727 cm^{-1}.

N-*tert*-Butoxycarbonyl-2-phenylpyrrole (4) (General description of a Stille reaction) A two-necked flask (100 ml) was charged with bromobenzene (3.15 g, 20.0 mmol), N-*tert*-butoxycarbonyl-2-trimethylstannylpyrrole (**3**, 6.62 g, 20.0 mmol), toluene (30 ml) and aqueous Na_2CO_3 (1 M, 30 ml). After deaeration and storage under an argon atmosphere, tetrakis(triphenylphosphine)palladium(0) (2 mol%) was added. The mixture was heated under reflux for two days, after which it was allowed to cool to RT. The organic and aqueous layers were separated and the aqueous layer was extracted with Et_2O (3 x 20 ml). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated. Final purification by column chromatography (300 g SiO_2, CH_2Cl_2 : hexane (1:2), R_f = 0.40) gave **4** as a colorless oil (3.91 g, 16.1 mmol, 80%).
^{1}H-NMR ($CDCl_3$): δ 7.38-7.26 (m, 6H, H-phenyl, H-5), 6.22 (t, J = 3.3 Hz, 1H, H-4), 6.18 (dd, J = 3.3 and 1.8 Hz, 1H, H-3), 1.33 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.3 (C=O), 135.0/134.4 (C-2/C-*ipso* (phenyl)), 129.1/127.5 (C-*ortho*/C-*meta*), 127.1 (C-*para*), 122.5 (C-5), 114.3 (C-3), 110.5 (C-4), 83.4 (C-q (BOC)), 27.5 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 270 nm. IR (KBr): 2980, 2934, 1739, 1471, 1395, 1315, 1256, 1151, 1074, 972, 849, 775, 730 cm^{-1}.

4H: Removal of the *t*-BOC group was accomplished by thermolysis; heating neat **4** for 20-30 min at 190°C under inert atmosphere, gave the deprotected form (**4H**) in quantitative yield.
^{1}H-NMR ($CDCl_3$): δ 8.42 (broad singlet, 1H, N-H), 7.47 (dd, J = 8.4 and 1.2 Hz, 2H, H-*ortho*), 7.36 (tt, J = 7.9 and 1.6 Hz, 2H, H-*meta*), 7.20 (tt, J = 7.4 and 1.3 Hz, 1H, H-*para*), 6.86 (td, J = 2.6 and 1.5 Hz, 1H, H-5), 6.53 (ddd, J = 3.4, 2.6 and 1.5 Hz, 1H, H-3), 6.30 (dt, J = 3.4 and 2.6 Hz, 1H, H-4) ppm. ^{13}C-NMR ($CDCl_3$): δ 132.7/131.9 (C-2/C-*ipso* (phenyl)), 128.9 (C-*ortho*), 126.2 (C-*para*), 123.8 (C-*meta*), 118.8 (C-5), 110.1 (C-3), 105.9 (C-4) ppm.
(N.B. **4H** can also be prepared starting from benzoyl chloride and allylamine. The resulting amide, which is formed in 100% yield, can then be transformed into the corresponding benzimidoyl chloride using phosgene (97% yield), after which a final reaction with potassium *tert*-butoxide results in **4H** (67% yield)).[71]

N-*tert*-Butoxycarbonyl-2-bromo-5-phenylpyrrole (5) (General description of a NBS bromination reaction of pyrrole derivatives) A solution of N-*tert*-butoxycarbonyl-2-phenylpyrrole (**4**, 1.04 g, 4.3 mmol) in THF (20 ml) was cooled to -70°C, blanketed by argon. N-Bromosuccinimide (NBS, 0.76 g, 4.3 mmol) was added in portions, after which stirring was continued for 30 min at -70°C. The reaction mixture was then stored at 3°C overnight, after which Na_2SO_3 (0.81 g, 6.5 mmol) was added. The mixture was stirred for another 15 min and the solvent was evaporated. CCl_4 (20 ml) was added, the mixture was filtered and the filtrate concentrated, yielding pure N-*tert*-butoxycarbonyl-2-bromo-5-phenylpyrrole (**5**, 1.38 g, 4.3 mmol, 100%) as a slightly red oil.
^{1}H-NMR ($CDCl_3$): δ 7.37-7.24 (m, 5H, H-phenyl), 6.30 (d, J = 3.3 Hz, 1H, H-3), 6.16 (d, J = 3.6 Hz, 1H, H-4), 1.30 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.5 (C=O), 136.6/134.0 (C-2/C-*ipso* (phenyl)), 128.1/127.9 (C-*ortho*/C-*meta*), 127.3 (C-*para*), 114.9 (C-3), 112.6 (C-4), 101.9 (C-2), 84.9 (C-q (BOC)), 27.2 (C-methyl (BOC)) ppm.
(N.B. **5** as well as other halogenated pyrrole derivatives are sensitive compounds. Preferably, they should be used without delay; otherwise, one should store them at low temperature (-20°C) under inert atmosphere).

N-*tert*-Butoxycarbonyl-2-phenyl-5-trimethylstannylpyrrole (6) A solution of 2,2,6,6-tetramethylpiperidine (1.31 g, 9.27 mmol) and THF (25 ml) was cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in *n*-hexane, 6.1 ml, 9.76 mmol) was added dropwise, after which the solution was stirred for 15 min at -70°C and 30 min at RT. The mixture was again cooled to -70°C and a solution of N-*tert*-butoxycarbonyl-2-phenylpyrrole (**4**, 2.14 g, 8.80 mmol) in THF (5 ml) was added gradually. The solution was stirred for 90 min at -70°C, after which a solution of trimethylstannyl chloride (1.97 g, 9.89 mmol) in THF (5 ml) was added dropwise. Stirring was continued for another 4 h at -70°C and overnight at RT. Then the reaction mixture was concentrated, and Et_2O (30 ml) and water (30 ml) were added. The organic and aqueous layers were separated and the aqueous fraction was extracted with Et_2O (2x20 ml). The combined organic fractions were dried ($MgSO_4$), filtered and concentrated, yielding **6** as a white crystalline solid (3.47 g, 8.54 mmol, 97%).
^{1}H-NMR ($CDCl_3$): δ 7.35-7.23 (m, 5H, H-phenyl), 6.38 (d, J = 3.1 Hz, 1H, H-4), 6.27 (d, J = 3.0 Hz, 1H, H-3), 1.18 (s, 9H, H-methyl (BOC)), 0.30 (s, 9H, H-methyl (stannyl)) ppm. ^{13}C-NMR ($CDCl_3$): δ 151.5 (C=O), 138.2/137.6/135.9 (C-2/C-5/C-*ipso* (phenyl)), 128.0/127.5 (C-*ortho*/C-*meta*), 126.8 (C-

para), 121.4 (C-4), 115.4 (C-3), 83.3 (C-q (BOC)), 27.2 (C-methyl (BOC)), -7.5 (C-methyl (stannyl)) ppm.

N,N'-Di-*tert*-butoxycarbonyl-5,5'-dibromo-2,2'-bipyrrole (7)[58] N,N'-Di-*tert*-butoxycarbonyl-2,2'-bipyrrole (85.0 mg, 0.256 mmol) was dissolved in THF (4.5 ml) and cooled to -70°C, blanketed by argon. NBS (91.0 mg, 0.511 mmol) was added and the mixture was stirred for 30 min at -70°C. Then it was allowed to warm to 3°C, at which temperature it was kept for 3 h. Na_2SO_3 (a few mg) was added and the solvent was evaporated. CCl_4 (10 ml) was added to the residue, the mixture was stirred for 10 min and filtered. The solvent was then evaporated, resulting in **7** as a slightly red oil (124.2 mg, 0.253 mmol, 99%).
^{1}H-NMR ($CDCl_3$): δ 6.31 (d, J = 3.5 Hz, 2H, H-4,4'), 6.13 (d, J = 3.5 Hz, 2H, H-3,3'), 1.36 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.0 (C=O), 128.1 (C-2,2'), 115.7/115.1 (C-3,3', C-4,4'), 102.5 (C-5,5'), 84.9 (C-q (BOC)), 27.5 (C-methyl (BOC)) ppm.

2,5-Dibromothiophene (8)[59] A vigorously stirred mixture of thiophene (41.85 g, 497 mmol), 48% aqueous HBr (150 ml) and Et_2O (100 ml) was cooled to -10°C. A solution of Br_2 (160.0 g, 1.00 mol) in 48% aqueous HBr (150 ml) was added over a 25 min period, after which stirring was continued for another 45 min at +10°C. The layers were then separated and the aqueous layer was extracted with CH_2Cl_2 (4 x 60 ml). The combined organic fractions were washed with water (2 x 100 ml), dried ($MgSO_4$), filtered and concentrated. Distillation of the resulting liquid gave pure **8** (110.85 g, 458 mmol, 92%). Bp.: 78-80°C (10 mm Hg).
^{1}H-NMR ($CDCl_3$): δ 6.83 (s, 2H, H-3,4) ppm. ^{13}C-NMR ($CDCl_3$): δ 130.4 (C-3,4), 111.5 (C-2,5) ppm. IR (KBr): 3096, 1518, 1412, 1203, 982, 947, 784 cm^{-1}.

5,5'-Dibromo-2,2-bithiophene (9)[60] In the absence of light, NBS (3.20 g, 18.0 mmol) was added in portions to a stirred solution of 2,2'-bithiophene (1.50 g, 9.0 mmol) in DMF (10 ml), blanketed by argon. The mixture was stirred for 3 h, after which it was poured into ice-water. The precipitate was filtered and washed with water. Recrystallization from ethanol afforded **9** as a slightly yellow solid (2.20 g, 6.8 mmol, 76%). Mp.: 145°C (Lit.: yield 88%, mp. 146°C).
^{1}H-NMR ($CDCl_3$): δ 6.96 (d, J = 4.1 Hz, 2H, H-4,4'), 6.85 (d, J = 3.8 Hz, 2H, H-3,3') ppm. ^{13}C-NMR ($CDCl_3$): δ 137.8 (C-2), 130.6 (C-4), 124.1 (C-3), 111.5 (C-5) ppm. IR (KBr): 1504, 1416, 1197, 1058, 970, 867, 794, 626, 456 cm^{-1}.

5,5''-Dibromo-2,2':5',2''-terthiophene (10)[60] Compound **10** was prepared following the same procedure as described for **9**. Starting from 2,2':5',2''-terthiophene (0.200 g, 0.805 mmol), NBS (0.290 g, 1.63 mmol) and DMF (10 ml), pure **10** was obtained as a yellow solid (0.304 g, 0.75 mmol, 93%). (Lit.: yield 84%, mp. 159-160°C).
^{1}H-NMR ($CDCl_3$): δ 6.99 (s, 2H, H-3',4'), 6.97 (d, J = 3.7 Hz, 2H, H-4,4''), 6.90 (d, J = 3.7 Hz, 2H, H-3,3'') ppm.

N-*tert*-Butoxycarbonyl-2,5-di-(5-bromo-2-thienyl)pyrrole (11) A solution of 2,2,6,6-tetramethylpiperidine (1.52 g, 10.77 mmol) in THF (15 ml) was cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in *n*-hexane, 7.5 ml, 12.0 mmol) was added dropwise, after which the solution was stirred for

15 min at -70°C and 30 min at RT. Then the mixture was again cooled to -70°C and a solution of N-*tert*-butoxycarbonyl-2,5-di(2-thienyl)pyrrole[61] (1.66 g, 5.01 mmol) in THF (5 ml) was added gradually, followed by stirring for 90 min at this temperature. Finally, a solution of trimethylstannyl chloride (1.10 g, 5.50 mmol) in THF (5 ml) was added dropwise. Stirring was continued for another 4 h at -70°C and overnight at RT. The solvent was evaporated and Et_2O (30 ml) and water (30 ml) were added. The organic and aqueous layers were separated and the aqueous layer was extracted with Et_2O (2x20 ml). The combined organic fractions were dried ($MgSO_4$), filtered and concentrated resulting in pure N-*t*-BOC-2,5-di(5-trimethylstannyl-2-thienyl)pyrrole (3.16 g, 4.81 mmol, 96%). This compound was dissolved in THF (15 ml) and cooled to -70°C, blanketed by argon. NBS (1.73 g, 9.70 mmol) was added and the mixture was stirred at -70°C for 30 min and for another 18 h at 3°C. Then Na_2SO_3 (0.5 g) was added and the solvent was evaporated. CCl_4 (50 ml) was added and the mixture was stirred for 15 min. Finally, the mixture was filtered and concentrated to give **11** as a solid (2.24 g, 4.57 mmol, 95%). Mp.: 100-101°C.
^{1}H-NMR ($CDCl_3$): δ 7.00 (d, J = 3.8 Hz, 2H, H-3 (th)), 6.83 (d, J = 3.8 Hz, 2H, H-4 (th)), 6.30 (s, 2H, H-3,4 (pyr)), 1.31 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.8 (C=O), 135.9 (C-2 (th)), 129.6 (C-4 (th)), 128.0 (C-2,5 (pyr)), 127.6 (C-3 (th)), 114.4 (C-3,4 (pyr)), 112.1 (C-5 (th)), 85.0 (C-*ipso* (BOC)), 27.2 (C-methyl (BOC)) ppm. IR (KBr): 2972, 1748, 1488, 1420, 1368, 1300, 1254, 1135, 962, 790 cm^{-1}.

2-Bromo-5-methylthiophene (12)[59] A three-necked flask (50 ml) was charged with 2-methylthiophene (5.01 g, 51 mmol), Et_2O (4 ml) and 48% aqueous HBr solution (12 ml) and cooled to -20°C. 35% Aqueous H_2O_2 (5.01 g, 44.2 mmol) was added over 30 min, in which period the temperature was allowed to raised to +10°C. After complete addition of H_2O_2 the mixture was brought to RT and stirred for another 30 min. The layers were then separated and the aqueous phase was extracted with pentane (5 x 20 ml). The combined organic fractions were washed with brine (2 x 50 ml) and water (2 x 50 ml), dried ($MgSO_4$) and the solvent was evaporated. Finally, distillation resulted in pure **12** as a colorless oil (5.44 g, 30.7 mmol, 69%). Bp.: 42°C (12 mmHg).
^{1}H-NMR ($CDCl_3$): δ 6.82 (d, J = 3.6 Hz, 1H, H-3), 6.51 (dt, J = 3.5 and 0.8 Hz,1H, H-4), 2.42 (d, J = 0.8 Hz, 3H, H-methyl) ppm. ^{13}C-NMR ($CDCl_3$): δ 141.3 (C-5), 129.5 (C-3), 125.4 (C-4), 108.5 (C-2), 15.4 (C-methyl) ppm.

N-*tert*-Butoxycarbonyl-2,5-diphenylpyrrole (13) A Stille reaction between bromobenzene (0.71 g, 4.50 mmol) and **6** (1.83 g, 4.50 mmol) in toluene (25 ml) and aqueous Na_2CO_3 (1 M, 25 ml) in the presence of $Pd(PPh_3)_4$ (2 mol%), was performed as described for **4**. After 2 days this resulted in a dark mixture, which was subjected to work-up. Finally, column chromatography (40 g SiO_2, hexane : CH_2Cl_2 (2:1), R_f = 0.49) and subsequent recrystallization from ethanol, resulted in pure **13** as a white, crystalline solid (1.14 g, 3.56 mmol, 79%). Mp.: 120°C.
^{1}H-NMR ($CDCl_3$): δ 7.43-7.28 (m, 10H, H-phenyl), 6.23 (s, 2H, H-3,4), 1.17 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.8 (C=O), 136.2/134.1 (C-2,5/C-*ipso* (phenyl)), 128.8/127.8 (C-*ortho*/C-*meta*), 127.2 (C-*para*), 112.1 (C-3,4), 83.9 (C-q (BOC)), 27.1 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 290 nm. IR (KBr): 3073-2933, 1746, 1605, 1486, 1444, 1305, 1146, 643-701 cm^{-1}. GC-MS: 319 (M^+), 263, 219, 115, 57. FD-MS: calcd. 319.40; found 319.3.

13H: Thermal deprotection of the *t*-BOC groups was performed as described for **4H**. ^{1}H-NMR (THF-d_8): δ 10.40 (broad s, 1H, N-H), 7.63 (d, J = 7.4 Hz, 4H, H-*ortho*), 7.31 (t, J = 7.4 Hz, 4H, H-*meta*), 7.12 (t, J = 7.4 Hz, 2H, H-*para*), 6.51 (dd, J = 3.5 and 2.5 Hz, 2H, H-3,4) ppm. UV-Vis (CH_3CN): 328 nm.

N,N'-Di-*tert*-butoxycarbonyl-5,5'-diphenyl-2,2'-bipyrrole (14) A Stille reaction between **5** (0.310 g, 0.96 mmol) and **6** (0.408 g, 1.00 mmol) in toluene (6 ml) and aqueous Na_2CO_3 (1 M, 6 ml) in the presence of $Pd(PPh_3)_4$ (2 mol%), was performed as described for **4**. After work-up procedures a dark oil was obtained, which was purified by column chromatography (15 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.28). This resulted in pure **14** as a white solid (0.25 g, 0.52 mmol, 54%).
^{1}H-NMR ($CDCl_3$): δ 7.38-7.28 (m, 10H, H-phenyl), 6.27 (d, J = 3.2 Hz, 2H, H-3,3'/H-4,4'), 6.24 (d, J = 3.4 Hz, 2H, H-3,3'/H-4,4'), 1.25 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$) δ 149.3 (C=O), 136.6/134.6 (C-5,5'/C-*ipso* (phenyl)), 128.4/127.8 (C-*ortho*/C-*meta*), 128.1 (C-2,2'), 127.0 (C-*para*), 114.4 (C-4,4'), 112.6 (C-3,3'), 83.4 (C-q (BOC)), 27.4 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 295 nm. IR (KBr): 2973, 1741, 1370, 1307, 1157, 1122, 968, 851, 796, 752, 698 cm^{-1}.
14H: Thermal deprotection of the *t*-BOC groups was performed as described for **4H**. ^{1}H-NMR (THF-d_8): δ 10.33 (broad s, 2H, N-H), 7.56 (d, J = 7.4 Hz, 4H, H-*ortho*), 7.28 (t, J = 7.4 Hz, 4H, H-*meta*), 7.08 (t, J = 7.4 Hz, 2H, H-*para*), 6.48 (dd, J = 3.5 and 2.5 Hz, 2H, H-3,3'/H-4,4'), 6.37 (dd, J = 3.5 and 2.5 Hz, 2H, H-3,3'/H-4,4') ppm. UV-Vis (CH_3CN): 360 nm. IR (KBr): 3435, 1598, 1488, 1296, 1054, 757, 692, 508 cm^{-1}. FD-MS: calcd. 284.36; found 284.3.

N,N',N''-Tri-*tert*-butoxycarbonyl-5,5''-diphenyl-2,2':5',2''-terpyrrole (15) A Stille reaction between **6** (0.218 g, 0.54 mmol) and **2** (0.060 g, 0.25 mmol) in toluene (1 ml) and aqueous Na_2CO_3 (1 M, 1 ml) in the presence of $Pd(PPh_3)_4$, was performed as described for **4**. After work-up procedures a dark green solid was obtained. Purification by column chromatography (10 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.20) resulted in pure **15** (70 mg, 0.11 mmol, 43%).
^{1}H-NMR ($CDCl_3$): δ 7.40-7.30 (m, 10H, H-phenyl), 6.28 (s, 2H, H-3',4'), 6.26 (d, J = 3.4 Hz, 2H, H-3,3''/H-4,4''), 6.23 (d, J = 3.4 Hz, 2H, H-3,3''/H-4,4''), 1.34 (s, 9H, H-methyl (BOC')), 1.26 (s, 18H, H-methyl (BOC, BOC'')) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.2 (C=O (BOC, BOC'')), 149.0 (C=O (BOC')), 136.5/134.7 (C-5,5''/C-*ipso* (phenyl)), 128.7/127.7 (C-2,2''/C-2',5'), 128.3/127.8 (C-*ortho*/C-*meta*), 126.9 (C-*para*), 114.2/113.9 (C-3,3''/C-4,4''), 112.8 (C-3',4'), 83.3 (C-q (BOC, BOC'')), 82.8 (C-q (BOC')), 27.6 (C-methyl (BOC')), 27.4 (C-methyl (BOC, BOC'')) ppm. UV-Vis (CH_3CN): 301 nm.
15H: Thermal deprotection of the *t*-BOC groups was performed as described for **4H**. ^{1}H-NMR (THF-d_8): δ 10.23 (broad s, 2H, N-H and NH''), 10.12 (broad s, 1H, N-H'), 7.55 (m, 4H, H-*ortho*), 7.28 (m, 4H, H-*meta*), 7.08 (m, 2H, H-*para*), 6.47 (s, 2H, H-3',4'), 6.31 (m, 4H, H-3,3'', H-4,4'') ppm. UV-Vis (CH_3CN): 374 nm.

N,N',N'',N'''-Tetra-*tert*-butoxycarbonyl-5,5'''-diphenyl-2,2':5',2'':5'',2'''-quaterpyrrole (16) A Stille reaction between **6** (0.124 g, 0.304 mmol) and **7** (70 mg, 0.14 mmol) in toluene (2 ml) and aqueous Na_2CO_3 (1 M, 2 ml) in the presence of $Pd(PPh_3)_4$, was performed as described for **4**. After work-up procedures a dark oil was obtained. Purification by column chromatography (10 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.10) gave pure **16** as a brown solid (45 mg, 0.06 mmol, 39%).

^{1}H-NMR ($CDCl_3$): δ 7.38-7.26 (m, 10H, H-phenyl), 6.26 (d, J = 3.3 Hz, 2H, H-3,3‴/H-4,4‴), 6.22 (s, 4H, H-3′,4″, H-4′,3″), 6.19 (d, 2H, J = 3.3 Hz, H-3,3‴/H-4,4‴), 1.29 (s, 18H, H-methyl (BOC)), 1.24 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.3 (C=O), 148.9 (C=O), 136.4/134.8 (C-5,5‴, C-*ipso* (phenyl)), 128.7/128.3/127.6 (C-2,2‴/C-2′,5″/C-5′,2″), 128.8/127.7 (C-*ortho*/C-*meta*), 126.9 (C-*para*), 114.4/113.9/113.8/112.7 (C-3,3‴/C-4,4‴/C-3′,4″/C-4′,3″), 83.2 (C-q (BOC)), 82.8 (C-q (BOC)), 27.7 (C-methyl (BOC)), 27.4 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 299 nm.

16H: Thermal deprotection of the *t*-BOC groups was performed as described for **4H**. ^{1}H-NMR (THF-d_8): δ 10.21 (broad s, 2H, N-H), 10.09 (broad s, 2H, N-H), 7.56 (m, 4H, H-*ortho*), 7.28 (m, 4H, H-*meta*), 7.08 (m, 2H, H-*para*), 6.48/6.28 (2 x m, 2 x 4H, H-3,3‴, H-4,4‴, H-3′,4″, H-4′,3″) ppm. UV-Vis (CH_3CN): 373 nm.

2,5-Di(N-*tert*-butoxycarbonyl-5-phenyl-2-pyrrolyl)thiophene (17) A Stille reaction between **6** (0.4082 g, 1.005 mmol) and **8** (0.1219 g, 0.504 mmol) in toluene (2 ml) and aqueous Na_2CO_3 (1 M, 2 ml) in the presence of $Pd(PPh_3)_4$, was performed as described for **4**. After work-up procedures and column chromatography (40 g SiO_2, hexane : CH_2Cl_2 (1:1), R_f = 0.43), pure **17** was obtained as a red-brown glassy compound (0.0438 g, 0.10 mmol, 20%).

^{1}H-NMR ($CDCl_3$): δ 7.41-7.28 (m, 10 H, H-phenyl), 7.07 (s, 2H, H-3,4 (th)), 6.38 (d, J = 3.5 Hz, 2H, H-3 (pyr)), 6.24 (d, J = 3.5 Hz, 2H, H-4 (pyr)), 1.25 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.6 (C=O), 136.7/134.4/134.0 (C-2,5 (th)/C-*ipso* (phenyl)/C-5 (pyr)), 128.4/127.9 (C-*ortho*/C-*meta*), 127.8/127.2/127.0 (C-3,4 (th)/C-2 (pyr)/C-*para*), 113.9/112.1 (C-3 (pyr)/C-4 (pyr)), 83.4 (C-q (BOC)), 27.1 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 331 nm. IR (KBr): 2977, 1750, 1302, 1141, 842-698 cm^{-1}.

17H: Thermal deprotection of the *t*-BOC groups was performed as described for **4H**. ^{1}H-NMR (THF-d_8): δ 10.53 (broad s, 2H, N-H), 7.62 (d, J = 7.4 Hz, 4H, H-*ortho*), 7.32 (t, J = 7.4 Hz, 4H, H-*meta*), 7.13 (t, J = 7.4 Hz, 2H, H-*para*), 7.06 (s, 2H, H-3,4 (th)), 6.51 (dd, J = 3.5 and 2.5 Hz, 2H, H-3/H-4 (pyr)), 6.40 (dd, J = 3.5 and 2.5 Hz, 2H, H-3/H-4 (pyr)) ppm. UV-Vis (CH_3CN): 390 nm.

5,5′-Di(N-*tert*-butoxycarbonyl-5-phenyl-2-pyrrolyl)-2,2′-bithiophene (18) A Stille reaction between **9** (0.1530 g, 0.472 mmol) and **6** (0.4268 g, 1.051 mmol) in toluene (8 ml) and aqueous Na_2CO_3 (1 M, 8 ml) in the presence of $Pd(PPh_3)_4$, was performed as described for **4**. After work-up procedures, column chromatography (40 g SiO_2, hexane : CH_2Cl_2 (1:1), R_f = 0.27) and subsequent recrystallization from the same eluent, pure **18** was obtained as a red-brown crystalline solid (75 mg, 0.12 mmol, 24%). Mp.: 159°C.

^{1}H-NMR ($CDCl_3$): δ 7.41-7.30 (m, 10H, H-phenyl), 7.12/7.04 (2xd, J = 3.7 Hz, 4H, H-3/H-4 (th)), 6.39 (d, J = 3.5 Hz, 2H, H-3 (pyr)), 6.25 (d, J = 3.4 Hz, 2H, H-4 (pyr)), 1.24 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR($CDCl_3$): δ 149.6 (C=O), 137.2/137.0/134.0/133.4 (C-*ipso* (phenyl)/C-5 (pyr)/C-2,2′ (th)/C-5,5′ (th)), 128.4/128.2/128.0/127.3/123.3 (C-3,3′ (th)/C-4,4′ (th)/C-2 (pyr)/C-*ortho*/C-*meta*/C-*para*), 114.1/112.1 (C-3 (pyr)/C-4 (pyr)), 84.4 (C-q (BOC)), 27.2 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 364 nm. IR (KBr): 2978, 1751, 1295, 841-698 cm^{-1}.

18H: Thermal deprotection of the *t*-BOC groups was performed as described for **4H**. ^{1}H-NMR (THF-d_8): δ 10.55 (broad s, 2H, N-H), 7.62 (d, J = 7.4 Hz, 4H, H-*ortho*), 7.31 (t, J = 7.4 Hz, 4H, H-*meta*), 7.13 (t, J = 7.4 Hz, 2H, H-*para*), 7.12 (d, J = 3.8 Hz, 2H, H-3/H-4 (th)), 7.09 (d, J = 3.8 Hz, 2H, H-

3/H-4 (th)), 6.50 (dd, J = 3.5 and 2.5 Hz, 2H, H-3/H-4 (pyr)), 6.40 (dd, J = 3.5 and 2.5 Hz, H-3/H-4 (pyr)) ppm. UV-Vis (CH_3CN): 427 nm.

5,5''-Di(N-*tert*-butoxycarbonyl-5-phenyl-2-pyrrolyl)-2,2',5',2''-terthiophene (19) A Stille reaction between **6** (0.33g, 0.81 mmol) and **10** (0.16 g, 0.40 mmol) in toluene (2 ml) and aqueous Na_2CO_3 (1 M, 2 ml) in the presence of $Pd(PPh_3)_4$, was performed as described for **4**. After work-up procedures and column chromatography (20 g SiO_2, EtOAc : hexane (1:9), R_f = 0.30), pure **19** was obtained (60 mg, 0.08 mmol, 21%).

^{1}H-NMR ($CDCl_3$): δ 7.40-7.29 (m, 10H, H-phenyl), 7.11 (d, J = 3.7 Hz, 2H, H-3,3''/H-4,4''), 7.08 (s, 2H, H-3',4'), 7.05 (d, J = 3.7 Hz, 2H, H-3,3''/H-4,4''), 6.39 (d, J = 3.5 Hz, 2H, H-3 (pyr)), 6.24 (d, J = 3.4 Hz, 2H, H-4 (pyr)), 1.24 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.0 (C=O), 134.1, 130.9, 128.8, 128.7, 128.5, 128.1, 127.9, 127.4, 127.1, 124.4, 124.2, 123.4, 114.1/112.2 (C-3/C-4 (pyr)), 84.5 (C-q (BOC)), 27.2 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 419 nm.

19H: Thermal deprotection of the *t*-BOC groups was performed as described for **4H**. ^{1}H-NMR (THF-d_8): δ 10.57 (broad s, 2H, N-H), 7.62 (d, J = 7.4 Hz, 4H, H-*ortho*), 7.32 (t, J = 7.4 Hz, 4H, H-*meta*), 7.13 (m, 8H, H-*para*, H-3',4', H-3,3'', H-4,4''), 6.51 (dd, J = 3.5 and 2.5 Hz, 2H, H-3/H-4 (pyr)), 6.42 (dd, J = 3.5 and 2.5 Hz, H-3/H-4 (pyr)) ppm. UV-Vis (CH_3CN): 431 nm.

1,2-Di(N-*tert*-butoxycarbonyl-5-phenyl-2-pyrrolyl)benzene (20) Performing a Stille reaction as described for **4** between 1,2-dibromobenzene (0.238 g, 1.01 mmol) and **6** (0.818 g, 2.01 mmol) in toluene (5 ml) and aqueous Na_2CO_3 (1 M, 5 ml) with $Pd(PPh_3)_4$ (2 mol%), finally resulted in a dark oil. Purification by column chromatography (40 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.27) gave a colorless oil (0.2004 g, 0.36 mmol, 35%).

^{1}H-NMR ($CDCl_3$): δ 7.43-7.32 (m, 4H, *o*-phenylene unit), 7.32-7.22 (m, 10H, H-*o,m,p* (end-capped phenyl)), 6.13 (d, J = 3.3 Hz, 2H, H-3/H-4 (pyr)), 6.07 (d, J = 3.3 Hz, 2H, H-3/H-4 (pyr)), 1.12 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.2 (C=O), 135.8/135.0/134.8/134.7 (C-*ipso* (end-capped phenyl)/C-*ipso* (*o*-phenylene unit)/C-2/C-5), 130.0/128.8/128.3/127.6/126.9 (C-*o,m,p* (end-capped phenyl)/C-*o,m* (*o*-phenylene unit)), 113.0/112.4 (C-3/C-4), 83.1 (C-q (BOC)), 27.1 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 280 nm. IR (KBr): 2979, 1747, 1306, 1145, 978, 846-698 cm^{-1}.

1,3-Di(N-*tert*-butoxycarbonyl-5-phenyl-2-pyrrolyl)benzene (21) Performing a Stille reaction as described for **4** between 1,3-dibromobenzene (0.238 g, 1.01 mmol) and **6** (0.816 g, 2.01 mmol) in toluene (5 ml) and aqueous Na_2CO_3 (1 M, 5 ml) with $Pd(PPh_3)_4$ (2 mol%) as catalyst, finally resulted in a dark oil. Purification by column chromatography (40 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.49) gave a colorless oil (0.3045 g, 0.54 mmol, 54%).

^{1}H-NMR ($CDCl_3$): δ 7.47 (m, 1H, H-2 (*m*-phenylene unit)), 7.42-7.28 (m, 13 H, H-*o,m,p* (end-capped phenyl), C-4, C-5, C-6 (*m*-phenylene unit)), 6.26 (d, J = 3.4 Hz, 2H, H-3/H-4 (pyr)), 6.23 (d, J = 3.4 Hz, 2H, H-3/H-4 (pyr)), 1.18 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.8 (C=O), 136.3/136.1/134.4/133.9 (C-2/C-5/C-*ipso* (end-capped phenyl)/C-1,3 (*m*-phenylene unit)), 129.0/128.8/127.8/127.6/127.2 (C-*o,m,p* (end-capped phenyl)/C-2,4,5,6 (*m*-phenylene unit)), 112.3/112.2 (C-3/C-4 (pyr)), 83.9 (C-q (BOC)), 27.1 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 294 nm. IR (KBr): 2979, 1744, 1302, 1141, 846-699 cm^{-1}.

1,4-Di(N-*tert*-butoxycarbonyl-5-phenyl-2-pyrrolyl)benzene (22) A Stille reaction between 1,4-dibromobenzene (0.1180 g, 0.50 mmol) and **6** (0.4062 g, 1.00 mmol) in toluene (2 ml) and aqueous Na_2CO_3 (1 M, 2 ml) in the presence of $Pd(PPh_3)_4$, was performed as described for **4**. After work-up procedures, column chromatography (40 g SiO_2, hexane : CH_2Cl_2 (1:1), R_f = 0.39) and subsequent recrystallization from hexane, pure **22** was obtained as a slightly brown, crystalline solid (0.0421 g, 0.075 mmol, 15%). Mp.: 139°C.

^{1}H-NMR ($CDCl_3$): δ 7.43-7.28 (m, 14H, H-*o,m,p* (end-capped phenyl), H-2,3,5,6 (*p*-phenylene unit)), 6.28/6.25 (2xd, J = 3.4 and 3.5 Hz, 4H, H-3/H-4 (pyr)), 1.22 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 150.3 (C=O), 136.4/136.0/134.1/ 132.8 (C-*ipso* (end-capped phenyl)/C-1,4 (*p*-phenylene unit)/C-2/C-5), 128.8/128.1/127.8/127.2 (C-*o,m,p* (end-capped phenyl)/C-2,3,5,6 (*p*-phenylene unit)), 112.3/112.2 (C-3/C-4 (pyr)), 84.1 (C-q (BOC)), 27.1 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 310 nm. IR (KBr): 2980, 1751, 1303, 1144, 847-698 cm^{-1}. FD-MS: calcd. 560.82; found 560.6.

22H: Thermal deprotection of the *t*-BOC groups was performed as described for **4H**. ^{1}H-NMR (THF-d_8): δ 10.40 (broad s, 2H, N-H), 7.65 (s, 4H, H-2,3,5,6 (*p*-phenylene unit)), 7.63 (d, J = 7.4 Hz, 4H, H-*ortho* (end-capped phenyl)), 7.31 (t, J = 7.4 Hz, 4H, H-*meta* (end-capped phenyl)), 7.12 (t, J = 7.4 Hz, 2H, H-*para* (end-capped phenyl)), 6.54 (dd, J = 3.5 Hz, J= 2.5 Hz, H-3,4 (pyr)) ppm. UV-Vis (CH_3CN): 371 nm.

1,3,5-Tri(N-*tert*-butoxycarbonyl-5-phenyl-2-pyrrolyl)benzene (23) Performing a Stille reaction as described for **4** between 1,3,5-tribromobenzene (0.162 g, 0.51 mmol) and **6** (0.614 g, 1.51 mmol) in toluene (5 ml) and aqueous Na_2CO_3 (1 M, 5 ml) with $Pd(PPh_3)_4$ (2 mol%) as catalyst, resulted in a dark oil. Purification by column chromatography (40 g SiO_2, CH_2Cl_2 : hexane (1:2), R_f = 0.13), finally gave **23** as a slightly brown oil (0.1134 g, 0.14 mmol, 27%).

^{1}H-NMR ($CDCl_3$): δ 7.43–7.26 (m, 15H, H-*o,m,p*), 7.18-7.13 (s, 3H, H-2,4,6 (central phenylene unit)), 6.25 (d, J = 3.4 Hz, 3H, H-3/H-4 (pyr)), 6.22 (d, J = 3.4 Hz, 3H, H-3/H-4 (pyr)), 1.20 (s, 27H, H-methyl (BOC)) ppm.

4,4'-Di(N-*tert*-butoxycarbonyl-5-phenyl-2-pyrrolyl)biphenyl (24) A Stille reaction between 4,4'-dibromobiphenyl (0.1511 g, 0.484 mmol) and **6** (0.4065 g, 1.001 mmol) in toluene (2 ml) and aqueous Na_2CO_3 (1 M, 2 ml) in the presence of $Pd(PPh_3)_4$, was performed as described for **4**. After work-up procedures, column chromatography (40 g SiO_2, hexane : CH_2Cl_2 (3:2), (R_f = 0.16) and subsequent recrystallization from the same eluent, pure **24** was isolated as a slightly brown, crystalline solid (0.065 g, 0.10 mmol, 21%).

^{1}H-NMR ($CDCl_3$): δ 7.67 (d, J = 8.4 Hz, 4H, H-2 (biphenyl)), 7.49 (d, J = 8.3 Hz, 4H, H-3 (biphenyl)), 7.45-7.31 (m, 10H, H-*o,m,p* (end-capped phenyl)), 6.31/6.27 (2xd, J = 3.4 Hz, 4H, H-3/H-4 (pyr)), 1.20 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 150.3 (C=O), 139.5/136.5/135.9/134.1/133.1 (C-2 (pyr)/C-5 (pyr)/C-1 (biphenyl)/C-4 (biphenyl)/C-ipso (end-capped phenyl)), 129.1/126.4/128.8/127.8/127.2 (C-2 (biphenyl)/C-3 (biphenyl)/C-*o,m,p* (end-capped phenyl)), 112.4/112.3 (C-3/C-4 (pyr)), 84.1 (C-q (BOC)), 27.1 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 323 nm. IR (KBr): 2973, 1748, 1310, 1145, 847-699 cm^{-1}.

24H: Thermal deprotection of the *t*-BOC groups was performed as described for **4H**. ^{1}H-NMR (THF-d_8): δ 10.46 (broad s, 2H, N-H), 7.74 (d, J = 2.0 Hz, 4H, H-2 (biphenyl)), 7.72 (d, J = 2.0 Hz, 4H, H-3

(biphenyl)), 7.63 (d, J = 7.4 Hz, 4H, H-*ortho*), 7.33 (t, J = 7.4 Hz, 4H, H-*meta*), 7.13 (t, J = 7.4 Hz, 2H, H-*para*), 6.59 (dd, J = 3.5 and 2.5 Hz, H-3/H-4 (pyr)), 6.55 (dd, J = 3.5 and 2.5 Hz, H-3/H-4 (pyr)) ppm. UV-Vis (CH_3CN): 371 nm.

N-*tert*-Butoxycarbonyl-2,5-di[2{5(N-*tert*-butoxycarbonyl)-5-phenyl-2-pyrrolyl)thienyl}]pyrrole (25)[64] A Stille reaction between **6** (0.486 g, 1.005 mmol) and **11** (0.243 g, 0.497 mmol) in toluene (2 ml) and aqueous Na_2CO_3 (1 M, 2 ml) in the presence of $Pd(PPh_3)_4$, was performed as described for **4**. After work-up procedures, column chromatography (40 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.25) and recrystallization from hexane, pure **25** was obtained as a solid (58 mg, 0.07 mmol, 14%). Mp.: 122-123°C.

^{1}H-NMR ($CDCl_3$): δ 7.41-7.28 (m, 10H, H-phenyl), 7.08/7.03 (2xd, J = 3.7 Hz, 4H, H-3, H-4 (th)), 6.37 (d, J = 3.6 Hz, 2H, H-3 (outer pyr)), 6.35 (s, 2H, H-3,4 (inner pyr)), 6.23 (d, J = 3.3 Hz, 2H, H-4 (outer pyr)), 1.36 (s, 9H, H-methyl (inner BOC)), 1.22 (s, 18H, H-methyl (outer BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.5 (C=O (outer BOC)), 149.4 (C=O (inner BOC)), 136.7, 134.4, 134.3, 134.0, 128.7, 128.3, 128.3, 127.8, 127.2, 127.0, 126.6, 113.9/113.6/112.1 (C-β (pyr)), 84.6 (C-q (inner BOC)), 84.2 C-q (outer BOC)), 27.2 (C-methyl (inner BOC)), 27.1 (C-methyl (outer BOC)) ppm. UV-Vis (CH_3CN): 346 nm. IR (KBr): 2978, 1750, 1300, 1141, 842-698 cm^{-1}.

N-*tert*-Butoxycarbonyl-2-(5-methyl-2-thienyl)pyrrole (26) Performing a Stille reaction as described for **4** between **3** (1.0158 g, 3.08 mmol) and **12** (0.5411 g, 3.06 mmol) in toluene (12 ml) and aqueous Na_2CO_3 (1 M, 12 ml) with $Pd(PPh_3)_4$ (2 mol%), resulted in a dark oil. Purification by column chromatography (40 g SiO_2, CH_2Cl_2 : hexane (1:2), R_f = 0.39), finally gave **26** as a slightly green oil (0.340 g, 1.29 mmol, 42%).

^{1}H-NMR ($CDCl_3$): δ 7.32 (dd, J = 3.9 and 2.3 Hz, 1H, H-5 (pyr)), 6.83 (d, J = 3.8 Hz, 1H, H-3 (th)), 6.64 (dt, 1H, H-4 (th)), 6.26 (dd, J = 3.9 and 2.3 Hz, 1H, H-3 (pyr)), 6.18 (t, J = 3.7 Hz, 1H, H-4 (pyr)), 2.47 (s, 3H, H-methyl), 1.43 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.9 (C=O), 140.0 (C-5 (th)), 132.3 (C-2 (pyr)), 127.2 (C-2 (th)), 124.5/122.7 (C-3 (th)/C-5 (pyr)), 116.0 (C-3 (pyr)), 110.4 (C-4 (pyr)), 83.5 (C-q (BOC)), 27.6 (C-methyl (BOC)), 15.2 (C-methyl) ppm.

1,3-Di(N-*tert*-butoxycarbonyl-2-pyrrolyl)benzene (27) Performing a Stille reaction as described for **4** between **3** (5.00 g, 17.48 mmol) and 1,3-dibromobenzene (2.06 g, 8.74 mmol) in toluene (60 ml) and aqueous Na_2CO_3 (1 M, 60 ml) with $Pd(PPh_3)_4$ (2 mol%), resulted in a dark oil after 72 h. Purification by column chromatography (150 g SiO_2, CH_2Cl_2 : hexane (1:3 to 2:1), R_f (2:1) = 0.33), finally yielded **27** as a slightly pink oil (1.81 g, 4.43 mmol, 51%).

^{1}H-NMR ($CDCl_3$): δ 7.35 (dd, J = 3.4 and 1.8 Hz, 2H, H-5 (pyr)), 7.33-7.25 (m, 4H, H-2,4,5,6 *m*-phenylene unit), 6.23 (t, J = 3.4 Hz, 2H, H-4), 6.20 (dd, J = 3.5 and 1.8 Hz, 2H, H-3), 1.36 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.3 (C=O), 134.7/133.7 (C-1,3 (*m*-phenylene unit), C-2 (pyr)), 129.9/128.0/126.6 (C-1,3,4 (*m*-phenylene unit)), 122.5 (C-5 (pyr)), 114.3/110.5 (C-3/C-4 (pyr)), 83.5 (C-q (BOC)), 27.5 (C-methyl (BOC)) ppm.

(N.B. N-*t*-BOC-2-(3-tolyl)pyrrole (1.27 g, 3.93 mmol, 45%) was isolated as a by-product during column chromatography; ^{1}H-NMR ($CDCl_3$): δ 7.35 (dd, 1H, H-5 (pyr)), 7.23-7.08 (m, 4H, H-2,4,5,6), 6.22 (t, 1H, H-4), 6.18 (dd, 1H, H-3), 2.36 (s, 3H, H-methyl), 1.34 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.4 (C=O, 136.8/135.1/134.3 (C-2 (pyr)/C-1/C-3), 129.9/127.8/127.4/126.2/

122.3 (C-5 (pyr))/C-2/C-4/C-5/C-6), 114.1 (C-3 (pyr)), 110.4 (C-4 (pyr)), 83.3 (C-q (BOC)), 27.5 (C-methyl (BOC)), 21.3 (C-methyl) ppm).

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Chapter 3

WELL-DEFINED AND FUNCTIONAL OLIGOPYRROLES: STUDIES TOWARD FUTURE APPLICATIONS

Abstract: *Several well-defined and functional oligopyrroles are synthesized by the Stille reaction and investigated for their specific properties. A series of N-t-BOC-protected D-π-A oligopyrroles shows surprising nonlinear optical behavior when investigated with Hyper Rayleigh Scattering. Going from one to three pyrrole units inserted between a 4-nitrophenyl and a 4-methoxyphenyl group, the UV-Vis absorptions almost remain unaltered, whereas the β-values increase significantly. A D-π-A oligomer with a bithienyl spacer shows an even higher β-value. N-Dodecyl-2,5-di{2[5(N-dodecyl-5-phenyl)pyrrolyl]thienyl}pyrrole, also prepared by a sequence of functionalization and Stille reactions, is investigated by scanning tunnelling microscopy in order to study its structural characteristics. Physisorbed on a graphite surface, these molecules form highly ordered monolayers consisting of couples forming linear aromatic 'backbones'. Finally, the redox properties of two series of oligopyrroles, being diphenyl-α-oligopyrroles (Ph-p$_n$-Ph) and di(phenylpyrrolyl)-α-oligothiophenes (Ph-p-t$_n$-p-Ph), are investigated. In case of the first series, a decrease of the first and the second oxidation potential is observed going from one to four pyrrole units; however, in case of the oligothiophene series, the first oxidation potential unexpectedly increases going from one to three thiophene units, whereas the second oxidation potential decreases.*

3.1 *(Nonlinear) optical properties of D-π-A substituted oligopyrroles*

3.1.1 *Introduction*

Over the past 15 years there has been a growing interest in the design and synthesis of new organic molecules with large second order molecular nonlinearities for applications in optical signal processing, optical computing and telecommunications.[1-6] Many of these so-called nonlinear optical (NLO) materials, which possess the ability to double the frequency of light, are donor-acceptor substituted π-conjugated molecules (D-π-A molecules) such as functionalized benzenes, stilbenes, azobenzenes and acetylenes.[3-8] More recently, also extended π-conjugated systems such as oligo- and polyenes, -phenylenes and -(phenylene

vinylene)s[9-11], as well as aliphatic polymers with NLO chromophores in the side chains[12,13], have been prepared and studied for their second order nonlinear hyperpolarizabilities (β).

A special class of NLO materials are heteroaromatic compounds.[14-16] Here, by far, most attention has been paid to oligo- and polythiophenes because of the availability of synthetic routes toward these systems.[17-23] Hitherto, however, no experimental data have been reported on D-π-A molecules based on oligo- and/or polypyrroles, simply because the synthetic strategies toward these systems are not at hand. The only data known are those of Morley who reported on the *calculated* hyperpolarizabilities of polythiophene, polyfuran and polypyrrole derivatives[24]; he predicted the largest values for polythiophenes, followed by polypyrroles and the smallest values for polyfurans (figure 3.1).

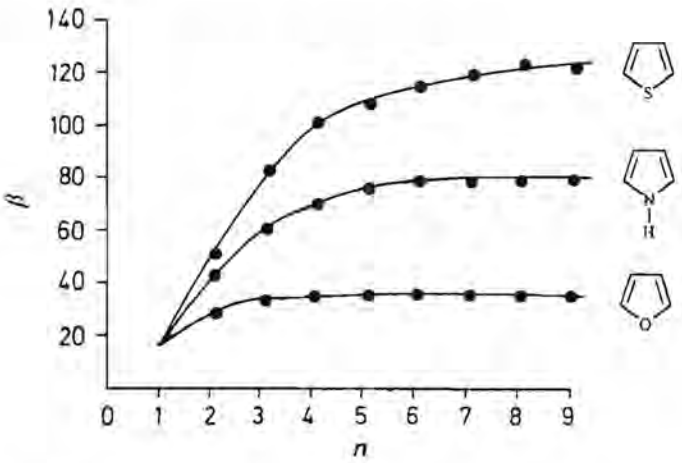


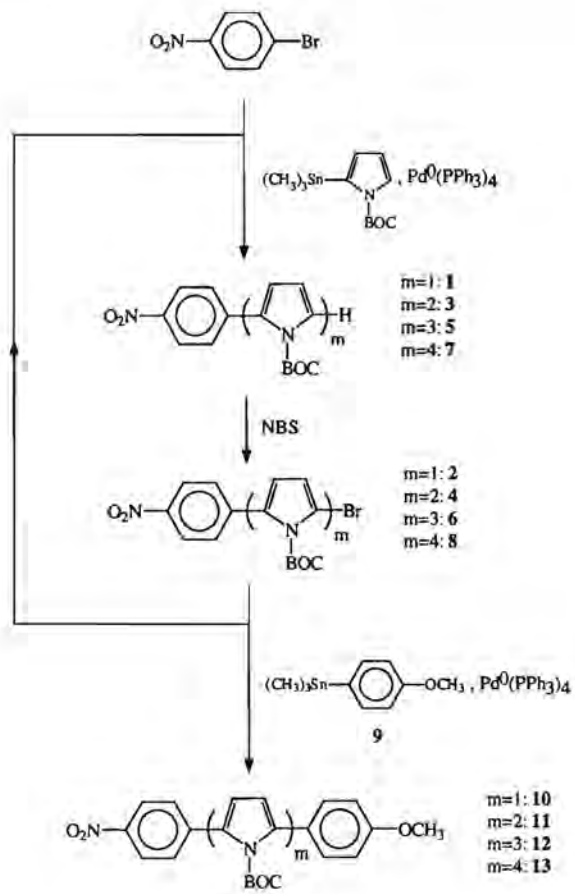
Figure 3.1: *Effect of increasing chain length (n) on the calculated hyperpolarizability (β) of polyheteroaromatics Me_2N-$[Ar]_n$-NO_2.*[24]

In order to study the (nonlinear) optical properties of NLO materials based on pyrrole, we have applied the Stille reaction for the synthesis of the first series of D-π-A oligopyrroles. Since the mechanistic studies (Chapter 2) suggested the feasibility to prepare donor and acceptor substituted pyrrole derivatives, the step to push-pull molecules was easily imagined. Performing a repetitive sequence of functionalization and Stille reactions resulted in four D-π-A oligomers, which were subsequently investigated by UV-Vis spectroscopy and Hyper Rayleigh Scattering. From these studies it appeared that the hyperpolarizability values of these systems are surprisingly high.

3.1.2 *Synthesis and (nonlinear) optical properties of a series of N-t-BOC-protected D-π-A oligopyrroles*

3.1.2.1 *Synthesis and characterization*

The synthesis of the D-π-A oligopyrroles is based on the Pd-catalyzed cross coupling reaction between an organostannane and an aryl halide, which was discussed extensively in Chapter 2. Applying the knowledge, obtained from the mechanistic studies, that the reactivity of an aryl bromide increases with the introduction of an electron withdrawing substituent[25-28], we used the reaction sequence as outlined in scheme 3.1.



Scheme 3.1: *Synthesis of four D-π-A oligopyrroles by a repetitive sequence of functionalization and Stille reactions.*

N-*t*-BOC-2-(4-nitrophenyl)pyrrole **1** was prepared by the Stille reaction between 4-bromo-1-nitrobenzene and N-*t*-BOC-2-trimethylstannylpyrrole[29]. By performing this coupling reaction in the two-phase system of toluene and aqueous Na_2CO_3 (1 M) with 2 mol% of $Pd^0(PPh_3)_4$ as catalyst, **1** was isolated as a yellow solid in 53% yield. Bromination of **1** using standard bromination conditions (NBS, THF, -70°C), resulted in N-*t*-BOC-2-bromo-5-(4-nitrophenyl)pyrrole **2** in quantitative yield. This compound was then coupled with N-*t*-BOC-2-trimethylstannylpyrrole using the same conditions as described for the synthesis of **1**. The resulting compound, N,N'-di-*t*-BOC-5-(4-nitrophenyl)-2,2'-bipyrrole **3** (53% yield), was subsequently brominated at the free α-pyrrolyl position, yielding N,N'-di-*t*-BOC-5'-bromo-5-(4-nitrophenyl)-2,2'-bipyrrole **4** in 99%. Repetition of this sequence of Stille reaction-bromination steps, gave the oligomers **5-8** (**5**: 24%, **6**: 98%, **7**: 48%, **8**: 92%). A final Stille reaction between the α-brominated species **2**, **4**, **6** and **8**, and 4-trimethylstannylanisole **9** (prepared from 4-bromoanisole using *n*-BuLi and trimethylstannyl chloride), afforded four D-π-A oligopyrroles **10-13**, which, after extensive purification (column chromatography and recrystallization), were isolated in moderate yields (20-47%). During the Stille reactions it was observed that the reactivity of the halide decreased by increasing the number of pyrrole units. This is due to the decreasing activating influence of the nitro substituent, resulting in longer reaction times. All compounds were fully characterized by NMR (^1H and ^{13}C), UV-Vis, IR and/or HR-MS spectroscopy.

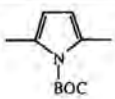
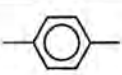
3.1.2.2 *(Nonlinear) optical properties*

Table 3.1 shows the optical and nonlinear optical properties of the oligomers prepared above. The latter were measured by means of Hyper Rayleigh Scattering (HRS) in chloroform with *p*-nitroaniline as reference.[30] A Nd:YAG laser at λ = 1064 nm provided the fundamental beam and the second harmonic (SH) was generated at λ = 532 nm, from which the molecular hyperpolarizability, β, was determined. The four D-π-A oligomers **10-13** all show three absorption maxima in the UV-Vis spectra (figure 3.2). The first one, at ~240 nm, is a transition that is observed in every pyrrole derivative, and that does not shift with the number of pyrrole units. The second absorption maximum ($\lambda_{max,2}$) is situated at ~285 nm and corresponds to the π–π^* transition of the N-*t*-BOC protected diphenyl-α-oligopyrrole part (Ph-p_n-Ph; figure 3.3). The third absorption maximum ($\lambda_{max,3}$), situated at ~365 nm, is most probably the charge transfer (CT) transition of the 2-(4-nitrophenyl)pyrrolyl part (O_2N-Ph-p). Going to more extended oligomers, $\lambda_{max,2}$ shows a bathochromic shift of 28 nm, indicating that conjugation does not increase significantly. The latter is due to the presence of the bulky *tert*-butoxycarbonyl groups, which prevents the system to become coplanar. $\lambda_{max,3}$ even undergoes a slight hypsochromic shift (13 nm) going from **10** to **13** (figure 3.3). The extinction coefficients (ε) of the π-π^* transition increase going to higher oligomers, whereas those of

the charge transfer transition hardly change. Furthermore, the extinction coefficient at 532 nm, being the wavelength at which the SH signal is measured, is very small and nearly constant in all four cases.

Table 3.1: *Optical (λ_{max}) and nonlinear optical (β) properties of D-π-A oligopyrroles in $CHCl_3$ (n.m. = not measured).*

	$\lambda_{max,2}$ (nm, ε)	$\lambda_{max,3}$ (nm, ε)	β (10^{-30} esu)	ε at 532 nm ($l.mol^{-1}.cm^{-1}$)
O_2N-Ph-p (**1**)	245 (1.02 x 10^4)	345 (1.03 x 10^4)	55	0.010 x 10^4
O_2N-Ph-p-p (**3**)	255 (1.20 x 10^4)	364 (1.28 x 10^4)	60	0.027 x 10^4
O_2N-Ph-p-Ph-OCH_3 (**10**)	269 (1.42 x 10^4)	376 (1.29 x 10^4)	82	0.026 x 10^4
O_2N-Ph-p-p-Ph-OCH_3 (**11**)	286 (1.66 x 10^4)	366 (1.36 x 10^4)	177	0.056 x 10^4
O_2N-Ph-p-p-p-Ph-OCH_3 (**12**)	294 (1.84 x 10^4)	364 (1.24 x 10^4)	277	0.039 x 10^4
O_2N-Ph-p-p-p-p-Ph-OCH_3 (**13**)	297 (n.m.)	363 (n.m.)	n.m.	n.m.
p-Ph-OCH_3 (**14**)	275 (0.81 x 10^4)	-	< 30	0.008 x 10^4

p =  ; Ph = 

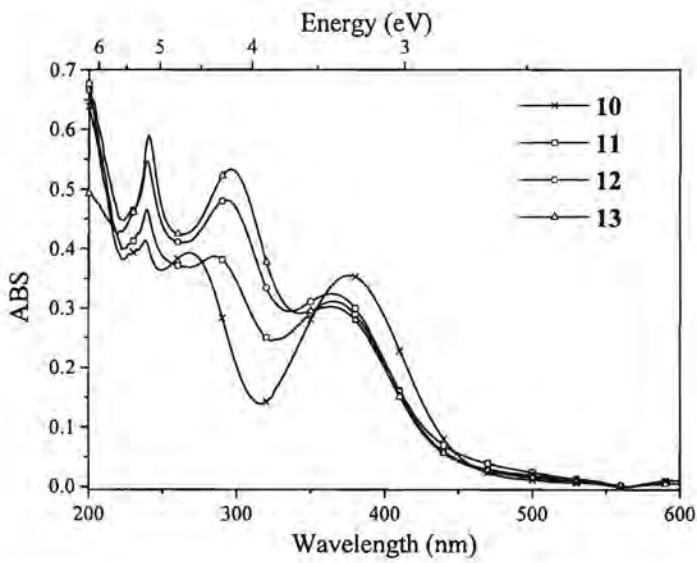


Figure 3.2: *UV-Vis absorption spectra of the N-t-BOC protected D-π-A oligopyrroles **10-13**.*

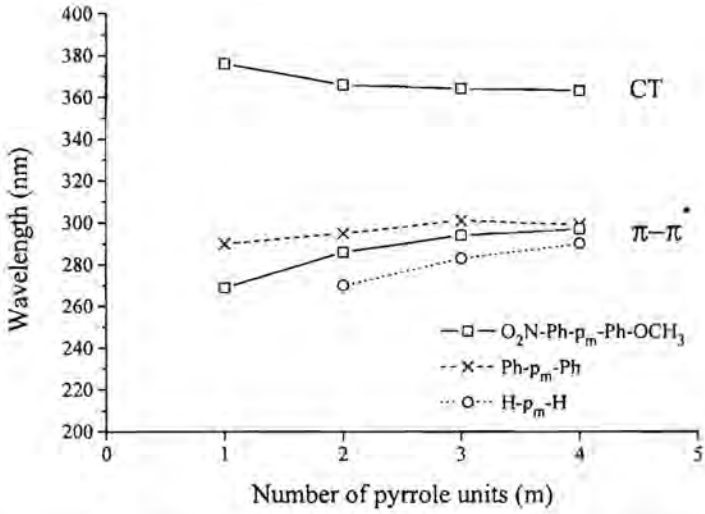


Figure 3.3: *UV-Vis absorption data of three series of N-t-BOC protected oligopyrroles, being O_2N-Ph-p_m-Ph-OCH_3 (m = 1-4), Ph-p_m-Ph (m = 1-4)[31] and H-p_m-H (m = 2-4)[32] (CT = charge transfer transition).*

HRS-measurements reveal that, although the linear optical data in this series of oligomers are quite similar, the hyperpolarizability (β) values increase significantly (82, 177 and 277 x 10^{-30} esu for **10**, **11** and **12**, respectively). In case of **13** we were not able to obtain a valid β-value since the isolated amount of this oligomer was too small.

The following explanation is suggested for this surprising nonlinear optical behavior, which was also, although far less pronounced, observed by Zyss *et al.* for series of oligophenylenes.[11,33,34] Surveying the experimental data in table 3.1, it appears that only the π–π^* transitions follow the increase of the hyperpolarizability values to some extent; the position of the absorption maximum slightly increases (25 nm going from **10** to **12**), whereas the corresponding extinction coefficients increase quite significantly (from 1.42 x 10^4 to 1.84 x 10^4 $l.mol^{-1}.cm^{-1}$). This observation leads to the assumption that it might not just be the highest wavelength transition (in this case the charge transfer transition) that determines the value of the hyperpolarizability, but that lower wavelength transitions (in this case the π–π^* transition) also contribute substantially to this value. In other words, a simple two-level model to describe these nonlinear optical data is no longer sufficient; at least a three-level model is required.

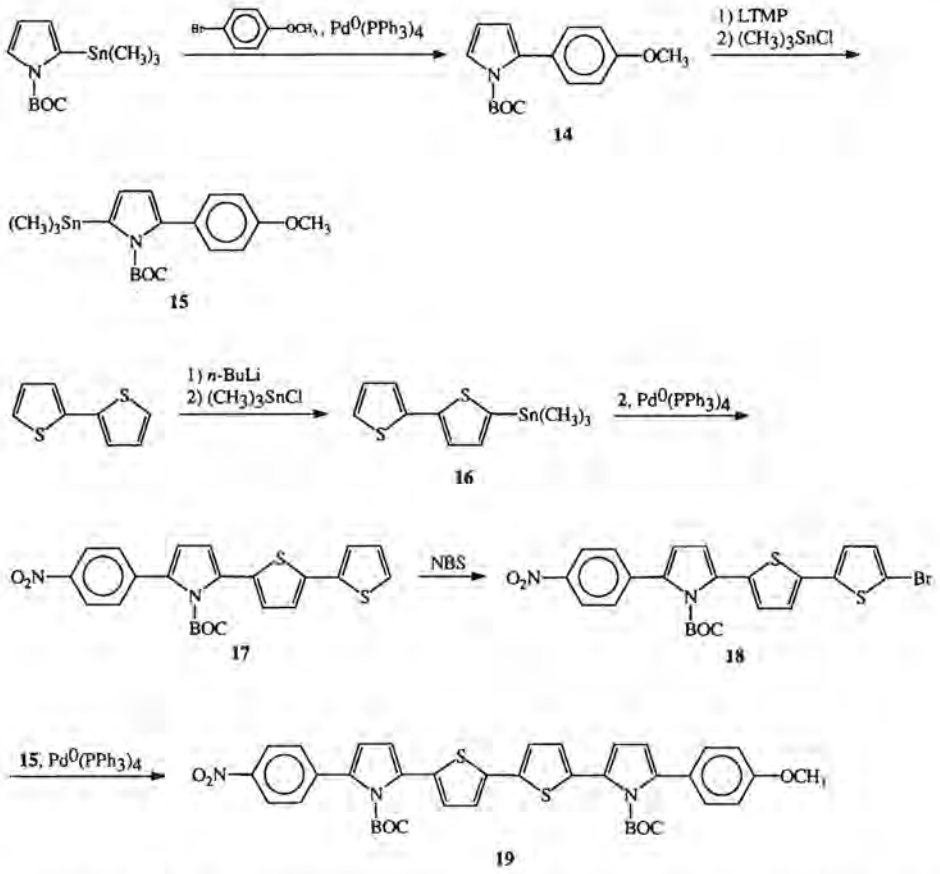
If this assumption is correct, it should be possible to increase the hyperpolarizability by shifting the π–π^* transition to higher wavelength. In order to check this hypothesis, we designed and constructed a molecule that we expected to have a much higher π–π^* transition. This D-π-A oligomer, 5-{N-*t*-BOC-2''-[5''(4-methoxyphenyl)]pyrrolyl}-5'-{N-*t*-BOC-2'''-

[5'''(4-nitrophenyl)]pyrrolyl}-2,2'-bithiophene **19**, is more coplanar due to the bithienyl spacer and, therefore, exhibits a π–π^* transition around 365 nm (the absorption maximum of the aromatic skeleton, being Ph-p-t_2-p-Ph[35], is located at 364 nm in CH_3CN). It is expected that **19** only shows one absorption band, consisting of both transitions, while its β-value is expected to be significantly higher.

3.1.3 *Synthesis and (nonlinear) optical properties of 5-{N-t-BOC-2''-[5''(4-methoxyphenyl)]pyrrolyl}-5'-{N-t-BOC-2'''-[5'''(4-nitrophenyl)]pyrrolyl}-2,2'- bithiophene*

3.1.3.1 *Synthesis and characterization*

Analogous to the four D-π-A oligopyrroles **10-13**, the Stille reaction was applied for the synthesis of 5-{N-*t*-BOC-2''-[5''(4-methoxyphenyl)]pyrrolyl}-5'-{N-*t*-BOC-2'''-[5'''(4-nitrophenyl)]pyrrolyl}-2,2'-bithiophene (**19**) (scheme 3.2). First, N-*t*-BOC-2-(4-methoxyphenyl)pyrrole **14** was prepared from N-*t*-BOC-2-trimethylstannylpyrrole[29] and 4-bromoanisole using standard Stille reaction conditions. After isolation by column chromatography (48% yield), **14** was directly stannylated at the free α-pyrrolyl position using LTMP and trimethylstannyl chloride, to give N-*t*-BOC-2-(4-methoxyphenyl)-5-trimethylstannylpyrrole **15** in 96% yield. The central part, 5-trimethylstannyl-2,2'-bithiophene **16**, was prepared from 2,2-bithiophene using *n*-BuLi and trimethylstannyl chloride (66% yield). Subsequent coupling with N-*t*-BOC-2-bromo-5-(4-nitrophenyl)pyrrole **2** resulted in N-*t*-BOC-2-(5-[2,2'-bithienyl])-5-(4-nitrophenyl)pyrrole **17** (55% yield), which was then brominated with NBS in DMF at RT. Unfortunately, bromination did not only occur at the α-thienyl position but also at the β-position of the pyrrole unit; this is due to the high temperature at which **17** is brominated. However, after column chromatography and recrystallization, N-*t*-BOC-2-(5'-bromo-5-[2,2'-bithienyl])-5-(4-nitrophenyl)pyrrole **18** could be isolated in 43% yield. A final Stille reaction between **15** and **18** resulted in the desired D-π-A-oligopyrrole **19** (34% yield). All isolated compounds were fully characterized by NMR (^{1}H and ^{13}C), UV-Vis, IR and/or HR-MS spectroscopy.



Scheme 3.2: *Synthesis of D-π-A oligopyrrole **19** by a sequence of functionalization and Stille reactions.*

3.1.3.2 *(Nonlinear) optical properties*

Figure 3.4 shows the optical (UV) and nonlinear optical (β) properties of oligomer **19**. Only one absorption maximum is observed at 378 nm ($\varepsilon = 3.11 \times 10^4$ l.mol^{-1}.cm^{-1}; $\varepsilon_{532} = 0.053 \times 10^4$l.mol^{-1}cm^{-1}), indicating that the π–π^* transition has indeed shifted underneath the charge transfer transition. Furthermore, the β-value, 440 x 10^{-30} esu, is much higher than for all former molecules. This β-value clearly indicates that the abovementioned hypothesis, which states that both the π–π^* and the charge transfer transition contribute to the hyperpolarizability, is correct.

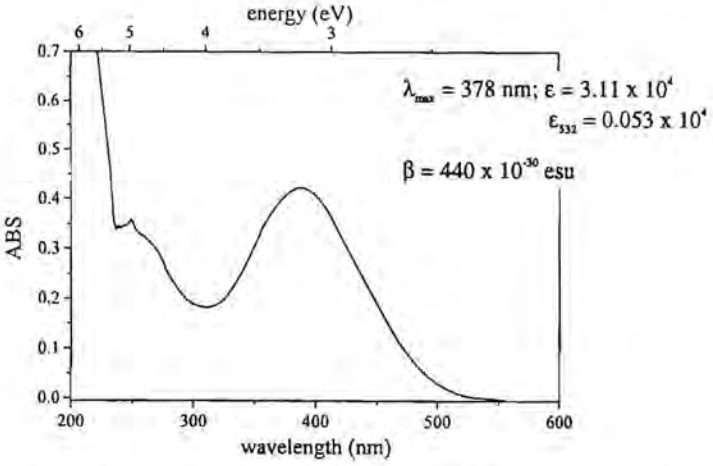


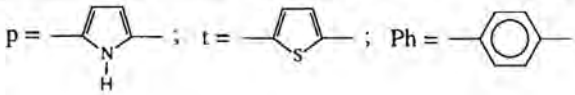
Figure 3.4: *Optical and nonlinear optical properties of D-π-A oligomer* ***19****.*

3.1.4 *Hyperpolarizability measurements on deprotected D-π-A oligopyrroles.*

The *t*-BOC groups of some oligomers were thermally removed as described in Chapter 2 (heating for 20-30 min at 190°C under inert atmosphere). The optical and nonlinear optical properties of the resulting deprotected analogs, which were measured by the same methods and under the same conditions as applied for the *t*-BOC protected derivatives, are listed in table 3.2.

Table 3.2: *Optical (λ_{max}) and nonlinear optical (β) properties of some deprotected oligomers in $CHCl_3$ (n.m. = not measured).*

	$\lambda_{max,2}$(nm)	$\lambda_{max,3}$ (nm)	β (10^{-30} esu)
O_2N-Ph-p (**1H**)	250	374	n.m.
O_2N-Ph-p-p (**3H**)	292	451	n.m.
O_2N-Ph-p-Ph-OCH_3 (**10H**)	295	431	450
O_2N-Ph-p-p-Ph-OCH_3 (**11H**)	328	479	1390
O_2N-Ph-p-p-p-Ph-OCH_3 (**12H**)	355	496	n.m.
O_2N-Ph-t-Ph-OCH_3 [36]	295	400	320



The UV-Vis spectra of the deprotected oligomers show substantial red shifts for the π–π^* and the charge transfer absorption maxima due to increased coplanarity and, thus, increased π-conjugation (figure 3.5). Furthermore, the β-values of the deprotected pyrrole derivatives **10H** and **11H** are much higher compared to their N-*t*-BOC protected analogs. Once more, this demonstrates the important contribution of conjugation to the hyperpolarizability. However, in case of **11H** the extinction coefficient at 532 nm is quite significant, which results in a large resonance enhancement of β. In case of **10H** the extinction coefficient at 532 nm has a value that is comparable with those of N-*t*-BOC protected oligomers.

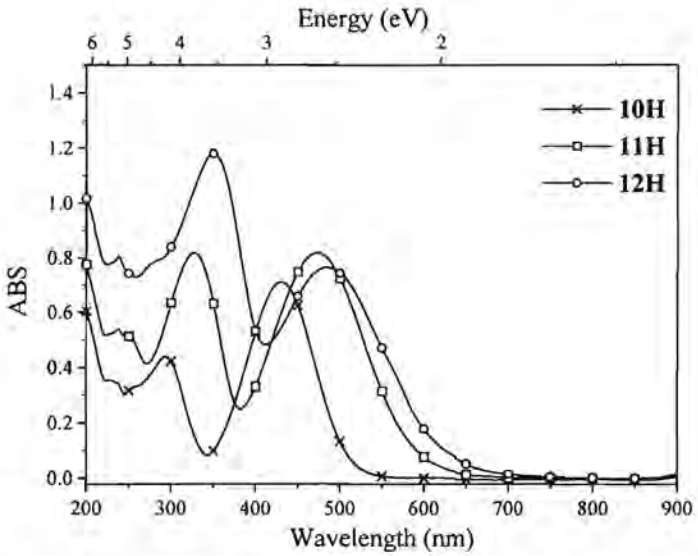
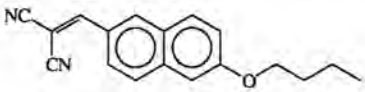


Figure 3.5: *UV-Vis absorption spectra of the deprotected D-π-A oligopyrroles **10H-12H**.*

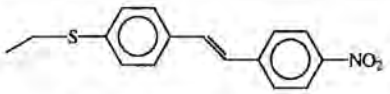
The availability of **10H** also opens the way to compare the optical and nonlinear optical properties of this compound with those of its thiophene analog (O_2N-Ph-t-Ph-OCH_3)[36]. The UV-Vis data of the latter also show two absorption maxima in $CHCl_3$ (295 and 400 nm), while hyperpolarizability measurements, performed under exactly the same conditions, give a β-value of 320 x 10^{-30} esu. This value is lower than that for **10H**, which is in agreement with the optical data (π–π^* transitions are identical, whereas the charge transfer transition of **10H** is 31 nm higher). However, these observations are in contradiction with the calculations of Morley who predicted the highest β-value for the thiophene derivative.[24]

3.1.5 *Conclusions*

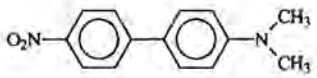
The knowledge obtained in Chapter 2, that an electron-withdrawing substituent at the aryl halide has a strong and positive influence on the proceeding of a Stille coupling reaction, has been applied to the synthesis of the first D-π-A oligopyrroles. After a repetitive sequence of functionalization and Stille reactions, a series of oligomers with one to four pyrrole units between a MeO-phenyl donor and a O_2N-phenyl acceptor side was isolated in moderate yields. Optical measurements showed two important absorption maxima for all four oligomers; the first one, situated at ~285 nm, corresponds to the π–π^* transition of the N-*t*-BOC protected diphenyl-α-oligopyrrole part (Ph-p_n-Ph), while the second one, situated at ~365 nm, was attributed to the charge transfer transition. Although the positions of both absorption maxima hardly shift going from small to larger oligomers, nonlinear optical measurements (obtained by Hyper Rayleigh Scattering) do show a significant increase for the β-values up to the trimer (82, 177 and 277 x 10^{-30} esu, respectively). These observations are explained by the assumption that it is not just the charge transfer transition that determines the value of the hyperpolarizability, but that lower transitions (i.e. π–π^* transition) also contribute. The latter was checked by studying another D-π-A system, containing a bithienyl spacer between 2-(4-nitrophenyl)-5-pyrrolyl and 2-(4-methoxyphenyl)-5-pyrrolyl termini. This molecule showed only one absorption band at 378 nm, indicating that the π–π^* transition has shifted underneath the charge transfer transition, whereas the β-value was much higher (440 x 10^{-30} esu).



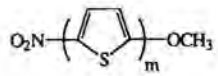
$\lambda_{max}(CHCl_3)$: 397 nm
β (HRS, $CHCl_3$): 79 x 10^{-30} esu



$\lambda_{max}(CHCl_3)$: 378 nm
β (HRS, $CHCl_3$): 147 x 10^{-30} esu



$\lambda_{max}(CHCl_3)$: 390 nm
β (EFISH, $CHCl_3$): 50 x 10^{-30} esu



m=1: $\lambda_{max}(CCl_4)$: 349 nm
β (EFISH, CCl_4): 8 x 10^{-30} esu

m=2: $\lambda_{max}(CCl_4)$: 418 nm
β (EFISH, CCl_4): 46 x 10^{-30} esu

m=3: $\lambda_{max}(CCl_4)$: 452 nm
β (EFISH, CCl_4): 162 x 10^{-30} esu

Scheme 3.3: *Other NLO compounds with their specific (nonlinear) optical properties.*[37]

If one compares this β-value with that of other NLO molecules with similar optical properties, it appears that the β-value of our mixed system is substantially higher (scheme 3.3).[37] Furthermore, comparison with the D-π-A oligothiophenes as prepared by Effenberger *et al.*[23] shows large differences.

Some thermally deprotected D-π-A oligomers were also investigated. This resulted in substantial red shifts for both absorption maxima, while the β-values increased dramatically. The latter is explained by increased π-conjugation and large resonance enhancement due to significant absorption at 532 nm.

3.2 *Mixed oligomers for Scanning Tunnelling Microscopy studies*

3.2.1 *Introduction*

One of the most challenging goals of molecular electronics is to develop devices that are based on individual molecules or small aggregates, rather than on large molecular ensembles. Up to now, such synthetic molecular devices still remain a challenge. However, considerable progress has been made in preparing molecular materials, which, for instance, can be efficient electron conductors.[38] Moreover, various methods have been developed to assemble functional molecules in ordered ultrathin molecular layers on solid substrates.[39] However, since conventional characterization methods average over some macroscopic number of molecules, it is often difficult to determine whether a certain property is a condensed matter phenomenon or the effect of a single molecule. It is desirable, therefore, to address individual molecules, and to determine their properties *in situ* and non-destructively.

Scanning tunnelling microscopy (STM), based on the quantum mechanical phenomenon of electron tunnelling, is a technique that allows a very local investigation on a preselected area at a surface or interface.[40-42] Figure 3.6 shows a schematic representation of a STM-microscope.[40,43]

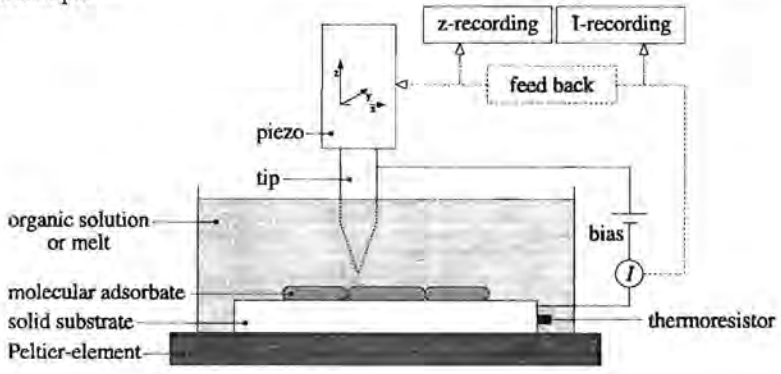


Figure 3.6: *The STM-microscope*[40,43]

Its essential features are a sharp metallic tip (Pt/Ir, W), a piezo element, which allows for the three-dimensional control of the tip position with an accuracy better than 0.1 Å, and a solid substrate on which the molecules are physisorbed. The substrate is often 'highly oriented pyrolytic graphite' (HOPG), a material that is both chemically and mechanically inert and exhibits atomically flat and perfect crystallites of the order of a micrometer in diameter. By bringing the tip at such a close proximity to the physisorbed molecules that the electronic orbitals of the outermost atoms of the tip and of the sample will spatially overlap, a tunnelling current will flow when an electrical potential difference is applied between the two. Maintaining the tip height constant and measuring the current, I, while scanning in the x and y directions, produces a map of I(x,y) versus x and y.[44] Since different parts of molecules show different currents, this map provides topological information on the surface and therefore on the orientation, size and shape of individual molecules.

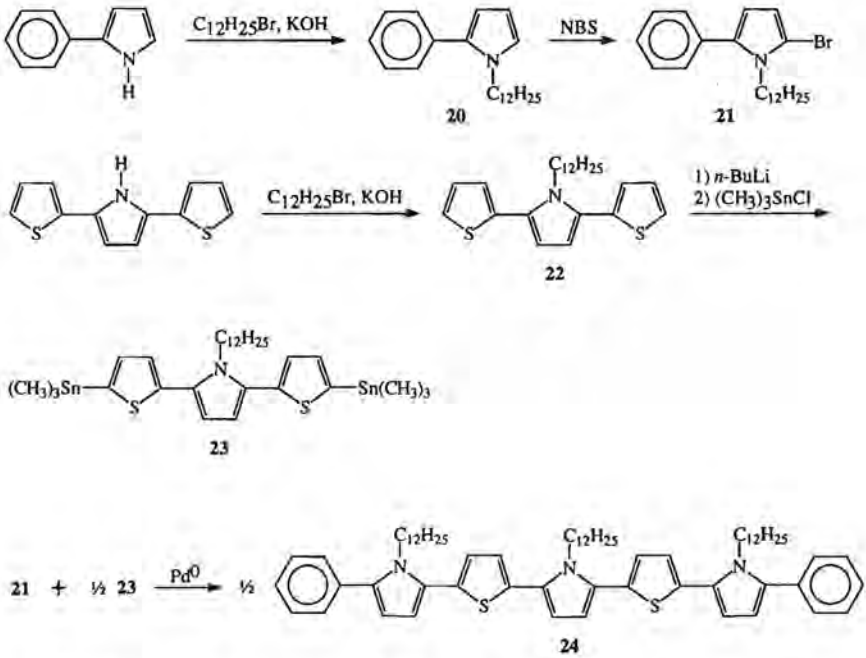
Numerous polymers[42,45,46] and charge transfer crystals[46-48] have been investigated by STM. However, this technique is relatively new for oligomers. In order to apply STM to oligomers, two basic requirements should be taken into account. The first is the prerequisite that the molecules have a reasonable electrical conductivity; the second requirement prescribes that these oligomers have a limited mobility on the HOPG surface. In case of oligomers consisting of (hetero)aromatic units, the first requirement is not a problem. However, in order to fulfil the second one, the oligomers have to be substituted with alkyl or alkoxy chains.

In literature there are only a few reports on oligomers being investigated by STM. Rabe and Stabel showed that both α,ω-dihexylsexithiophene and 2,5-didodecylsexithiophene form highly oriented monolayers at the interface between an organic solution and the basal plane of graphite.[49] Together with Bäuerle *et al.*, they observed similar behavior when investigating other, both regioselectively and non-regioselectively substituted oligothiophenes.[50] At the same time that we performed our experiments, Cava *et al.* reported on similar experiments with mixed oligomers that were prepared by ring closure reactions of 1,4-diketones.[51,52] They observed five different domain structures in which the intramolecular structure revealed that the aromatic units all have a *trans* conformation and form triangularly shaped blocks.[53,54] The latter is the result of two different N-alkyl substituents in one molecule.

In this study, STM has been applied to study structural characteristics of a N-dodecyl substituted oligomer consisting of pyrrole, thiophene and benzene, that was prepared by a sequence of functionalization and Stille reactions.

3.2.2 *Synthesis and characterization*

The Stille reaction has been applied to prepare N-dodecyl substituted oligomers[55-57] (scheme 3.4). Starting from 2-phenylpyrrole, which can be prepared by thermal deprotection of N-*t*-BOC-2-phenylpyrrole[57,58], or by the base catalyzed ring closure of an imidoyl chloride[59], we first alkylated this compound at nitrogen using KOH and dodecyl bromide in DMSO at RT.[60] After column chromatography N-dodecyl-2-phenylpyrrole (**20**, 44% yield) was selectively brominated at the α-position using standard bromination conditions (NBS, THF, -70°C).[61] The resulting N-dodecyl-2-bromo-5-phenylpyrrole (**21**, 98% yield) constitutes the blocking parts of compound **24**.



Scheme 3.4: *Synthesis of compound **24** by a sequence of functionalization and Stille reactions.*

The preparation of the central part started with 2,5-di(2-thienyl)pyrrole[62]. This compound was first N-alkylated under the same conditions as described for **20**, giving pure N-dodecyl-2,5-di(2-thienyl)pyrrole **22** after column chromatography (70% yield). Besides **22**, we also isolated N,3-didodecyl-2,5-di(2-thienyl)pyrrole (6% yield), the product of double alkylation. Compound **22** was then distannylated using *n*-BuLi and trimethylstannyl chloride.[63] The resulting N-dodecyl-2,5-di(5-trimethylstannyl-2-thienyl)pyrrole (**23**, 100% yield) was finally coupled with two equivalents of **21** using $Pd^0(PPh_3)_4$ as catalyst. This led to

N-dodecyl-2,5-di{2[5(N-dodecyl-5-phenyl)pyrrolyl]thienyl}pyrrole **24** in 6% yield. The low yield of this reaction is mainly the result of small scale synthesis in combination with extremely difficult purification.

3.2.3 *STM-measurements*

A saturated solution of **24** in phenyloctane was prepared and deposited on a freshly cleaved HOPG surface. Figure 3.7 shows the STM images of the highly ordered monolayers that were derived from this.[64]

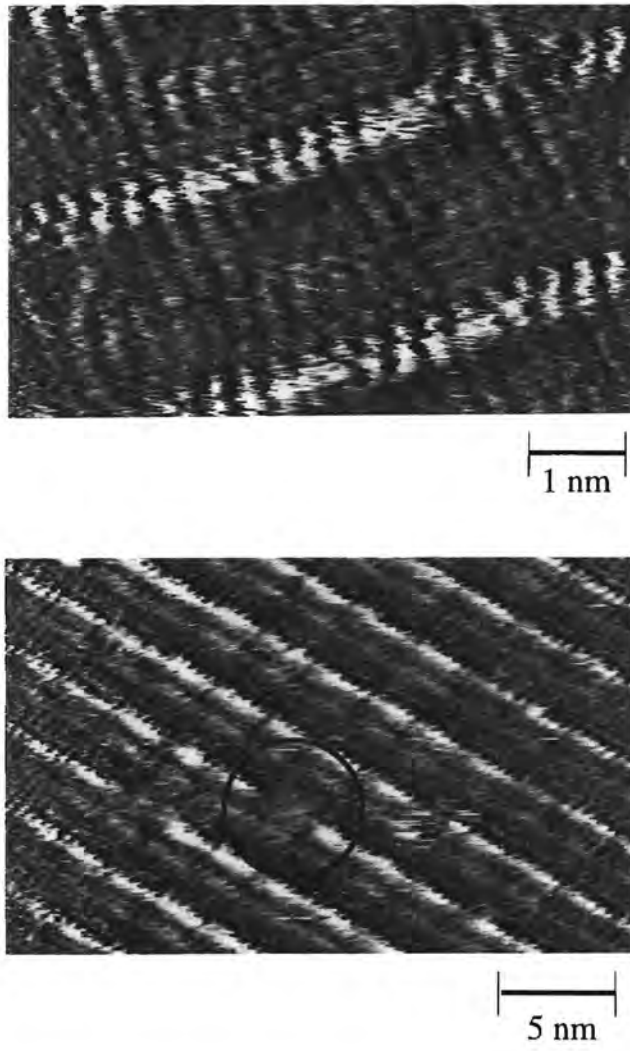


Figure 3.7: *Scanning tunnelling microscopy images of compound* ***24****.*

The first image shows two white bands, which represent the electron-rich parts of the molecules, being the aromatic units. The distance between these two bands appears to be exactly twice the length of a dodecyl chain, suggesting that the alkyl chains of two oligomers do not interdigitate but are lying against each other, as is shown in the representation in figure 3.8. One can also observe that two oligomers form couples ('Doppellamellen') with the aromatic units lying against each other. All these couples form aromatic 'backbones'. Unfortunately, it is not possible to see where one couple ends and where the next one starts. Therefore, the second image was a nice shot. Here one can observe the absence of one couple (two 'missing molecules'), which suggests the final representation as shown in figure 3.8.

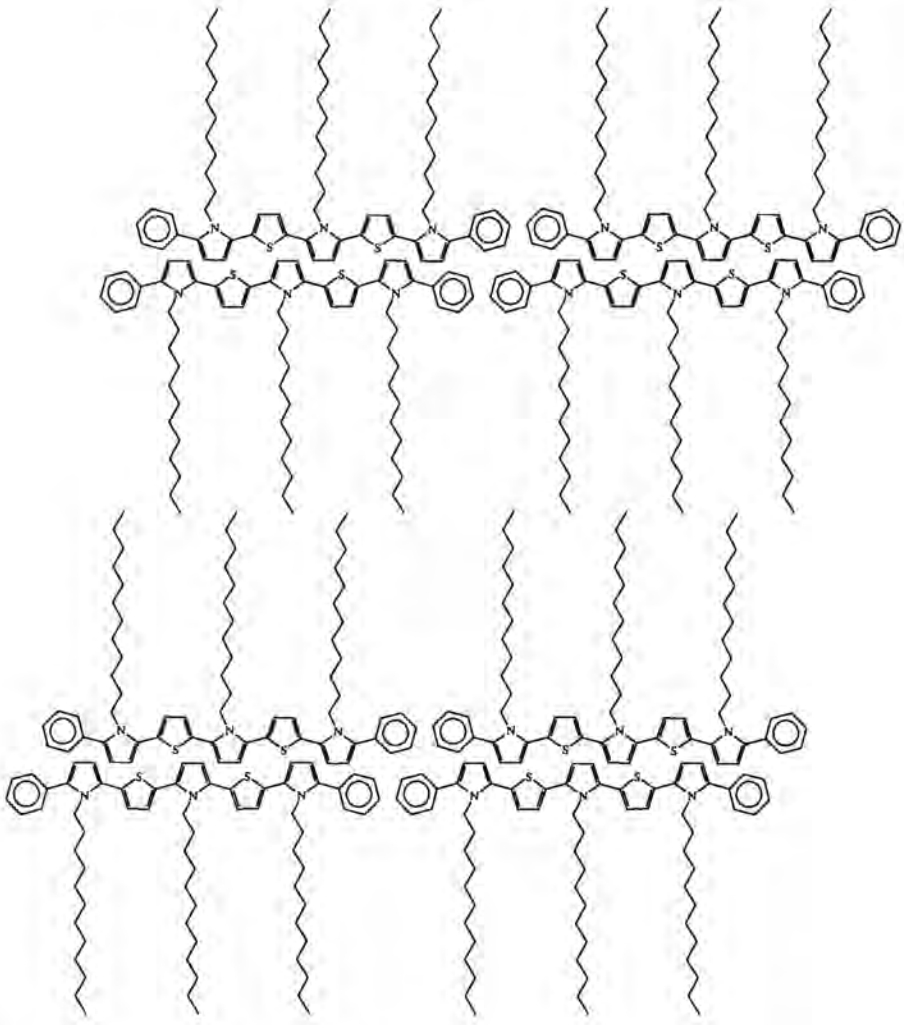


Figure 3.8: *Representation of highly ordered monolayers of* ***24*** *on HOPG.*

Although the two-dimensional crystallization of this oligomer supplies new information about their molecular packing structure on HOPG, one oligomer is not enough to draw general conclusions on this point. This is confirmed by the fact that the results as derived by Cava *et al.* on comparable mixed oligomers, show totally different packing patterns.[53]

3.2.4 *Conclusions*

A sequence of functionalization and Stille reactions has been applied to prepare N-dodecyl-2,5-di{2[5(N-dodecyl-5-phenyl)pyrrolyl]thienyl}pyrrole **24**. After tedious purification, this molecule was investigated by scanning tunnelling microscopy. These studies show that highly ordered monolayers are formed when the molecules are physisorbed on a HOPG surface. The STM images also reveal that they form couples with the aromatic units lying against each other, and the alkyl chains lying against each other; however, the latter do not interdigitate. Furthermore, these couples form linear aromatic backbones.

3.3 *Studies on the redox behavior of two series of α-oligoheteroaromatic compounds*

3.3.1 *Introduction*

π-Conjugated homopolymers such as polypyrrole, polyaniline, polyphenylene and poly(3-alkylthiophene)s have been subject of considerable attention in recent years because of their interesting electrical and optical properties.[65] In contrast, the preparation and properties of heteroaryl copolymers have received far less attention.[66] Introducing structurally different units in a single π-conjugated polymer chain, however, may lead to new properties, which are tuneable by the sequence of the different units in the polymer. The recent development of novel low band gap polymers consisting of alternating structures of donor and acceptor moieties may serve as an example of the new properties that can be obtained from π-conjugated copolymers.[67]

Many of the electronic and optical properties of π-conjugated polymers are related to their redox properties and have been associated with nonlinear soliton, polaron and bipolaron excitations.[68] Conjugated oligomers with a well-defined chemical structure have been successfully used to assess optical and redox properties of semi-conducting polymers in detail, particularly in studying effects of (effective) conjugation length. Numerous experimental[69-73] and theoretical[74] studies on various π-conjugated homo-oligomers have shown that the energy of the π–π^* transition as well as the first and second oxidation potentials decrease proportionally with the inverse conjugation length. Detailed studies are

available on the electronic structure of oligothiophene radical cations, radical cation π-dimers and dications, being molecular analogs for polaronic and bipolaronic charge carriers in doped conjugated polymers.[69]

The redox properties of oligomers consisting of different aromatic units have received little attention. Recently, Cava *et al.* have studied mixed thienylpyrrole oligomers containing up to seven units without reporting on particular properties deviating from homo-oligomers.[75] Here we report on the electrochemical properties of two series of phenyl-blocked oligomers being diphenyl-α-oligopyrroles (Ph-p_n-Ph, n = 1-4) and di(phenylpyrrolyl)-α-oligothiophenes (Ph-p-t_n-p-Ph, n = 1-3) (figure 3.9).

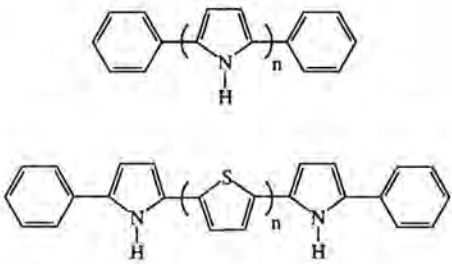


Figure 3.9: *Molecular structures of Ph-p_n-Ph (n = 1-4) and Ph-p-t_n-p-Ph (n = 1-3).*

3.3.2 *Results and discussion*

As shown in Chapter 2, the oligomers Ph-p_n-Ph (n = 1-4) and Ph-p-t_n-p-Ph (n = 1-3) were prepared by Stille reactions followed by thermal removal of the *t*-BOC groups (compounds **13H-19H**). The UV-Vis absorption spectra of both series reveal that the onset of the π–π^* transition (E_g, table 3.3) shifts to lower energies with increasing number of units, consistent with the expected behavior for increasing π-conjugation. Figure 3.10 shows that both series exhibit an approximately linear behavior of E_g as a function of the inverse conjugation length of the oligomer (1/m, m = total number of aromatic units in the oligomer).

Using cyclic voltammetry, Ph-p_n-Ph oligomers are found to exhibit two chemically reversible oxidation waves for $n \geq 2$ (figure 3.11a). For n = 1, polymerization occurs, resulting in a dark-red film on the working electrode. The chemical stability of Ph-p_n-Ph monocation radicals and dications is significantly enhanced as compared to P_n.[70] Chemically reversible one-electron oxidation for P_n has been observed starting at n = 3 for scan rates over 1000 mV/s, while the second one-electron oxidation wave becomes reversible at n = 5.[70] As expected for π-conjugated oligomers, E^0_1 and E^0_2 of Ph-p_n-Ph decrease approximately linearly with the reciprocal number of units (figure 3.12).

Table 3.3: *Electrochemical data[a] and onset of the π–π* absorption[b].*

oligomer	E_{pa1} (V)	E_{pc1} (V)	E_{pa2} (V)	E_{pc2} (V)	E_g (eV)
Ph-p-Ph	[c]	-	-	-	3.44
Ph-p_2-Ph	0.42	0.33	1.09	1.00	3.05
Ph-p_3-Ph	0.16	0.10	0.64	0.57	2.89
Ph-p_4-Ph	0.06	-0.04	0.43	0.32	2.78
Ph-p-t-p-Ph	0.47	0.36	0.86	0.75	2.72
Ph-p-t_2-p-Ph	0.54	0.43	0.70	0.60	2.52
Ph-p-t_3-p-Ph[d]	0.66	0.55	0.66	0.55	2.39

[a] *Potentials in $CH_2Cl_2/Bu_4N^+PF_6^-$ (0.1 M) vs. SCE, oligomer concentration c = 0.5-10 mM.*
[b] *Absorption spectra recorded in acetonitrile*
[c] *Irreversible oxidation wave.*
[d] *A broad oxidation wave is observed, assigned to a coalescence of E_{pa1} and E_{pa2}.*

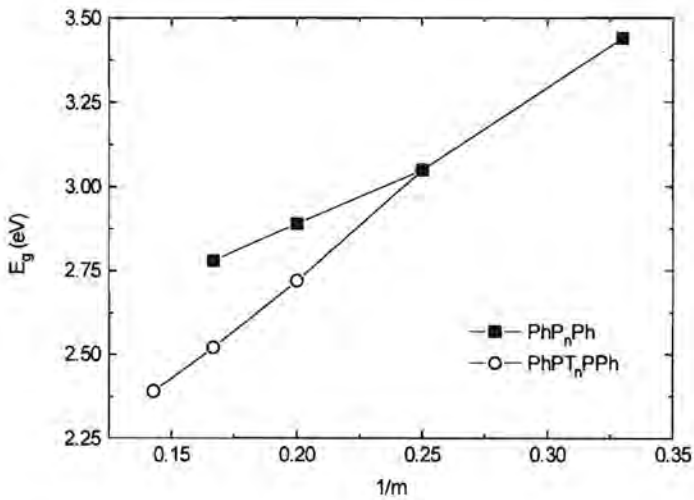


Figure 3.10: *Onset of the π-π* transition of the Ph-p_n-Ph and Ph-p-t_n-p-Ph oligomers in acetonitrile solution vs. inverse conjugation length (1/m; m being the total number of aromatic units in the oligomer).*

The redox behavior of the Ph-p-t_n-p-Ph series is dramatically different from that of the Ph-p_n-Ph oligomers. Figure 3.11b shows that the first oxidation wave for Ph-p-t_n-p-Ph occurs at a higher potential as compared to Ph-p_2-Ph, despite the longer conjugation length and the decreased onset of the π–π^* transition. Further augmenting the number of thiophene units between the two pyrrole units, results in a steady increase of E^0_1 (figure 3.12), while E^0_2 continues to decrease. For Ph-p-t_3-p-Ph the first and second oxidation potential coalesce into a single broad oxidation wave.

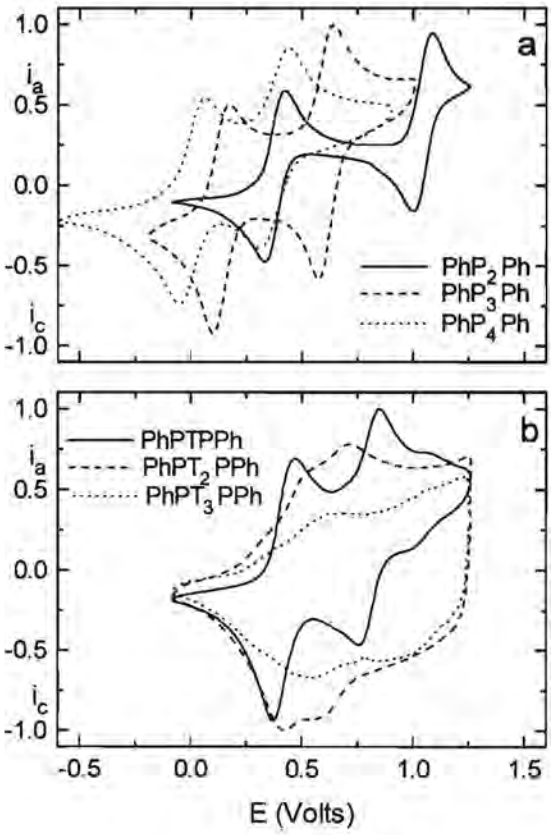


Figure 3.11: *Cyclic voltammograms of Ph-p_n-Ph (a) and Ph-p-t_n-p-Ph (b) in CH_2Cl_2/ $Bu_4N^+PF_6^-$ (0.1 M) solution, scanned at 100 mV/s. Potential vs. SCE, internally calibrated vs. Fc/Fc$^+$.*

E.E. Havinga developed a Hückel band model to rationalize the abovementioned data. These calculations appear to be in fair agreement and explain the general behavior (figure 3.12).[76] Temperature-dependent UV-Vis-NIR measurements revealed the existence of so-called π-dimers; the latter are formed upon dimerization of two cation radicals. Although these species were already known in oligothiophene chemistry, this is the first time that they are observed for phenyl-blocked homo- and co-oligomers.[77,78]

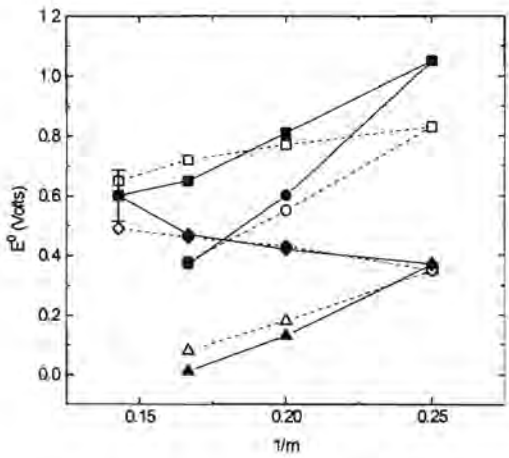


Figure 3.12: *First and second oxidation potentials (vs. SCE) as function of inverse conjugation length (1/m) for Ph-p_n-Ph (m = n+2, ▲ and ●) and Ph-p-t_n-p-Ph (m = n+4, ◆ and ■). Closed markers refer to experimental data, open markers to calculated values using Hückel band model.*

3.3.3 *Conclusions*

The redox properties of two series of phenyl-blocked α-oligoheteroaromatic compounds, consisting of pyrrole and/or thiophene units, have been investigated. Cyclic voltammetry studies on diphenyl-α-oligopyrroles (Ph-p_n-Ph) reveal two chemically reversible oxidation waves for $n \geq 2$, with decreasing potentials for larger n. For di(phenylpyrrolyl)-α-oligothiophenes (Ph-p-t_n-p-Ph), in contrast, we observe an increase of the first and a decrease of the second oxidation potential going from n = 1 to n = 3. The band gap in both series follows the expected decreasing behavior with increasing conjugation length. We find a good agreement between the experimental oxidation potentials and those calculated from a Hückel band model.

3.4 *Overall conclusions/Outlook*

The Pd-catalyzed cross coupling reaction has proved to be an important tool in the synthesis of well-defined and functional oligomers based on pyrrole. Applying the right conditions, suggested by the methodological studies (Chapter 2), we have been able to introduce several functionalities that gave rise to new compounds with interesting properties. Although this is just the beginning of an interesting new period of research, it may be hoped that further investigation of the structure-property relationship may soon lead to comparable molecules that can be applied in electrical and/or optical devices.

At the same time, these well-defined oligomeric materials have proved to be ideal models for their polymeric analogs. By applying the aforementioned synthetic strategies to the preparation of more extended structures, while maintaining full control over molecular weight, polydispersity and regioselectivity, new polymeric materials will emerge, which could be applied in the advanced materials of the twenty-first century.

3.5 *Experimental section*

For general remarks concerning chemicals and analysis techniques, the reader is referred to section 2.6. Hyper Rayleigh Scattering measurements were performed using a Nd:YAG laser (Spectra-Physics, DCR-3, 10 Hz), resulting in infrared laser pulses (1064 nm, 8 ns, 3-4 mJ).[30] The home-built scanning tunnelling microscope, together with some procedures, has been described elsewhere.[79,80] The tunnelling tips were electrochemically etched (2N KOH + 6N NaCN) from 0.25 mm diameter Pt/Ir (80:20) wire. For STM measurements a saturated solution (2 x 10^{-3} M) of **24** in phenyloctane (Aldrich 98%) was used.[64] All experiments on deprotected oligomers were performed under rigorously inert conditions (water < 1 ppm; oxygen < 3 ppm). Cyclic voltammograms were obtained in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$) as supporting electrolyte using a Potentioscan Wenking POS73 potentiostat. A platinum disk (diameter 5 mm) was used as working electrode, the counter electrode was a platinum plate (5 x 5 mm), and a saturated calomel electrode (SCE) was used as reference electrode, internally calibrated vs. Fc/Fc^+.

N-*tert*-Butoxycarbonyl-2-(4-nitrophenyl)pyrrole (1) A mixture of N-*t*-BOC-2-trimethylstannyl-pyrrole[29] (9.03 g, 27.4 mmol), 1-bromo-4-nitrobenzene (5.24 g, 25.9 mmol), toluene (40 ml) and aqueous Na_2CO_3 (1 M, 40 ml) was deaerated and stored under argon. $Pd(PPh_3)_4$ (0.48 g, 0.42 mmol) was added and the reaction mixture was heated under reflux for 2 days. After this period, water and Et_2O (both 100 ml) were added, the two phases were separated and the aqueous phase was extracted twice with Et_2O (100 ml). The combined organic fractions were dried ($MgSO_4$), filtered and

concentrated. The remaining dark solid was then recrystallized (hexane : CH_2Cl_2 (3:1)). The residue, remaining after evaporation of the filtrate, was purified by column chromatography (250 g SiO_2, CH_2Cl_2 : hexane (2:1), R_f = 0.56) and recrystallized. Both fractions gave **1** as a yellow solid (4.27 g, 14.8 mmol, 53%). Mp.: 120-121°C.
^{1}H-NMR ($CDCl_3$): δ 8.22 (d, J = 9.0 Hz, 2H, H-*meta*), 7.51 (d, J = 9.0 Hz, 2H, H-*ortho*), 7.41 (dd, J = 3.3 and 1.8 Hz, 1H, H-5), 6.32 (dd, J = 3.3 and 1.8 Hz, 1H, H-3), 6.28 (t, J = 3.3 Hz, 1H, H-4), 1.44 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.8 (C=O), 146.5 (C-NO_2), 140.6 (C-*ipso* (phenyl), 132.7 (C-2), 129.5 (C-*meta*), 124.3 (C-5), 122.9 (C-*ortho*), 116.5 (C-3), 111.1 (C-4), 84.4 (C-q (BOC)), 27.6 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 245 (1.02 x 10^4) and 345 (1.03 x 10^4) nm. IR (KBr): 3147, 2982, 2937, 1743, 1598, 1508, 1341, 1307, 1145, 976, 854, 772, 758 cm^{-1}.
1H: Thermal deprotection of the *t*-BOC groups was accomplished by heating neat **1** for 20-30 min at 190°C under inert atmosphere. UV-Vis ($CHCl_3$): 250 and 374 nm.

N-*tert*-Butoxycarbonyl-2-bromo-5-(4-nitrophenyl)pyrrole (2) A mixture of N-*tert*-butoxycarbonyl-2-(4-nitrophenyl)pyrrole (**1**, 0.557 g, 1.93 mmol) and THF (20 ml) was cooled to -70°C, blanketed by argon. N-Bromosuccinimide (NBS, 0.345 g, 1.94 mmol) was added, after which the mixture was stirred at -70°C for 20 min. After this period it was allowed to warm to 3°C at which temperature it was kept for another 18 h. Na_2SO_3 (0.5 g) was added, the mixture was stirred for 10 min and the solvent was evaporated. CCl_4 (40 ml) was added, the mixture was stirred for 5 min, filtered and concentrated. A yellow solid remained, being pure **2** (0.700 g, 1.91 mmol, 99%).
^{1}H-NMR ($CDCl_3$): δ 8.23 (d, J = 8.8 Hz, 2H, H-*meta*), 7.45 (d, J = 8.96 Hz, 2H, H-*ortho*), 6.37 (d, J = 3.6 Hz, 1H, H-3/H-4), 6.33 (d, J = 3.6 Hz, 1H, H-3/H-4), 1.43 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.0 (C=O), 146.5 (C-NO_2), 140.0 (C-*ipso* (phenyl)), 134.3 (C-5), 128.1 (C-*meta*), 123.4 (C-*ortho*), 115.6/114.9 (C-3/C-4), 104.6 (C-2), 86.0 (C-q (BOC)), 27.4 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 248 and 349 nm.

N,N'-Di-*tert*-butoxycarbonyl-5-(4-nitrophenyl)-2,2'-bipyrrole (3) A Stille reaction between N-*t*-BOC-2-trimethylstannylpyrrole[29] (2.06 g, 6.24 mmol) and **2** (2.28 g, 6.21 mmol) in toluene (10 ml) and aqueous Na_2CO_3 (1 M, 10 ml) in the presence of $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol), was performed as described for **1**. After work-up procedures a dark green liquid remained, which was purified by column chromatography (200 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.12). Subsequent recrystallization from a mixture of CH_2Cl_2 and hexane gave **3** as a yellow solid (1.49 g, 3.29 mol, 53%). Mp.: 122°C.
^{1}H-NMR ($CDCl_3$): δ 8.23 (d, J = 9.0 Hz, 2H, H-*meta*), 7.48 (d, J = 8.8 Hz, 2H, H-*ortho*), 7.43 (dd, J = 3.3 and 1.9 Hz, 1H, H-5'), 6.36 (d, J = 3.4 Hz, 1H, H-4), 6.28-6.23 (m, 3H, H-3, H-3', H-4'), 1.40 (s, 9H, H-methyl (BOC')), 1.24 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.1 (C=O), 148.9 (C=O), 146.3 (C-NO_2), 140.8 (C-*ipso* (phenyl)), 134.1 (C-5), 129.8/125.3 (C-2/C-2'), 128.6 (C-*meta*), 123.2 (C-*ortho*), 122.2 (C-5'), 116.2/114.7/114.5/110.5 (C-3/C-4/C-3'/C-4'), 84.0 (C-q (BOC)), 83.6 (C-q (BOC)), 27.7 (C-methyl (BOC)), 27.3 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 255 (1.20 x 10^4) and 364 (1.28 x 10^4) nm. IR (KBr): 2986, 2936, 1750, 1596, 1515, 1333, 1312, 1259, 1155, 1110, 970, 852, 794, 733 cm^{-1}.
3H: Thermal deprotection of the *t*-BOC groups was accomplished as described for **1H**. UV-Vis ($CHCl_3$): 292 and 451 nm.

N,N'-Di-*tert*-butoxycarbonyl-5'-bromo-5-(4-nitrophenyl)-2,2'-bipyrrole (4) The bromination of **3** (0.252 g, 0.56 mmol) in THF (5 ml) with NBS (0.1033 g, 0.580 mmol) was performed as described for **2**. This finally resulted in pure **4** as a slightly red oil (0.295 g, 0.554 mmol, 99%).
^{1}H-NMR ($CDCl_3$): δ 8.24 (d, J = 8.9 Hz, 2H, H-*meta*), 7.48 (d, J = 8.8 Hz, 2H, H-*ortho*), 6.37 (2 x d, J = 3.6 Hz, 2 x 1H, H-4, H-4'), 6.25-6.22 (2 x d, J = 3.5 Hz, 2 x 1H, H-3, H-3'), 1.41 (H-methyl (BOC'), 1.27 (H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.9 (C=O), 148.0 (C=O), 146.4 (C-NO_2), 140.6 (C-*ipso* (phenyl)), 134.5-127.7 (C-2, C-5, C-2'), 128.6 (C-*meta*), 123.3 (C-*ortho*), 115.7/115.6/115.0/114.8 (C-3/C-4/C-3'/C-4'), 102.6 (C-5'), 84.8 (C-q (BOC)), 84.7 (C-q (BOC)), 27.6 (C-methyl (BOC)), 27.4 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 255 and 358 nm.

N,N',N''-Tri-*tert*-butoxycarbonyl-5-(4-nitrophenyl)-2,2':5',2''-terpyrrole (5) A Stille reaction between N-*t*-BOC-2-trimethylstannylpyrrole[29] (0.7187 g, 2.18 mmol) and **4** (1.154 g, 2.17 mmol) in toluene (3.5 ml) and aqueous Na_2CO_3 (1 M, 3.5 ml) in the presence of $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), was performed as described for **1**. The remaining dark liquid was purified by column chromatography (150 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.10), which gave **5** as a reddish oil (0.322 g, 0.52 mmol, 24%).
^{1}H-NMR ($CDCl_3$): δ 8.23 (d, J = 8.9 Hz, 2H, H-*meta*), 7.49 (d, J = 9.0 Hz, 2H, H-*ortho*), 7.43 (dd, J = 3.4 and 1.9 Hz, 1H, H-5''), 6.39 (d, J = 3.4 Hz, 1H, H-4), 6.26-6.19 (m, 4H, H-3, H-3', H-4', H-4''), 6.17 (dd, J = 3.5 and 1.9 Hz, 1H, H-3''), 1.41 (s, 9H, H-methyl (BOC'')), 1.27 (s, 9H, H-methyl (BOC)), 1.26 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.0 (C=O), 148.9 (C=O), 148.8 (C=O), 146.2 (C-NO_2), 140.8 (C-*ipso* (phenyl)), 134.3/130.7/127.9/127.0/126.2 (C-2/C-5/C-2'/C-5'/C-2''), 128.5 (C-*meta*), 123.2 (C-*ortho*), 121.9 (C-5''), 115.4/115.1/114.3/113.8/110.3 (C-3/C-4/C-3'/C-4'/C-3''/C-4''), 84.3 (C-q (BOC)), 83.3 (C-q (BOC)), 82.9 (C-q (BOC)), 27.7 (C-methyl (BOC)), 27.5 (C-methyl (BOC)), 27.4 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 283 and 366 nm.

N,N',N''-Tri-*tert*-butoxycarbonyl-5''-bromo-5-(4-nitrophenyl)-2,2':5',2''-terpyrrole (6) The bromination of **5** (0.327 g, 0.527 mmol) in THF (5 ml) with NBS (0.0949 g, 0.533 mmol) was performed as described for **2**. This finally resulted in pure **6** as a red oil (0.320 g, 0.516 mmol, 98%).
^{1}H-NMR ($CDCl_3$): δ 8.23 (d, J = 8.9 Hz, 2H, H-*meta*), 7.50 (d, J = 8.9 Hz, 2H, H-*ortho*), 6.38 (d, J = 3.4 Hz, 1H, H-4/H-4''), 6.34 (d, J = 3.4 Hz, 1H, H-4/H-4''), 6.25-6.13 (4 x d, J = 3.4 Hz, 4 x 1H, H-3, H-3', H-3'',H-4'), 1.39 (s, 9H, H-methyl (BOC'')), 1.29 (H-methyl (BOC)), 1.25 (H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.9 (C=O), 148.7 (C=O), 148.1 (C=O), 146.3 (C-NO_2), 140.9 (C-*ipso* (phenyl)), 134.4/130.4/128.7/127.8/127.4 (C-2/C-5/C-2'/C-5'/C-2''), 128.6 (C-*meta*), 123.2 (C-*ortho*), 115.7/115.1/114.9/114.5/114.4/114.3 (C-3/C-4/C-3'/C-4'/C-3''/C-4''), 102.2 (C-5''), 84.6 (C-q (BOC)), 84.2 (C-q (BOC)), 83.6 (C-q (BOC)), 27.9 (C-methyl (BOC)), 27.7 (C-methyl (BOC)), 27.5 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 283 and 361 nm.

N,N',N'',N'''-Tetra-*tert*-butoxycarbonyl-5-(4-nitrophenyl)-2,2':5',2'':5'',2'''-quaterpyrrole (7)
A Stille reaction between N-*t*-BOC-2-trimethylstannylpyrrole[29] (0.038 g, 0.115 mmol) and **6** (0.058 g, 0.083 mmol) in toluene (0.5 ml) and aqueous Na_2CO_3 (1 M, 0.5 ml) in the presence of $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), was performed as described for **1**. The remaining dark liquid was purified by column chromatography (6 g SiO_2, CH_2Cl_2 : hexane (3:1), R_f = 0.12) yielding **7** as a red oil (31.6 mg, 0.040 mmol, 48%).

^{1}H-NMR ($CDCl_3$): δ 8.23 (d, J = 8.9 Hz, 2H, H-*meta*), 7.50 (d, J = 8.9 Hz, 2H, H-*ortho*), 7.40 (dd, J = 3.2 and 1.9 Hz, 1H, H-5'''), 6.39 (d, J = 3.5 Hz, 1H, H-4), 6.27-6.16 (m, 7H, H-3, H-3', H-3'', H-3''', H-4', H-4'', H-4'''), 1.41 (s, 9H, H-methyl (BOC''')), 1.32 (s, 9H, H-methyl (BOC)), 1.29 (s, 9H, H-methyl (BOC)), 1.25 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.0 (2 x C=O), 148.9 (C=O), 148.8 (C=O), 146.3 (C-NO_2), 141.1 (C-*ipso* (phenyl)), 134.2/130.8/127.9/127.7/127.0/ 126.6 (C-2/C-5/C-2'/C-5'/C-2''/C-5''/C-2'''), 128.6 (C-*meta*), 123.2 (C-*ortho*), 121.9 (C-5'''), 115.4/ 115.2/114.5/114.5/113.9/110.2 (C-3/C-4/C-3'/C-4'/C-3''/C-4''/C-3'''/C-4'''), 84.2 (C-q (BOC)), 83.1 (C-q (BOC)), 82.7 (2 x C-q (BOC)), 27.8 (C-methyl (BOC)), 27.7 (2 x C-methyl (BOC)), 27.5 (C-methyl (BOC)) ppm.

N,N',N'',N'''-Tetra-*tert*-butoxycarbonyl-5'''-bromo-5-(4-nitrophenyl)-2,2':5',2'':5'',2'''-quaterpyrrole (8) The bromination of **7** (31.6 mg, 0.0403 mmol) in THF (3 ml) with NBS (7.2 mg, 0.0405 mmol) was performed as described for **2**. This finally gave pure **8** as a red oil (32.0 g, 0.037 mmol, 92%).

^{1}H-NMR ($CDCl_3$): δ 8.23 (d, J = 8.8 Hz, 2H, H-*meta*), 7.50 (d, J = 8.8 Hz, 2H, H-*ortho*), 6.38 (d, J = 3.5 Hz, 1H, H-4/H-4'''), 6.33 (d, J = 3.6 Hz, 1H, H-4/H-4'''), 6.28-6.14 (m, 6H, H-3, H-3', H-3'', H-3''', H-4', H-4''), 1,40 (s, 9H, H-methyl (BOC''')), 1.28 (s, 9H, H-methyl (BOC)), 1.27 (s, 9H, H-methyl (BOC)), 1.25 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.0 (C=O), 148.8 (C=O), 148.6 (C=O), 148.2 (C=O), 146.3 (C-NO_2), 141.0 (C-*ipso* (phenyl)), 134.2/130.7/128.8/ 128.3/128.2/ 127.4/127.0 (C-2/C-5/C-2'/C-5'/C-2''/C-5''/C-2'''), 128.6 (C-*meta*), 123.2 (C-*ortho*), 115.6/115.1/ 114.8/114.6/114.5/114.3/114.0 (C-3/C-4/C-3'/C-4'/C-3''/C-4''/C-3'''/C-4'''), 102.1 (C-5'''), 84.4 (C-q (BOC)), 84.2 (C-q (BOC)), 83.4 (C-q (BOC)), 83.1 (C-q (BOC)), 27.7 (C-methyl (BOC)), 27.6 (2 x C-methyl (BOC)), 27.5 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 290 and 362 nm.

4-Trimethylstannylanisol (9) A two-necked flask containing 4-bromoanisole (0.561 g, 3.00 mmol) and THF (8 ml) was cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 2.0 ml, 3.2 mmol) was added over a 10 min period, after which the mixture was stirred at -70°C for 1 h. Then a solution of trimethylstannyl chloride (0.63 g, 3.16 mmol) in THF (2 ml) was added and the mixture was stirred at -70°C for another 4 h. After this period the mixture was allowed to warm to RT. After 16 h at RT it was poured into water (15 ml) and extracted with Et_2O (3 x 10 ml). The combined organic fractions were dried ($MgSO_4$), filtered and concentrated resulting in **9** as a colorless liquid (0.80 g, 3.0 mmol, 98%).

^{1}H-NMR ($CDCl_3$): δ 7.40 (d, J = 8.5 Hz, 2H, H-3), 6.91 (d, J = 8.6 Hz, 2H, H-2), 3.77 (s, 3H, H-methoxy), 0.27 (s, 9H, H-methyl (stannyl)) ppm. ^{13}C-NMR ($CDCl_3$): δ 159.8 (C-1), 137.3 (C-4), 137.0 (C-3), 113.9 (C-2), 54.9 (C-methoxy), -9.5 (C-methyl (stannyl)) ppm. IR (KBr): 2977, 2910, 2835, 1588, 1566, 1496, 1459, 1277, 1243, 1181, 1076, 1033, 809, 769, 528 cm^{-1}.

N-*tert*-Butoxycarbonyl-2-(4-methoxyphenyl)-5-(4-nitrophenyl)pyrrole (10) A Stille reaction between **2** (0.94 g, 1.93 mmol) and **9** (0.565 g, 2.08 mmol) in toluene (5 ml) and aqueous Na_2CO_3 (1 M, 5 ml) in the presence of $Pd(PPh_3)_4$ (35 mg, 0.030 mmol), was performed as described for **1**. This resulted in a red oil, which was purified by column chromatography (70 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.15) and subsequent recrystallization (mixture of CH_2Cl_2 and hexane) to give **10** as a yellow solid (0.359 g, 0.910 mmol, 47%).

^{1}H-NMR ($CDCl_3$): δ 8.24 (d, J = 8.9 Hz, 2H, H-*meta* (Ph-NO_2)), 7.54 (d, J = 8.9 Hz, 2H, H-*ortho* (Ph-NO_2)), 7.33 (d, J = 8.8 Hz, 2H, H-*ortho* (Ph-OCH_3)), 6.94 (d, J = 8.8 Hz, 2H, H-*meta* (Ph-OCH_3)), 6.39 (d, J = 3.4 Hz, 1H, H-4), 6.22 (d, J = 3.5 Hz, 1H, H-3), 3.85 (s, 3H, H-methoxy), 1.21 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 159.3 (C-OCH_3), 149.5 (C=O), 146.2 (C-NO_2), 140.5 (C-*ipso* (Ph-NO_2)), 138.3/133.5 (C-2/C-5), 130.3 (C-*ortho* (Ph-OCH_3)), 128.5 (C-*meta* (Ph-NO_2)), 125.9 (C-*ipso* (Ph-OCH_3)), 123.2 (C-*ortho* (Ph-NO_2)), 114.6 (C-4), 113.2 (C-*meta* (Ph-OCH_3)), 112.4 (C-3), 84.0 (C-q (BOC)), 55.2 (OCH_3), 27.1 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 269 (1.42 x 10^4) and 376 (1.29 x 10^4) nm. IR (KBr): 2979, 2938, 1739, 1597, 1514, 1496, 1340, 1305, 1243, 1175, 1143, 1109, 978, 850, 802, 749 cm^{-1}. HR-MS: mass calcd. 394.1529; mass found 394.1525. GC-MS: 394 (M^+), 338, 295, 294, 293, 279, 277, 57.

10H: Thermal deprotection of the *t*-BOC groups was accomplished as described for **1H**. ^{1}H-NMR (THF-d_8): δ 10.63 (s, 1H, N-H), 8.19 (d, J = 9.0 Hz, 2H, H-*meta* (Ph-NO_2)), 7.81 (d, J = 9.1 Hz, 2H, H-*ortho* (Ph-NO_2)), 7.60 (d, J = 9.0 Hz, 2H, H-*ortho* (Ph-OCH_3)), 6.95 (d, J = 9.0 Hz, 2H, H-*meta* (Ph-OCH_3)), 6.83 (dd, J = 3.9 and 2.5 Hz, 1H, H-4), 6.50 (dd, J = 3.8 and 2.5 Hz, 1H, H-3), 3.79 (s, 3H, H-methoxy) ppm. UV-Vis ($CHCl_3$): 295 and 431 nm.

N,N'-Di-*tert*-butoxycarbonyl-5-(4-methoxyphenyl)-5'-(4-nitrophenyl)-2,2'-bipyrrole (11)

A Stille reaction between **4** (0.266 g, 0.500 mmol) and **9** (0.148 g, 0.55 mmol) in toluene (3 ml) and aqueous Na_2CO_3 (1 M, 3 ml) in the presence of $Pd(PPh_3)_4$ (31 mg, 0.027 mmol), was performed as described for **1**. This resulted in a dark liquid, which was purified by column chromatography (25 g SiO_2, CH_2Cl_2 : hexane (1:2), R_f = 0.02). Subsequent recrystallization from a mixture of CH_2Cl_2 and hexane, finally gave **11** as a yellow solid (0.102 g, 0.211 mmol, 42%).

^{1}H-NMR ($CDCl_3$): δ 8.23 (d, J = 8.9 Hz, 2H, H-*meta* (Ph-NO_2)), 7.50 (d, J = 8.8 Hz, 2H, H-*ortho* (Ph-NO_2)), 7.29 (d, J = 8.7 Hz, 2H, H-*ortho* (Ph-OCH_3)), 6.92 (d, J = 8.7 Hz, 2H, H-*meta* (Ph-OCH_3)), 6.41 (d, J = 3.4 Hz, 1H, H-4'), 6.32 (d, J = 3.4 Hz, 1H, H-3/H-3'), 6.26 (d, J = 3.4 Hz, 1H, H-3/H-3'), 6.19 (d, J = 3.4 Hz, 1H, H-4), 3.83 (s, 3H, H-methoxy), 1.32 (s, 9H, H-methyl (BOC)), 1.26 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 158.8 (C-OCH_3), 149.2 (C=O), 149.1 (C=O), 146.3 (C-NO_2), 140.8 (C-*ipso* (Ph-NO_2)), 136.6/134.3/130.3/126.9 (C-2/C-5/C-2'/C-5'), 129.6 (C-*ortho* (Ph-OCH_3)), 128.5 (C-*meta* (Ph-NO_2)), 126.8 (C-*ipso* (Ph-OCH_3)), 123.2 (C-*ortho* (Ph-NO_2)), 115.0/114.6/113.3/112.2 (C-3/C-4/C-3'/C-4'), 113.3 (C-*meta* (Ph-OCH_3)), 84.2 (C-q (BOC)), 83.4 (C-q (BOC)), 55.2 (OCH_3), 27.4 (C-methyl (BOC)), 27.3 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 286 (1.66 x 10^4) and 366 (1.36 x 10^4) nm. IR (KBr): 2980, 2934, 1745, 1597, 1515, 1369, 1344, 1307, 1248, 1152, 1032, 971, 850, 794, 750 cm^{-1}. HR-MS: mass calcd. 559.2319; mass found 559.2319.

11H: Thermal deprotection of the *t*-BOC groups was accomplished as described for **1H**. ^{1}H-NMR (THF-d_8): δ 10.61 (s, 1H, N-H'), 10.32 (s, 1H, N-H), 8.17 (d, J = 8.8 Hz, 2H, H-*meta* (Ph-NO_2)), 7.74 (d, J = 8.3 Hz, 2H, H-*ortho* (Ph-NO_2)), 7.51 (d, J = 8.4 Hz, 2H, H-*ortho* (Ph-OCH_3)), 6.90 (d, J = 9.0 Hz, 2H, H-*meta* (Ph-OCH_3)), 6.81 (broad s, 1H, H-4'), 6.45 (broad s, 2H, H-3, H-3'), 6.39 (broad s, 1H, H-4), 3.78 (s, 3H, H-methoxy) ppm. UV-Vis ($CHCl_3$): 328 and 479 nm

N,N',N''-Tri-*tert*-butoxycarbonyl-5-(4-methoxyphenyl)-5''-(4-nitrophenyl)-2,2':5',2''-terpyrrole (12) A Stille reaction between **6** (0.302 g, 0.432 mmol) and **9** (0.133 g, 0.491 mmol) in toluene (2 ml) and aqueous Na_2CO_3 (1 M, 2 ml) in the presence of $Pd(PPh_3)_4$ (58 mg, 0.050 mmol), was performed as described for **1**. This resulted in a dark liquid, which was purified by column

chromatography (15 g SiO_2, CH_2Cl_2 : hexane (1:1), $R_f = 0.06$), giving pure **12** as an oil (0.063 g, 0.087 mmol, 20%).

^{1}H-NMR ($CDCl_3$): δ 8.23 (d, J = 8.8 Hz, 2H, H-*meta* (Ph-NO_2)), 7.51 (d, J = 8.8 Hz, 2H, H-*ortho* (Ph-NO_2)), 7.29 (d, J = 8.9 Hz, 2H, H-*ortho* (Ph-OCH_3)), 6.92 (d, J = 8.8 Hz, 2H, H-*meta* (Ph-OCH_3)), 6.39 (d, J = 3.5 Hz, 1H, H-4''), 6.27-6.18 (m, 5H, H-3, H-3', H-3'', H-4, H-4'), 3.86 (s, 3H, H-methoxy), 1.33 (s, 9H, H-methyl (BOC)), 1.29 (s, 9H, H-methyl (BOC)), 1.25 (H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 158.7 (C-OCH_3), 149.3 (C=O), 149.0 (C=O), 148.9 (C=O), 146.3 (C-NO_2), 141.0 (C-*ipso* (Ph-NO_2)), 136.4/134.3/130.7/128.3/127.8/127.1 (C-*ipso* (Ph-OCH_3)/C-2/C-5/C-2'/C-5'/C-2''/C-5''), 129.5 (C-*ortho* (Ph-OCH_3)), 128.6 (C-*meta* (Ph-NO_2)), 123.2 (C-*ortho* (Ph-NO_2)), 115.2/114.4/114.4/114.3/113.9/112.3 (C-3/C-3'/C-3''/C-4/C-4'/C-4''), 113.3 (C-*meta* (Ph-OCH_3)), 84.2 (C-q (BOC)), 83.3 (C-q (BOC)), 83.1 (C-q (BOC)), 55.2 (OCH_3), 27.6 (C-methyl (BOC)), 27.5 (2 x C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 294 (1.84 x 10^4) and 364 (1.24 x 10^4) nm. IR (KBr): 2979, 1743, 1597, 1514, 1369, 1308, 1260, 1149, 1132, 1105, 1022, 849, 793 cm^{-1}. HR-MS: mass calcd. 724.3108; mass found 724.3077.

12H: Thermal deprotection of the *t*-BOC groups was accomplished as described for **1H**. UV-Vis ($CHCl_3$): 355 and 496 nm.

N,N',N'',N'''-Tetra-*tert*-butoxycarbonyl-5-(4-methoxyphenyl)-5'''-(4-nitrophenyl)-2,2':5',2'':5'',2'''-quaterpyrrole (13) A Stille reaction between **8** (33 mg, 0.038 mmol) and **9** (18.7 mg, 0.069 mmol) in toluene (1 ml) and aqueous Na_2CO_3 (1 M, 1 ml) in the presence of $Pd(PPh_3)_4$ (7.2 mg, 0.006 mmol), was performed as described for **1**. This resulted in a dark liquid, which was purified by column chromatography (6 g SiO_2, CH_2Cl_2 : hexane (3:1), $R_f = 0.33$) and gave pure **13** as an oil (8.6 mg, 0.010 mmol, 25%).

^{1}H-NMR ($CDCl_3$): δ 8.23 (d, J = 9.0 Hz, 2H, H-*meta* (Ph-NO_2)), 7.50 (d, J = 8.9 Hz, 2H, H-*ortho* (Ph-NO_2)), 7.28 (d, J = 8.8 Hz, 2H, H-*ortho* (Ph-OCH_3)), 6.91 (d, J = 8.8 Hz, 2H, H-*meta* (Ph-OCH_3)), 6.38 (d, J = 3.5 Hz, 1H, H-4'''), 6.28-6.16 (m, 7H, H-3, H-3', H-3'', H-3''', H-4, H-4', H-4''), 3.86 (s, 3H, H-methoxy), 1.29 (s, 9H, H-methyl (BOC)), 1.28 (2 x s, 2 x 9H, H-methyl (BOC)), 1.25 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 158.7 (C-OCH_3), 149.1 (2 x C=O), 148.8 (2 x C=O), 146.3 (C-NO_2), 141.1 (C-*ipso* (Ph-NO_2)), 136.3/134.2/130.8/128.1/128.0/127.2/127.0 (C-*ipso* (Ph-OCH_3)/C-2/C-5/C-2'/C-5'/C-2''/C-5''/C-2'''/C-5'''), 129.6 (C-*ortho* (Ph-OCH_3)), 128.6 (C-*meta* (Ph-NO_2)), 123.2 (C-*ortho* (Ph-NO_2)), 113.3 (C-*meta* (Ph-OCH_3)), 115.1/114.6/114.5/114.3/ 114.0/ 113.9/113.3/112.2 (C-3/C-4/C-3'/C-4'/C-3''/C-4''/C-3'''/C-4'''), 84.2 (C-q (BOC)), 83.2 (C-q (BOC)), 83.1 (C-q (BOC)), 82.9 (C-q (BOC)), 55.2 (OCH_3), 27.7 (C-methyl (BOC)), 27.5 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 297 and 363 nm. IR (KBr): 2963, 1738, 1598, 1515, 1395, 1369, 1311, 1260, 1092, 798, 698 cm^{-1}.

13H: Thermal deprotection of the *t*-BOC groups was accomplished as described for **1H**. UV-Vis (CH_3CN): 360 and 474 nm.

N-*tert*-Butoxycarbonyl-2-(4-methoxyphenyl)pyrrole (14) A Stille reaction between N-*t*-BOC-2-trimethylstannylpyrrole[29] (0.60 g, 1.82 mmol) and 4-bromoanisole (0.34 g, 1.82 mmol) in toluene (5 ml) and aqueous Na_2CO_3 (1 M, 5 ml) in the presence of $Pd(PPh_3)_4$ (45 mg, 0.039 mol), was performed as described for **1**. The resulting dark liquid was purified by column chromatography (25 g SiO_2, CH_2Cl_2 : hexane (1:3), $R_f = 0.08$) giving **15** as a colorless oil (0.24 g, 0.88 mmol, 48%).

^{1}H-NMR ($CDCl_3$): δ 7.32 (dd, J = 3.4 and 1.8 Hz, 1H, H-5), 7.27 (d, J = 8.8, 2H, H-*ortho*), 6.88 (d, J = 8.8 Hz, 2H, H-*meta*), 6.20 (t, J = 3.3 Hz, 1H, H-4), 6.13 (dd, J = 3.2 and 1.8 Hz, 1H, H-3), 3.82 (s, 3H, H-methoxy), 1.38 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 158.8 (C-OCH_3), 149.4 (C=O), 134.8 (C-2), 130.3 (C-*ortho*), 126.8 (C-*ipso* (phenyl)), 122.1 (C-5), 113.9 (C-3), 113.0 (C-*meta*), 110.4 (C-4), 83.3 (C-q (BOC)), 55.2 (OCH_3), 27.6 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 275 (0.81 x 10^4) nm.

N-*tert*-Butoxycarbonyl-2-(4-methoxyphenyl)-5-trimethylstannylpyrrole (15) A mixture of 2,2,6,6-tetramethylpiperidine (0.125 g, 0.887 mmol) in THF (3 ml) was cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 0.60 ml, 0.96 mmol) was slowly added and the solution was stirred for 10 min at -70°C. Then it was allowed to warm to 0°C and again cooled to -70°C. A mixture of **15** (0.222 g, 0.810 mmol) in THF (2 ml) was slowly added and stirring was continued for 45 min at -70°C. Then trimethylstannyl chloride (0.20 g, 1.00 mmol) in THF (1.5 ml) was slowly added, after which the mixture was stirred for 3 h at -70°C and for another 16 h at RT. The solvent was evaporated and water (10 ml) was added. Extraction with Et_2O (3 x 10 ml) followed by drying ($MgSO_4$), filtration and evaporation of the solvent, finally resulted in pure **16** (0.339 g, 0.778 mmol, 96%).

^{1}H-NMR ($CDCl_3$): δ 7.23 (d, J = 8.8 Hz, 2H, H-*ortho*), 6.87 (d, J = 8.8 Hz, 2H, H-*meta*), 6.37 (d, J = 3.1 Hz, 1H, H-4), 6.22 (d, J = 3.0 Hz, 1H, H-3), 3.82 (s, 3H, H-methoxy), 1.21 (s, 9H, H-methyl (BOC)), 0.27 (s, 9H, H-methyl (stannyl)) ppm. ^{13}C-NMR ($CDCl_3$): δ 158.7 (C-OCH_3), 151.6 (C=O), 137.9/137.1 (C-2/C-5), 130.2 (C-*ortho*), 128.2 (C-*ipso* (phenyl)), 121.1 (C-4), 115.1 (C-3), 112.9 (C-*meta*), 83.2 (C-q (BOC)), 55.3 (OCH_3), 27.3 (C-methyl (BOC)), -7.5 (C-methyl (stannyl)) ppm.

5-Trimethylstannyl-2,2′-bithiophene (16) A solution of 2,2′-bithiophene (1.01 g, 6.02 mmol) in THF (15 ml) was cooled to 0°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 3.8 ml, 6.08 mmol) was slowly added, after which the mixture was stirred at RT for 1.5 h. Then it was cooled to -70°C and a solution of trimethylstannyl chloride (1.20 g, 6.02 mmol) in THF (5 ml) was slowly added. After this addition the mixture was stirred for 4 h at -70°C and for another 12 h at RT. The dark mixture was concentrated and water (30 ml) was added. After extraction with Et_2O (3 x 25 ml), the combined organic fractions were dried ($MgSO_4$). Filtration followed by evaporation of the solvent resulted in a dark oil. Purification by column chromatography (65 g Al_2O_3, hexane, R_f = 0.34) finally gave a colorless liquid (1.20 g, 3.65 mmol, 61%).

^{1}H-NMR ($CDCl_3$): δ 7.27 (d, J = 3.4 Hz, 1H, H-4), 7.16 (m, 2H, H-3′, H-5′), 7.07 (d, J = 3.3 Hz, 1H, H-3), 6.98 (dd, J = 3.5 and 1.9 Hz, 1H, H-4′), 0.37 (s, 9H, H-methyl (stannyl)) ppm. UV-Vis ($CHCl_3$): 313 nm. IR (KBr): 3105-3050, 2981, 2913, 1413, 1195, 1050, 945, 796, 774, 692, 534 cm^{-1}.

N-*tert*-Butoxycarbonyl-2-(5-(2,2′-bithienyl))-5-(4-nitrophenyl)pyrrole (17) A Stille reaction between **2** (0.735 g, 2.00 mmol) and **16** (0.675 g, 2.05 mmol) in toluene (5 ml) and aqueous Na_2CO_3 (1 M, 5 ml) in the presence of $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), was performed as described for **1**. The resulting dark liquid was purified by column chromatography (60 g SiO_2, CH_2Cl_2 : hexane (3:4), R_f = 0.29), which finally gave **17** as a red oil (0.497 g, 1.10 mmol, 55%).

^{1}H-NMR ($CDCl_3$): δ 8.24 (d, J = 8.9 Hz, 2H, H-*meta*), 7.55 (d, J = 8.9 Hz, 2H, H-*ortho*), 7.24 (dd, J = 5.1 and 1.4 Hz, 1H, H-3′ (th)/H-5′ (th)), 7.20 (dd, J = 5.1 and 1.4 Hz, 1H, H-3′ (th)/H-5′ (th)), 7.13

(d, J = 3.7 Hz, 1H, H-3 (th)/H-4 (th)), 7.06 (d, J = 3.7 Hz, 1H, H-3 (th)/H-4 (th)), 7.03 (dd, J = 5.0 and 3.7 Hz, 1H, H-4' (th)), 6.43 (d, J = 3.5 Hz, 1H, H-3 (pyr)/H-4 (pyr)), 6.40 (d, J = 3.5 Hz, 1H, H-3 (pyr)/H-4 (pyr)), 1.28 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.1 (C=O), 146.4 (C-NO_2), 140.2 (C-*ipso* (phenyl)), 138.0, 136.9, 134.6, 132.5, 130.3, 128.7, 128.4 (C-*meta*), 127.8, 124.5, 123.7, 123.3, 123.3 (C-*ortho*), 114.7/114.6 (C-3/C-4), 85.2 (C-q (BOC)), 27.2 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 355 (1.69 x 10^4) nm.

N-*tert*-Butoxycarbonyl-2-(5'-bromo-5-(2,2'-bithienyl))-5-(4-nitrophenyl)pyrrole (18) A solution of **17** (0.497 g, 1.10 mmol) in DMF (6 ml) was blanketed by argon. A solution of NBS (0.199 g, 1.12 mmol) in DMF (5 ml) was slowly added and the mixture was stirred for 18 h at RT. Then the solution was poured into ice-water (30 ml) and extracted with Et_2O (3 x 25 ml). The combined organic fractions were dried ($MgSO_4$), filtered and concentrated. Column chromatography (30 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.40) followed by recrystallization (hexane) finally gave **18** as an orange solid (0.251 g, 0.472 mmol, 43%).
^{1}H-NMR ($CDCl_3$): δ 8.25 (d, J = 8.8 Hz, 2H, H-*meta*), 7.54 (d, J = 8.9 Hz, 2H, H-*ortho*), 7.06/6.99/6.93/6.93 (4 x d, J = 3.8 Hz, 4 x 1H, H-3/H-3'/H-4/H-4' (th)), 6.42/6.39 (d, J = 3.5 Hz, 1H, H-3/H-4 (pyr)), 1.27 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.0 (C=O), 146.5 (C-NO_2), 140.2 (C-*ipso* (phenyl)), 136.8, 134.7, 133.1, 130.6, 130.0, 128.9, 128.7, 128.5 (C-*meta*), 123.8, 123.6, 123.3 (C-*ortho*), 114.9/114.6 (C-3/C-4), 111.1 (C-Br), 85.3 (C-q (BOC)), 27.2 (C-methyl (BOC)) ppm.

5-{N-*t*-BOC-2''-[5''(4-methoxyphenyl)]pyrrolyl}-5'-{N-*t*-BOC-2'''-[5'''(4-nitrophenyl)]pyrrolyl}-2,2'-bithiophene (19) A Stille reaction between **16** (0.251 g, 0.472 mmol) and **18** (0.223 g, 0.512 mmol) in toluene (7 ml) and aqueous Na_2CO_3 (1 M, 7 ml) in the presence of $Pd(PPh_3)_4$ (55 mg, 0.048 mmol), was performed as described for **1**. The resulting dark liquid was purified by column chromatography (40 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.16). Subsequent recrystallization (hexane : CH_2Cl_2 (9:1)) gave **19** as an orange solid (0.116 g, 0.16 mmol, 34%).
^{1}H-NMR ($CDCl_3$): δ 8.26 (d, J = 8.8 Hz, 2H, H-*meta* (Ph-NO_2)), 7.54 (d, J = 9.0 Hz, 2H, H-*ortho* (Ph-NO_2)), 7.32 (d, J = 8.8 Hz, 2H, H-*ortho* (Ph-OCH_3)), 7.13-7.02 (4 x d, J = 3.7 Hz, 4 x 1H, H-3, H-3', H-4, H-4' (th)), 6.90 (d, J = 8.8 Hz, 2H, H-*meta* (Ph-OCH_3)), 6.43-6.38 (3 x d, J = 3.4 Hz, 1H, H-3'', H-3''', H-4''' (pyr)), 6.19 (d, J = 3.4 Hz, 1H, H-4'' (pyr)), 3.86 (s, 3H, H-methoxy), 1.29 (s, 9H, H-methyl (BOC)), 1.25 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 159.1 (C-OCH_3), 149.7 (C=O), 149.2 (C=O), 146.5 (C-NO_2), 140.3 (C-*ipso* (Ph-NO_2)), 138.0, 136.9, 136.7, 134.7, 134.1, 132.5, 130.3, 129.8, 128.8, 128.5, 127.7, 127.6, 126.5, 123.5, 123.4, 123.2, 114.8, 114.6, 114.1, 113.4, 111.8, 85.4 (C-q (BOC)), 84.3 (C-q (BOC)), 55.3 (OCH_3), 27.3 (C-methyl (BOC)), 27.2 (C-methyl (BOC)) ppm. UV-Vis ($CHCl_3$): 378 nm (3.10 x 10^4). IR (KBr): 2977, 1749, 1596, 1515, 1498, 1369, 1341, 1299, 1248, 1177, 1141, 1110, 1033, 842 cm^{-1}. Anal.: calcd. N 5.81, C 64.71, H 5.15; found N 5.49, C 64.89, H 5.13. FD-MS: calcd. 723.87; found 723.4.

N-Dodecyl-2-phenylpyrrole (20) KOH (0.96 g, 17.1 mmol) and DMSO (3 ml) were introduced in a 2-necked flask and stirred under inert atmosphere. A solution of 2-phenylpyrrole[59] (1.06 g, 7.4 mmol) in DMSO (4 ml) was slowly added, after which the mixture was stirred for 90 min. Then dodecyl bromide (1.82 g, 7.3 mmol) was added dropwise and stirring was continued for another 18 h. The

mixture was poured into water (70 ml) and extracted with hexane, CH_2Cl_2 and Et_2O (each 50 ml). The combined organic fractions were dried ($MgSO_4$), filtered and concentrated, resulting in a dark oil. Column chromatography (30 g, SiO_2, hexane, R_f = 0.18) finally resulted in **20** as a colorless oil (1.00 g, 3.2 mmol, 44%).
^{1}H-NMR ($CDCl_3$): δ 7.38-7.26 (m, 5H, H-*ortho*, -*meta*, -*para*), 6.74 (dd, J = 2.6 and 2.0 Hz, 1H, H-5), 6.20 (t, J = 2.8 Hz, 1H, H-4), 6.17 (dd, J = 3.6 and 1.8 Hz, 1H, H-3), 3.90 (t, J = 7.5 Hz, 2H, N-C$\underline{H}_2$), 1.63 (t, J = 6.7 Hz, 2H, N-CH$_2$-C$\underline{H}_2$), 1.36-1.12 (m, 18H, -C$\underline{H}_2$-), 0.88 (t, J = 6.9 Hz, 3H, -CH$_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 134.3/133.8 (C-2/C-*ipso* (phenyl)), 128.9/128.3 (C-*ortho*/C-*meta*), 126.7 (C-*para*), 121.8 (C-5), 108.6/107.7 (C-3/C-4), 47.1 (N-$\underline{C}$H$_2$), 31.9, 31.4, 29.6 (2 peaks), 29.5, 29.4, 29.3, 29.1, 26.6, 22.7 (-$\underline{C}$H$_2$-), 14.1 (-$\underline{C}$H$_3$) ppm.

N-Dodecyl-2-bromo-5-phenylpyrrole (21) A solution of N-dodecyl-2-phenylpyrrole (**20**, 0.597 g, 1.92 mmol) in THF (10 ml) was cooled to -70°C, blanketed by argon. NBS (0.330 g, 1.85 mmol) was added, after which the solution was stirred at this temperature for 30 min. Then it was brought to 3°C at which temperature it was kept, unstirred, for another 18 h. Na_2CO_3 (50 mg) was added and the mixture was stirred for 15 min. The solvent was then evaporated, CCl_4 (20 ml) was added, the mixture was stirred for 10 min and filtered. Finally, the filtrate was concentrated, resulting in a slightly red oil, pure **21** (0.71 g, 1.81 mmol, 98%).
^{1}H-NMR ($CDCl_3$): δ 7.41-7.31 (m, 5H, H-*ortho*, -*meta*, -*para* (phenyl)), 6.22 (d, J = 3.7 Hz, 1H, H-3), 6.16 (d, J = 3.7 Hz, 1H, H-4), 3.93 (t, J = 7.7 Hz, 2H, N-C$\underline{H}_2$), 1.59 (m, 2H, N-CH$_2$-C$\underline{H}_2$), 1.36-1.10 (m, 18H, -C$\underline{H}_2$-), 0.88 (t, J = 6.9 Hz, 3H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 135.5/133.6 (C-5/C-*ipso* (phenyl)), 129.0/128.4 (C-*ortho*/C-*meta*), 127.3 (C-*para*), 110.6/109.4 (C-3/C-4), 102.8 (C-2), 45.9 (N-$\underline{C}$H$_2$), 31.9, 30.7, 29.6 (2 peaks), 29.5, 29.4, 29.3, 28.9, 26.3, 22.7 (-$\underline{C}$H$_2$-), 14.1 (-$\underline{C}$H$_3$) ppm.

N-Dodecyl-2,5-di(2-thienyl)pyrrole (22) Performing a reaction with KOH (0.88 g, 15.7 mmol), 2,5-di(2-thienyl)pyrrole (1.15 g, 5.0 mmol) and dodecyl bromide (1.87 g, 7.5 mmol) as described for **20** (however, this time in the absence of light), resulted in a dark oil. Column chromatography (80 g, SiO_2, hexane, R_f = 0.32) finally gave pure **22** as an oil (1.40 g, 3.50 mmol, 70%).
^{1}H-NMR ($CDCl_3$): δ 7.33 (dd, J = 4.6 and 1.8 Hz, 2H, H-5 (th)), 7.12-7.07 (m, 4H, H-3, H-4 (th)), 6.36 (d, J = 0.9 Hz, 2H, H-3,4 (pyr)), 4.14 (t, J = 7.9 Hz, 2H, N-C$\underline{H}_2$), 1.58 (t, J = 7.9 Hz, 2H, N-CH$_2$-C$\underline{H}_2$), 1.38-1.12 (m, 18H, -C$\underline{H}_2$-), 0.91 (t, J = 7.1 Hz, 3H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 135.0 (C-2 (th)), 128.2/127.2/125.9/125.2 (C-2,5 (pyr)/C-3/C-4/C-5 (pyr)), 110.7 (C-3,4 (pyr)), 45.1 (N-$\underline{C}$H$_2$), 31.9, 31.1, 29.6 (2 peaks), 29.5, 29.3 (2 peaks), 28.9, 26.3, 22.7 (-$\underline{C}$H$_2$-), 14.1 (-CH$_3$) ppm.
(N.B. Besides **22**, we also isolated N,3-di(dodecyl)-2,5-di(2-thienyl)pyrrole (0.16 g, 0.28 mmol, 6%) by column chromatography (hexane, R_f = 0.46): ^{1}H-NMR ($CDCl_3$): δ 7.39 (dd, J = 5.2 and 1.1 Hz, 1H, H-α (th)), 7.26 (dd, J = 4.7 and 1.7 Hz, 1H, H-α (th)), 7.09 (dd, J = 5.2 and 3.5 Hz, 1H, H-β (th)), 7.06-7.02 (m, 2H, H-β (th)), 6.99 (dd, J = 3.5 and 1.1 Hz, 1H, H-β (th)), 6.24 (s, 1H, H-4 (pyr)), 3.95 (t, J = 7.9 Hz, 2H, N-C$\underline{H}_2$), 2.39 (t, J = 7.8 Hz, 2H, pyr-C$\underline{H}_2$), 1.58-1.40 (m, 4H, N-CH$_2$-C$\underline{H}_2$ and pyr-CH$_2$-C$\underline{H}_2$), 1.38-1.00 (m, 36H, -C$\underline{H}_2$-), 0.88 (2 x t, J = 7.0 Hz, 6H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 135.4, 133.7, 128.7, 127.2, 126.9 (2 peaks), 126.5, 125.5, 125.2, 124.6, 124.1, 110.5, 45.1, 31.9, 31.3, 31.2, 29.7, 29.6, 29.5, 29.3 (2 peaks), 28.8, 26.4, 26.3, 22.7, 14.1 (2 peaks) ppm.

N-Dodecyl-2,5-di(5-trimethylstannyl-2-thienyl)pyrrole (23) N-Dodecyl-2,5-di(2-thienyl)pyrrole (**22**, 0.632 g, 1.63 mmol) was dissolved in THF (10 ml) and cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 2.25 ml, 3.6 mmol) was slowly added and the solution was stirred at this temperature for 10 min. Then it was brought to -40°C at which temperature it was stirred for 45 min. After this period it was again cooled to -70°C and a solution of $(CH_3)_3SnCl$ (0.70 g, 3.51 mmol) in THF (5 ml) was added dropwise. The solution was stirred for another 90 min, after which it was slowly warmed to RT. After 1 h the solvent was evaporated and Et_2O and water were added. The aqueous phase was extracted with Et_2O and the combined organic fractions were dried ($MgSO_4$), filtered and concentrated resulting in a dark green oil, pure **23** (1.18 g, 1.63 mmol, 100%).
^{1}H-NMR ($CDCl_3$): δ 7.17 (dd, J = 3.4 and 0.7 Hz, 2H, H-3/H-4 (th)), 7.14 (dd, J = 3.3 and 0.6 Hz, 2H, H-3/H-4 (th)), 6.32 (d, J = 0.7 Hz, 2H, H-3,4 (pyr)), 4.14 (t, J = 7.8 Hz, 2H, N-C$\underline{H}_2$), 1.60 (t, J = 7.2 Hz, 2H, N-CH$_2$-C$\underline{H}_2$), 1.37-1.10 (m, 18H, -C$\underline{H}_2$-), 0.88 (t, J = 6.6 Hz, 3H, -CH$_3$), 0.39 (2 x s, 18H, H-methyl (stannyl)) ppm. ^{13}C-NMR ($CDCl_3$): δ 140.9, 137.4, 135.3, 128.5, 126.6, 110.4 (C-3,4 (pyr)), 45.1 (N-$\underline{C}H_2$), 31.9, 31.1, 29.6 (2 peaks), 29.5, 29.4, 29.3, 28.9, 26.4, 22.7 (-$\underline{C}H_2$-), 14.1 (-$\underline{C}H_3$), -8.2 (C-methyl (stannyl)) ppm.

N-Dodecyl-2,5-di{2[5(N-dodecyl-5-phenyl)pyrrolyl]thienyl}pyrrole (24) A solution of N-dodecyl-2-bromo-5-phenylpyrrole (**21**, 194.8 mg, 0.499 mmol) and N-dodecyl-2,5-di(5-trimethylstannyl-2-thienyl)pyrrole (**23**, 183.0 mg, 0.252 mmol) in toluene (3 ml) and aqueous Na_2CO_3 (1 M, 3 ml) was deaerated and stored under argon. $Pd(PPh_3)_4$ (3 mol%) was added and the mixture was heated under reflux for two days. Et_2O and water were added and the phases were separated. The aqueous phase was extracted with Et_2O and the organic fractions were combined, dried ($MgSO_4$), filtered and concentrated. The resulting dark oil was purified by column chromatography (30 g Al_2O_3, hexane to CH_2Cl_2 : hexane (1:5), R_f (1:3) = 0.79), which gave pure **24** as an oil (15 mg, 0.015 mmol, 6%).
^{1}H-NMR ($CDCl_3$): δ 7.45-7.29 (m, 10H, H-*ortho*, -*meta*, -*para*), 7.04 (s, 4H, H-β (th)), 6.41 (d, J = 3.6 Hz, 2H, H-3 (outer pyrrole units)), 6.39 (s, 2H, H-3,4 (inner pyrrole unit)), 6.23 (d, J = 3.6 Hz, 2H, H-4 (outer pyrrole units)), 4.25 (t, J = 7.5 Hz, 2H, N-C$\underline{H}_2$ (inner pyrrole unit)), 4.15 (t, J = 7.9 Hz, 4H, N-C$\underline{H}_2$ (outer pyrrole units)), 1.65 (m, 6H, N-CH$_2$-C$\underline{H}_2$ (inner and outer pyrrole units)), 1.38-1.00 (m, 54H, -C$\underline{H}_2$-), 0.88 (2 x t, 9H, -CH$_3$ (inner and outer pyrrole units)) ppm. ES-MS: mass calculated 1017; mass found 1016.7.

3.6 References

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37 The naphthalene and stilbene derivatives (top of scheme 3.3) represent unpublished results from the Department of Chemistry and the Center for Research on Molecular Electronics and Photonics, Catholic University of Leuven, Celestijnenlaan, 200 D, B-3001 Leuven, Belgium, which were measured with the same equipment and under the same conditions as our compounds. The biphenyl and oligothiophene derivatives (bottom of scheme 3.3) are examples from literature, which were measured with EFISH (ref. 7 and 23, respectively).

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Chapter 4

SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED 3-ALKYLPYRROLES

ON THE WAY TO REGIOREGULAR POLYPYRROLES

Abstract: *3-Alkylpyrroles have been known for many years but hitherto little effort has been put in functionalizing these compounds. Here we present the results of detailed studies on the halogenation and stannylation of two types of N-protected 3-hexylpyrroles, being N-phenylsulfonyl and N-t-BOC protected species. Halogenation experiments reveal that selective α-mono- and α,α-disubstitution can easily be achieved for both types using NBS or NCS in THF at -70°C. An exception is the synthesis of N-t-BOC-2-bromo-3-hexylpyrrole; the latter can, however, be prepared by a slight adaptation (DMF instead of THF as solvent). Concerning stannylation experiments, none of the N-phenylsulfonyl protected 3-hexylpyrroles can be stannylated selectively. In case of N-t-BOC protected 3-hexylpyrroles, α-stannylation can be performed; however, just the 5-position is functionalized by direct lithiation (LTMP) and subsequent stannylation ($(CH_3)_3SnCl$). When performing a NBS bromination on an α-trimethylstannyl substituted pyrrole derivative, a stannyl-bromo exchange reaction takes place, the latter being an excellent method to prepare α-monobromo pyrroles. Finally, the Stille reaction has been applied in our first attempts to prepare regioregular oligo- and polypyrroles.*

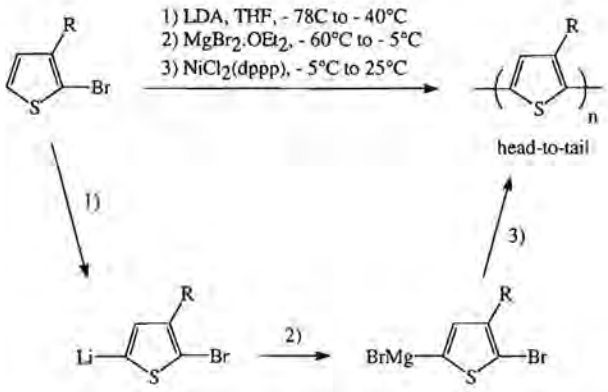
4.1 *Introduction*

π-Conjugated polymers have become an important part of polymer chemistry since their properties have been shown to be of great interest for application in electrical and optical devices.[1,2] The extended π-conjugation in these polymers, however, makes them highly intractable and infusible. As a result, the synergism of metallic properties and polymer processing is not achieved with the parent polymers, such as polypyrrole. This lack of solubility and processability as well as problems related to the characterization of these polymers, have been overcome by the introduction of flexible side chains. Well-known in this

context are alkyl and alkoxy substituted polyphenylenes[3,4] and poly(phenylene vinylene)s[5,6], and polyheteroaromatics like polypyrroles[7-11] and polythiophenes.[12-14]

In many cases introduction of side chains introduces a number of regioisomeric relationships, originating from combinations of head-to-head (HH) and/or head-to-tail (HT) configurations.[15,16] Head-to-head coupling of alkyl groups is sterically unfavorable for coplanarity and, hence, causes a significant loss of conjugation. Head-to-tail coupling, however, does not prevent conjugation to a large extent. The difference in coplanarity between head-to-head and head-to-tail couplings shows the subtleness in the trade-off between resonance energy and steric hindrance in substituted polyaromatics.

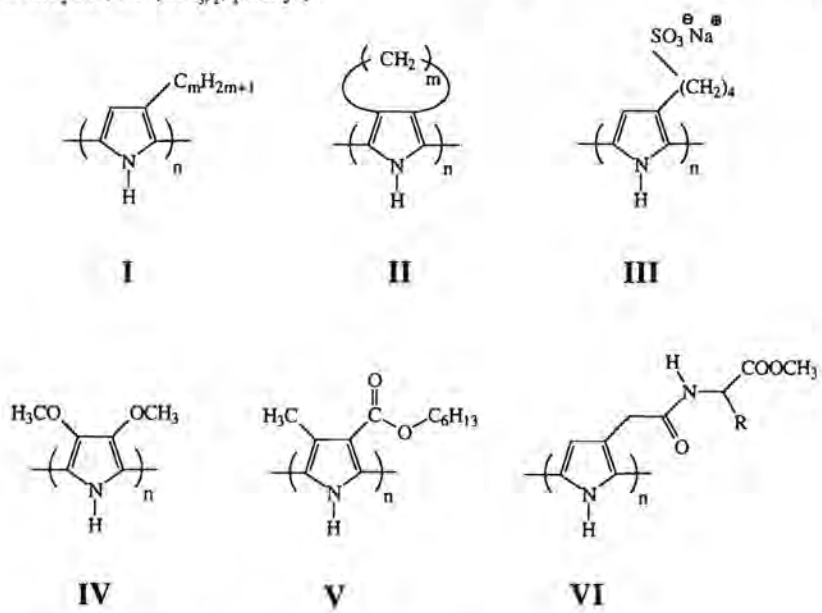
Hitherto, only oligo- and polythiophenes have been prepared in a regioregular fashion. In 1990 Wudl *et al.* were the first to prepare regioregular head-to-head poly(3-alkylthiophene)s both by chemical and electrochemical polymerization of 3,3'-dialkyl-2,2'-bithiophenes.[17] Although these polymers absorbed light at shorter wavelengths than their regiorandom analogs, this was not reflected in the conductivity. A few years later, McCullough *et al.* were the first to prepare regioregular head-to-tail polythiophenes.[18-22] Applying the Kumada coupling on functionalized 3-alkylthiophenes, they obtained over 98% head-to-tail coupled polymers in yields ranging from 33 to 69% (scheme 4.1). These polymers exhibit enhanced conducting and optical properties when compared to regiorandom materials. The conductivity of poly(3-dodecylthiophene) reaches values up to 1000 Scm^{-1}, whereas for the regiorandom material the conductivity is limited to 20 Scm^{-1}. Furthermore, the difference in absorption maximum is indicative for enhanced coplanarity in these systems. Another intriguing property of these systems is the temperature and solvent dependence of the UV-absorption, which arises from aggregation and a conformational change in the aromatic backbone.[23,24]



Scheme 4.1: *Synthesis of regioregular polythiophenes as developed by McCullough.*[18-22]

Recently, two other routes have become available to achieve regioregularity in polythiophenes. Rieke *et al.* applied the Negishi coupling using 3-alkyl-2-(bromozincio)-5-bromothiophenes and a Ni(dppe)Cl_2 catalyst[25,26], while Canadian and Swedish scientists simultaneously prepared the first regioregular polythiophenes by means of an oxidative coupling reaction with $FeCl_3$.[27,28] Furthermore, the first regioregular oligothiophenes have been synthesized and investigated: applying both the Kumada and the Stille reaction, Barbarella *et al.* prepared head-to-tail oligomers containing up to three repeating units[29-31], which appeared to be interesting models to study conformational properties.

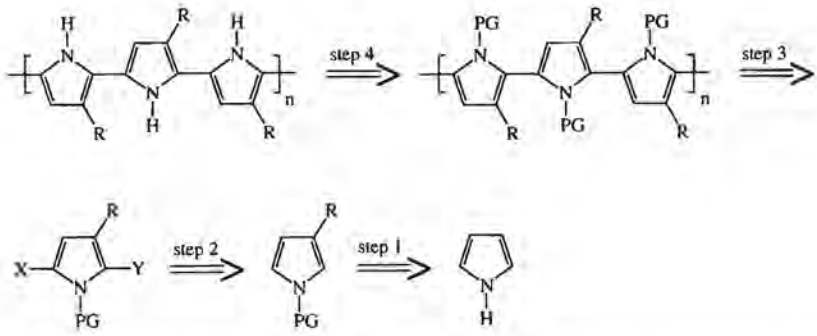
Oligo- and polypyrrole chemistry is still waiting for its first regioregular 3-substituted derivatives. Up to now only regiorandom polypyrroles have been prepared. Scheme 4.2 shows some examples. Well-known are the poly(3-alkylpyrrole)s with different chain lengths (**I**, m = 2, 6, 8, 10, 12, 15, 18)[7], and the bicyclic poly(3,4-alkanopyrrole)s (**II**)[32] as prepared by Wegner *et al.* Another example are the water-soluble self-doped polypyrroles as reported by Meijer *et al.* (**III**).[33] Here the sodium salt of pyrrole-3-alkanesulfonic acid acts as monomer as well as electrolyte for the electrochemical polymerization. Other examples are alkoxy (**IV**)[11] and ester (**V**)[8] substituted polypyrroles, and polymers with chiral side chains (**VI**, R = CH_2OH, $CH(CH_3)_2$, phenyl).[34]



Scheme 4.2: *Examples of substituted polypyrroles.*

There are two important reasons for the fact that regioregular oligo- and polypyrroles have not been prepared yet. First of all, there is hardly any knowledge on the synthesis of functionalized 3-alkylpyrroles (scheme 4.3, step 2). Secondly, there is a lack of knowledge on

asymmetric coupling reactions to bring about the desired regioregular couplings (step 3). However, with the knowledge that we gained on the asymmetric Stille reaction (Chapter 2), we have a powerful tool in hand to investigate asymmetric coupling reactions with functionalized 3-alkylpyrroles.

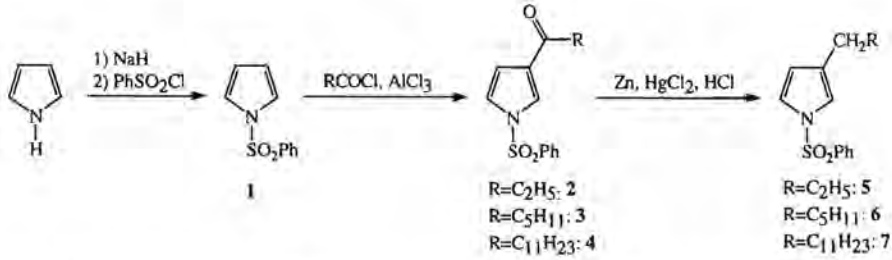


Scheme 4.3: *Retrosynthetic route toward regioregular polypyrroles (PG=protecting group).*

In order to prepare regioregular polypyrroles, the route as depicted in scheme 4.3 was followed. Pyrrole was first protected with an appropriate protecting group, after which the pyrrole unit was selectively alkylated at the 3-position (step 1). In the next step the N-protected 3-alkylpyrrole was functionalized (step 2). Since we wanted to apply the Stille reaction, this step intended selective halogenation and stannylation in order to prepare a bifunctional monomer. Finally, attempts were made to polymerize this monomer in order to prepare the desired regioregular polymer (step 3). In the following sections we will mainly focus on step 2, being the synthesis of functionalized 3-alkylpyrroles. Furthermore, the first attempts toward N-protected regioregular oligo- and polypyrroles are discussed.

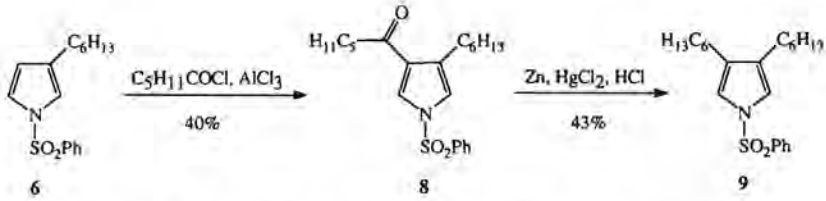
4.2 *Attempts toward regioregular polypyrroles*

The synthesis of a regioregular head-to-tail polypyrrole started from pyrrole. Pyrrole is a "π-excessive" heteroaromatic compound that, because of its electron-richness, can easily be attacked by electrophilic reagents. A well-known reaction is the Friedel-Crafts acylation of pyrroles, which, in case a phenylsulfonyl (SO_2Ph) group is attached to the annular nitrogen atom, selectively substitutes the 3-position of the pyrrole unit (scheme 4.4).[7,35-38] Pyrrole was first protected with the phenylsulfonyl group by a sequence of anion formation (NaH), followed by the addition of phenylsulfonyl chloride. The resulting N-phenylsulfonylpyrrole **1** (83% yield)[39], was subsequently reacted with an appropriate acyl chloride or anhydride, using $AlCl_3$ as Lewis acid, which gave a number of 3-acylated pyrrole derivatives (**2-4**) in quantitative yields.



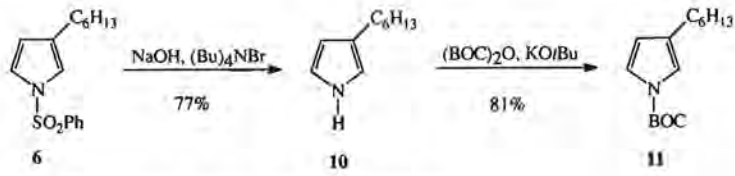
Scheme 4.4: *Synthesis of 3-alkylpyrroles by a sequence of Friedel-Crafts acylation and Clemmensen reduction.*

In the next step the acyl group was reduced to yield the desired 3-alkylpyrroles under mild conditions. This reaction was performed by a Clemmensen reduction[40,41]. Applying amalgamated zinc (Zn and $HgCl_2$) in the two-phase system of toluene and concentrated HCl (36%), the acylated pyrroles were easily transformed into their reduced species. After work-up procedures and column chromatography, the corresponding N-phenylsulfonyl-3-alkyl-pyrroles were isolated in yields of 100% (R = C_2H_5 (**5**)), 61% (R = C_5H_{11} (**6**)) and 45% (R = $C_{11}H_{23}$ (**7**)), respectively. In case of N-phenylsulfonyl-3-hexylpyrrole (**6**), repetition of the acylation/reduction sequence resulted in N-phenylsulfonyl-3,4-dihexylpyrrole **9** (scheme 4.5).



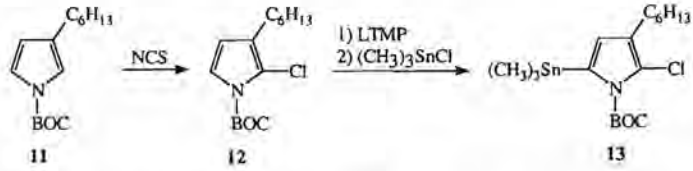
Scheme 4.5: *Synthesis of N-phenylsulfonyl-3,4-dihexylpyrrole (9).*

In oligo- and polypyrrole chemistry there are no data available regarding the influence of the phenylsulfonyl group on a Stille reaction. Since we had our doubts about the stability of this group under Stille coupling conditions, and about possible steric and/or electronic influences, we also investigated the *tert*-butoxycarbonyl (*t*-BOC) protecting group, which is compatible with pyrrole-Stille chemistry (scheme 4.6).[42-44] Removal of the phenylsulfonyl group of **6** was performed under basic conditions[45]; applying aqueous NaOH (5 M)/methanol with tetrabutylammonium bromide as phase-transfer catalyst, resulted in 3-hexylpyrrole **10** in 77% yield. Subsequent protection with the *t*-BOC group, using $(BOC)_2O$ and KO*t*Bu in THF[46], gave N-*t*-BOC-3-hexylpyrrole **11** (81% yield).



Scheme 4.6: *Synthesis of N-t-BOC-3-hexylpyrrole (11).*

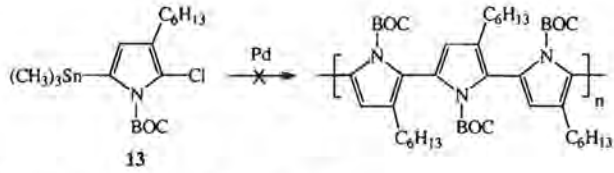
For the regioregular synthesis of poly(N-*t*-BOC-3-hexylpyrrole-2,5-diyl) *via* the asymmetric Stille reaction, a bifunctional monomer is required, meaning that N-*t*-BOC-3-hexylpyrrole **11** had to be halogenated and stannylated selectively. Halogenation reactions with **11** were performed following the general halogenation procedure as discussed in Chapter 2 (NXS, THF, -70°C).[42,47-49] Using one equivalent of NCS, N-*t*-BOC-2-chloro-3-hexylpyrrole (**12**) was prepared in good yield; however, there was still some starting compound (**11**) left. In order to achieve total conversion, we added 1.15 equivalent of NCS resulting in the quantitative formation of **12**. Selective stannylation of **12** at the 5-position was accomplished by direct lithiation with LTMP, followed by the addition of trimethylstannyl chloride as discussed in Chapter 2 (THF, -70°C; scheme 4.7). The resulting compound, N-*t*-BOC-2-chloro-3-hexyl-5-trimethylstannylpyrrole (**13**), is a bifunctional pyrrole derivative that can be used directly in a Stille polymerization.



Scheme 4.7: *Synthesis of N-t-BOC-2-chloro-3-hexyl-5-trimethylstannylpyrrole (13).*

Since it is well-known that aryl bromides are far more reactive in the Stille reaction than the corresponding chlorides, we investigated the synthesis of the bromo analog of **13** as well. Therefore, **11** was treated with one equivalent of NBS under exactly the same conditions as described above. However, much to our surprise, this reaction did not give the desired monobrominated pyrrole derivative. In fact, several compounds were found including starting material, 2- and 5-monobrominated and 2,5-dibrominated N-*t*-BOC-3-hexylpyrrole. The latter clearly indicates the absence of preferential bromination at the 2-position, a phenomenon that has been observed for NBS bromination of 3-alkylthiophenes.

With the knowledge gained in Chapter 2 on pyrrole-Stille reactions, we performed the Stille polymerization in the two-phase system of toluene and aqueous Na_2CO_3 (1 M) (scheme 4.8).

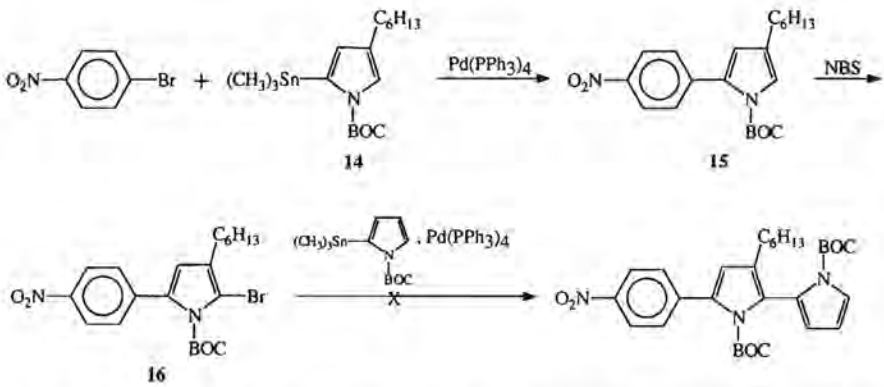


Scheme 4.8: *Stille polymerization of monomer* ***13****.*

After two and four days with $Pd^{0}(PPh_3)_4$ as catalyst, it appeared that only partial destannylation had occurred; there was not the slightest indication for the formation of any desired product(s), neither by TLC nor by ^{1}H-NMR spectroscopy. Performing the same reaction with $Pd^{II}(PPh_3)_2Cl_2$ gave the same result. Apparently, it seems that due to the chloro substituent, the reactivity is so low, that only destannylation is observed. Since the synthesis of N-*t*-BOC-2-bromo-3-hexyl-5-trimethylstannylpyrrole was not possible at this stage of research, we decided to study well-defined regioregular oligomers first.

4.3 *Attempts toward regioregular oligopyrroles*

In order to prepare a series of regioregular oligopyrroles, we started from an activated aryl halide since the methodological studies (Chapter 2) had demonstrated that such a species is far more reactive than a non-activated aryl halide. Therefore, a Stille reaction was performed under standard coupling conditions (toluene/aqueous Na_2CO_3 (1 M), $Pd^{0}(PPh_3)_4$) using 4-bromo-nitrobenzene and N-*t*-BOC-2-trimethylstannyl-4-hexylpyrrole (**14**). The latter was prepared from **11** in a similar fashion as described for **13** (scheme 4.9).



Scheme 4.9: *Synthesis of oligo(3-hexylpyrrole) derivatives using an activated aryl halide.*

After 4 days under reflux conditions, N-*t*-BOC-2-(4-nitrophenyl)-4-hexylpyrrole (**15**) was isolated in 49% yield. This compound was then selectively brominated at the free α-pyrrolyl position using standard bromination conditions (NBS, THF, -70°C), which gave N-*t*-BOC-2-bromo-3-hexyl-5-(4-nitrophenyl)pyrrole (**16**) in quantitative yield. Subsequent coupling of **16** with N-*t*-BOC-2-trimethylstannylpyrrole[53], however, did not give the desired oligomer. In fact, the only products obtained were debrominated and destannylated starting compounds, and the homo-coupling product of N-*t*-BOC-2-trimethylstannylpyrrole, being N,N'-di-*t*-BOC-2,2'-bipyrrole. Similarly, the 'activated' reaction between **14** and **16**, as well as the 'non-activated' reactions between N-*t*-BOC-2-bromo-4-hexylpyrrole and N-*t*-BOC-2-trimethylstannylpyrrole, and N-*t*-BOC-2-trimethylstannyl-4-hexylpyrrole and N-*t*-BOC-2-bromopyrrole were unsuccessful.

These results forced us to conclude that, applying the abovementioned substituents and conditions, the Stille reaction is not the appropriate route to prepare regioregular oligo- and polypyrrole derivatives.[50] An explanation for this unexpected result might be two-fold. First of all, it seems obvious that steric influences play an important role in these reactions. Since the Pd-catalysts applied here are quite bulky because of the PPh_3 ligands, it will be difficult to approach the carbon-halogen bond in order to form the planar PdL_2ArX complex. Both the alkyl chain and the *t*-BOC group contribute to this. Secondly, it seems plausible that some kind of electronic effect is involved as well. This is confirmed by the fact that it is not possible to couple 3-alkylpyrroles along the 5-position, being the situation in which the alkyl chain is directed away from the reaction centre.

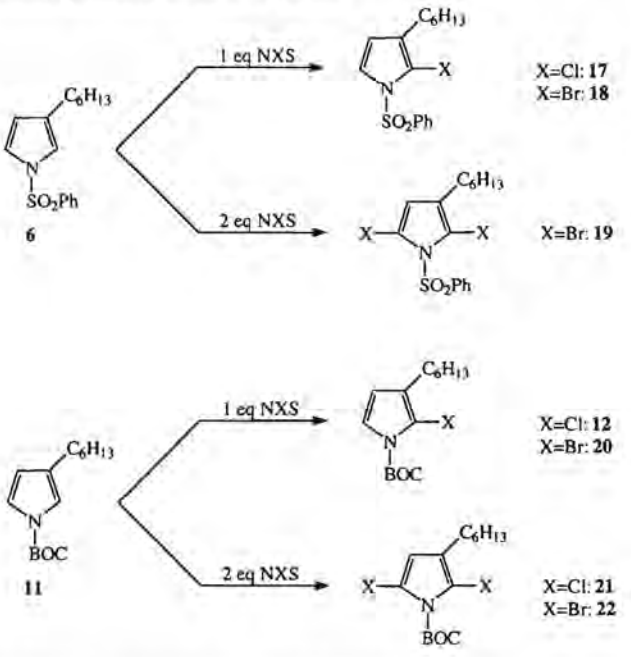
4.4 *Detailed studies on the functionalization of N-protected 3-hexylpyrroles*

Although our first attempts toward regioregular oligo- and polypyrroles did not yield the desired products, new and important information was obtained about the limitations of the Stille reaction. Apparently, the reactivity of the pyrrole unit changes drastically by the introduction of an alkyl chain at the 3-position. In the following, the functionalization of N-protected 3-hexylpyrroles will be discussed in more detail.

4.4.1 *Halogenation of N-protected 3-hexylpyrroles*

Halogenation reactions of N-phenylsulfonyl-3-hexylpyrrole (**6**) and N-*t*-BOC-3-hexylpyrrole (**11**) were performed following the standard procedures discussed in Chapter 2. In case of N-phenylsulfonyl-3-hexylpyrrole (**6**) both mono- and dihalogenation reactions were performed in THF at -70°C with one and two equivalents of NXS, respectively (scheme 4.10).[57] After continuous stirring for 30 minutes, the reaction mixtures were brought to 3°C at

which temperature they were kept, unstirred, overnight. Subsequent work-up procedures finally gave the desired products in 90-95% yields.



Scheme 4.10: *Selective halogenation of 3-hexylpyrroles using NXS.*

Halogenation of N-*t*-BOC-3-hexylpyrrole (**11**) was performed under the same conditions with comparable yields. However, as mentioned in section 4.2, there was one exception, being the synthesis of N-*t*-BOC-2-bromo-3-hexylpyrrole (**20**). When the reaction was performed as described above, this resulted in several products, including starting material, 2- and 5-monobrominated and 2,5-dibrominated 3-hexylpyrrole. Therefore, we investigated this reaction more closely. After a number of attempts, it was finally performed in DMF at -60°C (N.B. DMF is a common solvent for NBS-bromination reactions of thiophenes[51]). In this way, **20** was formed in quantitative yield without the formation of any by-products.

In case of the halogenation reactions performed in THF, small amounts of by-products (5-10%) were obtained. These by-products were most probably the result of allylic halogenation of the hexyl chain (^{1}H-NMR revealed signals between 3.9 and 4.9 ppm in case of chlorination and signals between 3.3 and 4.2 ppm in case of bromination). Since these by-products must be formed by a radical mechanism, it is obvious that, in case the reaction is performed in DMF, the amount of by-products is much lower; HBr is an intermediate in the radical mechanism, which is neutralized by DMF, but not by THF. However, as the removal of DMF requires higher temperatures, all halogenation reactions, with the exception of the

preparation of **20**, were performed in THF, since halogenated pyrrole derivatives are notorious for their thermal instability.

Two final remarks: all halogenation experiments show that 3-hexylpyrroles can be halogenated to the desired mono- and dibrominated species using NXS in THF at -70°C (DMF in case of **20**). However, just like other N-substituted halopyrroles, one has to handle these compounds with great care since they are quite unstable, even at room temperature. Therefore, all compounds were directly used, or stored under argon at low temperatures (-20°C). A second issue is the synthesis of N-*t*-BOC-2-bromo-3-hexyl-5-trimethylstannyl-pyrrole. Although this compound could probably be prepared at this stage of research by a sequence of NBS/DMF-bromination and subsequent stannylation as discussed for **13**, we did not prepare it since the activated oligomer studies had already shown that this monomer would most probably not polymerize either.

4.4.2 *Stannylation of N-protected 3-hexylpyrroles*

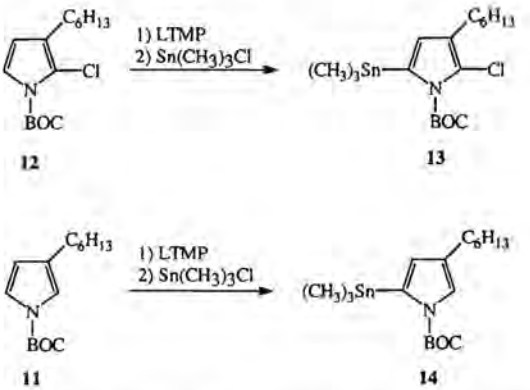
For the regiospecific stannylation and, thus, lithiation of N-substituted 3-hexylpyrroles, both the direct and indirect route were investigated. Since the 2-position can easily be halogenated, the 5-position is preferred for stannylation, which is also favorable from a steric point of view (for a pliable addition to the Pd-complex, the stannyl substituent should be easily accessible). Unfortunately, the electron-donating effect of the hexyl substituent directs lithiation toward the 2-position. Therefore, a sterically hindered base, like LTMP, LDA or *t*-BuLi, is required for anion formation.

First of all, we tried to stannylate N-phenylsulfonyl protected 3-hexylpyrroles. Starting from N-phenylsulfonyl-3-hexylpyrrole (**6**), lithiation with LTMP at -70°C in THF followed by the addition of trimethylstannyl chloride at the same temperature, showed that several products were formed; however, the desired product was not present in the mixture (in the ^{1}H-NMR one expects two doublets with coupling constants of about 2.2 Hz at positions of 6.2 (β-proton) and 7.3 ppm (α-proton) in case of 5-stannylation or doublets at similar positions with coupling constants of about 3.6 Hz in case of 2-stannylation). In fact, it seemed as if *ortho* lithiation of the phenyl ring had taken place. However, since the mixture consisted of many products and there was no indication for the desired product, no attempts were made to investigate these products.

Stannylation of N-phenylsulfonyl-2-bromo-3-hexylpyrrole (**18**) showed similar results. Both with LTMP and LDA, numerous stannylated products were formed. However, again there was no indication of the desired product to be formed. When *t*-BuLi was used, we did not observe any stannylation. The only products found after work-up procedures were starting material and debrominated product. The latter is a strong indication that, although

lithiation has definitely taken place, substitution with the trimethylstannyl group is not possible for steric reasons.

Stannylation of N-*t*-BOC protected 3-hexylpyrroles gave better results (scheme 4.11). As shown in section 4.2, N-*t*-BOC-2-chloro-3-hexyl-5-trimethylstannyl-pyrrole (**13**) can be prepared starting from monochloro derivative **12** by direct lithiation (LTMP) and subsequent stannylation ($(CH_3)_3SnCl$) in THF at -70°C. Similarly, N-*t*-BOC-3-hexylpyrrole (**11**) can be transferred into N-*t*-BOC-2-trimethylstannyl-4-hexylpyrrole (**14**) (61% yield after column chromatography (Al_2O_3)).



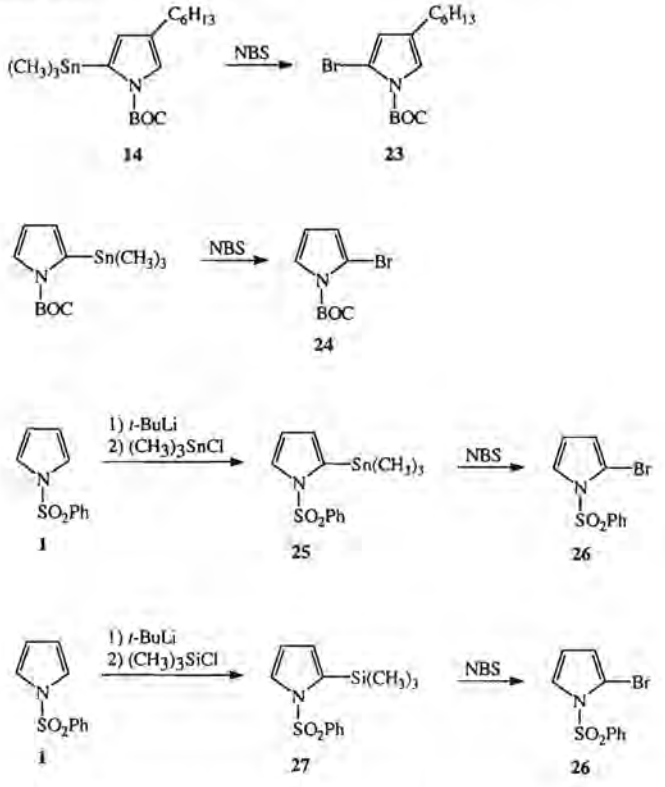
Scheme 4.11: *Selective stannylation of N-t-BOC protected 3-alkylpyrroles.*

From these stannylation experiments it can be concluded that when a N-phenylsulfonyl protected 3-hexylpyrrole is involved, some stannylated products are formed but none is the desired α-trimethylstannylpyrrolyl derivative. In case of *t*-BOC protected 3-hexylpyrroles, the direct route leads to appropriately stannylated products, being **13** and **14**.

4.4.3 *The stannyl-bromo exchange reaction*

With a convenient route toward N-*t*-BOC-2-trimethylstannyl-4-hexylpyrrole (**14**), it should be possible to prepare N-*t*-BOC-2-bromo-3-hexyl-5-trimethylstannylpyrrole by bromination of the remaining α-position with NBS. Therefore, this reaction was performed using standard bromination conditions (NBS, THF, -70°C) (scheme 4.12). However, much to our surprise, the only product that we obtained was N-*t*-BOC-2-bromo-4-hexylpyrrole (**23**), which, after filtration over SiO_2 in order to remove N-trimethylstannyl succinimide, also appeared to be a remarkably stable product (97% yield). Instead of bromination of the 2-position, a stannyl-bromo exchange reaction had taken place.[52]

In order to test the generality of this reaction and to investigate the origin of the stability, we subsequently tried to synthesize N-*t*-BOC-2-bromopyrrole (**24**) from N-*t*-BOC-2-trimethylstannylpyrrole[53]. Although this compound had once been described by Chen and Cava[54,55], it was generally considered to be an extremely unstable compound. Applying the same conditions as for **23**, compound **24** was indeed formed as a stable colorless oil (97% yield). Then we investigated this mild substitution reaction on a trimethylstannyl substituted pyrrole bearing a N-phenylsulfonyl group. Therefore, N-phenylsulfonyl-2-trimethylstannyl-pyrrole (**25**) was prepared by first making the anion using the procedure of Levy *et al.*[56], followed by reaction with trimethylstannyl chloride (59% yield). Subsequent application of the stannyl-bromo exchange reaction resulted in N-phenylsulfonyl-2-bromopyrrole (**26**) as a stable white solid (99% yield). Finally, we tried to perform this reaction on a trimethyl*silyl* substituted pyrrole. Therefore, N-SO_2Ph-2-trimethylsilylpyrrole (**27**) was prepared using *t*-BuLi and trimethylsilyl chloride.[56] Although this compound was far more difficult to prepare (yield 23%), it also quantitatively yielded the corresponding 2-monobrominated pyrrole **26** upon reaction with NBS.



Scheme 4.12: *α-Monobrominated pyrrole derivatives by the stannyl/silyl-bromo exchange reaction.*

From the experiments described above, it is clear that this mild substitution reaction is a perfect route to prepare α-monobrominated pyrrole derivatives under neutral conditions in quantitative yields. Although the same compounds can also be prepared from the corresponding trimethylsilyl derivatives, the synthesis of the latter is more difficult and, therefore, less preferred. The surprisingly good thermal stability of the products makes this route a far more convenient one than direct bromination routes such as that developed by Chen and Cava.[54,55] This difference in stability is possibly due to the formation of neutral trimethylstannyl succinimide instead of the more acidic succinimide.

4.5 *Conclusions*

In order to study the functionalization of N-protected 3-hexylpyrroles, two different 3-hexylpyrroles were synthesized starting from pyrrole. N-Phenylsulfonyl-3-hexylpyrrole was prepared by first protecting the annular nitrogen with a phenylsulfonyl group (NaH, $PhSO_2Cl$), after which it was selectively alkylated at the 3-position by means of a Friedel-Crafts/Clemmensen reduction sequence. Subsequent deprotection of the phenylsulfonyl group followed by protection with the *t*-BOC group, yielded N-*t*-BOC-3-hexylpyrrole.

Halogenation of both 3-hexylpyrroles was performed using standard halogenation procedures (NXS, THF, -70°C). Hereby, both 2-mono- and 2,5-dihalogenated products could be obtained in high yields (85-100%). A minor side-reaction was the occurrence of allylic halogenation of the alkyl chain. An exception of the halogenation strategy was the synthesis of N-*t*-BOC-2-bromo-3-hexylpyrrole. Due to the high reactivity, the selectivity of bromination decreased dramatically, giving rise to a number of products. However, when changing the solvent from THF to DMF, this compound could also be prepared in excellent yield.

Stannylation appeared to be more difficult. Neither N-phenylsulfonyl-3-hexylpyrrole nor one of its halogenated derivatives could be stannylated selectively due to steric and electronic influences of the hexyl and phenylsulfonyl substituents. In case of N-*t*-BOC protected 3-hexylpyrroles, direct stannylation with LTMP and trimethylstannyl chloride, did result in the formation of two organostannanes: N-*t*-BOC-2-trimethylstannyl-4-hexylpyrrole and N-*t*-BOC-2-chloro-3-hexyl-5-trimethylstannylpyrrole. However, stannylation underneath the hexyl chain appeared impossible.

An attempt to transform N-*t*-BOC-2-trimethylstannyl-4-hexylpyrrole into the difunctional compound N-*t*-BOC-2-bromo-3-hexyl-5-trimethylstannylpyrrole applying the same halogenation conditions as described above, resulted in the formation of N-*t*-BOC-2-bromo-4-hexylpyrrole. A similar exchange reaction was observed upon the addition of NBS to N-*t*-BOC-2-trimethylstannylpyrrole (resulting in the most interesting and up to now almost inaccessible compound N-*t*-BOC-2-bromopyrrole), to N-phenylsulfonyl-2-trimethylstannyl-

pyrrole and to N-phenylsulfonyl-2-trimethylsilylpyrrole, giving rise to the quantitative formation of very stable α-monobromo derivatives in all cases.

Finally, some attempts were made to prepare regioregular oligo- and polypyrroles by means of the Stille reaction. However, neither the polymerization of N-*t*-BOC-2-chloro-3-hexyl-5-trimethylstannylpyrrole nor the synthesis of regioregular oligomers using a nitro-activated arylhalide resulted in these species. Therefore, it was concluded that, due to a combination of steric and electronic effects, this coupling reaction is not the right tool in combination with the substituents and conditions applied in these studies. Possibly, the use of a less space demanding substituent or another coupling reaction is required. For the latter, these functionalization experiments might be of great importance.

4.6 *Experimental section*

For general remarks concerning chemicals and analysis techniques, the reader is referred to section 2.6.

N-Phenylsulfonylpyrrole (1)[39] A solution of pyrrole (13.42 g, 200 mmol) in THF (120 ml) was cooled to 0°C, blanketed by argon. NaH (5.80 g, 242 mmol) was added in small portions over a 20 min period, after which the mixture was stirred at RT for another 15 min. Then it was again cooled to 0°C and phenylsulfonyl chloride (35.33 g, 200 mmol) was added dropwise. The temperature was raised to RT and the mixture was stirred for another 2 h. THF was evaporated and the residue was dissolved in Et_2O (200 ml) and water (200 ml). The two phases were separated and the aqueous phase was extracted with Et_2O (3 x 150 ml). The combined organic fractions were washed with brine (2 x 150 ml) and water (1 x 150 ml), dried ($MgSO_4$), filtered and concentrated. Finally, the resulting dark solid was recrystallized from methanol, and gave white crystals (34.25 g, 165 mmol, 83%). Mp.: 89°C (Lit.: 89-89.5°C).
^{1}H-NMR ($CDCl_3$): δ 7.85 (d, J = 8.3 Hz, 2H, H-*ortho*), 7.56 (t, J = 7.4 Hz, 1H, H-*para*), 7.48 (t, J = 7.7 Hz, 2H, H-*meta*), 7.18 (t, J = 2.3 Hz, 2H, H-2,5), 6.29 (t, J = 2.3 Hz, 2H, H-3,4) ppm. ^{13}C-NMR ($CDCl_3$): δ 138.9 (C-*ipso* (phenyl), 133.8 (C-*para*), 129.3 (C-*ortho*), 126.6 (C-*meta*), 120.7 (C-2,5), 113.6 (C-3,4) ppm. IR (KBr): 3133-3062, 1583, 1535, 1481, 1452, 1363, 1169, 1059, 724, 686, 615 cm^{-1}. Anal.: calcd. N 6.76, C 57.95, H 4.38; found N 6.73, C 58.05, H 4.51.

N-Phenylsulfonyl-3-propanoylpyrrole (2) A suspension of anhydrous $AlCl_3$ (5.68 g, 42.6 mmol) in 1,2-dichloroethane (1,2-DCE, 150 ml) was cooled to 0°C, blanketed by argon. Then propanoic anhydride (20.8 g, 160 mmol) was added dropwise, after which the mixture was stirred at RT for 10 min. After cooling to 0°C again, a solution of N-phenylsulfonylpyrrole (**1**, 13.29 g, 64.1 mmol) in 1,2-DCE (50 ml) was added dropwise and the mixture was stirred overnight at RT. After this period the reaction mixture was quenched with ice-water (250 ml) and the product was extracted with Et_2O (3 x 150 ml). The combined organic fractions were washed with water (2 x 100 ml), dried ($MgSO_4$),

filtered and concentrated to yield a dark oil, that was directly used for the reduction (11.07 g, 42.0 mmol, 99%).
^{1}H-NMR ($CDCl_3$): δ 7.92 (d, J = 7.9 Hz, 2H, H-*ortho*), 7.74 (t, J = 1.9 Hz, 1H, H-2), 7.66 (t, J = 7.6 Hz, 1H, H-*para*), 7.55 (t, J = 8.2 Hz, 2H, H-*meta*), 7.15 (dd, J = 3.3 and 2.0 Hz, 1H, H-5), 6.70 (dd, J = 3.4 and 1.7 Hz, 1H, H-4), 2.76 (t, J = 7.4 Hz, 2H, CO-C$\underline{H}_2$-), 1.16 (t, J = 7.3 Hz, 3H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 195.5 (C=O), 138.1 (C-3), 135.1 (C-*para*), 130.3/127.7 (C-*ortho*/C-*meta*), 124.5/122.1 (C-2/C-5), 113.1 (C-4), 33.5 (CO-$\underline{C}H_2$-), 8.7 (-$\underline{C}H_3$) ppm. IR (KBr): 3143, 2984, 2974, 1675, 1482, 1369, 1173, 1120, 1073 cm^{-1}. UV-Vis (CH_3CN): 236 nm. Anal.: calcd. C 59.30, H 4.98, N 5.32; found C 59.95, H 4.76, N 5.24.

N-Phenylsulfonyl-3-hexanoylpyrrole (3) A suspension of anhydrous $AlCl_3$ (7.11 g, 53.3 mmol) in 1,2-dichloroethane (1,2-DCE, 90 ml) was cooled to 0°C, blanketed by argon. Then hexanoyl chloride (5.83 g, 43.3 mmol) was added dropwise, after which the mixture was stirred at RT for 10 min. After cooling to 0°C again, a solution of N-phenylsulfonylpyrrole (**1**, 6.91 g, 33.3 mmol) in 1,2-DCE (38 ml) was added dropwise and the mixture was stirred overnight at RT. The reaction was quenched with ice-water (150 ml) and the product was extracted with CH_2Cl_2 (3 x 100 ml). The combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. This resulted in a slightly brown solid, that was directly used for the reduction (10.0 g, 32.7 mmol, 98%).
^{1}H-NMR ($CDCl_3$): δ 7.92 (d, J = 8.0 Hz, 2H, H-*ortho*), 7.75 (t, J = 2.0 Hz, 1H, H-2), 7.67 (t, J = 7.4 Hz, 1H, H-*para*), 7.54 (t, J = 7.8 Hz, 2H, H-*meta*), 7.16 (dd, J = 3.3 and 2.2 Hz, 1H, H-5), 6.71 (dd, J = 3.7 and 1.3 Hz, 1H, H-4), 2.72 (t, J = 7.5 Hz, 2H, CO-C$\underline{H}_2$), 1.67 (m, 2H, CO-CH$_2$-C$\underline{H}_2$-), 1.32 (m, 4H, C$\underline{H}_2$-C$\underline{H}_2$-CH$_3$), 0.89 (m, 3H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 195.6 (C=O), 138.0 (C-*ipso* (Ph)), 134.5 (C-*para*), 129.6/127.0 (C-*ortho*/C-*meta*), 129.1 (C-3), 124.0/121.5 (C-2/C-5), 112.4 (C-4), 39.6 (CO-$\underline{C}H_2$), 31.3 (CO-CH$_2$-$\underline{C}H_2$), 23.9 ($\underline{C}H_2$-CH$_2$-CH$_3$), 22.4 ($\underline{C}H_2$-CH$_3$), 13.8 (-CH$_3$) ppm.

N-Phenylsulfonyl-3-dodecanoylpyrrole (4) A suspension of anhydrous $AlCl_3$ (7.92 g, 60 mmol) in CH_2Cl_2 (100 ml) was cooled to 0°C, blanketed by argon. Then dodecanoyl chloride (9.39 g, 42.9 mmol) was slowly added, after which the mixture was stirred at RT for 10 min. After cooling to 0°C again, a solution of N-phenylsulfonylpyrrole (**1**, 6.84 g, 33.0 mmol) in CH_2Cl_2 (38 ml) was added dropwise and the mixture was stirred overnight at RT. The reaction was quenched with ice-water (150 ml) and the product was extracted with Et_2O (3 x 100 ml). The combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. This gave a greenish solid, that was directly used for the reduction (12.8 g, 32.9 mmol, 99%).
^{1}H-NMR ($CDCl_3$): δ 7.93 (d, J = 7.8 Hz, 2H, H-*ortho*), 7.77 (t, J = 1.7 Hz, 1H, H-2), 7.66 (t, J = 7.5 Hz, 1H, H-*para*), 7.56 (t, J = 7.7 Hz, 2H, H-*meta*), 7.16 (dd, J = 3.3 and 2.2 Hz, 1H, H-5), 6.70 (dd, J = 3.1 and 1.5 Hz, 1H, H-4), 2.74 (t, J = 7.5 Hz, 2H, CO-C$\underline{H}_2$-), 1.68 (m, 2H, CO-CH$_2$-C$\underline{H}_2$-), 1.30 (m, 16H, (C$\underline{H}_2$)$_8$-CH$_3$), 0.89 (t, J = 6.9 Hz, 3H, -C$\underline{H}_3$) ppm.

N-Phenylsulfonyl-3-propylpyrrole (5) To a solution of N-phenylsulfonyl-3-propanoylpyrrole (**2**, 7.73 g, 29.4 mmol) in toluene (100 ml) and water (20 ml), amalgamated zinc was added. Amalgamated zinc was prepared by stirring a mixture of zinc powder (65.4 g, 1.0 mol) and mercuric chloride (6.79 g, 0.025 mol) in water (100 ml) and concentrated hydrochloric acid (36% HCl, 20 ml) for 15 min. The reaction mixture was stirred for 15 min, after which HCl (36%, 40 ml) was added.

The mixture was boiled under reflux for 20 h, during which 3 additional portions of HCl (36%, 3 x 25 ml) were added. After cooling, the layers were separated. The aqueous layer was extracted twice with Et_2O, after which the combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. The residual oil was purified by distillation, which resulted in a colorless liquid (7.35 g, 29.4 mmol, 100%). Bp.: 200°C (0.1 mmHg).
^{1}H-NMR ($CDCl_3$): δ 7.83 (d, J = 7.9 Hz, 2H, H-*ortho*), 7.58 (t, J = 7.4 Hz, 1H, H-*para*), 7.50 (t, J = 7.8 Hz, 2H, H-*meta*), 7.07 (dd, J = 2.9 and 2.3 Hz, 1H, H-5), 6.90 (broad s, 1H, H-2), 6.15 (dd, J = 3.1 and 1.6 Hz, 1H, H-4), 2.35 (t, J = 7.6 Hz, 2H, pyr-C$\underline{H}_2$-), 1.52 (m, 2H, -C$\underline{H}_2$-), 0.88 (t, J = 7.4 Hz, 3H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 139.2 (*C-ipso* (phenyl)), 133.6 (*C-para*), 130.0 (C-3), 129.2 (C-*ortho*), 126.6 (C-*meta*), 120.9/117.3 (C-2/C-5), 114.9 (C-4), 28.8 (pyr-$\underline{C}H_2$-), 23.1 (-$\underline{C}H_2$-), 13.7 (-CH_3) ppm. IR (KBr): 3139, 2959, 1448, 1369, 1253, 1175 cm^{-1}. UV-Vis (CH_3CN): 234 nm. Anal.: calcd. C 62.62, H 6.06, N 5.62; found 63.05, H 6.45, N 5.65.

N-Phenylsulfonyl-3-hexylpyrrole (6) To a solution of N-phenylsulfonyl-3-hexanoylpyrrole (**3**, 22.5 g, 75 mmol) in toluene (450 ml) and water (45 ml), amalgamated zinc was added. Amalgamated zinc was prepared by stirring a mixture of zinc powder (134.4 g, 1.9 mol) and mercuric chloride (12.62 g, 47.93 mmol) in water (250 ml) and concentrated hydrochloric acid (36% HCl, 25 ml) for 15 min. The reaction mixture was stirred for 15 min, after which HCl (36%, 150 ml) was added. The mixture was boiled under reflux for 20 h during which 3 additional portions of HCl (36%, 3 x 200 ml) were added. After cooling, the layers were separated. The aqueous layer was extracted twice with ether, and the combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. This yielded a slightly brown oil, pure **6** (13.21 g, 45.3 mmol, 61%).
^{1}H-NMR ($CDCl_3$): δ 7.83 (d, J = 8.5 Hz, 2H, H-*ortho*), 7.57 (t, J = 6.5 Hz, 1H, H-*para*), 7.47 (t, J = 7.6 Hz, 2H, H-*meta*), 7.07 (t, J = 2.6 Hz, 1H, H-5), 6.89 (broad s, 1H, H-2), 6.14 (dd, J = 3.1 and 1.6 Hz, 1H, H-4), 2.35 (t, J = 7.7 Hz, 2H, pyr-C$\underline{H}_2$), 1.48 (m, 2H, pyr-CH_2-C$\underline{H}_2$-), 1.27 (m, 6H, -(C$\underline{H}_2$)$_3$-CH_3), 0.86 (t, J = 6.7 Hz, 3H, -C$\underline{H}_3$) ppm.

N-Phenylsulfonyl-3-dodecylpyrrole (7) To a solution of N-phenylsulfonyl-3-dodecanoylpyrrole (**4**, 12.8 g, 32.9 mmol) in toluene (190 ml) and water (18 ml), amalgamated zinc was added. Amalgamated zinc was prepared by stirring a mixture of zinc powder (54.91 g, 840 mmol) and mercuric chloride (5.54 g, 20.9 mmol) in water (75 ml) and concentrated hydrochloric acid (36% HCl, 7.5 ml) by stirring for 15 min. The reaction mixture was stirred for 15 min and HCl (36%, 44 ml) was added. The mixture was boiled under reflux for 20 h, during which an additional portion of HCl (36%, 100 ml) was added. After cooling, the layers were separated. The aqueous layer was extracted twice with Et_2O and the combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. This yielded a viscous brown oil. Filtration of a solution in CH_2Cl_2 over SiO_2 followed by concentration, gave a colorless oil, that slowly crystallized. Recrystallization from ethanol finally yielded pure **7** as an oil (5.55 g, 14.8 mmol, 45%).
^{1}H-NMR ($CDCl_3$): δ 7.84 (d, J = 7.9 Hz, 2H, H-*ortho*), 7.57 (t, J = 7.6 Hz, 1H, H-*para*), 7.48 (t, J = 7.7 Hz, 2H, H-*meta*), 7.08 (t, J = 2.7 Hz, 1H, H-5), 6.92 (broad s, 1H, H-2), 6.15 (dd, J = 3.1 and 1.5, 1H, H-4), 2.38 (t, J = 7.7 Hz, 2H, pyr-C$\underline{H}_2$), 1.50 (m, 2H, pyr-CH_2-C$\underline{H}_2$-), 1.27 (m, 18H, -(C$\underline{H}_2$)$_9$-CH_3), 0.89 (t, J = 6.8 Hz, 3H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 139.2 (*C-ipso* (phenyl)), 133.5 (*C-para*),

130.2 (C-3), 129.2 (C-*ortho*), 126.5 (C-*meta*), 120.8/117.2 (C-2/C-5), 114.9 (C-4), 31.9 (pyr-$\underline{C}H_2$), 29.9-29.2 (-$\underline{C}H_2$-), 26.7 ($\underline{C}H_2$-CH_2-CH_3), 22.6 ($\underline{C}H_2$-CH_3), 14.0 ($\underline{C}H_3$) ppm.

N-Phenylsulfonyl-3-hexanoyl-4-hexylpyrrole (8) A suspension of anhydrous $AlCl_3$ (0.742 g, 5.4 mmol) in CH_2Cl_2 (7 ml) was cooled to 0°C, blanketed by argon. Hexanoyl chloride (0.541 g, 4.01 mmol) was slowly added, after which the resulting solution was stirred at 25°C for 10 min. Then it was cooled to 0°C again and a solution of N-phenylsulfonyl-3-hexylpyrrole (**6**, 0.90 g, 3.09 mmol) in CH_2Cl_2 (5 ml) was added dropwise. The mixture was stirred for 4 days at RT. Because the conversion was only 50% extra reagents were added; $AlCl_3$ (1.07 g) in CH_2Cl_2 (10 ml) and hexanoyl chloride (0.91 g) were stirred for 20 min and then added to the reaction mixture. After one more night at RT the reaction was quenched with ice-water, and the product was extracted with Et_2O. The combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. Column chromatography (25 g silica, CH_2Cl_2 : hexane (3:1), R_f = 0.26) yielded pure **8** as an oil (0.48 g, 1.23 mmol, 40%).
^{1}H-NMR ($CDCl_3$): δ 7.91 (d, J = 7.6 Hz, 2H, H-*ortho*), 7.69 (d, J = 2.4 Hz, 1H, H-2), 7.63 (t, J = 7.5 Hz, 1H, H-*para*), 7.53 (t, J = 6.8 Hz, 2H, H-*meta*), 6.90 (m, 1H, H-5), 2.73 (t, J = 7.3 Hz, 2H, CO-$\underline{C}H_2$), 2.56 (t, J = 6.9 Hz, 2H, pyr-$\underline{C}H_2$), 1.65 (m, 2H, CO-CH_2-$\underline{C}H_2$-), 1.47 (m, 2H, pyr-CH_2-$\underline{C}H_2$-), 1.28 (m, 10H, -($\underline{C}H_2$)-), 0.89 (m (t + t), 6H, -$\underline{C}H_3$ (hexyl and hexanoyl)) ppm.

N-Phenylsulfonyl-3,4-dihexylpyrrole (9) To a solution of N-phenylsulfonyl-3-hexanoyl-4-hexyl-pyrrole (**8**, 0.48 g, 1.23 mmol) in toluene (10 ml) and water (1 ml), amalgamated zinc was added. Amalgamated zinc was prepared by stirring a mixture of zinc powder (2.94 g, 41.7 mol) and mercuric chloride (0.281 g, 1.05 mmol) in water (4 ml) and concentrated hydrochloric acid (36% HCl, 0.4 ml) for 15 min. The reaction mixture was stirred for 15 min, after which HCl (36%, 1.5 ml) was added. The mixture was boiled under reflux for 72 h, during which an additional portion of HCl (36%, 2.5 ml) was added. After cooling, the layers were separated. The aqueous layer was extracted twice with Et_2O and the combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. This gave a thick brown oil, that was purified by column chromatography (15 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.45), yielding pure **9** as an oil (0.20 g, 0.53 mmol, 43%).
^{1}H-NMR ($CDCl_3$): δ 7.81 (d, J = 7.5 Hz, 2H, H-*ortho*), 7.57 (t, J = 8.0 Hz, 1H, H-*para*), 7.46 (t, J = 8.0 Hz, 2H, H-*meta*), 6.83 (s, 2H, H-2,5), 2.28 (t, J = 7.7 Hz, 4H, pyr-CH_2-), 1.48 (m, 4H, pyr-CH_2-$\underline{C}H_2$-), 1.27 (m, 12H, -($\underline{C}H_2$)$_3$-CH_3), 0.87 (t, J = 7.5 Hz, 6H, -$\underline{C}H_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 139.4 (C-*ipso* (phenyl)), 133.3 (C-*para*), 129.9 (C-3,4), 129.1 (C-*ortho*), 126.5 (C-*meta*), 117.4 (C-2,5), 31.6 (pyr-$\underline{C}H_2$-), 29.0 (pyr-CH_2-$\underline{C}H_2$-$\underline{C}H_2$), 25.1 (-$\underline{C}H_2$-CH_2-CH_3), 22.6 (-$\underline{C}H_2$-CH_3), 14.0 (-CH_3) ppm.

3-Hexylpyrrole (10) A mixture of N-phenylsulfonyl-3-hexylpyrrole (**6**, 5.17 g, 17.7 mmol) and tetrabutylammonium bromide (ca. 0.5 g) in 5 M NaOH (30 ml) and methanol (30 ml), was heated under reflux for 18 h. After evaporation of the methanol, the aqueous residue was extracted with Et_2O. The combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. This yielded a brown oil (2.05 g, 13.6 mmol, 77%), that was directly used for the *t*-BOC protection step.

^{1}H-NMR ($CDCl_3$): δ 8.28 (broad s, 1H, N-H), 6.69 (t, J = 2.3 Hz, 1H, H-5), 6.56 (s, 1H, H-2), 6.07 (t, J = 2.0 Hz, 1H, H-4), 2.49 (t, J = 7.5 Hz, 2H, pyr-C$\underline{H}_2$), 1.59 (m, 2H, pyr-CH$_2$-C$\underline{H}_2$-), 1.30 (m, 6H, -(C$\underline{H}_2$)$_3$-CH$_3$), 0.89 (t, J = 7.5 Hz, 3H, -C$\underline{H}_3$) ppm.

N-*tert*-Butoxycarbonyl-3-hexylpyrrole (11) A mixture of 3-hexylpyrrole (**10**, 2.86 g, 18.9 mmol), di-*tert*-butyl dicarbonate (4.99 g, 22.8 mmol), THF (130 ml) and potassium *tert*-butoxide (0.20 g, 1.8 mmol), was heated under reflux, blanketed by argon. After 18 h the mixture was cooled to RT. 2-Dimethylaminoethylamine (0.5 g, 6 mmol) was added and the mixture was stirred for another 30 min. Then the solvent was evaporated, the residue was dissolved in Et_2O and washed with dilute HCl (0.1 M), water and brine (each ca. 50 ml). The organic fractions were dried ($MgSO_4$), filtered and concentrated. Purification by column chromatography (150 g SiO_2, CH_2Cl_2 : hexane (1:3), R_f = 0.35) resulted in pure **11** (3.86 g, 15.4 mmol, 81%).
^{1}H-NMR ($CDCl_3$): δ 7.14 (s, 1H, H-2/H-5), 6.96 (s, 1H, H-2/H-5), 6.07 (dd, J = 3.2 and 1.7 Hz, 1H, H-4), 2.49 (t, J = 7.3 Hz, 2H, pyr-C$\underline{H}_2$), 1.59 (s, 9H, H-methyl (BOC)), 1.52 (m, 2H, pyr-CH$_2$-C$\underline{H}_2$-), 1.32 (m, 6H, -(C$\underline{H}_2$)$_3$-CH$_3$), 0.89 (t, J = 7.4 Hz, 3H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.9 (C=O), 128.1 (C-3), 119.8/116.4 (C-2/C-5), 112.9 (C-4), 82.9 (C-q (BOC)), 31.9 (pyr-$\underline{C}$H$_2$), 30.2 (pyr-CH$_2$-$\underline{C}$H$_2$), 29.0 (pyr-CH$_2$-CH$_2$-$\underline{C}$H$_2$), 27.9 (C-methyl (BOC)), 26.8 (-$\underline{C}$H$_2$-CH$_2$-CH$_3$), 22.6 (-$\underline{C}$H$_2$-CH$_3$), 14.0 (-$\underline{C}$H$_3$) ppm.

N-*tert*-Butoxycarbonyl-2-chloro-3-hexylpyrrole (12) A solution of N-*t*-BOC-3-hexylpyrrole (**11**, 1.257 g, 5.00 mmol) in THF (15 ml) was cooled to -70°C, blanketed by argon. N-Chlorosuccinimide (NCS, 0.800 g, 6.00 mmol)[57] was added and the mixture was stirred for 30 min at -70°C. Then the reaction mixture was brought to 3°C and kept at this temperature for 16 h. Na_2SO_3 (0.35 g) was added and the solution was stirred for 10 min. The solvent was evaporated, CCl_4 (20 ml) was added to the residue and the solution was stirred for another 15 min. Finally, the suspension was filtered and concentrated to yield pure **12** as an oil (1.41 g, 4.94 mmol, 99%).
^{1}H-NMR ($CDCl_3$): δ 7.17 (d, J = 3.7 Hz, 1H, H-5), 6.05 (d, J = 3.7 Hz, 1H, H-4), 2.39 (t, J = 7.6 Hz, 2H, pyr-C$\underline{H}_2$), 1.63 (s, 9H, H-methyl (BOC)), 1.54 (m, 2H, pyr-CH$_2$-C$\underline{H}_2$-), 1.30 (m, 6H, -(C$\underline{H}_2$)$_3$-CH$_3$), 0.90 (t, J = 6.9 Hz, 3H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.0 (C=O), 125.7 (C-3), 120.4 (C-5), 111.2 (C-4), 107.5 (C-2), 84.0 (C-q (BOC)), 31.6 (pyr-$\underline{C}$H$_2$), 29.4 (pyr-CH$_2$-$\underline{C}$H$_2$), 28.9 (pyr-CH$_2$-CH$_2$-$\underline{C}$H$_2$), 27.9 (C-methyl (BOC)), 25.4 ($\underline{C}$H$_2$-CH$_2$-CH$_3$), 22.5 ($\underline{C}$H$_2$-CH$_3$), 14.0 ($\underline{C}$H$_3$) ppm.
(N.B. Since α-halogenated pyrrole derivatives are quite sensitive when exposed to air, this procedure has to be performed under inert atmosphere as much as possible).

N-*tert*-Butoxycarbonyl-2-chloro-3-hexyl-5-trimethystannylpyrrole (13) 2,2,6,6-Tetramethylpiperidine (0.156 g, 1.1 mmol) was dissolved in THF (2 ml) and cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 0.75 ml, 1.2 mmol) was added dropwise, after which the mixture was brought to -10°C. After 5 min at this temperature, the mixture was again cooled to -78°C, after which a solution of N-*t*-BOC-2-chloro-3-hexylpyrrole (**12**, 0.285 g, 1.00 mmol) in THF (1.5 ml) was added. The mixture was stirred at this temperature for another 45 min and a solution of trimethylstannyl chloride (0.23 g, 1.15 mmol) in THF (1.5 ml) was added dropwise. The mixture was stirred for 4 h at -78°C, after which it was allowed to warm to RT. At this temperature it was stirred for another 16 h. The solvent was evaporated and the residue was dissolved in Et_2O (10 ml) and water (10 ml). The

aqueous layer was extracted with Et_2O and the combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. A final filtration over Al_2O_3 resulted in **13** as a green oil (0.159 g, 0.35 mmol, 35%).
^{1}H-NMR ($CDCl_3$): δ 6.21 (s, 1H, H-4), 2.37 (t, J = 7.5 Hz, 2H, pyr-C$\underline{H}_2$), 1.59 (s, 9H, H-methyl (BOC)), 1.57 (m, 2H, pyr-CH$_2$-C$\underline{H}_2$-), 1.32 (m, 6H, -(C$\underline{H}_2$)$_3$-CH$_3$), 0.88 (t, J = 6.9 Hz, 3H, -C$\underline{H}_3$), 0.12 (s, 9H, H-methyl (stannyl)) ppm. ^{13}C-NMR ($CDCl_3$): δ 150.4 (C=O), 135.7 (C-5), 126.9 (C-3), 121.6 (C-4), 115.2 (C-2), 84.4 (C-q (BOC)), 31.6 (pyr-$\underline{C}$H$_2$), 29.4 (pyr-CH$_2$-$\underline{C}$H$_2$), 29.0 (pyr-CH$_2$-CH$_2$-$\underline{C}$H$_2$), 27.8 (C-methyl (BOC)), 25.7 ($\underline{C}$H$_2$-CH$_2$-CH$_3$), 22.5 ($\underline{C}$H$_2$-CH$_3$), 14.0 ($\underline{C}$H$_3$), -7.5 (C-methyl (stannyl)) ppm.

N-*tert*-Butoxycarbonyl-2-trimethystannyl-4-hexylpyrrole (14) The reaction was performed as described for **13** using lithium-2,2,6,6-tetramethylpiperidide (1.58 mmol) in THF (3 ml), N-*t*-BOC-3-hexylpyrrole (**11**, 0.3786 g, 1.51 mmol) in THF (2 ml) and trimethylstannyl chloride (0.30 g, 1.5 mmol) in THF (2 ml). After work-up procedures, column chromatography (40 g Al_2O_3, hexane, R_f = 0.57) was applied to isolate **14** as a colorless liquid (0.38 g, 0.92 mmol, 61%).
^{1}H-NMR ($CDCl_3$): δ 7.13 (d, J = 1.3 Hz, 1H, H-5), 6.23 (d, J = 1.5 Hz, 1H, H-3), 2.41 (t, J = 7.7 Hz, 2H, pyr-C$\underline{H}_2$), 1.57 (s, 9H, H-methyl (BOC)), 1.57 (m, 2H, pyr-CH$_2$-C$\underline{H}_2$-), 1.31 (m, 6H, -(C$\underline{H}_2$)$_3$-CH$_3$), 0.89 (t, J = 6.8 Hz, 3H, -C$\underline{H}_3$), 0.23 (s, 9H, H-methyl (stannyl)) ppm. ^{13}C-NMR ($CDCl_3$): δ 150.5 (C=O), 134.6 (C-2), 129.2 (C-4), 123.5/120.0 (C-3/C-5), 82.9 (C-q (BOC)), 31.7 (pyr-$\underline{C}$H$_2$), 30.5-26.8 (CH$_2$-$\underline{C}$H$_2$-CH$_2$), 28.0 (C-methyl (BOC)), 22.6 ($\underline{C}$H$_2$-CH$_3$), 14.1 (-C$\underline{H}_3$), -7.8 (C-methyl (stannyl)) ppm.

N-*tert*-Butoxycarbonyl-2-(4-nitrophenyl)-4-hexylpyrrole (15) N-*t*-BOC-2-trimethylstannyl-4-hexylpyrrole (**14**, 1.00 g, 0.241 mmol) and 1-nitro-4-bromobenzene (0.494 g, 0.244 mmol) were dissolved in toluene (3 ml) and 1 M Na_2CO_3-solution (3 ml). After deaeration and storage under an argon atmosphere, tetrakis(triphenylphosphine)palladium(0) (0.082 g, 3 mol%) was added and the solution was heated under reflux for 96 h. The organic and aqueous layers were separated and the aqueous layer was extracted with Et_2O. The combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. Purification with column chromatography (35 g SiO_2, CH_2Cl_2 : hexane (2:5)) yielded **15** as an oil (0.44 g, 0.118 mmol, 49%).
^{1}H-NMR ($CDCl_3$): δ 8.20 (d, J = 9.0 Hz, 2H, H-*ortho*), 7.50 (d, J = 8.8 Hz, 2H, H-*meta*), 7.14 (d, J = 2.1 Hz, 1H, H-5), 6.21 (d, J = 2.1 Hz, 1H, H-3), 2.43 (t, J = 7.7 Hz, 2H, pyr-C$\underline{H}_2$-), 1.57 (m, 2H, pyr-CH$_2$-C$\underline{H}_2$-), 1.41 (s, 9H, H-methyl (BOC)), 1.38-1.29 (m, 6H, -(C$\underline{H}_2$)$_3$-CH$_3$), 0.89 (t, J = 6.8 Hz, 3H, -C$\underline{H}_3$) ppm.

N-*tert*-Butoxycarbonyl-2-bromo-3-hexyl-5-(4-nitrophenyl)pyrrole (16) The reaction between N-*t*-BOC-2-(4-nitrobenzene)-4-hexylpyrrole (**15**, 0.191 g, 0.51 mmol) and NBS (0.090 g, 0.51 mmol) in THF (5 ml) was performed as described for **12**. Yield of **16**: 0.23 g (0.51 mmol, 100%).
^{1}H-NMR ($CDCl_3$): δ 8.23 (d, J = 9.0 Hz, 2H, H-*ortho*), 7.43 (d, J = 8.8 Hz, 2H, H-*meta*), 6.27 (s, 1H, H-3), 2.45 (t, J = 7.7 Hz, 2H, pyr-C$\underline{H}_2$-), 1.56 (m, 2H, pyr-CH$_2$-C$\underline{H}_2$-), 1.41 (s, 9H, H-methyl (BOC)), 1.40-1.25 (m, 6H, -(C$\underline{H}_2$)$_3$-CH$_3$), 0.89 (t, J = 6.8 Hz, 3H, -C$\underline{H}_3$) ppm.

N-Phenylsulfonyl-2-chloro-3-hexylpyrrole (17) The reaction between N-phenylsulfonyl-3-hexylpyrrole (**6**, 0.295 g, 1.01 mmol) and NCS (0.155 g, 1.16 mmol)[57] in THF (4 ml) was performed as described for **12**. Yield of **17**: 0.32 g (0.98 mmol, 98%).
^{1}H-NMR ($CDCl_3$): δ 7.90 (d, J = 7.2 Hz, 2H, H-*ortho*), 7.59 (t, J = 7.6 Hz, 1H, H-*para*), 7.50 (t, J = 7.4 Hz, 2H, H-*meta*), 7.29 (d, J = 3.7 Hz, 1H, H-5), 6.17 (d, J = 3.7 Hz, 1H, H-4), 2.29 (t, J = 7.6 Hz, 2H, pyr-C$\underline{H}_2$), 1.47 (m, 2H, pyr-CH_2-C$\underline{H}_2$-), 1.23 (m, 6H, -(C$\underline{H}_2$)$_3$-CH_3), 0.84 (t, J = 6.8 Hz, 3H, -C$\underline{H}_3$) ppm.

N-Phenylsulfonyl-2-bromo-3-hexylpyrrole (18) The reaction between N-phenylsulfonyl-3-hexylpyrrole (**6**, 0.876 g, 3.01 mmol) and NBS (0.535 g, 3.00 mmol) in THF (12 ml) was performed as described for **12**. Yield of **18**: 1.11 g (3.00 mmol, 100%).
^{1}H-NMR ($CDCl_3$): δ 7.91 (d, J = 7.7 Hz, 2H, H-*ortho*), 7.60 (t, J = 7.4 Hz, 1H, H-*para*), 7.53 (t, J = 7.4 Hz, 2H, H-*meta*), 7.45 (d, J = 3.5 Hz, 1H, H-5), 6.21 (d, J = 3.5 Hz, 1H, H-4), 2.28 (t, J = 7.6 Hz, 2H, pyr-C$\underline{H}_2$), 1.44 (m, 2H, pyr-CH_2-C$\underline{H}_2$-), 1.22 (m, 6H, -(C$\underline{H}_2$)$_3$-CH_3), 0.85 (t, J = 6.9 Hz, 3H, -C$\underline{H}_3$) ppm.

N-Phenylsulfonyl-2,5-dibromo-3-hexylpyrrole (19) The reaction between N-phenylsulfonyl-3-hexylpyrrole (**6**, 0.582 g, 2.00 mmol) and NBS (0.713 g, 4.01 mmol) in THF (10 ml) was performed as described for **12**. Yield of **19**: 0.87 g (1.94 mmol, 97%).
^{1}H-NMR ($CDCl_3$): δ 8.01 (d, J = 7.5 Hz, 2H, H-*ortho*), 7.64 (t, J = 7.6 Hz, 1H, H-*para*), 7.55 (t, J = 7.4 Hz, 2H, H-*meta*), 6.27 (s, 1H, H-4), 2.30 (t, J = 7.5 Hz, 2H, pyr-C$\underline{H}_2$), 1.46 (m, 2H, pyr-CH_2-C$\underline{H}_2$), 1.27 (m, 6H, -(C$\underline{H}_2$)$_3$-CH_3), 0.86 (t, J = 6.8 Hz, 3H, -C$\underline{H}_3$) ppm.

N-*tert*-Butoxycarbonyl-2-bromo-3-hexylpyrrole (20) The reaction between N-*t*-BOC-3-hexylpyrrole (**11**, 0.364 g, 1.45 mmol) and NBS (0.257 g, 1.45 mmol) in DMF (5 ml) was performed as described for **12**. However, instead of carrying out the reaction at -70°C, it was performed just above the melting point of DMF (-60°C). Yield of **20**: 0.460 g (1.39 mmol, 96%)
^{1}H-NMR ($CDCl_3$): δ 7.30 (d, J = 3.7 Hz, 1H, H-5), 6.12 (d, J = 3.6 Hz, 1H, H-4), 2.39 (t, J = 7.7 Hz, 2H, pyr-C$\underline{H}_2$), 1.62 (s, 9H, H-methyl (BOC)), 1.55 (m, 2H, pyr-CH_2-C$\underline{H}_2$-), 1.30 (m, 6H, -(C$\underline{H}_2$)$_3$-CH_3), 0.90 (t, J = 6.8 Hz, 3H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.8 (C=O), 129.3 (C-3), 122.3 (C-5), 112.1 (C-4), 98.8 (C-2), 84.2 (C-q (BOC)), 31.6 (pyr-$\underline{C}H_2$), 30.2 (pyr-CH_2-$\underline{C}H_2$), 29.0 (pyr-CH_2-CH_2-$\underline{C}H_2$), 27.9 (C-methyl (BOC)), 26.9 ($\underline{C}H_2$-CH_2-CH_3), 22.5 ($\underline{C}H_2$-CH_3), 14.0 (-$\underline{C}H_3$) ppm.

N-*tert*-Butoxycarbonyl-2,5-dichloro-3-hexylpyrrole (21) The reaction between N-*t*-BOC-3-hexylpyrrole (**11**, 0.258 g, 1.07 mmol) and NCS (0.314 g, 2.35 mmol)[57] in THF (3 ml) was performed as described for **12**. Yield of **21**: 0.335 g (1.05 mmol, 98%).
^{1}H-NMR ($CDCl_3$): δ 6.01 (s, 1H, H-4), 2.38 (t, J = 7.5 Hz, 2H, pyr-C$\underline{H}_2$), 1.61 (s, 9H, H-methyl (BOC)), 1.60 (m, 2H, pyr-CH_2-C$\underline{H}_2$-), 1.30 (m, 6H, -(C$\underline{H}_2$)$_3$-CH_3), 0.90 (t, J = 6.9 Hz, 3H, -C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 146.7 (C=O), 124.1 (C-3), 120.3/115.2 (C-2/C-5), 111.7 (C-4), 85.5 (C-q (BOC)), 31.6 (pyr-$\underline{C}H_2$), 29.2 (2 (pyr-CH_2-$\underline{C}H_2$), 28.7 (pyr-CH_2-CH_2-$\underline{C}H_2$), 27.8 (C-methyl (BOC)), 25.4 ($\underline{C}H_2$-CH_2-CH_3), 22.5 ($\underline{C}H_2$-CH_2-CH_3), 14.0 ($\underline{C}H_3$) ppm.

N-*tert*-Butoxycarbonyl-2,5-dibromo-3-hexylpyrrole (22) The reaction between N-*t*-BOC-3-hexylpyrrole (**11**, 2.00 g, 7.96 mmol) and NBS (2.97 g, 16.7 mmol) in THF (25 ml) was performed as described for **12**. Yield of **22**: 3.11 g (7.60 mmol, 95%).
^{1}H-NMR (CCl_4 with $CDCl_3$ in internal capillary): δ 6.07 (s, 1H, H-4), 2.28 (t, J = 7.5 Hz, 2H, pyr-$C\underline{H}_2$), 1.55 (s, 9H, H-methyl (BOC)), 1.50 (m, 2H, pyr-CH_2-$C\underline{H}_2$-), 1.25 (m, 6H, -($C\underline{H}_2$)$_3$-CH_3), 0.83 (t, J = 6.9 Hz, 3H, -$C\underline{H}_3$) ppm. ^{13}C-NMR (CCl_4, ref. $CDCl_3$): δ 142.4 (C=O), 124.1 (C-3), 112.2 (C-4), 95.8(C-5), 94.9 (C-2), 80.7 (C-q (BOC)), 27.5 (pyr-$\underline{C}H_2$), 25.3 (pyr-CH_2-$\underline{C}H_2$), 24.7 (pyr-CH_2-CH_2-$\underline{C}H_2$), 23.9 (C-methyl (BOC)), 22.7 ($\underline{C}H_2$-CH_2-CH_3), 18.5 ($\underline{C}H_2$-CH_2-CH_3), 10.0 ($\underline{C}H_3$) ppm.

N-*tert*-Butoxycarbonyl-2-bromo-4-hexylpyrrole (23) N-BOC-2-trimethylstannyl-4-hexylpyrrole (**14**, 0.1571 g, 0.379 mmol) was dissolved in THF (2 ml) and cooled to -70°C, blanketed by argon. N-bromosuccinimide (NBS, 0.0682 g, 0.383 mmol) was added and the mixture was stirred for another 15 min at -70°C. Then it was allowed to warm to 3°C at which temperature it was kept for one night. Then Na_2SO_3 (50 mg) was added and the solvent was evaporated. CCl_4 (10 ml) was added to the residue, the suspension was filtered and the filtrate was concentrated. After column chromatography (10 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.75), **23** was obtained as a pale yellow liquid (0.1173 g, 0.355 mmol, 97%).
^{1}H-NMR ($CDCl_3$): δ 7.05 (dt, J = 2.2 and 1.0 Hz, 1H, H-5), 6.17 (d, J = 2.1 Hz, 1H, H-3), 2.35 (t, J = 7.9 Hz, 2H, pyr-$C\underline{H}_2$), 1.60 (s, 9H, H-methyl (BOC)), 1.51 (m, 2H, pyr-CH_2-$C\underline{H}_2$), 1.29 (m, 6H, -($C\underline{H}_2$)$_3$-CH_3), 0.88 (t, J = 6.9 Hz, 3H, -$C\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.1 (C=O), 127.5 (C-4), 119.5/118.3 (C-3/C-5), 99.9 (C-2), 84.3 (C-q (BOC)), 31.6 (pyr-$\underline{C}H_2$), 30.0-26.8 (CH_2-$\underline{C}H_2$-CH_2), 28.0 (C-methyl (BOC)), 22.6 ($\underline{C}H_2$-CH_3), 14.1 ($C\underline{H}_3$) ppm. MS: m/z (%) = 329 (M^+, 1.3), 331 ($M+2^+$, 1.5), 161 (36.6), 160 (21.3), 159 (39.4), 158 (17.6), 57 (100). IR (KBr): 3136, 2928, 2856, 1757, 1741, 1321, 1243, 1158, 1022, 852, 809, 759 cm^{-1}.

N-*tert*-Butoxycarbonyl-2-bromopyrrole (24) The reaction between N-BOC-2-trimethylstannylpyrrole[51] (0.2494 g, 0.756 mmol) and NBS (0.1350 g, 0.758 mmol) in THF (3 ml) was performed as described for **23**. After column chromatography (10 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.67), **24** was obtained as a colorless oil (0.1803 g, 0.733 mmol, 97%).
^{1}H-NMR ($CDCl_3$): δ 7.31 (dd, J = 3.5 and 1.9 Hz, 1 H, H-5), 6.29 (dd, J = 3.5 and 1.9 Hz, 1H, H-3), 6.15 (t, J = 3.5 Hz, 1H, H-4), 1.61 (s, 9H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.0 (C=O), 123.0 (C-5), 117.2 (C-3), 111.5 (C-4), 100.2 (C-2), 84.7 (C-q (BOC)), 27.9 (C-methyl (BOC)) ppm. MS: m/z (%) = 245 (M^+, 3.4), 247 ($M+2^+$, 3.6), 147 (29.1), 145 (29.4), 57 (100). IR (KBr): 3156, 3129, 2980, 2934, 1746, 1322, 1156, 847, 804, 767, 720 cm^{-1}.

N-Phenylsulfonyl-2-trimethylstannylpyrrole (25) A solution of N-phenylsulfonylpyrrole (**1**, 2.07 g, 9.99 mmol) in THF (12 ml) was cooled to -70°C, blanketed by argon. Then *t*-BuLi (1.5 M in hexane, 7.70 ml, 11.55 mmol) was added over a 20 min period, after which the mixture was allowed to warm to RT. After 30 min at this temperature, the mixture was again cooled to -70°C and trimethylstannyl chloride (2.28 g, 11.44 mmol) in THF (6 ml) was added. The mixture was kept for another 30 min at -70°C, after which the dark brown solution was allowed to warm to RT and stirred for one night. The solvent was evaporated and Et_2O (30 ml) and water (30 ml) were added. After extraction with Et_2O (3 x 25 ml) the combined organic fractions were washed with brine and water,

dried ($MgSO_4$), filtered and concentrated. Purification by column chromatography (200 g Al_2O_3, hexane, R_f = 0.08) afforded **25** as a colorless oil (2.20 g, 5.94 mmol, 59%).
^{1}H-NMR ($CDCl_3$): δ 7.63 (d, J = 8.3 Hz, 2H, H-*ortho*), 7.57 (t, J = 7.4 Hz, 1H, H-*para*), 7.47 (t, J = 7.6 Hz, 2H, H-*meta*), 7.41 (dd, J = 3.1 and 1.8 Hz, 1H, H-5), 6.47 (dd, J = 3.1 and 1.4 Hz, 1H, H-3), 6.43 (t, J = 3.0 Hz, 1H, H-4), 0.30 (s, 9H, H-methyl (stannyl)) ppm. ^{13}C-NMR ($CDCl_3$): δ 140.1 (C-*ipso* (phenyl)), 135.8 (C-2), 133.4 (C-*para*), 129.2 (C-*ortho*), 126.0 (C-*meta*), 125.7-124.3 (C-3, C-5), 114.6 (C-4), -7.3 (C-methyl (stannyl)) ppm.
(N.B. Besides **25**, N-(2-trimethylstannyl)phenylsulfonyl-2-trimethylstannylpyrrole (1.21 g, 2.27 mmol, 23%) was also isolated: ^{1}H-NMR ($CDCl_3$): δ 7.72 (d, J = 7.3 Hz, 1H, H-6 (phenyl)), 7.46 (t, J = 7.3 Hz, 1H, H-4 (phenyl)), 7.28 (m, 2H, H-5 (pyr) and H-5 (phenyl)), 6.76 (d, J = 7.1 Hz, 1H, H-3 (phenyl)), 6.52 (dd, J = 3.0 and 1.7 Hz, 1H, H-3 (pyr)), 6.44 (t, J = 3.0 Hz, 1H, H-4 (pyr)), 0.45 (s, 9H, H-methyl (stannyl (Ph))), 0.24 (s, 9H, H-methyl (stannyl (pyr))) ppm. ^{13}C-NMR ($CDCl_3$): δ 146.8, 141.8, 137.3, 136.2, 131.7, 129.0, 126.2, 125.1, 124.0, 114.2, -6.5, -7.5 ppm).

N-Phenylsulfonyl-2-bromopyrrole (26) Using N-phenylsulfonyl-2-trimethylstannylpyrrole (**25**, 0.3372 g, 0.911 mmol) and NBS (0.1622 g, 0.911 mmol) in THF (3 ml), the reaction was performed as described for **23**. After column chromatography (10 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.56), **26** was obtained as a white solid (0.2576 g, 0.900 mmol, 99%). Mp.: 86-87°C.
^{1}H-NMR ($CDCl_3$): δ 7.92 (d, J = 8.5 Hz, 2H, H-*ortho*), 7.63 (t, J = 7.5 Hz, 1H, H-*para*), 7.53 (t, J = 7.8 Hz, 2H, H-*meta*), 7.48 (dd, J = 3.6 and 1.9 Hz, 1H, H-5), 6.28 (dd, J = 3.6 and 1.9 Hz, 1H, H-3), 6.25 (t, J = 3.5 Hz, 1H, H-4) ppm. ^{13}C-NMR ($CDCl_3$): δ 138.0 (C-*ipso* (phenyl)), 134.2 (C-*para*), 129.2 (C-*ortho*), 127.7 (C-*meta*), 124.3 (C-5), 118.0 (C-3), 112.7 (C-4), 110.0 (C-2) ppm. MS: m/z (%) = 285 (M^+, 17.5), 287 (M+2$^+$, 18.0), 141 (73.8), 77 (100). IR (KBr): 3132, 3087, 1367, 1266, 1186, 1169, 1141, 727, 681, 611 cm^{-1}.

N-Phenylsulfonyl-2-trimethylsilylpyrrole (27) N-Phenylsulfonylpyrrole (**1**, 0.4145 g, 2.00 mmol) was dissolved in THF (2 ml) and cooled to -78°C, blanketed by argon. Over a 20-min period *t*-BuLi (1.5 M in hexane, 1.50 ml, 2.25 mmol) was added, after which the mixture was allowed to warm to RT. After 30 min at this temperature, the mixture was again cooled to -78°C and trimethylsilyl chloride (0.510 ml, 4.01 mmol) was added slowly. The mixture was kept at -78°C for another 30 min, after which the solution was allowed to warm to RT and stirred for another 16 h. The solvent was then evaporated and the residue was dissolved in Et_2O (30 ml) and water (30 ml). The aqueous phase was extracted with Et_2O and the combined organic fractions were washed with brine and water, dried ($MgSO_4$), filtered and concentrated. Purification by column chromatography (25 g Al_2O_3 : hexane, R_f = 0.20) afforded **27** as a colorless oil (0.128 g, 0.46 mmol, 23%).
^{1}H-NMR ($CDCl_3$): δ 7.62 (d, J = 8.4 Hz, 2H, H-*ortho*), 7.58 (t, J = 7.5 Hz, 1H, H-*para*), 7.47 (m, 3H, H-*meta* and H-5), 6.62 (m, 1H, H-3), 6.39 (t, J = 3.1 Hz, 1H, H-4), 0.32 (s, 9H, H-methyl (silyl)) ppm. ^{13}C-NMR ($CDCl_3$): δ 140.4 (C-*ipso* (phenyl)), 136.3 (C-2), 133.3 (C-*ortho*), 129.1 (C-*ortho*), 127.2 (C-5), 125.9 (C-*meta*), 125.7 (C-3), 113.4 (C-4), 0.04 (C-methyl (silyl)) ppm.

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Chapter 5

PYRROLE - SULFUR COMPOUNDS

ATTEMPTS TOWARD INTRINSICALLY CONDUCTING POLYMERS

Abstract: *The first attempts toward intrinsically conducting polymers based on pyrrole are made by incorporating the '+ - 0 0'-electronic structure, as present in polysulfur nitride, into an organic polymer. Therefore, two different types of oligomeric and polymeric pyrrole-sulfur compounds have been synthesized. First, a number of N-t-BOC protected oligo- and poly(pyrrole-2,5-diyl sulfide)s is prepared starting from α-brominated pyrroles using a lithiation/sulfuration sequence. Subsequent attempts to remove the t-BOC groups by thermolysis, however, result in the formation of insoluble black tars in all cases. The latter is most probably due to sulfur extrusion/polymerization. In order to overcome this problem, a poly(thienylthiothienylpyrrolyl) was prepared starting from N-t-BOC-3-dodecyl-2,5-di(2-thienyl)pyrrole and following the same strategy. In contrast to the former compounds, this polymer can be deprotected by thermolysis. However, in this case π-conjugation along the polymer backbone appears to be limited, both in the neutral and in the radical cationic form, due to a low degree of delocalization through the carbon-sulfur linkages.*

5.1 *Introduction*

For many years scientists have been searching for intrinsically conducting polymers, i.e. systems that are electrically conducting without the requirement of any external doping. In contrast, extrinsically conducting polymers need a considerable amount of dopant to induce conducting properties.[1,2] Hitherto, the search for intrinsically conducting polymers has resulted in a number of low band gap materials. One example is polyisothianaphthene (E_g = 1.0 eV), which is based on the idea that an appropriate balance between the aromatic and quinoid character of the π-conjugated backbone might lead to a polymer without Peierls distortion.[3,4] Other examples are Havinga's polysquaraines and polycroconaines (E_g = 0.5 eV; intrinsic conductivity = 10^{-5} S/cm)[5]; these systems are based on the idea that alternating donor and acceptor units lower the band gap.

Here we describe a new concept for an intrinsically conducting polymer. This so-called '+ - 0 0'-concept, as proposed by Havinga, is based on the idea that it should be

possible to prepare an organic analogue of polysulfur nitride $(SN)_x$, with similar electronic properties but improved processability. The most striking and important features of $(SN)_x$, an inorganic quasi-one-dimensional conducting polymer, are its metallic conductivity at low temperatures and the absence of a Peierls distortion.[6-10] Furthermore, $(SN)_x$ even becomes superconducting with a transition temperature T_c of 0.26 ± 0.03 K when measuring conductivity along the fibre axis.[11] This makes $(SN)_x$ the first inorganic superconducting polymer. A major disadvantage of this polymer, however, is the instability of its intermediates. This drawback has prevented a detailed exploration of the properties for a long time.

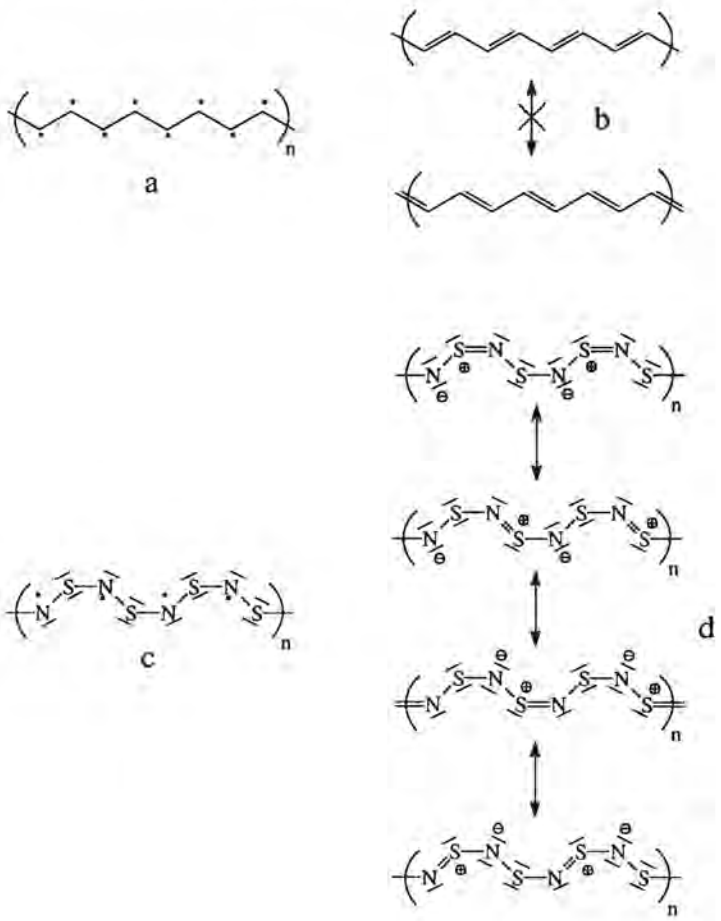


Figure 5.1: *Electronic structures of polyacetylene and polysulfur nitride $(SN)_x$: a) polyacetylene, polyradical form; b) polyacetylene, localized bonds; c) $(SN)_x$, polyradical form; d) $(SN)_x$, delocalization of charges on the polymeric backbone.*

The difference between polysulfur nitride and organic conducting polymers such as polyacetylene is related to the (de)localization of their π-electrons. In order to get good conductivity along a π-conjugated polymer chain, one needs an overall neutral structure with delocalized π-electrons. Polyacetylene, however, contains localized double bonds (figure 5.1b). The latter results in a band gap between the valence and conduction band, and hence in semi-conducting properties. On the contrary, in polysulfur nitride the localization of the double bonds would imply localization of charges on the polymeric backbone. Since charge localization is energetically unfavorable, polysulfur nitride will delocalize its charges (figure 5.1d). This suppresses the Peierls distortion and reduces the band gap close to zero (metallic conductivity).

As mentioned above, it is our goal to prepare an organic analogue of polysulfur nitride. Since we are interested in polymers based on pyrrole, we thought it relevant to replace the nitrogen atom by a pyrrolyl radical. The resulting organic polymer, poly(N-dehydro-pyrrole-2,5-diyl sulfide), would still be able to possess the desired '+ - 0 0'-electronic structure. The main difference, however, is the incorporation of additional sp^2 carbon atoms (figure 5.2). Still, due to the possibility of delocalizing the charges over the hetero-atoms in the polymeric backbone, poly(N-dehydro-pyrrole-2,5-diyl sulfide) might show a small band gap and could even be intrinsically conducting. [12] The easiest strategy to obtain this polymer would be by dehydrogenation of poly(pyrrole-2,5-diyl sulfide).

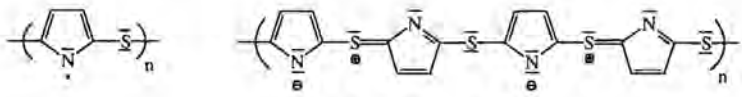
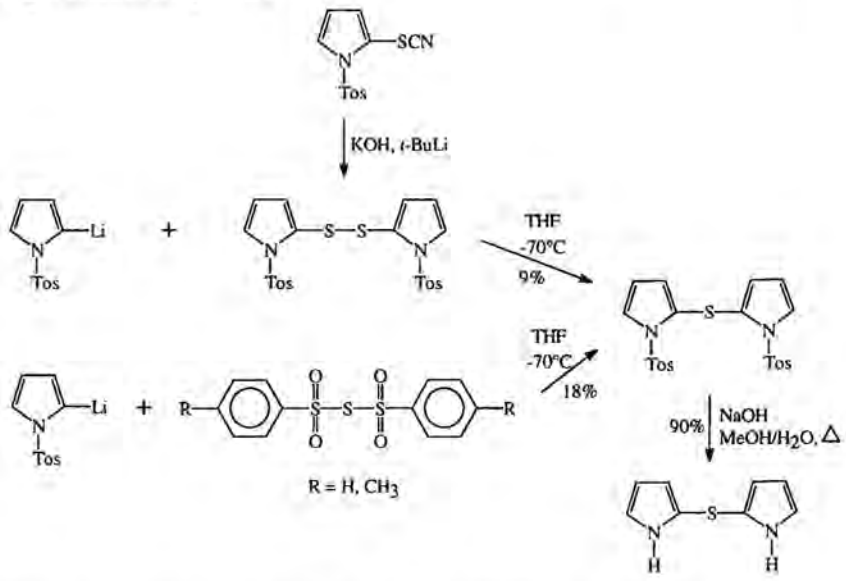


Figure 5.2: *Polyradical and '+ - 0 0'-structure of poly(N-dehydro-pyrrole-2,5-diyl sulfide).*

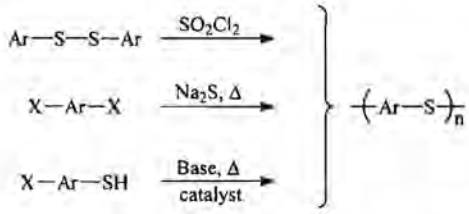
Very little is known about the coupling between pyrrole and sulfur. The 'closest' match with poly(pyrrole-2,5-diyl sulfide) is a report by Berlin, Ferraccioli and Pagani on the synthesis of bis(2-pyrrolyl) sulfide.[13] They developed two routes for the synthesis of bis(N-tosyl-2-pyrrolyl) sulfide starting from N-tosyl-2-lithiopyrrole (scheme 5.1). The first method consists in reacting this lithiopyrrole with N,N'-ditosyl-2,2'-dipyrrolyl disulfide, yielding the desired dipyrrolyl sulfide in only 9% after purification. The dipyrrolyldisulfide was prepared by air oxidation of sodium N-tosyl-2-pyrrolyl thiolate, formed *in situ* by alkaline hydrolysis of the N-tosyl-2-thiocyanatopyrrole. The second route is based on the successful preparation of dithienyl sulfides[14] and involves the reaction of N-tosyl-2-lithiopyrrole with bis(phenyl-sulfonyl) sulfide ($(PhSO_2)_2S$). This method doubled the yield of N-tosyl protected bis(2-pyrrolyl) sulfide to 18% after purification. The N-tosyl protecting groups of bis(N-tosyl-2-pyrrolyl) sulfide could be removed in aqueous NaOH/methanol at reflux temperature. The

yield of this deprotection step was high, 90% after distillation under reduced pressure, but Berlin noticed that this unprotected dipyrrolyl sulfide only possessed "a moderate stability to air and light at room temperature".



Scheme 5.1: *Synthesis of bis(2-pyrrolyl) sulfide as developed by Berlin et al.*[13]

A number of strategies are known to prepare arene sulfide polymers. Well-known is the reaction between a diaryl disulfide and sulfuryl chloride[15], condensation of a (hetero)aromatic dihalide with Na_2S[16,17] and the self-condensation of a halogenated (hetero)aromatic thiol[18] (scheme 5.2).

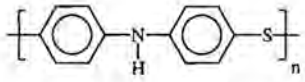


Scheme 5.2: *Synthetic routes toward arene sulfide polymers (X = halogen).*

Two arene sulfide polymers have been studied quite extensively over the past decades. The first one, poly(*p*-phenylene sulfide) (PPS), is a widely used nonrigid and processable engineering polymer that, in the undoped state, is a very good insulator (electronic conductivity $\sigma = 10^{-16}$ Scm^{-1}). However, when doped, conductivities of $\sigma = 1$ Scm^{-1} can be obtained in pressed pellets, whereas in AsF_5-doped PPS films, values as high as $\sigma =$ 200 Scm^{-1} have been reported for this polymer.[19] The second example is poly(2,5-thienyl

sulfide) (PTS), a heteroaromatic polymer that has also been investigated for its conducting and optical properties. Here conductivities up to $\sigma = 2 \times 10^{-5}$ Scm^{-1} have been measured upon doping with I_2.[16]

Very recently, Havinga and Müllen published on the properties of poly(phenylene-sulfidephenylenamine) (PPSA).[20] This polymer, being a combination of poly(*p*-phenylene sulfide) (PPS) and polyaniline (PAni), showed reasonable conductivity upon doping (~ 1 Scm^{-1}). However, when they tried to dehydrogenate a related oligomer, 4,4'-di(4'-methyldi-phenylamine-4-sulfanyl)diphenylamine, by UV irradiation in toluene containing dibenzoyl peroxide, they were able to detect the asymmetrical diradical species by ERS spectroscopy (figure 5.3).



PPSA

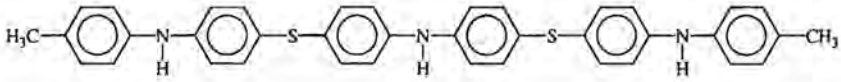
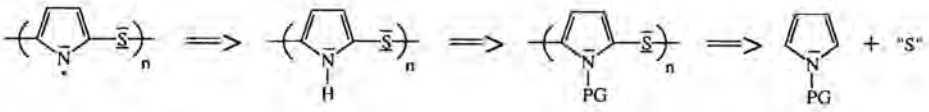


Figure 5.3: *Poly(phenylenesulfidephenylenamine) (PPSA) and a related oligomer.*[20]

To date, no reports have been published on the synthesis of poly(pyrrole-2,5-diyl sulfide). The synthesis of this polymer from pyrrole is to be considered rather difficult, since pyrrole is an electron-rich aromatic unit that easily undergoes oxidation and polymerization. The high reactivity of the pyrrole unit toward electrophiles prevents the use of reagents such as $SOCl_2$, unless it carries several substituents, including electron-withdrawing groups.[21-24] The general instability of pyrrole thiols[25] on the one hand, and the reluctance of pyrrole to undergo nucleophilic substitution on the other hand, hinder reactions between thiolates and halogenated pyrroles. However, since we are interested in the electronic properties of poly(N-dehydro-pyrrole-2,5-diyl sulfide), the retrosynthetic route as shown in scheme 5.3 has been developed. Stabilization of the pyrrole units may be achieved by the introduction of electron-withdrawing protecting groups at nitrogen. The N-protected poly(pyrrole-2,5-diyl sulfide) might be obtained by polymerization of an N-protected pyrrole derivative with a sulfurating agent ("S").

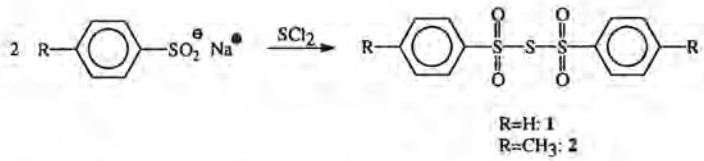


Scheme 5.3: *Retrosynthetic approach toward poly(N-dehydro-pyrrole-2,5-diyl sulfide).*

In the next sections two different types of oligomeric and polymeric pyrrole-sulfur compounds are prepared by adapting Berlin's route, and subsequently investigated.

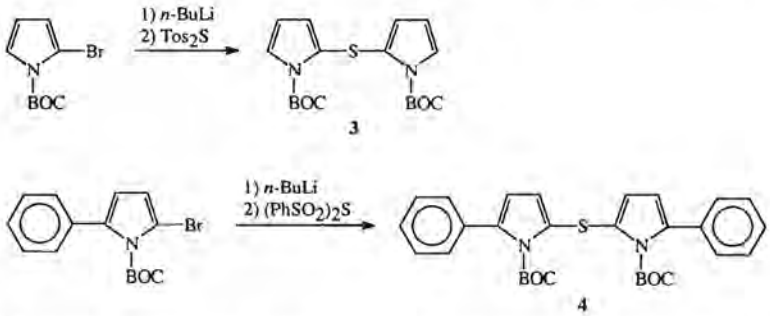
5.2 *Oligo- and poly(pyrrole-2,5-diyl sulfide)s*

For the synthesis of the smallest oligomer, bis(2-pyrrolyl) sulfide, we slightly adapted the second route as developed by Berlin *et al.*[13]. Bis(phenylsulfonyl) sulfide ($(PhSO_2)_2S$, **1**) and bis(*p*-tosyl) sulfide (Tos_2S, **2**) were used as sulfurating agents. These bis(arylsulfonyl) sulfides were prepared in comparable yields (45% and 51%, respectively) from the corresponding sodium arylsulfinates using SCl_2 (scheme 5.4).[14]



Scheme 5.4: *Synthesis of bis(arylsulfonyl) sulfides.*[14]

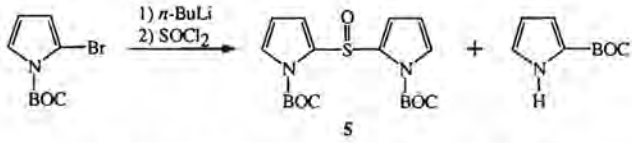
The synthesis of bis(N-*t*-BOC-2-pyrrolyl) sulfide (**3**) started from N-*t*-BOC-2-bromopyrrole, which, in itself, was prepared from N-*t*-BOC-2-trimethylstannylpyrrole by the stannyl-bromo exchange reaction, discussed in Chapter 4.[26] This monobromo derivative was first selectively α-lithiated with *n*-BuLi in THF at -70°C, and then treated with 0.5 eq of Tos_2S (scheme 5.5). After work-up and subsequent distillation to remove volatile impurities, pure **3** was obtained as a dark oil (96% yield). Attempts to transform this oil into a more convenient appearance (decoloration with activated carbon and subsequent precipitation in methanol), gave **3** as a slightly orange solid at the price of a significant loss of material (42% yield).



Scheme 5.5: *Synthesis of bis(N-t-BOC-2-pyrrolyl) sulfide (3) and bis(N-t-BOC-5-phenyl-2-pyrrolyl) sulfide (4), respectively.*

In a similar way bis(N-*t*-BOC-5-phenyl-2-pyrrolyl) sulfide (**4**) could be prepared. However, the yield (55%) was significantly lower due to difficult purification procedures (scheme 5.5).

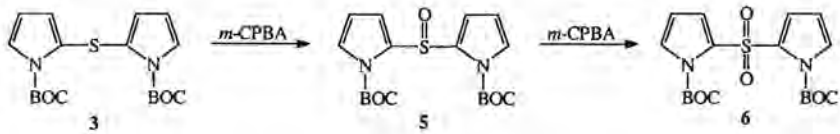
Since pyrrole itself already is a very electron-rich aromatic unit, which easily undergoes oxidation and oxidative polymerization, additional α-substitution with an electron-donating sulfur atom will make it even less stable. Therefore, we also prepared the oxidized forms of **3**: bis(N-*t*-BOC-2-pyrrolyl) sulfoxide (**5**) and bis(N-*t*-BOC-2-pyrrolyl) sulfone (**6**). In particular sulfoxide **5** might serve as a more stable precursor molecule for bis(2-pyrrolyl) sulfide and higher oligomers. The synthesis of bis(N-*t*-BOC-2-pyrrolyl) sulfoxide (**5**) was initially performed analogously as described for **3**, using $SOCl_2$ as sulfurating agent. Although **5** was the main product of this experiment, it could only be isolated in 52% yield after column chromatography. An interesting by-product, that could also be isolated was 2-*t*-BOC-pyrrole (scheme 5.6). This compound might be formed by a rearrangement during lithiation, the driving force being the formation of a more stable anion.



5

Scheme 5.6: *Synthesis of bis(N-t-BOC-2-pyrrolyl) sulfoxide (5) using $SOCl_2$.*

In order to inerease the yield of sulfoxide **5**, an alternative approach was investigated: oxidation of **3**. Using one equivalent of *m*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2, resulted in the quantitative formation of **5** within 45 minutes. Similarly, **5** could be transformed into bis(N-*t*-BOC-2-pyrrolyl) sulfone (**6**) in an obviously significantly slower oxidation step (scheme 5.7).

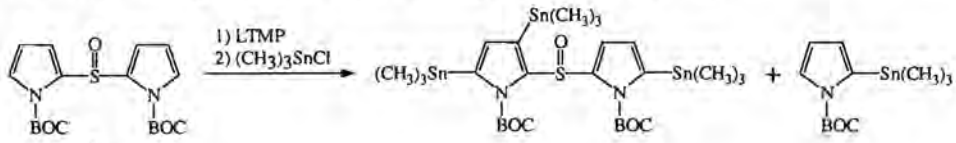


3 5 6

Scheme 5.7: *Synthesis of bis(N-t-BOC-2-pyrrolyl) sulfoxide (5) and -sulfone (6) via stepwise oxidation of bis(N-t-BOC-2-pyrrolyl) sulfide (4).*

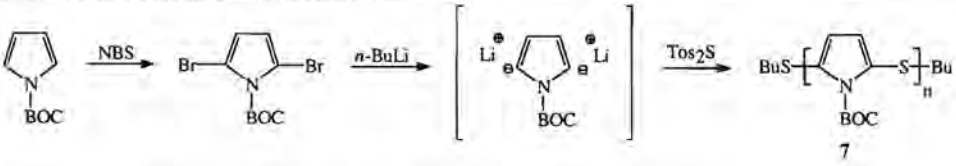
In order to prepare longer oligomers starting from **3**, **5** and **6**, attempts were made to functionalize these compounds. Much to our surprise, however, both bromination and stannylation experiments failed.[27] In case of mono- or dibromination of the α-pyrrolyl positions of **3** and **5** with NBS (THF, -70°C), several products were formed, including N-*t*-BOC-pyrrole, N-*t*-BOC-2-bromopyrrole and N-*t*-BOC-2,5-dibromopyrrole. The latter probably arise from the interaction of the sulfide or sulfoxide with an electrophile, which

weakens the α-pyrrolyl-sulfur bond to such an extent that cleavage occurs. In case of **3**, selective α-lithiation appeared to be very difficult with LTMP below -50°C. However, by raising the temperature above -40°C, the lithiation/stannylation sequence resulted in many products, but none stannylated, suggesting that side-reactions had already taken place before the addition of trimethylstannyl chloride. In case of **5**, distannylation in THF at -70°C did provide some stannylated products. However, after column chromatography only a tristannylated compound and N-*t*-BOC-2-trimethylstannylpyrrole could be isolated, the latter once more indicating that the C-S bond is easily cleaved (scheme 5.8).



Scheme 5.8: *Distannylation of bis(N-t-BOC-2-pyrrolyl) sulfoxide (5).*

The lithiation/sulfuration sequence was also applied to prepare the corresponding polymer of **3**, being poly(N-*t*-BOC-pyrrole-2,5-diyl sulfide) (**7**). Starting from N-*t*-BOC-pyrrole, this compound was first selectively dibrominated (NBS, THF, -70°C).[28] Subsequent α,α-dilithiation of N-*t*-BOC-2,5-dibromopyrrole using *n*-BuLi in THF at -70°C, followed by the addition of Tos_2S (1 eq), resulted in the formation of poly(N-*t*-BOC-pyrrole-2,5-diyl sulfide) **7** as a black oil (scheme 5.9).



Scheme 5.9: *Synthesis of poly(N-t-BOC-pyrrole-2,5-diyl sulfide) (7).*

^{1}H-NMR analysis of the crude oil revealed that it contained *n*-butylthio terminated oligomers; the latter is in line with the excess of *n*-BuLi used. Furthermore, size exclusion chromatography (SEC) showed the presence of high molecular weight material (figure 5.4).

In order to characterize the lower molecular weight oligomers separately, we fractionated the reaction mixture by column chromatography. Elution with a gradient of CH_2Cl_2 : hexane (1:1) to pure CH_2Cl_2, allowed the isolation of the monomer (**7a**, n = 1 contaminated with small amounts of monopyrrole derivatives), the dimer (**7b**, n = 2, purity > 98%) and the trimer (**7c**, n = 3, purity ~95%). In order to isolate the higher molecular weight oligomers, the column was flushed with $CHCl_3$/ethanol (99/1), yielding fraction 4 (**7d**). All fractions were characterized by NMR spectroscopy and SEC (figure 5.4).

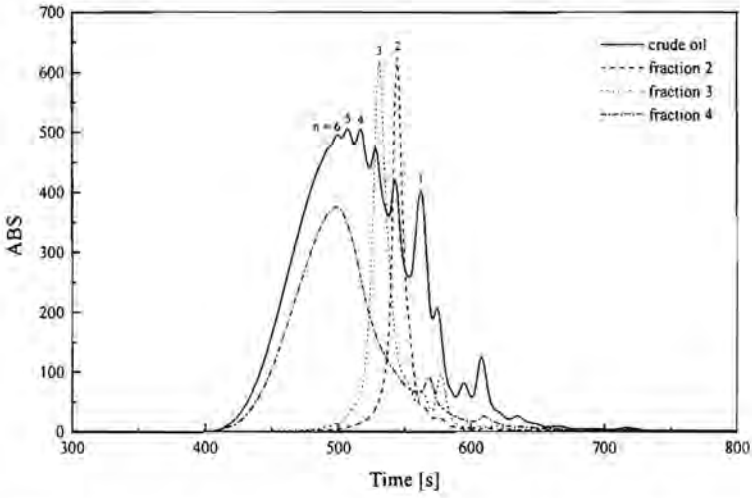


Figure 5.4: *SEC-analyses of crude poly(N-t-BOC-pyrrole-2,5-diyl sulfide) (7) and its fractionated oligomers.*

In order to prove that the '+ - 0 0'-concept can indeed be operative in pyrrole-sulfur compounds, the *t*-BOC groups of the model compounds, **3**, **4**, **5** and **6**, and the polymer, **7**, needed to be removed first. Therefore, as usual, we applied thermal deprotection as discussed in Chapter 2 (20-30 minutes at 190°C under vacuum).[29] However, much to our surprise, this deprotection step resulted in black insoluble tars in all cases. Apparently, the deprotected species easily undergo side-reactions under these conditions. A possible explanation might be the occurrence of sulfur-extrusion, a phenomenon known from porphyrin chemistry.[30] Hereby, a sulfur atom is eliminated by a combination of pericyclic processes. During one of the deprotection experiments we checked this by smelling above the flask (olfactory analysis). Hereby, we observed the indisputable proof: H_2S. Another related explanation might be that radicals are formed during this process; the latter are expected to be so reactive that polymerization immediately occurs. This could explain the insoluble character of the products formed upon thermolysis.

Since thermal deprotection destroys the α-pyrrolyl-sulfur bond, we also investigated the acid-catalyzed deprotection of *t*-BOC groups.[31] However, again undefined products were obtained, which once more pointed to polymerization. A final attempt to measure the conductivity of this polymer could not be performed, since the films were totally mutilated due to gas formation (CO_2, isobutene, H_2S) upon thermolysis.

The adaptation of Berlin's route has opened the way to prepare new pyrrole-sulfur compounds. Since selective α-lithiation of N-*t*-BOC-2-bromopyrrole with *n*-BuLi proceeds much easier than direct lithiation of N-tosylpyrrole, bis(N-*t*-BOC-2-pyrrolyl) sulfide (**3**) can be prepared in much higher yields compared to Berlin's bis(N-tosyl-2-pyrrolyl) sulfide (96%

vs. 18%). The latter is most probably due to the higher stability of the *t*-BOC group in the presence of an α-pyrrolyl anion, compared to the tosyl group. In a similar way, the first N-*t*-BOC protected poly(pyrrole-2,5-diyl sulfide) was prepared. However, since deprotection of the *t*-BOC groups appeared to be a major problem, there were two possibilities to continue this study. First of all, we could switch to the tosyl group and prepare poly(N-tosyl-pyrrole-2,5-diyl sulfide). The second possibility implied modification of the N-*t*-BOC protected polymer **7**. In order to verify the feasibility of the first option, we studied the synthesis of bis(N-phenylsulfonyl-2-pyrrolyl) sulfide from N-phenylsulfonyl-2-bromopyrrole, *n*-BuLi and Tos_2S. The yield of this reaction appeared to be comparable to that of Berlin (15%), which made us decide to choose for the second option.

5.3 *Poly(thienylthiothienylpyrrolyl)*

Since deprotection of the *t*-BOC groups turned out to be a major problem in case of the oligo- and poly(pyrrole-2,5-diyl sulfide)s, we designed a new polymer by modifying polymer **7**. This new polymer, poly{5[β-dodecyl-2(2{2-thienylthio}-5-thienyl)pyrrolyl]}, was chosen for a number of reasons. First of all, we hoped that by incorporating thiophene units between pyrrole and sulfur, a kind of buffer zone would be formed, which separates these electron-rich parts. This might result in more stable species under thermolytic conditions. Secondly, introduction of dodecyl chains will circumvent the expected solubility and processability problems of the polymer after removal of the *t*-BOC groups. A third reason for preparing this polymer, is the availability of the monomeric unit, N-*t*-BOC-3-dodecyl-2,5-dithienylpyrrole[32], and the knowledge on the formation of 2-thienyl-sulfur bonds.[14,33] A disadvantage of incorporating thiophene units, however, is their expected negative influence on the effectuation of the '+ - 0 0'-electronic structure. Since one out of every four thiophene units will be forced into an energetically unfavorable quinoid state, this might result in a more elevated band gap (figure 5.5).[12]

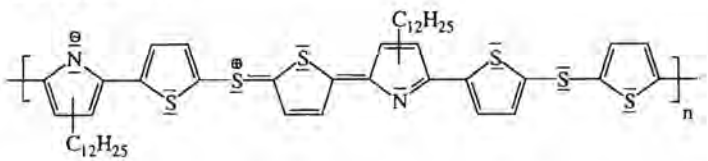
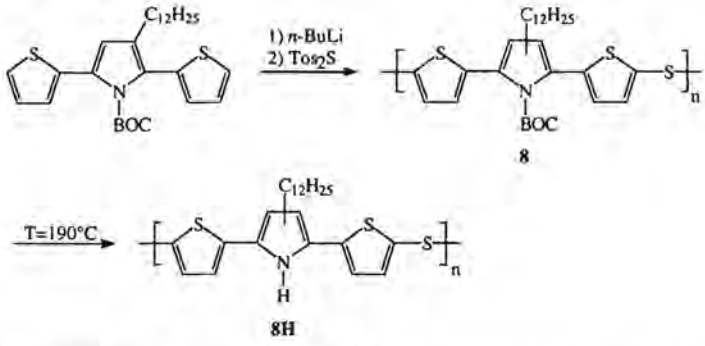


Figure 5.5: *'+ - 0 0'-Electronic structure of poly[N-dehydro-5[β-dodecyl-2(2{2-thienylthio}-5-thienyl)pyrrolyl]].*

For the synthesis of **8**, we once more applied the adapted Berlin-route. N-*t*-BOC-3-dodecyl-2,5-dithienylpyrrole[32] was first selectively lithiated at the free α-thienyl positions,

using *n*-BuLi in THF at -70°C, after which Tos_2S (1 eq) was added (scheme 5.10). Subsequent work-up gave the desired, regiorandom polymer **8** as a green oil. Size exclusion chromatographic analysis of the polymer showed the chromatogram as depicted in figure 5.6. Due to the exclusion limit of the column, all high molecular weight material is detected at 340 seconds, resulting in the deviating shape of the SEC-chromatogram. Still, a molecular weight (M_p) of 1.5 x 10^4 $gmol^{-1}$, based on polystyrene standards, could be calculated.



Scheme 5.10: *Synthesis of poly{5[N-t-BOC-β-dodecyl-2(2{2-thienylthio}-5-thienyl)pyrrolyl]} (8) and its deprotected form (8H).*

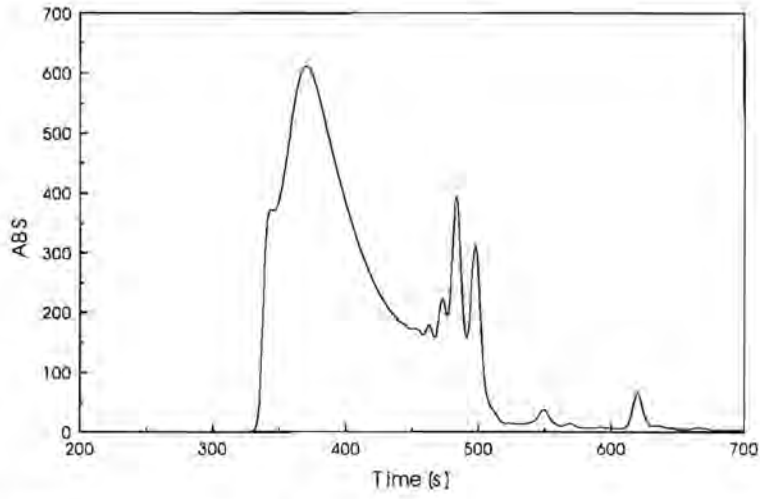
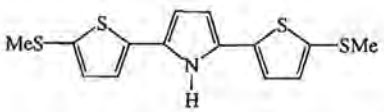


Figure 5.6: *SEC-chromatogram of polymer 8.*

Investigation of the possible '+ - 0 0'-behavior within this polymer started with thermal deprotection of the *t*-BOC groups (20-30 minutes at 190°C under vacuum; scheme

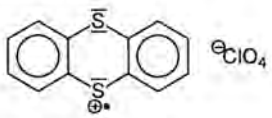
5.10). This indeed resulted in the quantitative formation of **8H**. The latter was checked with ^{1}H-NMR, which clearly indicated the presence of the N-H signal at 8.0 ppm, and with UV-Vis, showing a small bathochromic shift of the π-π^* wavelength transition of 34 nm compared to **8**.

Cyclic voltammetric measurements performed on the unprotected polymer **8H** revealed an oxidation potential of 0.88 V. When one compares this value to that of a reference compound, being 2,5-di(5-methylthio-2-thienyl)pyrrole[34],



the oxidation potential of the latter is significantly lower (0.58 V). This difference is mostly due to the fact that the cation radical of the reference compound is stabilized by two, strongly electron-releasing, thiomethoxy groups, whereas cation radicals in polymer **8H** are only stabilized by one, moderately electron-releasing, thioaryl group per repeating unit. This effect appears to be much stronger than the stabilizing effect of the dodecyl chains, which are attached to the polymer. Both compounds also showed reversible redox curves, indicating that a stable cation radical state is formed on the cyclic voltammetry time-scale.

In order to investigate the delocalization of (di)cation radicals in polymer **8H** and the reference compound, UV/Vis/NIR measurements were performed. Therefore, **8H** and the reference compound were oxidized under inert atmosphere by adding portions of a solution of thianthrenium perchlorate in dichloromethane.



Thianthrenium perchlorate

In case of 2,5-di(5-methylthio-2-thienyl)pyrrole, two absorption bands appeared at 1.31 eV and 2.16 eV, respectively; these are attributed to the cation radical of 2,5-di(5-methylthio-2-thienyl)pyrrole (figure 5.7a). The other two bands at 1.61 eV and 2.43 eV, respectively, arise from dimerization of cation radicals, a phenomenon earlier observed for oligothiophenes[35] and oligopyrroles.[36] Polymer **8H** shows two absorption bands at 1.38 eV and 2.31 eV, respectively, for the cation radical state. These two absorption bands seem to be superpositions of the 1.31/1.61 bands and the 2.16/2.43 bands of 2,5-di(5-methylthio-2-thienyl)pyrrole. Similarly, the absorption bands for the dication diradical states of the reference compound and the polymer appear at comparable positions (figure 5.7b). Since in 2,5-di(5-methylthio-2-thienyl)pyrrole the cation radical is definitely localized on the aromatic units, this strongly suggests that the positive charges in the polymer are also localized on the 2,5-dithienyl-

pyrrole triad, thus indicating that the degree of conjugation through the carbon-sulfur linkages is limited. This explanation is supported by the low conductivity (0.1 Scm^{-1}), measured in films of **8H** after doping with iodine. Although this value is not very high, it is still much higher than that of PTS ($\sigma = 2 \times 10^{-5}$ Scm^{-1}) as mentioned in the introduction. Furthermore, comparison with AsF_5-doped PPS ($\sigma = 200$ Scm^{-1}) is not appropriate since this dopant is so strong that it actually mutates this polymer by intrachain bridging toward dibenzothiophene linkages.[37]

Since we have not made any attempt to dehydrogenate polymer **8H**, we cannot make any statement about the '+ - 0 0'-concept. However, the UV/Vis/NIR measurements seem to point to localization of charges on the aromatic triads of chemically oxidized **8H**.

Although the ultimate goal, development of an intrinsically conducting polypyrrole, has not been reached, this study has shown that pyrrole-sulfur compounds are - albeit not easily - accessible. Therefore, these results can be of great use for future studies on the chemistry of the pyrrole-sulfur bond.

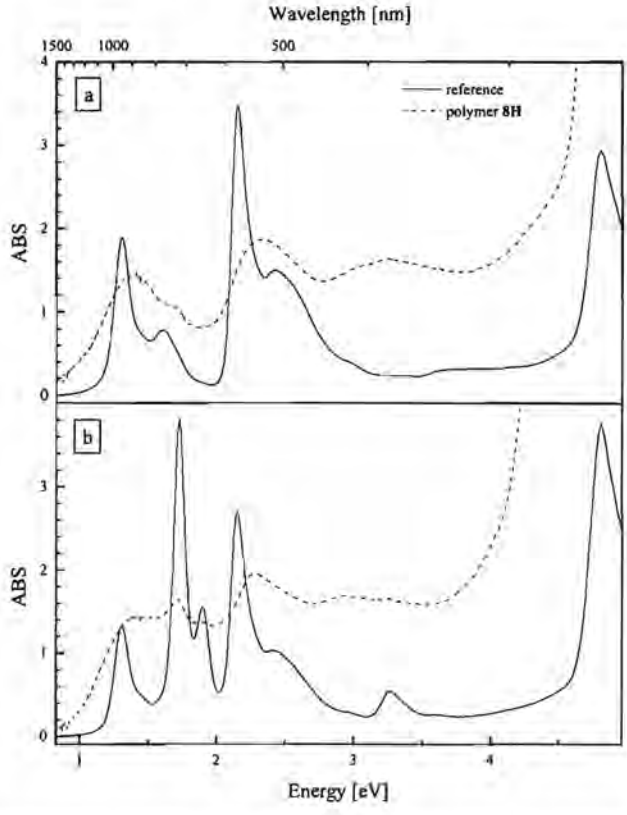


Figure 5.7: *UV/Vis/NIR spectra of a) the cation radical state, b) dication diradical state of polymer **8H** and reference compound 2,5-di(5-methylthio-2-thienyl)pyrrole.*

5.4 *Conclusions*

Although our attempts to transfer the '+ - 0 0'-electronic structure, as present in polysulfur nitride, into pyrrole-sulfur compounds have not resulted in an intrinsically conducting polypyrrole, a lot of new and important knowledge has been obtained on the chemistry of pyrrole-sulfur compounds.

First of all, bis(N-*t*-BOC-2-pyrrolyl) sulfide, -sulfoxide, -sulfone and poly(N-*t*-BOC-pyrrole-2,5-diyl sulfide) were synthesized in high yields by a slight but significant modification of the only synthetic strategy known in literature to prepare an N-protected pyrrole-sulfur compound. Both sulfides could be prepared by a sequence of lithiation (*n*-BuLi) and subsequent sulfuration (Tos_2S) in THF at -70°C using N-*t*-BOC-2-bromopyrrole and N-*t*-BOC-2,5-dibromopyrrole, respectively. Bis(N-*t*-BOC-2-pyrrolyl) sulfoxide and -sulfone were synthesized from bis(N-*t*-BOC-2-pyrrolyl) sulfide by selective, stepwise oxidation with *m*-CPBA. Attempts to remove the *t*-BOC groups by thermolysis, all resulted in the formation of insoluble black tars. The latter are probably caused by sulfur extrusion in combination with polymerization.

A second type of pyrrole-sulfur compounds was poly{5[N-*t*-BOC-*β*-dodecyl-2(2{2-thienylthio}-5-thienyl)pyrrolyl]}. The latter was synthesized from N-*t*-BOC-3-dodecyl-2,5-dithienylpyrrole applying the same sequence as described above. Although this compound could indeed be deprotected by thermolysis, UV/Vis/NIR studies on the deprotected oxidized species revealed that π-conjugation along the polymer backbone is limited and that localization of charges on the aromatic triads takes place. Although the latter does not prove whether the '+ - 0 0'-electronic structure can be incorporated into pyrrole-sulfur compounds, it was the ultimate result that we could obtain from these studies.

5.5 *Experimental section*

For general remarks concerning chemicals and analysis techniques, the reader is referred to section 2.6. The UV/Vis/NIR spectroelectrochemical measurements were performed in CH_2Cl_2 using a Perkin Elmer Lambda 900 UV/Vis spectrophotometer. Cyclic voltammograms were obtained in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte using a Potentioscan Wenking POS 73 potentiostat. A platinum disk (diameter 5 mm) was used as working electrode, the counter electrode was a platinum plate (5x5 mm) and a Standard Calomel Electrode (SCE) or Ag/AgCl electrode was used as reference electrode.

Bis(phenylsulfonyl) sulfide (1)[14] To a mechanically stirred suspension of sodium phenylsulfinate (32.83 g, 0.200 mol) in toluene (750 ml), a solution of SCl_2 (10.55 g, 0.102 mol) in toluene (50 ml) was slowly added. The mixture was stirred for 1 day, after which the precipitate was filtered. The

filtrate was concentrated, yielding a yellow solid. Crystallization of this solid, using di-*i*-propyl ether and toluene, yielded **1** as a white solid (14.0 g, 0.045 mol, 45%). Mp.: 129-130°C (Lit.: 128-130°C).[14] ^{1}H-NMR ($CDCl_3$): δ 8.00 (d, J = 7.7 Hz, 4H, H-*ortho*), 7.69 (t, J = 7.4 Hz, 2H, H-*para*), 7.57 (t, J = 7.8 Hz, 4H, H-*meta*) ppm. ^{13}C-NMR ($CDCl_3$): δ 144.2 (C-1), 134.9 (C-*para*), 129.3/128.0 (C-*ortho*/C-*meta*) ppm. Anal.: calcd. C 45.84, H 3.21; found C 45.84, H 3.24.

Bis(*p*-tosyl) sulfide (2)[14] To a mechanically stirred suspension of sodium *p*-tosylate (89.80 g, 0.504 mol) in toluene (950 ml), a solution of SCl_2 (25.84 g, 0.251 mol) in toluene (50 ml) was slowly added. The mixture was stirred overnight, after which the precipitate was filtered. From the filtrate the solvent was evaporated, yielding a pink solid. After three recrystallizations (toluene) in order to remove bis(*p*-tosyl) disulfide, pure **2** was obtained as a white solid (44.05 g, 0.129 mol, 51%). Mp.: 134-135°C.

^{1}H-NMR ($CDCl_3$): δ 7.85 (d, J = 8.4 Hz, 4H, H-*ortho*), 7.32 (d, J = 8.2 Hz, 4H, H-*meta*), 2.43 (s, 6H, H-methyl) ppm. ^{13}C-NMR ($CDCl_3$): δ 146.2 (C-1), 141.2 (C-*para*), 129.8/127.9 (C-*ortho*/C-*meta*), 21.7 (C-methyl) ppm. Anal.: calcd. C 49.10; H 4.12; found C 49.58, H 3.90.

Bis(N-*tert*-butoxycarbonyl-2-pyrrolyl) sulfide (3) N-*t*-BOC-2-bromopyrrole (2.72 g, 11.1 mmol) was dissolved in THF (40 ml) and cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 7.5 ml, 12 mmol) was slowly added and the solution was stirred for 15 min at -70°C. Then bis(*p*-tosyl) sulfide (**2**, 1.89 g, 5.52 mmol) was added in small portions, after which the mixture was stirred for another 15 min at -70°C. The mixture was then allowed to reach RT, poured into water (200 ml) and extracted with Et_2O (3 × 80 ml). The combined organic fractions were washed with aqueous Na_2CO_3 (0.25 M, 150 ml) and water (2 × 150 ml), dried ($MgSO_4$), filtered and concentrated, yielding a black oil (2.18 g). Distillation by means of Kügelrohr (100°C, 0.2 mm Hg, 1 h) removed all volatile impurities, whereas the residual black oil contained pure **3** (1.94 g, 5.32 mmol, 96%). Subsequent decoloration with activated carbon and precipitation in methanol, yielded **3** as a slightly orange solid (0.84 g, 2.30 mmol, 42%). Mp.: 88-89°C.

^{1}H-NMR ($CDCl_3$): δ 7.37 (dd, J = 3.5 and 1.9 Hz, 2H, H-5), 6.16 (t, J = 3.4 Hz, 2H, H-4), 5.98 (dd, J = 3.5 and 1.9 Hz, 2H, H-3), 1.51 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 148.9 (C=O), 124.7 (C-2), 123.2 (C-5), 117.7 (C-3), 111.2 (C-4), 84.4 (C-q (BOC)), 27.8 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 228 nm. IR (KBr): 2977, 2934, 1758, 1733, 1455, 1394, 1370, 1336, 1318, 1284, 1154, 1099, 1056, 994, 845, 736 cm^{-1}. Anal.: calcd. C 59.32, H 6.64, N 7.69; found C 59.45, H 6.54, N 7.36.

Bis(N-*tert*-butoxycarbonyl-5-phenyl-2-pyrrolyl) sulfide (4) A solution of N-*t*-BOC-2-bromo-5-phenylpyrrole (0.61 g, 1.89 mmol) in Et_2O (2 ml) was cooled to -78°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 1.074 ml, 1.72 mmol) was added dropwise, after which stirring was continued for 30 min at -78°C. Then bis(phenylsulfonyl) sulfide (**1**, 0.2682 g, 0.85 mmol) was added in small portions and the mixture was stirred for 2½ h at -78°C. Then the solution was allowed to reach RT and stirred for an additional 3 days. The solution was then poured into water, extracted with Et_2O, dried ($MgSO_4$), filtered and concentrated. The remaining dark red oil (0.71 g) was purified by column chromatography (50 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.16), yielding pure **4** as an oil (0.24 g, 0.46 mmol, 55%).

^{1}H-NMR ($CDCl_3$): δ 7.37-7.27 (m, 10H, Ph), 6.19 (d, J = 3.4 Hz, 2H, H-3/H-4), 6.16 (d, J = 3.6 Hz, 2H, H-3/H-4), 1.29 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 149.2 (C=O), 137.5 (C-*ipso* (Ph)), 134.5 (C-5), 128.2/127.9/127.2 (C-*o,m,p* (Ph)), 126.3 (C-2), 116.6 (C-4), 112.9 (C-3), 84.5 (C-q (BOC)), 27.3 (C-methyl (BOC)) ppm.

Bis(N-*tert*-butoxycarbonyl-2-pyrrolyl) sulfoxide (5) using thionyl chloride A solution of N-*t*-BOC-2-bromopyrrole (2.43 g, 9.87 mmol) in THF (40 ml) was cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 6.6 ml, 10.6 mmol) was slowly added, after which the solution was stirred for 10 min at -70°C. Thionyl chloride (0.36 ml, 4.96 mmol) was added dropwise and the solution was stirred for another 15 min at -70°C. Then, the solution was allowed to reach RT, poured into water (200 ml) and extracted with Et_2O (2 × 80 ml). The combined organic fractions were washed with aqueous Na_2CO_3 (0.25 M, 150 ml) and water (2 × 150 ml), dried (Na_2SO_4), filtered and concentrated, yielding a black oil (1.93 g). After column chromatography (200 g Al_2O_3, CH_2Cl_2, R_f = 0.31), pure **5** was obtained as a colorless oil, which slowly crystallized (0.97 g, 2.55 mmol, 52%). Mp.: 119-120°C.

^{1}H-NMR ($CDCl_3$): δ 7.44 (dd, J = 3.2 and 1.9 Hz, 2H, H-5), 6.49 (broad s, 2H, H-3), 6.27 (t, J = 3.4 Hz, 2H, H-4), 1.54 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 147.8 (C=O), 135.0 (C-2), 124.8 (C-5), 118.0 (C-3), 111.3 (C-4), 86.0 (C-q (BOC)), 27.7 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 234 nm. IR (KBr): 3129, 2981, 2935, 1748, 1396, 1372, 1320, 1260, 1154, 1099, 1054, 992, 842, 739 cm^{-1}. Anal.: calcd. C 56.82, H 6.36, N 7.36; found C 56.70, H 6.60, N 6.92.

Bis(N-*tert*-butoxycarbonyl-2-pyrrolyl) sulfoxide (5) *via* oxidation To a solution of bis(N-*t*-BOC-2-pyrrolyl) sulfide (**3**, 0.4237 g, 1.163 mmol) in CH_2Cl_2 (4 ml), *m*-chloroperbenzoic acid (techn. 70%, 0.2902 g, 1.177 mmol) was slowly added. After stirring for 45 min at RT, the solution was poured into water (50 ml) and extracted with Et_2O (3 × 25 ml). The combined organic fractions were washed with aqueous Na_2CO_3 (0.25 M, 50 ml) and water (2 × 50 ml), dried (Na_2SO_4), filtered and concentrated, yielding pure **5** as a slightly orange oil, which slowly crystallized (0.45 g, 1.163 mmol, 100%).

Bis(N-*tert*-butoxycarbonyl-2-pyrrolyl) sulfone (6) *via* oxidation Bis(N-*t*-BOC-2-pyrrolyl) sulfoxide (**5**, 0.45 g, 1.163 mmol) was dissolved in CH_2Cl_2 (4 ml) and *m*-chloroperbenzoic acid (techn. 70%, 0.2880 g, 1.17 mmol) was slowly added. After stirring for 3 h at RT, the solution was poured into water (50 ml) and extracted with Et_2O (3 × 25 ml). The combined organic fractions were washed with aqueous Na_2CO_3 (0.25 M, 50 ml) and water (2 × 50 ml), dried (Na_2SO_4), filtered and concentrated, yielding **6** as a slightly orange oil, which slowly crystallized (0.45 g, 1.14 mmol, 98%). Mp.: 134-135°C.

^{1}H-NMR ($CDCl_3$): δ 7.49 (dd, J = 3.1 and 2.0 Hz, 2H, H-5), 6.79 (dd, J = 3.7 and 2.0 Hz, 2H, H-3), 6.23 (t, J = 3.4 Hz, 2H, H-4), 1.52 (s, 18H, H-methyl (BOC)) ppm. ^{13}C-NMR ($CDCl_3$): δ 146.9 (C=O), 131.2 (C-2), 127.0 (C-5), 123.5 (C-3), 109.6 (C-4), 86.1 (C-q (BOC)), 27.3 (C-methyl (BOC)) ppm. UV-Vis (CH_3CN): 232 nm. IR (KBr): 3130, 2975, 2934, 1764, 1401, 1374, 1341, 1290, 1264, 1216, 1149, 1116, 1096, 1065, 1004, 840, 766, 742, 647, 625 cm^{-1}. Anal.: calcd. C 54.53, H 6.10, N 7.10; found C 55.41, H 5.85, N 6.71.

(N.B. From ^{1}H-NMR it was deduced that **6** contained 7% of **5**; the presence of the latter can be prevented by using a small excess of *m*-CPBA. Analyses were performed on pure **6**).

Poly(N-*tert*-butoxycarbonyl-pyrrole-2,5-diyl sulfide) (7) N-*t*-BOC-2,5-dibromopyrrole (2.32 g, 7.14 mmol) was dissolved in THF (36 ml) and cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 10.7 ml, 17.1 mmol) was slowly added, after which the solution was stirred for 1 h at -70°C. Bis(*p*-tosyl) sulfide (**2**, 2.46 g, 7.18 mmol) was added in small portions and the mixture was stirred for another hour at -70°C. The mixture was then allowed to reach RT, stirred for 2 h, poured into water (300 ml) and extracted with Et_2O (3 × 200 ml). The combined organic layers were washed with water (2 × 300 ml), dried ($MgSO_4$) and concentrated, yielding 1.82 g of a black oil, **7**. The smaller oligomers present in this oil were separated by column chromatography (130 g SiO_2, gradient CH_2Cl_2 : hexane (1:3) *via* CH_2Cl_2/ethanol (500/1) to $CHCl_3$/ethanol (100/1)), affording four fractions: fraction 1 (monomer **7a**, 0.05 g), fraction 2 (dimer **7b**, 0.01 g), fraction 3 (trimer **7c**, 0.02 g) and fraction 4 (higher oligomers **7d**, 0.76 g, ~50%).

N-*tert*-Butoxycarbonyl-2,5-bis(*n*-butylthio)pyrrole (7a) ^{1}H-NMR ($CDCl_3$): δ 6.17 (s, 2H, H-3,4), 2.78 (t, J = 7.5 Hz, 4H, -S-C$\underline{H}_2$-), 1.70-1.54 (m, 4H, -S-CH_2-C$\underline{H}_2$-), 1.65 (s, 9H, H-methyl (BOC)), 1.54-1.36 (m, 4H, -C$\underline{H}_2$-CH_3), 0.90 (t, J = 7.5 Hz, 6H, -CH_2-C$\underline{H}_3$) ppm.

Bis(N-*tert*-butoxycarbonyl-5-(*n*-butylthio)-2-pyrrolyl) sulfide (7b) ^{1}H-NMR ($CDCl_3$): δ 6.12 (d, J = 3.6 Hz, 2H, H-4), 6.01 (d, J = 3.6 Hz, 2H, H-3), 2.80 (t, J = 7.5 Hz, 4H, -S-C$\underline{H}_2$-), 1.70-1.54 (m, 4H, -S-CH_2-C$\underline{H}_2$-), 1.55 (s, 18H, H-methyl (BOC)), 1.54-1.35 (m, 4H, -C$\underline{H}_2$-CH_3), 0.93 (t, J = 7.5 Hz, 6H, -CH_2-C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$) δ: 149.0 (C=O), 129.3 (C-5), 125.6 (C-2), 117.4/114.9 (C-3/C-4), 85.4 (C-q (BOC)), 34.7 (-S-C$\underline{H}_2$-), 30.6 (-S-CH_2-C$\underline{H}_2$-), 27.8 (C-methyl (BOC)), 22.0 (-C$\underline{H}_2$-CH_3), 13.6 (-CH_2-C$\underline{H}_3$) ppm.

N-*tert*-Butoxycarbonyl-2,5-bis[N-*tert*-butoxycarbonyl-5′-(*n*-butylthio)-2′-pyrrolylthio]pyrrole (7c) ^{1}H-NMR ($CDCl_3$): δ 6.12 (d, J = 3.6 Hz, 2H, H-3′/H-4′), 6.10 (d, J = 3.6 Hz, 2H, H-3′/H-4′), 5.93 (s, 2H, H-3,4), 2.80 (t, J = 7.5 Hz, 4H, -S-C$\underline{H}_2$-), 1.70-1.54 (m, 4H, -S-CH_2-C$\underline{H}_2$-), 1.55 (s, 18H, H-methyl (BOC′)), 1.54-1.35 (m, 4H, -C$\underline{H}_2$-CH_3), 1.48 (s, 9H, H-methyl (BOC)), 0.93 (t, J = 7.5 Hz, 6H, -CH_2-C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$) δ: 148.9 (C=O (BOC,BOC′)), 129.8 (C-5′), 127.8 (C-2′), 125.0 (C-2,5), 118.2 (C-4′), 116.9 (C-3′), 114.5 (C-3,4), 85.4 (C-q (BOC,BOC′)), 34.8 (-S-C$\underline{H}_2$-), 30.6 (-S-CH_2-C$\underline{H}_2$-), 27.8 (C-methyl (BOC′)), 27.7 (C-methyl (BOC)), 22.0 (-C$\underline{H}_2$-CH_3), 13.6 (-CH_2-C$\underline{H}_3$) ppm.

Poly[(N-*tert*-butoxycarbonylpyrrole-2,5-diyl) sulfide] (7d) ^{1}H-NMR ($CDCl_3$): δ 6.5-5.8 (m, Py-H), 2.9-2.7 (m, -S-C$\underline{H}_2$-), 1.8-1.1 (m, BOC,-(C$\underline{H}_2$)$_2$-CH_3), 1.1-0.8 (m, -CH_2-C$\underline{H}_3$) ppm. ^{13}C-NMR ($CDCl_3$) δ: 149 (C=O), 132-126 (C-α (Py)), 120-114 (C-β (Py)), 86 (C-q (BOC)), 35 (-S-C$\underline{H}_2$-), 31 (-S-CH_2-C$\underline{H}_2$), 29-27 (C-methyl (BOC)), 22 (-C$\underline{H}_2$-CH_3), 14 (-CH_2-C$\underline{H}_3$) ppm.

Poly{5[N-*t*-BOC-β-dodecyl-2(2{2-thienylthio}-5-thienyl)pyrrolyl]} (8) A solution of N-*tert*-butoxycarbonyl-3-dodecyl-2,5-di(2-thienyl)pyrrole[32] (0.8176 g, 1.636 mmol) in THF (7 ml) was cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 2.15 ml, 3.44 mmol) was added in 5 min and the solution was stirred for 30 min. Then bis(*p*-tosyl) sulfide (**2**, 0.570 g, 1.66 mmol) was added in portions, after which the mixture was stirred for another 15 min at -70°C. Then it was allowed to reach RT, poured into water and extracted with Et_2O. The combined organic layers were dried ($MgSO_4$), filtered and concentrated, yielding **8** as a green oil (0.8 g).

^{1}H-NMR ($CDCl_3$) δ: 7.16-6.79 (m, 4H, H-β (th)), 6.21, 6.19 (s, 1H, H-β (pyr)), 2.30 (m, 2H, pyr-$C\underline{H}_2$-), 1.48 (m, 2H, pyr-CH_2-$C\underline{H}_2$-), 1.3-1.1 (m, 27H, -CH_2-($C\underline{H}_2$)$_9$-CH_3, H-methyl (BOC)), 0.88 (m, 3H, -CH_2-$C\underline{H}_3$) ppm. UV-Vis ($CHCl_3$): 334 nm. IR (film on KBr): 2924, 2852, 1748, 1462, 1368, 1307, 1148, 803 cm^{-1}.

8H: Thermolysis of neat **8** at 190°C under vacuum for 15 min, gave pure **8H** in quantitative yield. ^{1}H-NMR ($CDCl_3$): δ 8.0 (m, 1H, N-H), 7.1-6.8 (m, 4H, H-β (th)), 6.2 (m, 1H, H-β (pyr)), 2.5 (m, 2H, pyr-$C\underline{H}_2$-), 1.6 (m, 2H, pyr-CH_2-$C\underline{H}_2$-), 1.3 (m, 18H, -CH_2-($C\underline{H}_2$)$_6$-CH_3), 0.9 (m, 3H, -CH_2-$C\underline{H}_3$) ppm. UV-Vis (CH_2Cl_2): 377 nm. UV-Vis ($CHCl_3$): 368 nm.

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Chapter 6

WELL-DEFINED OLIGO(PYRROLE-2,5-DIYL)S BY THE ULLMANN REACTION

Abstract: *The Ullmann reaction has been applied to polymerize N-t-BOC-2,5-dibromopyrrole into well-defined oligo(N-t-BOC-pyrrole-2,5-diyl)s. After optimization of the reaction conditions, i.e. using one weight equivalent of Cu-bronze in DMF at 100°C for 1 hour, oligomers containing up to 25 repeating pyrrole units are obtained. Starting from 5,5'- and 5,5''-dibrominated N-t-BOC protected bi- and terpyrrole as monomers, the polymerization is slower and a lower degree of polymerization is observed, yielding oligomers with an even lower molecular weight than those resulting from N-t-BOC-2,5-dibromopyrrole. The first 20 oligomers of poly(N-t-BOC-pyrrole-2,5-diyl) have been isolated by means of preparative HPLC. Characterization of the individual oligomers shows that they are all hydrogen terminated and possess perfect 2,5-linkages: oligo(N-t-BOC-pyrrole-2,5-diyl)s. The isolated oligomers have been used to study the optical and electrical properties of the oligomers as a function of the chain length.*

6.1 *Introduction*

As shown in the former chapters, the Stille reaction is an interesting method to conduct asymmetric couplings and, therefore, to prepare well-defined and functional oligomers consisting of pyrrole and/or other π-conjugated units. However, besides the Stille reaction there are more methods to couple pyrroles. In Chapter 1 the possibilities of the Kumada, Suzuki, Negishi and Semmelhack/Yamamoto coupling were discussed. Here we will show that the 'old-fashioned' Ullmann reaction can also be applied for this purpose.

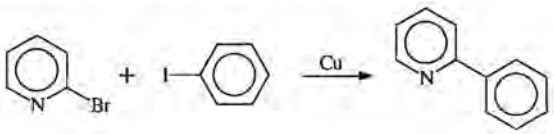
The Ullmann reaction is generally used as an intermolecular copper-mediated reductive homo-coupling of aromatic halides.[1-6]

$$2\ \text{Ar-X} \xrightarrow{\text{Cu}} \text{Ar-Ar}$$

The mechanism of the Ullmann reaction, which has been investigated quite extensively over the past decades, is still not fully understood.[3-8] It is proposed that the central mechanistic feature consists of the formation of an organocopper intermediate of unknown oxidation

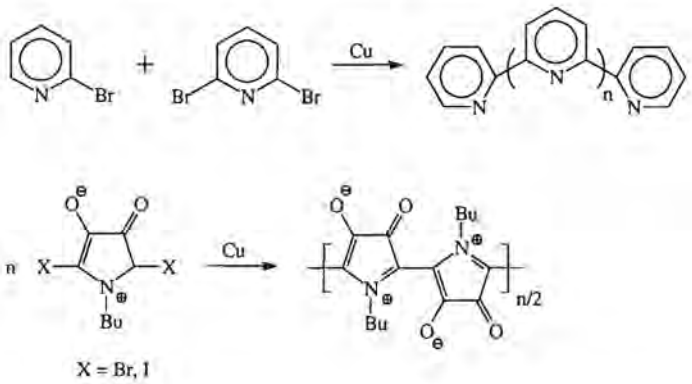
state.[9] However, the exact nature of this intermediate and the process by which it is formed and consumed, still remain obscure. The striking similarities between the homogeneous (Cu(I)) and the heterogeneous (Cu(0)) Ullmann reaction suggest that they are probably at least mechanistically related, indicating that Cu (III) intermediates might be involved, whereas the existence of radical intermediates is very unlikely.[7]

Since its discovery at the end of the nineteenth century, the Ullmann reaction has been used extensively in organic chemistry.[3-6,10] Although it is generally applied as a symmetric coupling reaction, there are several examples of asymmetric couplings[6,10-12], for instance the synthesis of 2-phenylpyridine (scheme 6.1, yield 50-55%).[6,13]



Scheme 6.1: *Illustration of an asymmetric Ullmann reaction.*

Concerning pyrrole derivatives, the Ullmann coupling has been applied quite frequently for the synthesis of building blocks for porphyrins.[14-17] In all cases N-unsubstituted pyrroles were dimerized to afford 2,2′-bipyrroles, or, as shown in scheme 1.4 (Chapter 1), a quaterpyrrole was obtained by dimerization of a monoiodo 2,2′-bipyrrole unit.[17] Simultaneously with our Ullmann studies, Sessler *et al.* used the Ullmann reaction to prepare a N-*t*-BOC protected 2,2′-bipyrrole.[18] Together with the present work, these are the only examples of Ullmann reactions performed with N-*t*-BOC protected pyrrole derivatives.



Scheme 6.2: *Two examples of the Ullmann reaction in macromolecular chemistry.*

In macromolecular chemistry the Ullmann reaction has only rarely been applied.[19-21] Two examples worth mentioning are the synthesis of oligopyridines, oligothiophenes and oligophenylenes during the 1930's[22-24], and the polymerization of azomethine ylide pyrroli-

nium oxide by Tour *et al.*[25,26] (scheme 6.2). The latter was performed following the work presented here.

In this chapter we will demonstrate that the Ullmann reaction appears to be a very good method to prepare a series of oligopyrroles. The latter is important to gain detailed insight into the structure-property relationship of these compounds. Starting from an α,α-dibrominated monomer, a mixture of perfectly α,α-linked N-*t*-BOC protected oligomers containing up to 25 pyrrole units is obtained. The latter is separated by preparative HPLC affording the first twenty individual oligomers on a 2-20 milligram scale, which allowed their investigation by several techniques.[27,28]

6.2 *Synthesis and characterization of the monomers*

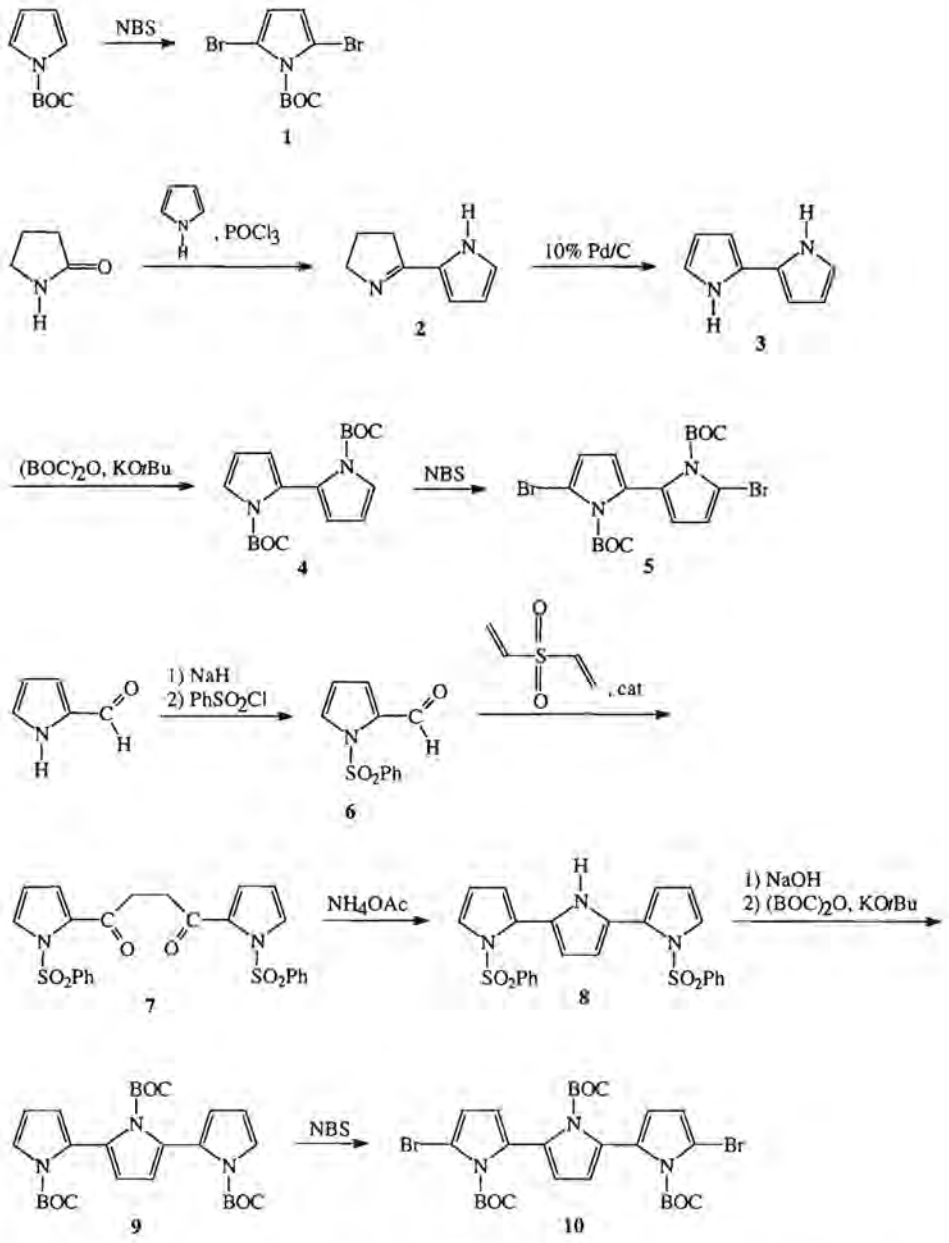
The N-*t*-BOC protected α,α-dibromopyrrole derivatives **1**, **5**, and **10** were used as the starting materials for the Ullmann polymerizations. The synthesis of these monomers is outlined in scheme 6.3. N-*tert*-Butoxycarbonyl-2,5-dibromopyrrole (**1**) was prepared from N-*tert*-butoxycarbonylpyrrole by selective dibromination of the latter with N-bromosuccinimide (NBS) using the procedure described by Martina *et al.*[29,30] Monomer **1**, which was obtained in 50% yield as a white solid after two recrystallizations, had to be stored under inert atmosphere at low temperatures (-20°C). If not, it easily decomposed into a black insoluble tar.

N,N'-Di-*tert*-butoxycarbonyl-5,5'-dibromo-2,2'-bipyrrole (**5**) was prepared from 2,2'-bipyrrole **3**. The latter was synthesized in two steps from pyrrole and 2-pyrrolidinone using the method of Rapoport *et al.*[31] The oxygen-sensitive 2,2'-bipyrrole was then protected with *tert*-butoxycarbonyl groups, after which it was selectively dibrominated with NBS to give **5** in an overall yield of 22% (from pyrrole).

Finally, N,N',N''-tri-*tert*-butoxycarbonyl-5,5''-dibromo-2,2':5',2''-terpyrrole (**10**) was prepared from 2-formylpyrrole in an overall yield of 12%. In the first three steps the terpyrrole unit was synthesized according to the procedure described by Merrill and LeGoff.[32] Subsequent removal of the phenylsulfonyl groups, directly followed by *t*-BOC protection of the oxygen-sensitive 2,2':5',2''-terpyrrole, gave N,N',N''-tri-*t*-BOC-2,2':5',2''-terpyrrole (**9**). In the last step this compound was selectively dibrominated with NBS, giving **10** in quantitative yield. Although these synthetic routes are combinations of steps published before, they are thought to be the most attractive ones (e.g. the synthesis of **9** by a Stille reaction has been described by Martina *et al.*[29,33]; however, as deduced by them, this route is far more difficult due to the latent instability of N-*t*-BOC-2,5-dibromopyrrole).

All monomers obtained are pure as checked by NMR spectroscopy; no monobrominated compounds or other impurities have been detected. Although both **5** and **10** proved to

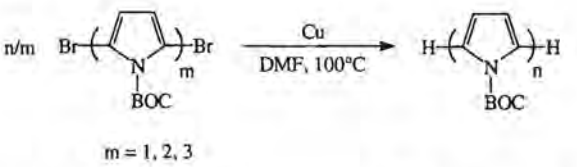
be more stable than monomer **1**, it is still necessary to handle these compounds with care (at low temperature under inert atmosphere).



Scheme 6.3: *Synthesis of the N-t-BOC protected dibromopyrrole monomers 1, 5 and 10.*

6.3 *Synthesis and characterization of oligo(N-t-BOC-pyrrole-2,5-diyl)s*

The polymerization of the monomers **1**, **5**, and **10** by the Ullmann reaction was performed by heating a mixture of the monomer, one weight equivalent of Cu-bronze and DMF (10 ml/g monomer) at 100°C under inert atmosphere (scheme 6.4).



Scheme 6.4: *Polymerization of N-t-BOC protected α,α-dibromopyrrole monomers (m=1-3) by the Ullmann reaction.*

After 1 hour in case of **1**, and 2 hours in case of **5** and **10**, the dark reaction mixtures were subjected to work-up procedures (extraction, filtration, evaporation). TLC (Al_2O_3) analysis of the resulting dark green oils showed that a large number of oligomers was formed in all three cases. After filtration over Al_2O_3 the reaction mixtures were analyzed in detail by analytical HPLC (reversed-phase chromatography using a gradient from methanol/water to methanol). The results of these HPLC analyses are shown in the figure 6.1, 6.2 and 6.3. These measurements revealed that in case of **1**, oligomers containing up to 25 pyrrole units were formed, whereas in case of **5** and **10**, oligomers containing up to 16 and 24 pyrrole units were obtained, respectively. In case of the bi- and terpyrrole monomers, substantial amounts of by-products were present as well.

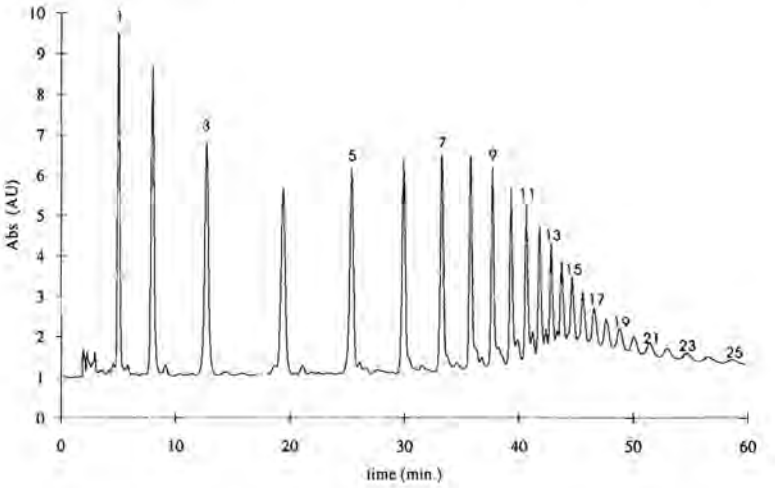


Figure 6.1: *HPLC analysis of the polymerization of 1.*

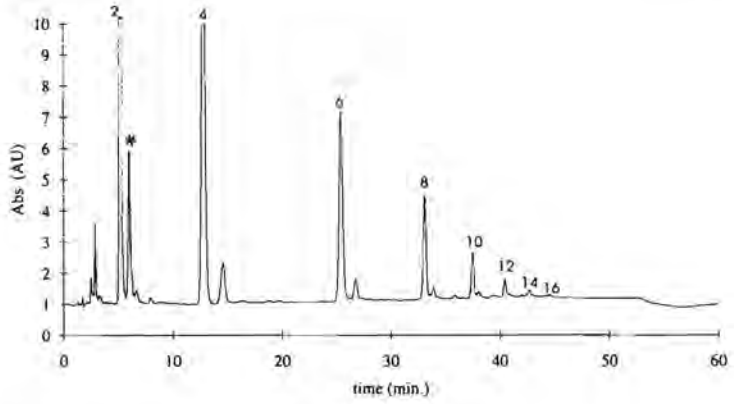


Figure 6.2: *HPLC analysis of the polymerization of* ***5****.*

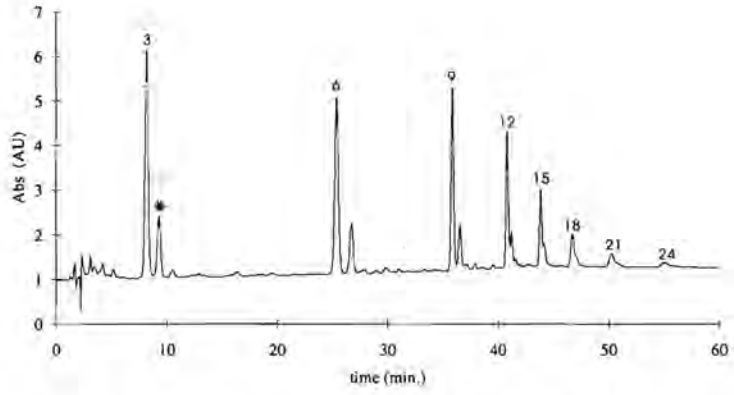


Figure 6.3: *HPLC analysis of the polymerization of* ***10****.*

In order to study the molecular structure of the oligomers obtained (e.g. what are the end-groups and what are the by-products in case of **5** and **10**?), preparative HPLC separations were performed on the complex reaction mixtures. Although HPLC is known to be of great use in the detection of oligomers[34,35], it was never, at the time of these experiments, applied to separate all oligomers from a polymerization reaction. Using preparative reversed-phase chromatography, we managed to isolate the first 20 individual oligomers on a 2-20 milligram scale from the reaction mixture of the polymerization of **1**. The purity of the isolated oligomers was checked by HPLC analysis and NMR-spectroscopy (^{1}H-NMR of all 20 isolated oligomers, ^{13}C-NMR of the first 10 oligomers, 2D-NMR to assign the peaks to the various H- and C-atoms). Up to 15 repeating units the samples featured a purity of at least

90%. In the higher oligomers a small fraction of unidentified UV absorbing impurity was detected by HPLC analysis. However, this impurity could not be detected by ^{1}H-NMR-spectroscopy.

The ^{13}C-NMR spectrum of the heptamer (n = 7) and the ^{1}H-NMR spectrum of the tridecamer (n = 13) are shown in the figures 6.4 and 6.5, respectively, together with their HPLC analyses (inserts). The ^{1}H-NMR spectra revealed that the oligomers are H-terminated as judged from the signals attributable to the α-H-atoms at δ = 7.40 ppm. All β-H-atoms give a multiplet around δ = 6.2 ppm. Going to higher oligomers the ratio between the number of α-H-atoms and the number of β-H-atoms changes as expected, while the shape of the multiplet almost resolves into a singlet. In the ^{13}C-NMR spectrum it proved to be far more difficult to assign peaks of the pyrrole unit for the higher oligomers. However, the resonances for the *t*-BOC group (both the carbonyl and the CH_3-group) are well-separated and the even-odd sequence can be measured as is shown in figure 6.4 for the heptamer. Final proof for the molecular structure of one of the oligomers (n = 13) was obtained by electrospray mass spectroscopy (ES-MS). The correct molar mass of 2186 (n = 13 (2147) complexed to K^+) was measured.

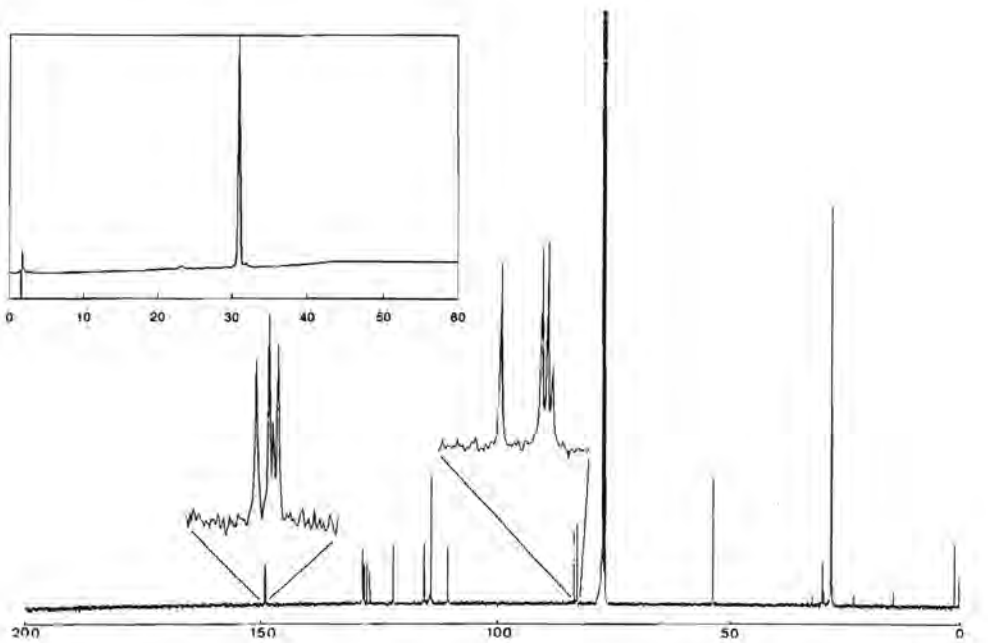


Figure 6.4: *^{13}C-NMR ($CDCl_3$) and HPLC analysis (inset) of the isolated heptamer (n=7).*

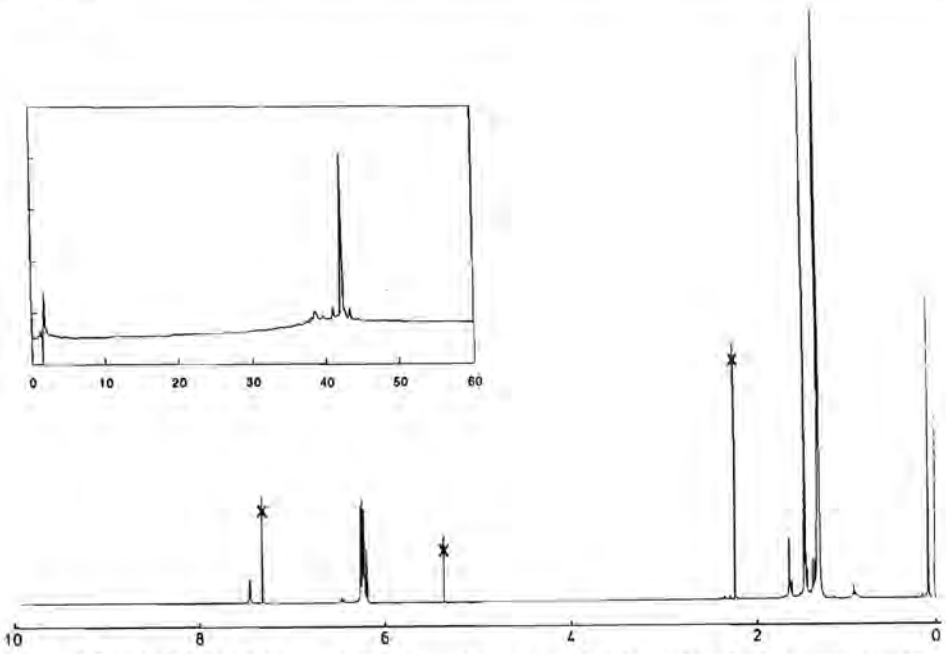


Figure 6.5: *^{1}H-NMR ($CDCl_3$) and HPLC analysis (inset) of the isolated tridecamer (n=13).*

As can be deduced from the figures 6.2 and 6.3, the Ullmann reactions of the bi- and terpyrrole monomers led to relatively many by-products. This is in sharp contrast to the clean reaction of **1**. After two hours of reaction time, each oligomer obtained from **5** and **10** was accompanied by a by-product, which represented at least 30% of the amount of H-terminated oligo(N-*t*-BOC-pyrrole-2,5-diyl). In order to clarify the structure of these by-products, the ones marked with an asterisk were also isolated by preparative HPLC. From mass- and NMR-spectroscopy it was concluded that these by-products are the corresponding *mono*brominated bi- and terpyrrole, N,N'-di-*tert*-butoxycarbonyl-5-bromo-2,2'-bipyrrole and N,N',N''-tri-*tert*-butoxy-carbonyl-5-bromo-2,2':5',2''-terpyrrole, respectively. All other by-products are, by analogy, proposed to be monobrominated N-*t*-BOC protected oligo(pyrrole-2,5-diyl)s (also the very small peaks in figure 6.1 are most probably monobrominated oligomers; formation of non 2,5-linked oligomers is not expected because this necessitates an unlikely bromine shift).

The reaction conditions applied here are the result of optimizing the Ullmann polymerization of **1**. The results under different conditions are shown in table 6.1. From these optimization experiments, it follows that enhanced temperatures (T > 70°C) are required to start the polymerization. However, too high temperatures result in more by-products and in removal of the *t*-BOC protecting groups. An effort to polymerize N-*t*-BOC-2,5-dichloro-pyrrole, the use of Cu^{2+} instead of Cu-bronze, or the addition of 17%(v/v) of water to the DMF, all result in a black insoluble tar.

The polymerization of the terpyrrole monomer **10** was also monitored by HPLC. We found that during the first 20 minutes there was an increase in the number of oligomers with a maximum of 8. After about 5 hours this number decreased until there were only 4 oligomers left after 88 hours. The amount of mono-brominated oligomers steadily decreased during the reaction; after 88 hours there were hardly any left. The decrease in the number of oligomers after 5 hours of reaction time is quite remarkable. This decrease is probably the result of (partial) deprotection giving rise to the formation of insoluble compounds.

Table 6.1: *Optimization of the Ullmann polymerization of* ***1****.*

monomer	solvent	T (°C)	time (h)	products
1	DMF	40	7	no reaction
1	DMF	80	2	oligomers up to 12 units
1	DMF	100	1	oligomers up to 25 units
1	DMF	120	5 min	oligomers up to 15 units, also by-products
1	THF	68	6	no reaction
1	NMP[a]	160	5 min	deprotection resulting in black insoluble tar
1	DMF/H_2O (5/1)	100	6	deprotection resulting in black insoluble tar
1	DMF[b]	100	2	deprotected monomer
2,5-dichloro	DMF	100	2	deprotection resulting in black insoluble tar

[a] N-Methylpyrrolidone. [b] Reaction with Cu^{2+} instead of Cu-bronze.

The NMR data of the isolated oligomers clearly show that the oligomers obtained by the Ullmann reaction possess hydrogen instead of bromine end groups at the α-positions. Evidently, a reductive debromination occurs, furnishing unreactive end groups in the Ullmann reaction products. Because of the absence of water during these reactions, these hydrogen atoms must come from the solvent (DMF), which is known to be relatively unstable at higher temperatures.

In contrast to the work of Martina *et al.*[29,33], the longest oligomers are not obtained starting from the longer monomers **5** and **10**, but starting from the monopyrrole monomer **1**. Both in case of **5** and **10** eight different oligomers are formed, while in case of **1** twenty-five different oligomers are obtained. This difference may be due to the higher stability and lower reactivity of the longer monomers compared to **1**. Extension of the reaction time, however, led to (partial) deprotection resulting in insoluble products.

The experimental data presented above, prompt us to propose a chain-reaction mechanism for the polymerization of N-*t*-BOC-2,5-dibromopyrrole. Since the mechanism of the Ullmann reaction is not known with certainty, the proposal made here is speculative at

this stage. First the reactive N-*t*-BOC-2,5-dibromopyrrole reacts with Cu to form N-*t*-BOC-2-Cu-5-bromopyrrole. In the next step this compound reacts with the growing chain, being a dibromo- or monobromo-oligopyrrole, which accomplishes an aryl-aryl coupling. Since the bromopyrrole unit in **1** is much more reactive than any other brominated oligomer, a new N-*t*-BOC-2-Cu-5-bromopyrrole intermediate is formed, which reacts with the growing chain. Simultaneous with propagation, competitive debromination leads to termination. In case of the reactive N-*t*-BOC-2,5-dibromopyrrole, this results in the formation of 25 oligomers, while in case of the dibrominated N-*t*-BOC protected bi- and terpyrrole the ratio between propagation and termination rate is lower, resulting in only 8 different oligomers. Future experiments in which the polymerization is monitored to record the consumption of monomer might be interesting to establish the mechanism.

6.4 *Properties of the oligomers*

The study of the properties of the isolated oligomers showed interesting results. First, UV-Vis spectra of all N-*t*-BOC protected oligomers were measured. The π-π^* wavelength transition of these oligopyrroles shows a bathochromic shift from 270 to 305 nm with an increasing number of repeating units (figure 6.6a, CH_3CN as solvent). An almost linear relation is found by plotting the bandgap energy versus 1/n (figure 6.6b). Despite the bulky protecting groups at nitrogen, responsible for a torsion angle of approximately 70°[29], some π-overlap is still present in the N-*t*-BOC protected oligo(pyrrole-2,5-diyl)s.

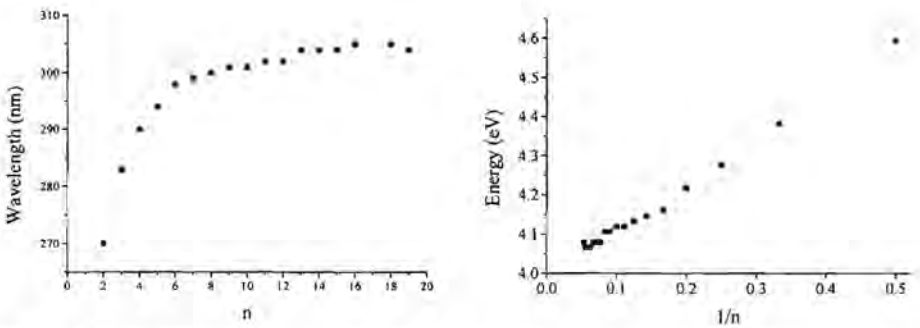


Figure 6.6: *(Left, 6a) π–π^* wavelength transition (λ_{max}) versus number of N-t-BOC protected pyrrole units in the oligomer (n). (Right, 6b) energy versus reciprocal number of N-t-BOC protected pyrrole units in the oligomer (1/n).*

Secondly, UV measurements of some deprotected oligomers were established. Therefore, these oligomers were heated at 190°C for 20-30 min under inert conditions. This

method leads to complete deprotection of oligomers up to n = 6. However, for n > 6 the deprotection could not be driven to completion. Unfortunately, there are no techniques available to detect the degree of deprotection, due to insolubility and extreme sensitivity to oxidation of the (partially) unprotected oligopyrroles. The UV-data recorded for the completely deprotected oligomers are in excellent agreement with the results described by Martina *et al.* (figure 6.7, CH_3CN as solvent).[29]

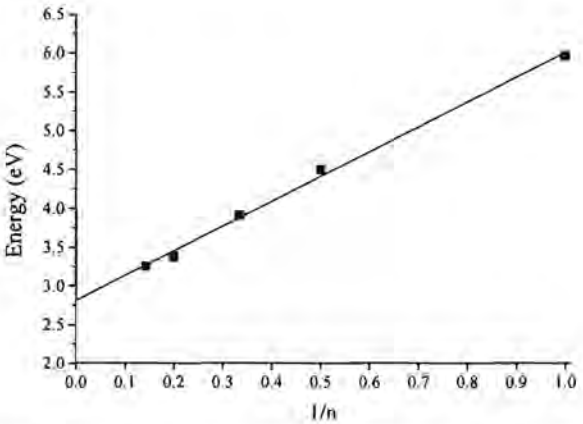


Figure 6.7: *π–π^* transition energy versus reciprocal number of pyrrole units in the deprotected oligomer (1/n).*

Some of the isolated oligomers were also used for conductivity experiments. These measurements were accomplished using the pentamer (n = 5), the decamer (n = 10) and the pentadecamer (n = 15). Therefore, thin films of the N-*t*-BOC protected oligomers were prepared, which were heated at 190°C for 1 hour. Doping of the fully deprotected pentamer films with I_2 afforded samples with conductivities as high as 100 Scm^{-1} (4-probe measurement). Similar conductivity experiments with decamer and pentadecamer films showed significantly lower conductivities in the range of 10^{-2} Scm^{-1}. The latter is most probably due to incomplete deprotection after heating (see above). Remaining *t*-BOC groups diminish the conjugation, which results in lower conductivities.

6.5 *Conclusions*

This study has shown that the Ullmann reaction is a good alternative for the Stille reaction in order to prepare well-defined N-*t*-BOC protected oligo(pyrrole-2,5-diyl)s. Oligomers containing up to 25 repeating pyrrole units are formed starting from the most reactive monomer, N-*t*-BOC-2,5-dibromopyrrole. Using preparative HPLC the first twenty

oligomers are isolated on a 2-20 mg scale and characterized by NMR- and UV-spectroscopy. These oligomers show an almost linear relationship between the bandgap energy and reciprocal number of repeating N-*t*-BOC protected pyrrole units. After thermal removal of the *t*-BOC groups, similar optical behavior is observed for the deprotected species. The latter, however, are only soluble up to the hexamer. Chemical oxidation of the deprotected pentamer shows a high conductivity of 100 Scm^{-1}. Without questioning the elegance of organic synthesis to well-defined oligomers, it is worth noting that in particular cases the relevant information on a series of oligomers is obtained much easier by the combination of oligomerization and chromatographic separation.

6.6 *Experimental section*

For general remarks concerning chemicals and analysis techniques, the reader is referred to section 2.6. HPLC separations were performed with a Pharmacia/LKB HPLC-system consisting of a Model 2252 LC-controller, two Model 2248 pumps, a Model 2510 uvicord SD detector operating at 276 nm, a Model 2211 superrac fraction collector and a Spark marathon autosampler. The stainless steel analytical (150 x 4.6 mm) and preparative (100 x 16 mm) columns were self-packed with Lichrosorb RP-18 (5 µm, 60 Å, 5 m, Merck, Darmstadt, Germany). The column temperature was 40°C and the samples were dissolved in a mixture of methanol and dichloromethane (9/1). Eluent A was methanol (HPLC-grade, Biosolve, Barneveld, Holland) and eluent B was water (milli-Q, Bedford, U.S.A.) with the following linear gradient profile: t = 0, 85% A, 15% B; t = 5 min, 85% A, 15% B; t = 40 min, 100% A; t = 60 min, 100% A; t = 65 min, 85% A, 15% B. This profile was slightly adjusted for the analysis of the oligomerization of the dibrominated bi- and terpyrrole (e.g. 80% A, 20% B instead of 85% A, 15% B). In this way a better separation was obtained. The flow rate was 1 ml/min for the analytical column and 6 ml/min for the preparative column.

N-*tert*-Butoxycarbonyl-2,5-dibromopyrrole (1)[30] N-*tert*-Butoxycarbonylpyrrole (16.75 g, 100 mmol) was dissolved in THF (570 ml) and cooled to -70°C, blanketed by argon. NBS (35.57 g, 200 mmol) was added in portions and the mixture was stirred at -70°C for 20 min. Then it was allowed to warm to 3°C at which temperature it was kept for 18 h. Na_2SO_3 (15.0 g, 119 mmol) was added to the solution and the solvent was evaporated. CCl_4 (300 ml) was added to the residue, the mixture was stirred for another 30 min, after which it was filtered and concentrated. The resulting solid was recrystallized twice from ethanol. During the first recrystallization the temperature was maintained below 45°C. After the second recrystallization a white solid (16.40 g, 50 mmol, 50%) was obtained, which was kept at -20°C under argon. Mp.: 84°C (Lit.: 79-80°C).
^{1}H-NMR ($CDCl_3$): δ 6.24 (s, 2H, H-3,4), 1.64 (s, 9H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 147.4 (C=O), 116.1 (C-3,4), 100.3 (C-2,5), 86.5 (C-q (BOC)), 27.8 (C-methyl (BOC)). IR (KBr): 3117, 2981, 2933, 1754, 1527, 1426, 1369, 1300, 1147, 1072, 994, 903, 835, 782 cm^{-1}.

2,2'-(1'-Pyrrolinyl)-pyrrole (2)[31] Pyrrole (40.57 g, 605 mmol) was cooled on an ice-bath under a nitrogen atmosphere. Phosphorus oxychloride (18.32 g, 120 mmol) was added over a 40-min period under vigorous stirring, followed by the addition of pyrrolidinone (12.12 g, 142 mmol) over a 70-min period. After the addition, the dark viscous liquid was stirred for another 50 min at RT when CH_2Cl_2 (70 ml) was added. The mixture was poured into an ice-cold solution of NaOAc (200 ml, 3 M), after which a solution of KOH (10 M) was slowly added until the pH reached a value of 10. During this addition the temperature was constantly maintained at 0°C. This finally resulted in a yellow aqueous fraction and a dark organic fraction. The organic fraction was separated and washed with H_2O (2 x 100 ml). The aqueous fraction was extracted with CH_2Cl_2 (3 x 100 ml) and the combined organic fractions were washed with H_2O (2 x 50 ml). Then the combined organic fractions were washed with a KH_2PO_4 solution in water (5 x 100 ml, 2 M) and the combined aqueous fractions were basified to pH 10 and extracted with CH_2Cl_2 (3 x 50 ml). The combined CH_2Cl_2 fractions were dried ($MgSO_4$), filtered and the solvent was evaporated. This resulted in a yellow solid (17.68 g). Sublimation (80°C, 0.2 mm Hg) gave a white solid (10.02 g, 75 mmol, 62%). Mp.: 168-169°C (Lit.: 162-163°C).
^{1}H-NMR ($CDCl_3$): δ 8.91 (s, 1H, N-H), 6.93 (dd, J = 2.6 and 1.4 Hz, 1H, H-5), 6.53 (dd, J = 3.5 and 1.3 Hz, 1H, H-3), 6.23 (dd, J = 3.5 and 2.7 Hz, 1H, H-4), 4.03 (tt, J = 7.2 and 1.6 Hz, 2H, H-5'), 2.90 (tt, J = 8.2 and 1.7 Hz, 2H, H-3'), 2.01 (q, J = 7.7 Hz, 2H, H-4'). ^{13}C-NMR ($CDCl_3$): δ 166.3 (C-2'), 127.9 (C-2), 121.9 (C-5), 112.8 (C-3), 109.2 (C-4), 60.5 (C-5'), 34.8 (C-3'), 22.6 (C-4'). IR (KBr): 3126, 2958, 2864, 1618, 1430, 1364, 1309, 1144, 1111, 1029, 974, 875, 844, 739 cm^{-1}.

2,2'-Bipyrrole (3)[31] A mixture of 2,2'-(1'-pyrrolinyl)pyrrole (**2**, 2.17 g, 16 mmol), 10% Pd/C (7.50 g, 16 mmol Pd) and triglyme (125 ml) was heated at 200°C under vigorous stirring for 2.5 h, continuously flushing with nitrogen. The hot mixture was filtered and the solvent was evaporated. The resulting dark green oil (1.9 g) was purified by chromatography (60 g SiO_2, CH_2Cl_2 as solvent, R_f = 0.28), which gave a green solid (1.11 g, 8.3 mmol, 54%).
^{1}H-NMR ($CDCl_3$): δ 8.23 (s, 1H, N-H), 6.77 (td, J = 2.6 and 1.5 Hz, 2H, H-5,5'), 6.24 (dd, J = 6.1 and 2.7 Hz, 2H, H-4,4'), 6.21 (td, J = 2.5 and 1.5 Hz, 2H, H-3,3'). ^{13}C-NMR ($CDCl_3$): δ 125.9 (C-2,2'), 117.6 (C-5,5'), 109.4 (C-3,3'), 103.5 (C-4,4').

N,N'-Di-*tert*-butoxycarbonyl-2,2'-bipyrrole (4) A mixture of 2,2'-bipyrrole (**3**, 0.26 g, 2.0 mmol), THF (12 ml), di-*tert*-butyl dicarbonate (0.88 g, 4.0 mmol) and potassium *tert*-butoxide (0.06 g, 0.5 mmol) was heated at reflux temperature for 4.5 h, blanketed by argon. Then the reaction mixture was cooled to RT and 2-dimethylaminoethylamine (45 mg, 0.5 mmol) was added. The mixture was stirred for another 15 min and the solvent was evaporated. The resulting oil was dissolved in Et_2O (40 ml) and washed with water (3 x 30 ml). The organic fraction was dried ($MgSO_4$), filtered and concentrated to afford a black oil. Column chromatography (25 g SiO_2, CH_2Cl_2 : hexane (1:1), R_f = 0.24) gave a colorless oil (0.43 g, 1.3 mmol, 66%).
^{1}H-NMR ($CDCl_3$): δ 7.40 (t, J = 2.6 Hz, 2H, H-5,5'), 6.20 (d, J = 2.6 Hz, 4H, H-3,3', H-4,4'), 1.39 (s, 18H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 149.1 (C=O), 126.0 (C-2,2'), 121.9 (C-5,5'), 115.3 (C-3,3'), 110.1 (C-4,4'), 83.0 (C-q (BOC)), 27.8 (C-methyl (BOC)).

N,N'-Di-*tert*-butoxycarbonyl-5,5'-dibromo-2,2'-bipyrrole (5) N,N'-Di-*tert*-butoxycarbonyl-2,2'-bipyrrole (**4**, 85.0 mg, 0.256 mmol) was dissolved in THF (4.5 ml) and cooled to -70°C. NBS (91.0

mg, 0.511 mmol) was added and the mixture was stirred for 30 min at -70°C. Then it was allowed to warm to 3°C at which temperature it was kept for 3 h. Na_2SO_3 (a few mg) was added and the solvent was evaporated. CCl_4 (10 ml) was added to the residue, the mixture was stirred for 10 min and filtered. The solvent was then evaporated, resulting in a slightly red oil (132.5 mg), which was directly used in the Ullmann polymerization.
^{1}H-NMR ($CDCl_3$): δ 6.31 (d, J = 3.5 Hz, 2H, H-4,4'), 6.13 (d, J = 3.5 Hz, 2H, H-3,3'), 1.36 (s, 18H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 148.0 (C=O), 128.1 (C-2,2'), 115.7/115.1 (C-3,3'/C-4,4'), 102.5 (C-5,5'), 84.9 (C-q (BOC)), 27.5 (C-methyl (BOC)).

N-Phenylsulfonyl-2-formylpyrrole (6)[32] 2-Formylpyrrole (4.76 g, 50.1 mmol) was dissolved in DMF (25 ml) in a nitrogen atmosphere at RT. NaH (1.56 g, 65.0 mmol) was added in portions and thereafter, the mixture was stirred for another 15 min. Then, phenylsulfonyl chloride (9.03 g, 51.1 mmol) was added dropwise over a 15-min period, after which the mixture was stirred for another 60 min. The mixture was then poured into ice-water (250 ml) and extracted with Et_2O (3 x 100 ml). The combined organic fractions were dried ($MgSO_4$), filtered and concentrated. The resulting beige solid (8.81 g, 37.5 mmol, 75%) was used directly for the synthesis of diketone **7**.
^{1}H-NMR ($CDCl_3$): δ 9.96 (s, 1H, H-ald.), 7.93 (d, J = 8.2 Hz, 2H, H-*ortho*), 7.65 (m, 2H, H-*para*, H-5), 7.55 (t, J = 7.8 Hz, 2H, H-*meta*), 7.17 (dd, J = 3.8 and 1.7 Hz, 1H, H-3), 6.43 (t, J = 3.4 Hz, 1H, H-4). ^{13}C-NMR ($CDCl_3$): δ 178.8 (C=O), 138.1 (C-*ipso* (phenyl)), 134.5 (C-*para*), 133.5 (C-2), 129.5 (C-*ortho* and C-5), 127.4 (C-*meta*), 124.9 (C-3), 112.5 (C-4).

1,4-Bis(N-phenylsulfonyl-2-pyrrolyl)-1,4-butanedione (7)[32] A mixture of N-phenylsulfonyl-2-formylpyrrole (**6**, 7.06 g, 30.0 mmol), 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (1.23 g, 4.6 mmol), NaOAc (0.63 g, 7.7 mmol) and ethanol (40 ml) was heated at reflux temperature under argon. Divinyl sulfone (1.76 g, 14.9 mmol) was added dropwise and the mixture was heated under reflux for another 17 h. The resulting precipitate was filtered, washed with ethanol, water and Et_2O (each 25 ml) and dried. A slightly brown solid was obtained (3.34 g, 6.7 mmol, 45%).
^{1}H-NMR ($CDCl_3$): δ 7.96 (d, J = 7.4 Hz, 4H, H-*ortho*), 7.80 (dd, J = 3.2 and 1.7 Hz, 2H, H-5), 7.58 (t, J = 7.4 Hz, 2H, H-*para*), 7.50 (t, J = 7.3 Hz, 4H, H-*meta*), 7.12 (dd, J = 3.8 and 1.7 Hz, 2H, H-3), 6.35 (t, J = 3.6 Hz, 2H, H-4), 3.04 (s, 4H, CH_2). ^{13}C-NMR ($CDCl_3$): δ 186.6 (C=O), 138.8 (C-*ipso* (phenyl)), 133.6 (C-*para*), 132.7 (C-2), 130.3 (C-5), 128.7-128.0 (C-*ortho*, C-*meta*), 123.9 (C-3), 110.5 (C-4), 32.9 (CH_2).

2,5-Bis(N-phenylsulfonyl-2-pyrrolyl)pyrrole (8)[32] A mixture of 1,4-bis(N-phenylsulfonyl-2-pyrrolyl)-1,4-butanedione (**8**, 2.57 g, 5.2 mmol), propionic acid (37 ml), acetic anhydride (7.5 ml, 79.4 mmol) and NH_4OAc (10.97 g, 142 mmol) was heated under reflux in a nitrogen atmosphere. After 18 h it was cooled to RT and the solvent was evaporated. H_2O (100 ml) was added to the residue and this mixture was neutralized with NaOH (2 M). The aqueous fraction was extracted with CH_2Cl_2 (3 x 50 ml) and the combined organic fractions were washed with $NaHCO_3$ (2 x 50 ml, 1 M), brine (2 x 50 ml) and dried ($MgSO_4$). After evaporation of the solvent a black solid was obtained. Column chromatography (50 g SiO_2, CH_2Cl_2 : hexane (3:1), R_f = 0.47) afforded a nicely smelling, slightly green solid (1.57 g, 3.3 mmol, 63%).

^{1}H-NMR ($CDCl_3$): δ 9.22 (s, 1H, N-H), 7.53 - 7.46 (m, 6H, H-*ortho*, H-*para*), 7.42 (dd, J = 3.1 and 2.0 Hz 2H, H-5,5''), 7.34 (t, 7.6 Hz, 4H, H-*meta*), 6.33-6.31 (m, 4H, H-3,3'', H-4,4''), 6.09 (d, J = 2.6 Hz, 2H, H-3', H-4'). ^{13}C-NMR ($CDCl_3$): δ 137.9 (C-*ipso* (phenyl)), 133.8 (C-*para*), 128.9/127.1(C-*ortho*/C-*meta*), 127.3 (C-2,2''), 123.8 (C-5,5''), 122.1 (C-2',5'), 115.7 (C-3,3''), 112.1/111.7 (C-3',4'/C-4,4'').

N,N',N''-Tri-*tert*-butoxycarbonyl-2,2':5',2''-terpyrrole (9) A deaerated solution of NaOH (1.05 g, 26 mmol) in methanol (20 ml) was charged with 2,5-bis(N-phenylsulfonyl-2-pyrrolyl)pyrrole (**8**, 0.80 g, 1.7 mmol) and heated under reflux for 2.5 h, blanketed by argon. The mixture was cooled to RT and extracted from a NH_4Cl solution in water (sat, 30 ml) with CH_2Cl_2 (3 x 15 ml). The combined organic fractions were washed with H_2O (2 x 20 ml), dried ($MgSO_4$) and concentrated. The resulting black solid (0.25 g) was used directly. Together with di-*tert*-butyl dicarbonate (1.50 g, 6.9 mmol), THF (12 ml) and potassium tert-butoxide (50 mg) it was heated under reflux for 18 h, blanketed by argon. Then dimethylaminoethylamine (0.20 g, 2.3 mmol) was added, the mixture was stirred for another 15 min, the solvent was evaporated and Et_2O (25 ml) was added. Extraction with dilute HCl (2 x 15 ml) and H_2O (2 x 10 ml) followed by drying ($MgSO_4$) of the organic fraction and evaporation of the solvent resulted in a dark oil. Column chromatography (50 g SiO_2, CH_2Cl_2 : hexane (2:1), R_f = 0.22) gave pure **9** (0.46 g, 0.9 mmol, 55%).
^{1}H ($CDCl_3$): δ 7.40 (dd, J = 3.3 and 1.9 Hz, 2H, H-5,5''), 6.20 (t, J = 3.3 Hz, 2H, H-4,4''), 6.15 (s, 2H, H-3',4'), 6.14 (dd, J = 3.3 and 1.9 Hz, 2H, H-3,3''), 1.39 (s, 18H, H-methyl (BOC and BOC'')), 1.21 (s, 9H, H-methyl (BOC')). ^{13}C-NMR ($CDCl_3$): δ 149.1 (C=O and C=O''), 149.0 (C=O'), 127.6/126.7 (C-2,2''/C-2',5'), 121.9 (C-5,5''), 115.3 (C-3,3''), 113.8 (C-3',4'), 110.3 (C-4,4''), 83.3 (C-q (BOC), C-q (BOC'')), 82.5 (C-q (BOC')), 27.8 (C-methyl (BOC), C-methyl (BOC'')), 27.6 (C-methyl (BOC')).

N,N',N''-Tri-*tert*-butoxycarbonyl-5,5''-dibromo-2,2':5',2''-terpyrrole (10) N,N',N''-Tri-*tert*-butoxycarbonyl-2,2':5',2''-terpyrrole (**9**, 108.9 mg, 0.219 mmol) was dissolved in THF (3 ml) and cooled to -70°C under argon. NBS (78.0 mg, 0.438 mmol) was added and the mixture was stirred for another 30 min at -70°C. Then the solution was allowed to warm to 3°C at which temperature it was kept for 3.5 h. Na_2SO_3 (a few mg) was added to the solution and the solvent was evaporated. CCl_4 (10 ml) was added, the mixture was stirred for another 15 min and filtered. After evaporation of the solvent a grey solid remained (141.1 mg), which was used directly in the Ullmann polymerization.
^{1}H-NMR ($CDCl_3$): δ 6.32 (d, J = 3.6 Hz, 2H, H-4,4''), 6.17 (s, 2H, H-3',4'), 6.10 (d, J = 3.6 Hz, 2H, H-3,3'') 1.37 (s, 18H, H-methyl (BOC), H-methyl (BOC'')), 1.26 (s, 9H, H-methyl (BOC')). ^{13}C-NMR ($CDCl_3$): δ 148.5 (C=O, C=O''), 148.0 (C=O'), 128.5/127.7 (C-2,2''/C-2',5'), 115.6-114.2 (C-3,3'', C-4,4'', C-3',4'), 102.2 (C-5,5''), 84.3 (C-q (BOC), C-q (BOC'')), 83.7 (C-q (BOC')), 27.6 (C-methyl (BOC), C-methyl (BOC'')), 27.5 (C-methyl (BOC')).

Polymerization of the monomers The Ullmann polymerization of the three monomers (**1**, **5** and **10**) was performed by heating a mixture of the monomer, DMF (10 ml/g monomer) and one weight equivalent of Cu-bronze under argon at 100°C. After some time (1 h in case of **1**, 2 h in case of **5** and **10**) the dark green mixture was poured into ice-water and extracted with Et_2O. The organic fractions

were dried ($MgSO_4$) and the solvent was evaporated to yield a dark oil, which was filtered over Al_2O_3 before HPLC analysis.

NMR-data of the isolated oligomers

n = 1: ^{1}H-NMR ($CDCl_3$): δ 7.23 (t, J = 2.2 Hz, 2H, H-2,5), 6.20 (t, J = 2.2 Hz, 2H, H-3,4), 1.58 (s, 9H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 148.8 (C=O), 119.9 (C-2,5), 111.7 (C-3,4), 83.4 (C-q (BOC)), 27.9 (C-methyl (BOC)).

n = 2: ^{1}H-NMR ($CDCl_3$): δ 7.40 (t, J = 2.6 Hz, 2H, H-5,5'), 6.20 (d, J = 2.6 Hz, 4H, H-3,3', H-4,4'), 1.39 (s, 18H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 149.1 (C=O), 126.0 (C-2,2'), 121.9 (C-5,5'), 115.3 (C-3,3'), 110.1 (C-4,4'), 83.0 (C-q (BOC)), 27.6 (C-methyl (BOC)). UV-Vis (CH_3CN): 270 nm.

n = 3: ^{1}H ($CDCl_3$): δ 7.40 (dd, J = 3.3 and 1.9 Hz, 2H, H-5,5''), 6.20 (t, J = 3.3 Hz, 2H, H-4,4''), 6.15 (s, 2H, H-3',4'), 6.14 (dd, J = 3.3 and 1.9 Hz, 2H, H-3,3''), 1.39 (s, 18H, H-methyl (BOC and BOC'')), 1.21 (s, 9H, H-methyl (BOC')). ^{13}C-NMR ($CDCl_3$): δ 149.1 (C=O and C=O''), 149.0 (C=O'), 127.6/126.7 (C-2,2''/C-2',5'), 121.9 (C-5,5''), 115.3 (C-3,3''), 113.8 (C-3',4'), 110.3 (C-4,4''), 83.3 (C-q (BOC), C-q (BOC'')), 82.5 (C-q (BOC')), 27.8 (C-methyl (BOC), C-methyl (BOC'')), 27.6 (C-methyl (BOC')). UV-Vis (CH_3CN): 283 nm.

n = 4: ^{1}H-NMR ($CDCl_3$): δ 7.40 (dd, J = 3.3 and 1.9 Hz, 2H, H-α), 6.22-6.13 (m, 8H, H-β), 1.42 (s, 18H, H-methyl (BOC and BOC'''), 1.26 (s, 18H, H-methyl (BOC' and BOC'')). ^{13}C-NMR ($CDCl_3$): δ 149.1, 148.9, 128.2, 127.5, 126.8, 121.9, 115.3, 113.9, 113.8, 110.2, 83.2, 82.7, 27.8, 27.7. UV-Vis (CH_3CN): 290 nm. FD-MS: calcd. 662.78; found 662.6.

n = 5: ^{1}H-NMR ($CDCl_3$): δ 7.40 (dd, J = 3.1 and 2.0 Hz, 2H, H-α), 6.21-6.14 (m, 10H, H-β), 1.41-1.24 (45H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 149.0, 148.9, 148.8, 128.3, 128.2, 127.5, 126.8, 121.8, 115.3, 113.9, 113.8, 110.2, 83.1, 82.8, 82.5 27.8, 27.7, 27.5. UV-Vis (CH_3CN): 294 nm.

n = 6: ^{1}H-NMR ($CDCl_3$): δ 7.40 (dd, J = 3.3 and 1.9 Hz, 2H, H-α), 6.22-6.15 (m, 12H, H-β), 1.43-1.25 (54H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 149.1, 148.9, 148.8, 128.4, 128.3, 128.1, 127.4, 126.9, 121.8, 115.3, 113.9, 113.8, 110.2, 83.2, 82.6, 82.5, 27.8, 27.7 (2 peaks). UV-Vis (CH_3CN): 298 nm.

n = 7: ^{1}H-NMR ($CDCl_3$): δ 7.40 (dd, J = 3.3 and 1.9 Hz, 2H, H-α), 6.23-6.15 (m, 14H, H-β), 1.43-1.27 (63H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 149.1, 148.9 (2 peaks), 148.8, 128.4, 128.2, 128.0, 127.4, 126.8, 121.8, 115.3, 113.9, 113.8, 110.2, 83.2, 82.6 (2 peaks), 82.5, 27.8 (2 peaks), 27.7. UV-Vis (CH_3CN): 299 nm.

n = 8: ^{1}H-NMR ($CDCl_3$): δ 7.40 (dd, J = 3.2 and 1.9 Hz, 2H, H-α), 6.23-6.15 (m, 16H, H-β), 1.43-1.27 (72H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 149.1, 148.9, 148.8 (2 peaks), 128.4, 128.3, 128.1, 128.0, 127.4, 126.8, 121.8, 115.3, 113.9, 113.8, 110.2, 83.2, 82.7, 82.5 (2 peaks), 27.8, 27.7 (2 peaks), 27.6. UV-Vis (CH_3CN): 300 nm.

n = 9: ^{1}H-NMR ($CDCl_3$): δ 7.40 (dd, J = 3.2 and 1.9 Hz, 2H, H-α), 6.23-6.15 (m, 18H, H-β), 1.41-1.25 (81H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 149.1, 148.9, 148.8 (2 peaks), 128.4, 128.3, 128.2, 128.1, 128.0, 127.4, 126.8, 121.8, 115.3, 113.9, 113.8, 110.2, 83.2, 82.7, 82.5 (2 peaks), 27.8, 27.7. UV-Vis (CH_3CN): 301 nm.

n = 10: ^{1}H-NMR ($CDCl_3$): δ 7.40 (dd, J = 3.2 and 1.9 Hz, 2H, H-α), 6.23-6.15 (m, 20H, H-β), 1.41-1.23 (90H, H-methyl (BOC)). ^{13}C-NMR ($CDCl_3$): δ 149.1, 148.9, 148.8, 128.4, 128.3, 128.2 (2 peaks), 128.0, 127.4, 126.8, 121.8, 115.3, 113.9, 110.2, 83.2, 82.7, 82.5, 27.8, 27.7. UV-Vis (CH_3CN): 301 nm.

From **n = 11** to **n = 20** only ^{1}H-NMR spectra were measured. These proton spectra were comparable to that of **n = 10** (just the ratios of peak intensities changed as expected). Furthermore, the positions of the absorption maxima, measured in CH_3CN, slightly increased up to 305 nm.

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Summary

This thesis describes the design, synthesis and characterization of well-defined and functional α,α-linked oligomers based on pyrrole, which can serve as models for their corresponding π-conjugated polymers, or as compounds with interesting electrical and/or optical properties on their own. Chapter 1 starts with a survey of pyrrole, oligopyrrole and polypyrrole chemistry. Besides the synthesis and properties of these species, a general overview is given on recent developments in organometallic aryl-aryl coupling methods. At the end of this chapter the aim of the research and the scope of this thesis are explained.

In chapter 2 the Pd-catalyzed cross coupling reaction involving organostannanes (Stille reaction) is applied to prepare well-defined oligopyrroles. First, some mechanistical aspects of this coupling reaction were investigated. These studies revealed that the kind of solvent, the type of halide and the electron-releasing/-withdrawing character of the substituents all strongly influence the course of this reaction. Subsequently, this knowledge was applied to prepare a large variety of well-defined oligomers consisting of pyrrole, thiophene and/or benzene units. Performing these coupling reactions for 2-3 days under reflux conditions in the two-phase system of toluene and aqueous Na_2CO_3 (1 M) with $Pd(PPh_3)_4$ as catalyst, resulted in the desired oligomers. Due to side-reactions, such as destannylation, methyl shift, deprotection of *t*-BOC groups and/or homo-coupling of organostannanes, the yields were not quantitative but ranged from 14% to 79%.

In chapter 3 the Stille reaction is applied to prepare several well-defined and functional oligopyrroles, which are studied for their specific properties. A series of N-*t*-BOC-protected D-π-A oligopyrroles showed surprising nonlinear optical behavior when investigated with Hyper Rayleigh Scattering. Going from one to three pyrrole units inserted between a 4-nitrophenyl and a 4-methoxyphenyl group, the UV-Vis absorptions almost remained unaltered, whereas the β-values increased significantly. A D-π-A oligomer with a bithienyl spacer showed an even higher β-value. N-Dodecyl-2,5-di{2[5(N-dodecyl-5-phenyl)-pyrrolyl]thienyl}pyrrole, also prepared by a sequence of functionalization and Stille reactions, was investigated by scanning tunnelling microscopy in order to study its structural characteristics. Physisorbed on a graphite surface, these molecules form highly ordered monolayers consisting of couples forming linear aromatic 'backbones'. Finally, the redox properties of two series of oligopyrroles, being diphenyl-α-oligopyrroles (Ph-p_n-Ph) and di(phenylpyrrolyl)-α-oligothiophenes (Ph-p-t_n-p-Ph), were investigated. These studies showed that the latter display unusual redox behavior with respect to the first oxidation potential.

Chapter 4 deals with the functionalization of 3-alkylpyrroles. Halogenation of N-phenylsulfonyl-3-hexylpyrrole and N-*t*-BOC-3-hexylpyrrole was achieved using N-chloro- or N-bromosuccinimide in THF at -70°C. An exception was the synthesis of N-*t*-BOC-2-bromo-

3-hexylpyrrole, which could only be prepared by a slight adaption (DMF instead of THF as solvent). Concerning stannylation experiments, none of the N-phenylsulfonyl protected 3-hexylpyrroles could be stannylated selectively. In case of N-*t*-BOC protected 3-hexylpyrroles, α-stannylation could be performed; however, just the 5-position was functionalized by direct lithiation (LTMP) and subsequent stannylation ($(CH_3)_3SnCl$). When performing an NBS bromination on an α-trimethylstannyl substituted pyrrole derivative, a stannyl-bromo exchange reaction took place, the latter being an excellent method to prepare α-monobromo pyrroles. Finally, attempts were make to prepare regioregular oligo- and polypyrroles. However, due to a combination of steric and electronic interactions this could not be accomplished by the Stille reaction.

In chapter 5 the first attempts toward intrinsically conducting polymers based on pyrrole are made by incorporating the '+ - 0 0'-electronic structure, as present in polysulfur nitride, into an organic polymer. Therefore, two different types of oligomeric and polymeric pyrrole-sulfur compounds were synthesized. First, a number of N-*t*-BOC protected oligo- and poly(pyrrole-2,5-diyl sulfide)s was prepared starting from α-brominated pyrroles, using a lithiation/sulfuration sequence. Subsequent attempts to remove the *t*-BOC groups by thermolysis, however, resulted in the formation of insoluble black tars in all cases. The latter is most probably due to sulfur extrusion/polymerization. In order to overcome this problem, a poly(thienylthiothienylpyrrolyl) was prepared starting from N-*t*-BOC-3-dodecyl-2,5-di(2-thienyl)pyrrole and following the same strategy. In contrast to the former compounds, this polymer could be deprotected by thermolysis. However, in this case π-conjugation along the polymer backbone appeared to be limited, both in the neutral and in the radical cationic form, due to a low degree of delocalization through the carbon-sulfur linkages.

In chapter 6 another organometallic coupling reaction, being the Ullmann reaction, is applied to polymerize N-*t*-BOC-2,5-dibromopyrrole into well-defined oligo(N-*t*-BOC-pyrrole-2,5-diyl)s. After optimization of the reaction conditions, oligomers containing up to 25 repeating pyrrole units were obtained. Starting from 5,5'- and 5,5''-dibrominated *t*-BOC protected bi- and terpyrrole as monomers, the polymerization was slower and a lower degree of polymerization was observed, yielding oligomers with an even lower molecular weight than those resulting from the smaller N-*t*-BOC-2,5-dibromopyrrole. The first 20 oligomers of poly(N-*t*-BOC-pyrrole-2,5-diyl) were isolated by means of preparative HPLC. Characterization of the individual oligomers showed that they are all hydrogen terminated and possess perfect 2,5-linkages. These oligomers were used to study the optical and electrical properties of the oligomers as a function of the chain length.

Samenvatting

Dit proefschrift beschrijft het ontwerp, de synthese en de karakterisering van goed gedefinieerde en funktionele α,α-gekoppelde oligomeren op basis van pyrrool, welke als modellen voor hun overeenkomstige π-geconjugeerde polymeren kunnen fungeren, of als verbindingen met interessante elektrische en/of optische eigenschappen van zichzelf. Hoofdstuk 1 begint met een overzicht over pyrrool-, oligopyrrool- en polypyrroolchemie. Behalve de synthese en de eigenschappen van deze verbindingen, wordt een algemeen overzicht gegeven over recente ontwikkelingen in organometallische aryl-aryl koppelingsmethoden. Aan het eind van dit hoofdstuk wordt het doel van dit onderzoek toegelicht.

In hoofdstuk 2 wordt de Pd-gekatalyseerde kruiskoppelingsreaktie met organostannanen toegepast op de synthese van goed gedefinieerde oligopyrrolen. Allereerst werden enkele mechanistische aspekten van deze koppelingsreaktie onderzocht. Deze studies lieten zien dat het soort oplosmiddel, het type halide en het elektronenstuwende/-zuigende karakter van de substituenten het verloop van deze reaktie sterk beïnvloeden. Vervolgens werd de opgedane kennis toegepast op de bereiding van een groot aantal goed gedefinieerde oligomeren op basis van pyrrool-, thiofeen- en benzeeneenheden. Door deze koppelingsreakties gedurende 2-3 dagen onder refluxcondities uit te voeren in het tweefasensysteem van tolueen en een waterige Na_2CO_3-oplossing (1M) met $Pd(PPh_3)_4$ as katalysator, werden de gewenste oligomeren verkregen. Als gevolg van bijreakties zoals destannylering, methyl-shift, verwijdering van *t*-BOC groepen en/of homo-koppeling van organostannanen, waren de opbrengsten niet kwantitatief maar varieerden van 14% tot 79%.

In hoofdstuk 3 wordt de Stille-reaktie toegepast op de synthese van verschillende goed gedefinieerde en funktionele oligopyrrolen, teneinde hun specifieke eigenschappen te bestuderen. Een serie N-*t*-BOC beschermde D-π-A-oligopyrrolen gaf verrassend niet-lineair-optisch gedrag te zien bij Hyper-Rayleigh-Scattering-metingen. Gaande van een naar drie pyrrooleenheden tussen een 4-nitrofenyl- en een 4-methoxyfenylgroep, bleef het UV-Vis-spectrum van de D-π-A-oligomeren nagenoeg onveranderd, terwijl de β-waarden duidelijk toenamen. Een D-π-A-oligomeer met een dithiënylspacer gaf een nog hogere β-waarde te zien. N-Dodecyl-2,5-di{2[5(N-dodecyl-5-fenyl)pyrrolyl]thiënyl}pyrrool, ook gesynthetiseerd via een sequentie van funktionaliserings- en Stille-reakties, werd onderzocht met scanning tunnelling microscopie om struktuurkarakteristieken te bestuderen. Fysisorptie van deze oligomeren op een grafietoppervlak, leidt tot geordende monolagen bestaande uit koppels, welke lineaire aromatische 'backbones' vormen. Tenslotte werden de redox-eigenschappen van twee series oligomeren, zijnde difenyl-α-oligopyrrolen (Ph-p_n-Ph) en di(fenylpyrrolyl)-α-oligothiofenen (Ph-p-t_n-p-Ph), onderzocht. Deze studies lieten zien dat de laatste afwijkend redoxgedrag met betrekking tot de eerste oxidatiepotentiaal vertoonden.

Hoofdstuk 4 behandelt de funkionalisering van 3-alkylpyrrolen. Halogenering van N-fenylsulfonyl-3-hexylpyrrool en N-*t*-BOC-3-hexylpyrrool werd bereikt door gebruik te maken van N-chloor- en N-broomsuccinimide in THF bij -70°C. Een uitzondering was de synthese van N-*t*-BOC-2-broom-3-hexylpyrrool, welke alleen door een kleine aanpassing kon worden verkregen (DMF in plaats van THF als oplosmiddel). Wat de stannyleringsexperimenten betreft, geen van de N-fenylsulfonyl beschermde 3-hexylpyrrolen kon selektief worden gestannyleerd. In het geval van N-*t*-BOC beschermde 3-hexylpyrrolen, kon α-stannylering wel worden bereikt. Echter, alleen de 5-positie werd gefunktionaliseerd door middel van direkte lithiëring gevolgd door stannylering ($(CH_3)_3SnCl$). In het geval van NBS-bromering van een α-trimethylstannyl-gesubstitueerd pyrroolderivaat, vond een stannyl-broom uitwisselingsreaktie plaats, welke een excellente methode blijkt te zijn voor het bereiden van α-monobroompyrrolen. Tot slot werden pogingen gedaan om regioregulaire oligo- en polypyrrolen te synthetiseren. Echter, als gevolg van een kombinatie van sterische en elektronische factoren bleek dat laatste niet mogelijk met de Stille-reaktie.

In hoofdstuk 5 worden de eerste pogingen in de richting van intrinsiek geleidende polymeren op basis van pyrrool beschreven door de '+ - 0 0'-elektronische struktuur, zoals aanwezig in polyzwavelnitride, in een organisch polymeer te incorporeren. Daartoe werden twee verschillende typen oligomere en polymere pyrrool-zwavel verbindingen gesynthetiseerd. Allereerst werd een aantal oligo- en poly(pyrrole-2,5-diyl sulfide)s gemaakt uitgaande van α-gebromeerde pyrrolen via een lithiërings/sulfureringssequentie. Pogingen om de *t*-BOC-groepen vervolgens thermolytisch te verwijderen, resulteerden echter in onoplosbare zwarte teren in alle gevallen. Dit laatste is hoogstwaarschijnlijk het gevolg van zwavelextrusie/polymerisatie. Om dit probleem te omzeilen, werd op analoge wijze een poly(thiënyl-thiothiënylpyrrolyl) bereid uitgaande van N-*t*-BOC-3-dodecyl-2,5-di(2-thiënyl)pyrrool. In tegenstelling tot de voorgaande verbindingen kon dit polymeer wel thermisch worden ontschermd. Echter, π-conjugatie langs de polymere backbone bleek, zowel in de neutrale als in de radikaal-kationische vorm, gelimiteerd als gevolg van geringe delokalisatie over zwavel.

In hoofdstuk 6 wordt een andere organometallische koppelingsreaktie, te weten de Ullmann-reaktie, toegepast om N-*t*-BOC-2,5-dibroompyrrool te polymeriseren tot goed gedefinieerde oligo(N-*t*-BOC-pyrrool-2,5-diyl)s. Na optimalisering van de reaktiecondities werden oligomeren tot een lengte van 25 opeenvolgende pyrrooleenheden vervaardigd. Uitgaande van 5,5'-and 5,5''-digebromeerde N-*t*-BOC beschermde bi- en terpyrroolmonomeren bleek de polymerisatie aanzienlijk langzamer, hetgeen in oligomeren met een lagere molmassa resulteerde. De eerste 20 oligomeren van poly(N-*t*-BOC-pyrrole-2,5-diyl) werden met behulp van preparatieve HPLC geïsoleerd. Karakterisering van de individuele oligomeren toonde aan dat ze alle waterstof-getermineerd zijn en perfekte 2,5-koppelingen bezitten. Deze oligomeren werden vervolgens gebruikt om de optische en elektrische eigenschappen als funktie van de ketenlengte te onderzoeken.

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L. Groenendaal, H.W.I. Peerlings, J.L.J. van Dongen, E.E. Havinga, J.A.J.M. Vekemans, E.W. Meijer "Oligopyrroles by the Ullmann reaction", *Polymer Preprints* **1994**, *207*, 194.

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L. Groenendaal, K. Pieterse, J.A.J.M. Vekemans, E.W. Meijer "Synthesis and characterization of N-*t*-BOC protected pyrrole-sulfur oligomers and polymers", *Synth. Commun.*, in press.

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L. Groenendaal, M.J. Bruining, J.A.J.M. Vekemans, E.E. Havinga, E.W. Meijer "Synthesis and (nonlinear)optical properties of a series of N-*t*-BOC protected D-π-A oligopyrroles", manuscript in preparation.

L. Groenendaal, J.A.E.H. van Haare, K. Pieterse, R.A.J. Janssen, E.W. Meijer "Synthesis and redox properties of a poly(thienylthiothienylpyrrolyl)", manuscript in preparation.

Curriculum Vitae

Lambertus ('Bert') Groenendaal werd op 13 september 1967 geboren te Dordrecht. Na het behalen van zijn MAVO (1983), HAVO (1985) en VWO diploma (1987) aan de scholengemeenschap 't Zwin in Oostburg, werd begonnen met de studie Scheikundige Technologie aan de Technische Universiteit Eindhoven. Het afstudeerwerk met als titel "Synthese van bipyrrolen als modelstoffen voor onderzoek naar polyradicalaire systemen", werd verricht in de vakgroep Organische Chemie onder begeleiding van dr. J.A.J.M. Vekemans en prof. dr. E.W. Meijer. In september 1992 behaalde hij zijn ingenieursdiploma. Van oktober 1992 tot oktober 1996 was hij als AIO-4 verbonden aan dezelfde vakgroep alwaar hij het onderzoek zoals beschreven in dit proefschrift verrichtte onder begeleiding van prof. dr. E.W. Meijer. In mei 1996 werd hem de tweede prijs voor Nederland van de DSM-prijs voor Chemie en Technologie toegekend. Vanaf januari 1997 zal hij gedurende een jaar werkzaam zijn als postdoc in de groep van prof. dr. J.M.J. Fréchet aan de universiteit van Berkeley (USA).

Dankwoord

Na vier jaren van experimenten doen, lezingen geven, artikelen schrijven maar ook instructies geven, stappen, begeleiden van studenten en heel, heel veel plezier, zit het er bijna op. Rest mij nog om al die mensen die op de een of andere manier een bijdrage hebben geleverd, hartelijk te danken.

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Eric Hendrickx (K.U. Leuven) en Andreas Stabel (Max Planck Institute for Polymer Research, Mainz) wil ik bedanken voor hun hulp bij het respectievelijk verrichten van de β-bepalingen en de STM-metingen. Prof. Wynberg en Wolter ten Hoeve ben ik zeer erkentelijk voor de synthetische tips en verbindingen die mij toekwamen.

Dankzij beurzen van de Nederlandse Organisatie voor Wetenschappelijk Onderzoek (N.W.O.) en Shell kreeg ik de mogelijkheden voor congres- en werkbezoeken.

Tenslotte wil ik in het bijzonder mijn ouders, mijn zus Lydia en mijn vrouw Bianca bedanken voor alle liefde, hulp en interesse in de afgelopen jaren.

Stellingen

behorende bij het proefschrift

The Chemistry of Oligopyrroles

Design, synthesis and characterization of well-defined
and functional α,α-linked oligomers

1. De destructieve destillatie van dierlijke bestanddelen heeft de pyrroolchemie geen windeieren gelegd.

   Anderson, T. *Trans. Roy. Soc. Edin.* **1857**, *XXI*, 571.
   Ho, C.-T.; Lee, K.N.; Jin, Q.Z. *J. Agric. Food Chem.* **1983**, *31*, 336.

2. De door Shin *et al.* beschreven synthese van blok-copolymeren op basis van oligothiofenen en *m*-fenyleeneenheden is onwaarschijnlijk.

   Kang, B.S.; Seo, M.-L.; Jun, Y.S.; Lee, C.K.; Skin, S.C. *J. Chem. Soc., Chem. Commun.* **1996**, 1167.

3. De afgelopen jaren heeft de dendrimeerchemie te lijden gehad van inflatie.

   Ottaviani, M.F.; Cossu, E.; Turro, N.J.; Tomalia, D.A. *J. Am. Chem. Soc.* **1995**, *117*, 4387.

4. Fosgeen kan bij de door Engel en Steglich gepubliceerde bereiding van N-(2-propenyl)benzimidoylchloride eenvoudig worden vervangen door thionylchloride.

   Engel, N.; Steglich, W. *Angew. Chem.* **1978**, *9*, 719.

5. Het bouwen van een polypyrrool-toren kan met recht een wetenschappelijk hoogstandje worden genoemd.

   Kranz, C.; Gaub, H.E.; Schuhmann, W. *Adv. Mater.* **1996**, *8*, 634.

6. De waargenomen (in)stabiliteit van een verbinding is niet altijd een intrinsieke eigenschap van die verbinding.

Chen, W.; Stephenson, E.K.; Cava, M.P.; Jackson, Y.A. *Organic Syntheses* **1991**, *70*, 151.
Hoofdstuk 4 van dit proefschrift.

7. Oligomeren kan men beschouwen als de kinderen onder de polymeren: hoe groter, hoe lastiger.

"Electronic Materials: The Oligomer Approach" (Eds.: Wegner, G.; Mullen, K.), VCH-Weinheim, Germany (1996).

8. Het geven van populaire namen aan nog niet gesynthetiseerde verbindingen levert geen enkele bijdrage aan de wetenschap.

Schulman, J.M.; Disch, R.L. *J. Am. Chem. Soc.* **1996**, *118*, 8470: Archimedene (C_{120}).
Nickon, A.; Silversmith, E.F. "Organic Chemistry: The Name Game", Pergamon Press: New York, pp. 87 (1987): Israelane/Helvetane ($C_{24}H_{24}$).

9. Het beschrijven van wetenschappelijke feiten in hun maatschappelijk kader verhoogt het leesgenot aanzienlijk.

Nicolaou, K.C. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 588.

10. De rechtspraak blijkt nogal eens krom.

11. Je kunt beter slecht zijn in goede vergelijkingen dan goed in slechte vergelijkingen.

Bert Groenendaal Eindhoven, 12 november 1996