New Diketopyrrolopyrrole(DPP)-Based Conjugated Polymers Prepared upon Palladium Catalyzed Polymerization and Electropolymerization Reactions

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To my parents and Ying

List of symbols

δ	Chemical shift
λ_{max}	Maximum absorption wavelength
λ_{em}	Maximum emission wavelength
Φ_f	Photoluminescence quantum yield
A	Ampere
ANT	Anthracene
BTH	Bithiophene
BTZ	2,1,3-Benzothiodiazole
CBZ	Carbazole
cm	Centimeter
CV	Cyclic voltammogram
DCM	Dichloromethane
DMF	N,N-Dimethylformamide
DMSO	Dimethylsulfoxide
DPP	1,4-Diketo-3,6-diphenylpyrrolo-[3,4-c]pyrrole
EC	Electrochromic
EDOT	3, 4-Ethylenedioxythiophene
EL	Electroluminescent
g	Gram
GPC	Gel-permeation chromatography
h	Hour
LED	Light emitting diode
min	Minute
mm	Millimeter
NMP	N-Methyl-2-pyrrolidon
NMR	Nuclear magnetic resonance
PDA	N,N'-Diphenyl-1,4-phenylenediamine
PL	Photoluminescence
PYRE	Pyrene
RT	Room temperature
SCE	Saturated calomel electrode
SEC	Size-exclusion chromatography

TBAN	4-t-Butylaniline
TBAPF$_6$	Tetrabutylammonium hexafluorophosphate
TH	Thiophene
THF	Tetrahydrofuran
TPA	Triphenylamine
UV	Ultraviolet
V	Volt
Vis	Visible light

Abstract

Synthesis and characteristic properties of new conjugated polymers and polyelectrolytes containing DPP-units in the main chain are described. The polymers are synthesized upon palladium-catalyzed Suzuki, Stille and Buchwald-Hartwig polycondensation and electropolymerization. Characteristic properties such as molecular weight, structure, optical and electrooptical properties of the polymers are studied using gel permeation chromatography, spectroscopic methods (UV/vis, Fluorescence, NMR spectroscopy), cyclic voltammetry and spectroelectrochemical characterization.

Using the Suzuki, Stille and Buchwald-Hartwig coupling, conjugated polymers are synthesized from dibromo-DPP or the boronic ester of DPP and derivatives of the carbazole (**CBZ**), triphenylamine (**TPA**), benzothiadiazole (**BTZ**), thiophene (**TH**), bithiophene (**BTH**), 3,4-ethylenedioxythiophene (**EDOT**), pyrene (**PYRE**) or N,N'-diphenyl-1,4-phenylene diamine (**PDA**). The molecular weights of the resulting polymers are between 4.3 and 16.5 kDa. The polymers are soluble in solvents such as toluene, chloroform or THF forming red to purple solutions with strong photoluminescence. Compared with the DPP monomer, the optical properties of the polymers are bathochromically shifted due to the increase of the conjugated system. Polymers in solution exhibit absorption maxima between 506 and 560 nm, and fluorescence maxima between 585 and 635 nm. The polymer **P-DPP-TPA** exhibits a photoluminescence quantum yield of 85 %, which is the highest value reported for DPP containing conjugated polymers so far. Polymers of DPP and **BTH**, **PDA** and **PYRE** exhibit reversible electrochromic properties upon electrochemical oxidation and reduction. The abrupt colour changes from purple to dark blue to black-green are observed.

Furthermore, a series of electropolymerizable DPP containing monomer have been successfully prepared using Suzuki, Stille or Buchwald-Hartwig coupling. The *in-situ* formed polymer films are robust and insoluble in common solvents. They exhibit a very good stability during oxidation reduction cycles together with electrochromic properties. The polymer films are useful as active materials in electrochromic devices showing colour changes from blue to transparent, brown-red to olive-green, purple-red to brown-red, and colourless to green.

Conjugated polyelectrolytes were synthesized from bis-bromohexyl-DPP or bis-sulfonylbutyl-DPP using Suzuki and Buchwald-Hartwig coupling. The resulting cationic and anionic polyelectrolytes are readily soluble in water and polar organic solvents such as methanol and DMSO. The polymers are non-luminescent in water, but exhibit photoluminescence quantum yields between 6.2 % and 49 % in DMSO.

Abstract

Ziel dieser Arbeit war die Herstellung und die Charakterisierung von konjugierten Polymeren mit DPP-Einheiten in der Hauptkette. Die Polymere wurden mit Hilfe der Suzuki, Stille und Buchwald-Hartwig Kupplung so wie durch Elektropolymerisation hergestellt. Die Eigenschaften der resultierenden Polymere (Molekulargewicht, UV/vis, Fluoreszenz, NMR Spektroskopie, Zyklovoltammetrische Untersuchungen und spektroelektrochemische Charakterisierung) wurden untersucht.

Mit Hilfe der Suzuki, Stille und Buchwald-Hartwig Kupplung, wurden Dibromo-DPP oder Diboronester-DPP mit Carbazol (**CBZ**), Triphenylamin (**TPA**), Benzothiadiazol (**BTZ**), Thiophen (**TH**), Bithiophen (**BTH**), 3,4-Ethylenedioxythiophen (**EDOT**), Pyrene (**PYRE**) oder N,N'-diphenyl-1,4-phenylene diamin (**PDA**) gekupplet. Die Molekulargewichte der erhaltenen Polymere liegen zwischen 4.3 und 16.5 kDa. Die Polymeren sind in gängigen Lösemitteln wie Toluol, Chloroform, Dichlormethan oder THF gut löslich. Dabei bilderen sie stark fluoreszierende Lösungen. Die Absorptionsmaxima liegen zwischen 506 und 560 nm, die Fluoreszenz maxima zwischen 585 und 635 nm.

Weiterhin wurden DPP-Polymere durch Elektropolymerisation herstellt. Die Polymere sind unter Farbwechsel Oxidationsbeständig.

Konjugierte Polyelektrolyte wurde mit Hilfe der Suzuki und Buchwald-Hartwig Kupplungs hergestellt. Die Polymeren sind löslich in Wasser, DMSO und Methanol.

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1. Introduction

1.1. Diketopyrrolopyrrole (DPP)

In 1974, Farnum, et al. [1] briefly reported the attempted synthesis of 2-azetinones according to the following reaction (Scheme 1.1). The desired reaction failed. Instead, the diphenyl DPP derivative was isolated in 5-20% yield.
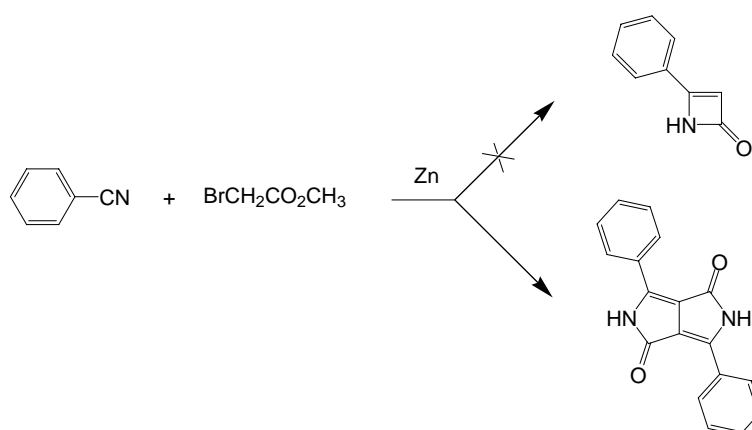
Scheme 1.1 Preparation of DPP (Farnum, et al. 1974)

However, the important physical properties of the DPPs such as high melting points (>350 ^{o}C), insolubility in most solvents and brilliant red colour remained unnoticed due to its too poor yield. In 1980, researchers from Ciba-Geigy (now Ciba Specialty Chemicals) took notice of this reaction in a compilation of interesting reactions published by Ranganathan in 1980[2]. Then the chemistry and applicatory properties were developed [3,4], and in 1986 the first DPP pigments have been developed and introduced to the market for conventional pigment applications like paints, plastics, fibers and inks.

Besides the original report from Farnum [1], there are several reports for the synthesis of DPP pigments [5-7]. Among all these methods, the succinic ester route is regarded as the best one [5,6]. In this route, succinic ester is condensed in a pseudo-Stobbe condensation with an aromatic nitrile in the presence of strong base to afford the desired DPP in a yield over 60% (Scheme 1.2). The key-step of the mechanism is the formation of pyrrolinone esters from the initially formed enaminoesters, then it can further react with another benzonitrile under basic conditions. Subsequent ring closure affords the DPP compounds.

Scheme 1.2 Preparation of DPP via the succinic ester route
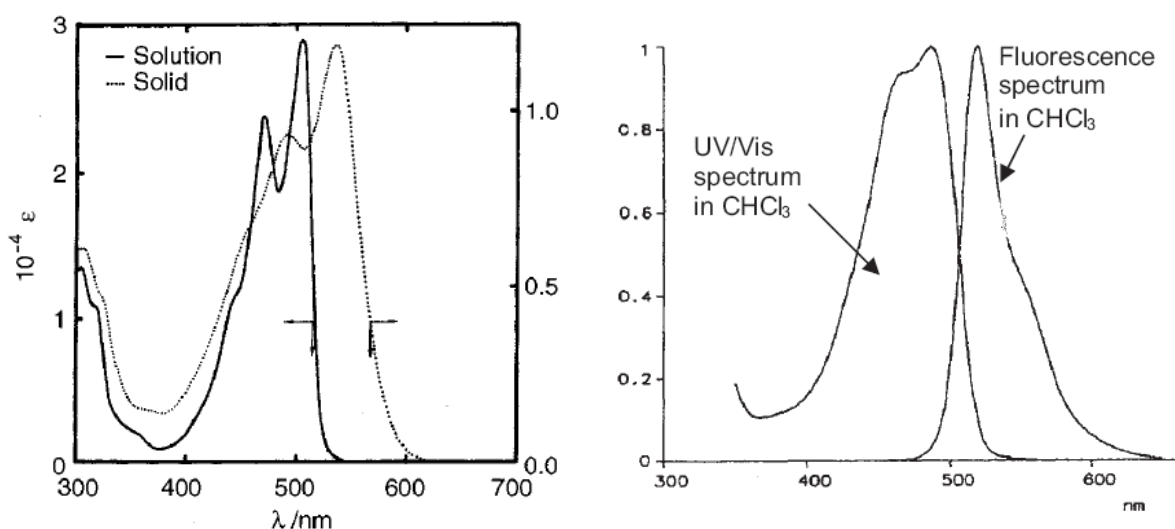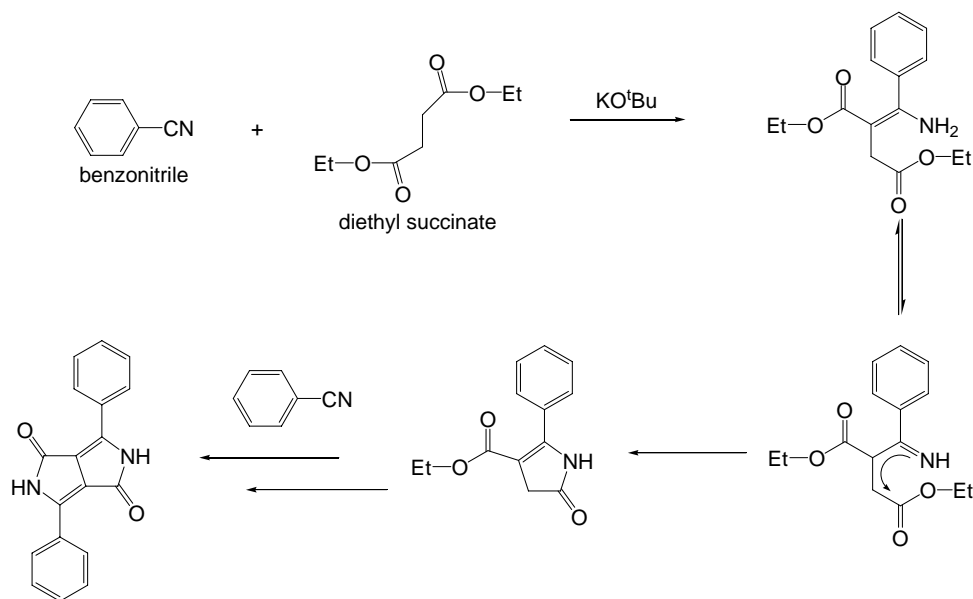
a) Absorption spectra of DPP in solution
(DMSO) and in the solid state

b) Absorption and emission spectra of DPP
in solution (CHCl$_3$)

Figure 1.1 UV/vis absorption and photoluminescence spectra of
diphenyl-diketopyrrolopyrrole

The synthesis of DPP pigments was discussed in a series of publications from Morton and Riggs[8-10]. More recently, the synthesis of unsymmetrical DPP[11,12] was reported. Some new synthetic methods such as the microwave route[13] have also been reported.

The diketopyrrolopyrrole is a bicyclic 8π electron system containing two lactam units. Typical DPP derivatives such as diphenyl-diketopyrrolopyrrole have melting points over 350 ^{o}C, a very low solubility in most solvents (<110 mg/L in DMF at 25 ^{o}C), an absorption in the

visible region with a molar extinction coefficient of 33,000 dm^{2}mol^{-1}, a strong photoluminescence with maximum between 500 nm and 600 nm. The UV/vis absorption[5,14,15] and photoluminescence[16] spectra of diphenyl-diketopyrrolopyrrole (see Scheme 1.1) are shown in Figure 1.1.

X-ray structure analyses [15,17-22] of diphenyl-diketopyrrolopyrrole pointed out that the whole molecule is almost in one plane. The phenyl rings are twisted out of the heterocyclic plane by 7°. The intermolecular hydrogen bonding between neighboring lactam NH and carbonyl units dominates the structure of DPP in the solid state. This in turn determines the molecular packing along the direction perpendicular to the DPP chromophore plane. The π-π interaction between the layers of DPPs is then understandable. The optimum interlayer distances between chromophore planes (3.36 Å) and between phenyl ring planes (3.54 Å) is short enough to warrant significant π-π interaction, the growth of crystals being also the strongest along this direction. Recent ab initio calculations [23-25] of the DPP molecules also confirmed this structure.

1.2.   The chemistry of DPP

Figure 1.2 depicts the possible reactive sites of the diaryl-DPP molecule and its corresponding reagents.

In this dissertation, only the basic reactions about the DPP itself are discussed below. Further detailed information can be found in the literature [8-10,26,27].
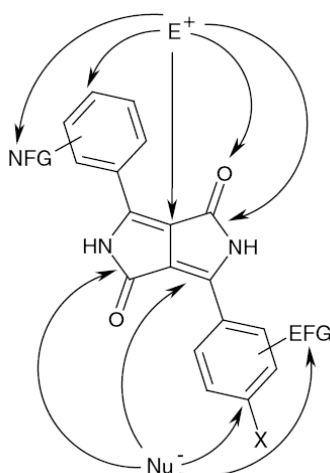
Figure 1.2 Potentially reactive centers in a diaryl-DPP derivative[27].

EFG: electrophilic functional group, e.g. CN, COOR

NFG: nucleophilic functional group, eg. OH, SH, NHR

X: halogen

1.2.1. N-Alkylation

The heterocyclic DPP moiety can be alkylated by alkyl halides or alkyl sulfonates. The following Scheme 1.3 is the example of N-methylation of diphenyl-DPP[28,29].
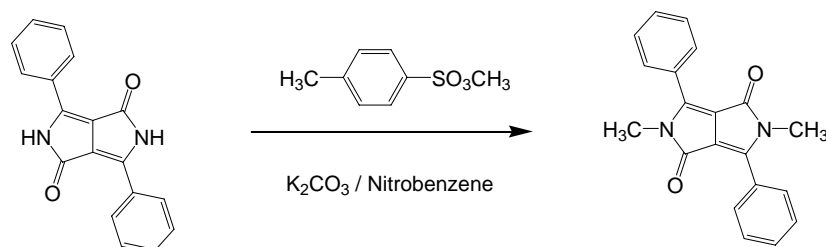
Scheme 1.3 The N-methylation of DPP

After the N-alkylation, the biggest change for DPP is the loss of intermolecular hydrogen bonding. The solubilities of the diaryl-DPPs are drastically raised upon N-alkylation. Compared with the unsubstituted diaryl-DPP (100mg/L in DMF at 25 $^{\circ}$C), the solubility of N-methyldiaryl-DPP is 3300 mg/L. The N-substituted DPP derivatives are generally fluorescent in solution with a maximum quantum yield up to 95%.

1.2.2. Electrophilic aromatic substitution

DPP can be sulfonated by oleum to form the disulfonic acid and the salts of the disulfonic acid. The sulfonation renders the DPP-derivatives water-soluble. The halogenation of diphenyl-DPP is difficult. With bromine gas, diphenyl-DPP can be transferred to 4,4'-dibromophenyl DPP. However, the chlorination does not form the corresponding compounds. This may be due to the reason that bromine is a better leaving group and a better nucleophile compared with chlorine[5].
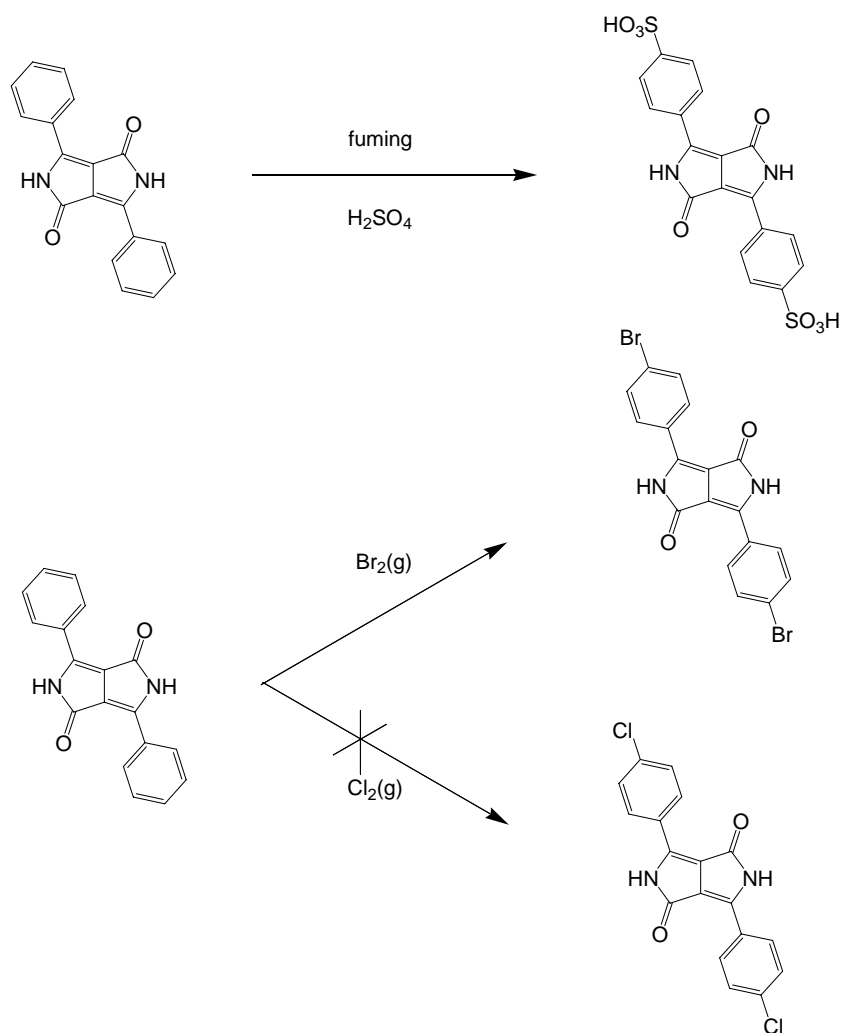
Scheme 1.4 Electrophilic aromatic substitution

1.2.3. Nucleophilic aromatic substitution

The nucleophilic aromatic substitution was reported in polar solvent at high temperature (Scheme 1.5)
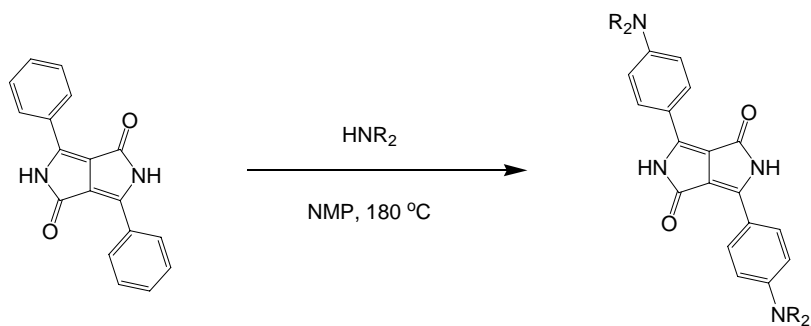
Scheme 1.5 Nucleophilic aromatic substitution

1.2.4. Transformations at the carbonyl group

The transformation at the carbonyl group of DPP has been investigated. The atom O can be replaced by S, N and C (Scheme 1.6).
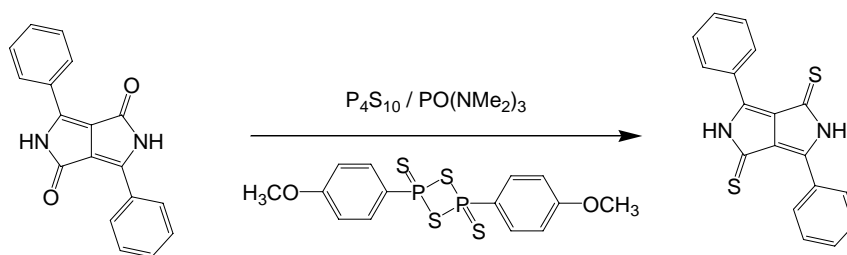
Scheme 1.6 DPP transformation reaction

1.3. Conjugated DPP polymers

DPPs are used as pigments in applications like paints, plastics, fibers and inks for years. However, since A. J. Heeger, A. G. MacDiarmid and H. Shirakawa found the conducting polyacetylenes and finally were awarded the Nobel Prize in 2000, this chromophore is interested for its promising properties in organic electronic applications. Due to the 8π electron system, DPP chromophore is an ideal building block for conjugated molecules, oligomers, polymers and dendrimers.

The very first DPP containing polymer was reported by L. Yu [30-32]. A series of DPP containing block copolymers were prepared by Stille polycondensation (Scheme 1.7).
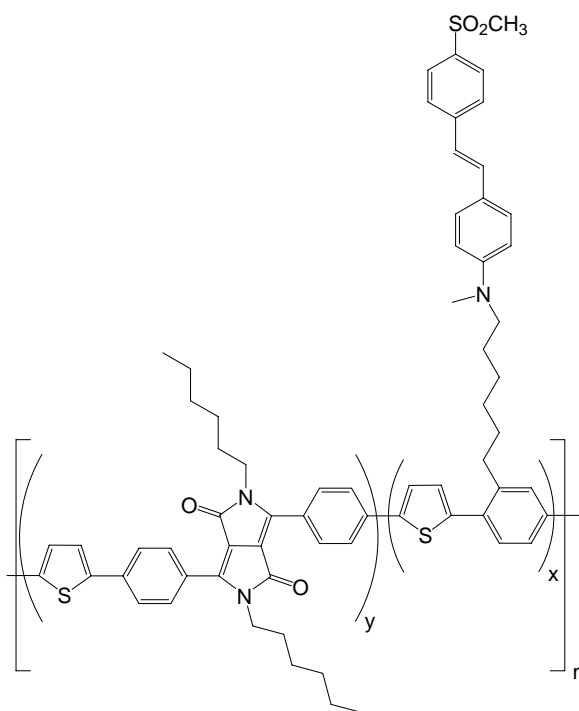
Scheme 1.7 The first reported DPP containing conjugated polymer

DPP-containing polymers have been prepared upon radical polymerization[33,34] and polymer modification[35]. In 1999[36], the polycondensation reaction for the preparation of DPP containing polymers was reported from our group. Copolyesters and copolyurethanes with 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP) units in the main chain were prepared (Scheme 1.8). Because the conjugation did not extend along the polymer chain, the polymer exhibited similar optical properties as the monomer. Polymer solutions were yellow to orange with an optical absorption maximum at 470 nm and a fluorescence maximum at 520 nm.
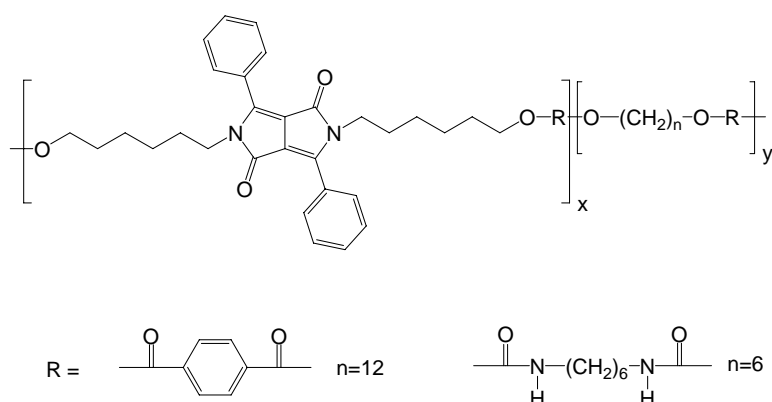
Scheme 1.8 Copolyesters and -urethanes with 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP) units in the main chain.

Smet and Dehaen reported synthetic work about rod-like diketopyrrolopyrrole oligomers and dendritic molecules containing DPP units[37,38]. DPP units used in the ligand system[39], as fluorescent Ca^{2+} indicator[40] and hydrogen gas sensors[41] have also been reported recently. Two different dendrimers using DPP unit as core have been synthesized by Verheijen and his colleagues[42] and the fluorescence quantum yield was over 80% for G3 dendrimers. Other important reports were concerned with liquid crystalline DPP derivatives [43] and with latent DPP pigments, which are transformed from the soluble N,N'-bis-(t-butoxycarbonyl)-3,6-diphenyl-1,4-diketo-pyrrolo[3,4-c]pyrrole into insoluble 3,6 diphenyl-1,4-diketo-pyrrolo[3,4-c]pyrrole upon heat treatment [44](Scheme 1.9).
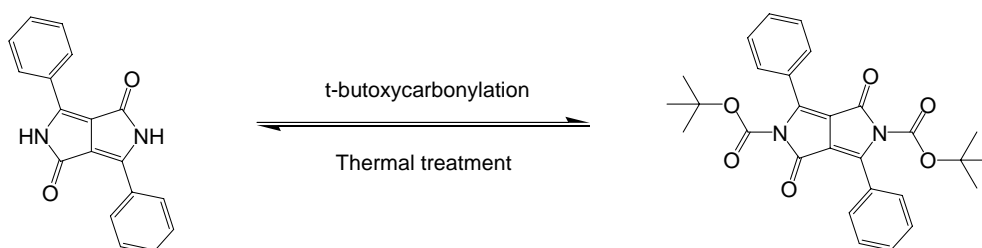
Scheme 1.9 Transformation of soluble DPP into insoluble DPP pigment

Following the very first report of multifunctional DPP polymers from L. Yu[30-32] (Scheme 1.7), a number of π-conjugated DPP-polymers and copolymers have been reported recently, which are promising materials for electronic applications because of their brilliant colours, photochemical stability and electroluminescent properties. Beyerlein et. al. synthesized the conjugated copolymers with DPP units and 1,4-phenylene units in the main chain[45] (Scheme 1.10). These polymers were used to fabricate a polymer light emitting device (PLED)[46].
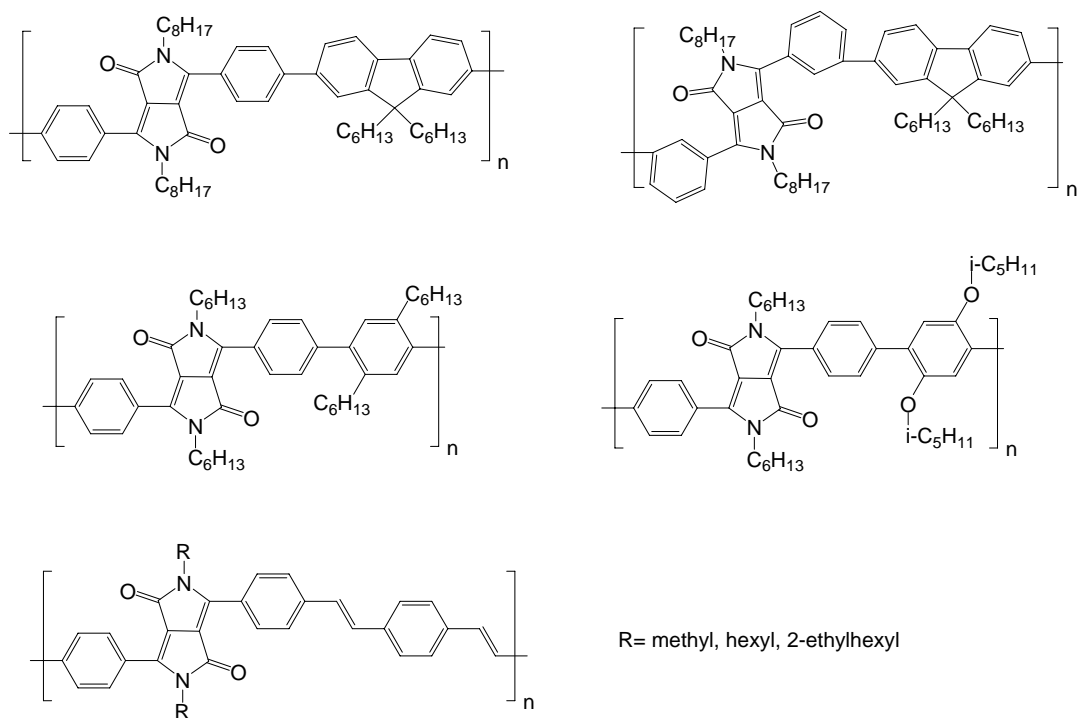
Scheme 1.10 Recent explore for the synthesis of DPP conjugated polymers.

Beyerlein also synthesized the conjugated polymers with DPP and fluorene in the main chain, the results were reported in his thesis. Cao and his colleagues reported a similar polymer in a recent publication[47]. I. Heim, another previous member in our group, synthesized a series of poly-DPP-vinylenes using Heck polycondensation reaction.[198]

1.4. Electroluminescent applications

The photoluminescence of π-conjugated molecules was found in the middle of the 19th century. However, until the middle of the 20th century, people did not know about the electroluminescence.

A typical conjugated polymer based electroluminescence device is shown in Figure 1.3.
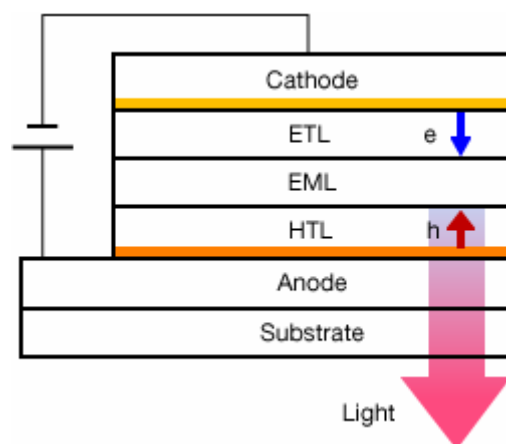
Figure 1.3 A typical electroluminescence device.

The principles of electroluminescent devices are depicted as follows:

- Organic multilayered thin films of electron transport layer (ETL), emitting materials layer (EML), and hole transport layer (HTL) are sandwiched between two metallic electrodes forming the anode and cathode on a transparent substrate.

- When a voltage is applied, charges are injected into the organic layers: electrons from the cathode, and holes from the anode.

- The electrons and holes form excitons through electrostatic interaction.

- Radiative recombination of excitons generates light.

The anode generally is an indium-tin oxide (ITO) coated glass, which is transparent and therefore the light can be emitted at this side. Typical hole transport materials are NPB, TPD, PVK, PMPS, PEDOT-PSS (Scheme 1.11) and typical electron transport materials are Alq_3, Znq_2, Beq_2, PBD, PPY and 4-AcNi (Scheme 1.12).

NPB

TPD

PVK

PEDOT-PSS

Scheme 1.11 Common hole transport materials

Alq$_3$

Znq$_2$

Beq$_2$

PPY

Ac—NH 4-AcNi

PBD

Scheme 1.12 Common electron transport materials
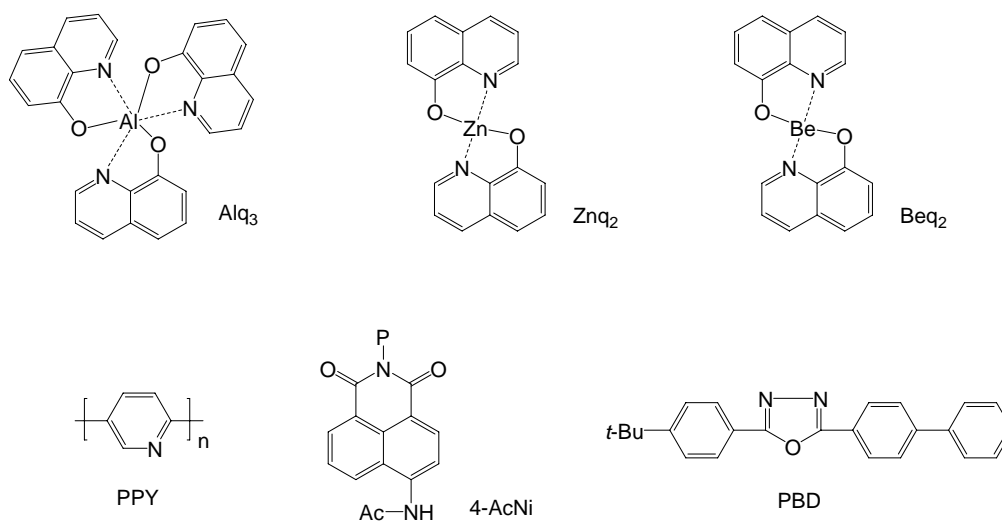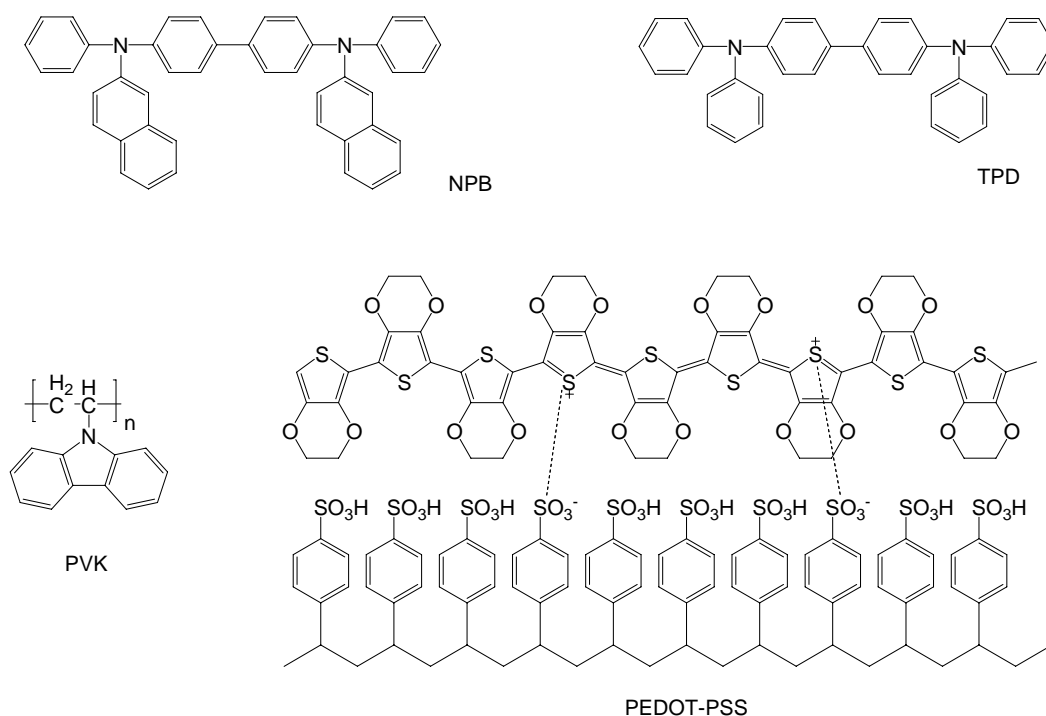
The following Figure 1.4 shows the band scheme of a single layer PLED system. The anode is ITO, a high work function material. The cathode is a low work function metal. The highest occupied molecular orbit (HOMO) of the emitting material should be a little bit higher than the work function of ITO. The lowest unoccupied molecular orbit (LUMO) of the emitting material should be a little bit lower than the work function of the metal. The injection barrier for hole ΔE_h and electron ΔE_e can be further adjusted by the additional hole transport layer and electron transport layer.

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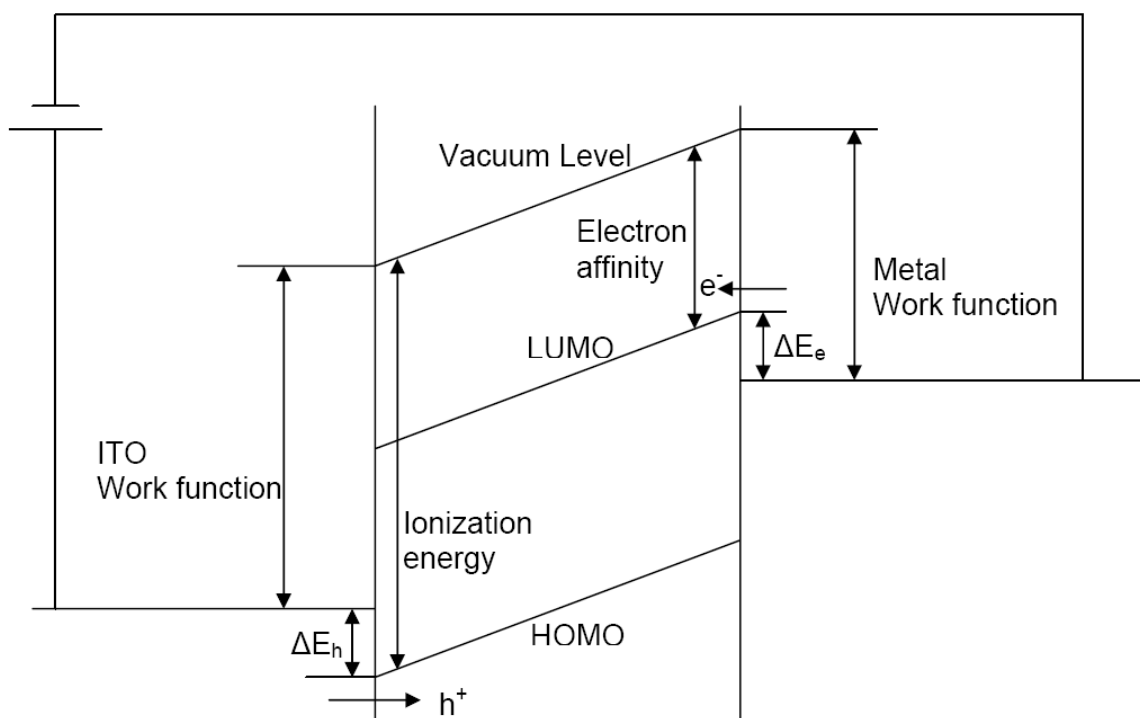
Figure 1.4 Schematic energy-level-diagram for single layer PLED system.

1.5. Electrochromic applications

Electrochromism is broadly defined as a reversible change of the optical absorption of a material induced by an external voltage, with many inorganic and organic species showing electrochromism throughout the electromagnetic spectrum. Conjugated polymers are a new class of electrochromic (EC) materials that have gained popularity due to their ease of processability, rapid response times, high optical contrast, and the ability to modify their structure to create multicolor electrochromism. A typical conjugated polymer based EC device is shown in Figure 1.5.
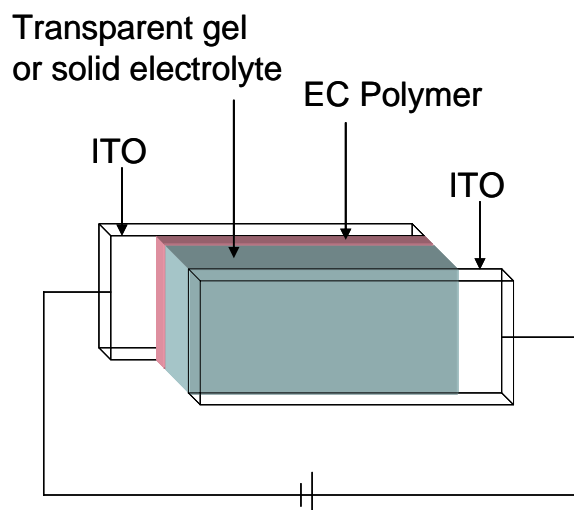
Figure 1.5 A typical electrochromic device.

Electrochromism in conjugated polymers occurs through changes in the electronic character accompanied by reversible insertion and extraction of ions in and from the polymer film upon electrochemical oxidation and reduction. In their neutral (insulating) states, these polymers show semiconducting behaviour with an energy gap between the valence band (HOMO) and the conduction band (LUMO). Upon electrochemical or chemical doping ("p-doping" for oxidation and "n-doping" for reduction, see Scheme 1.13), the band structure of the neutral polymer is modified, generating lower energy intraband transitions and creation of charge carriers (polarons and bipolarons), which are responsible for increased conductivity and change of physical absorption. Such optical and structural changes are reversible through repeated doping and dedoping over many redox cycles, making the conjugated polymers potentially useful in many applications.
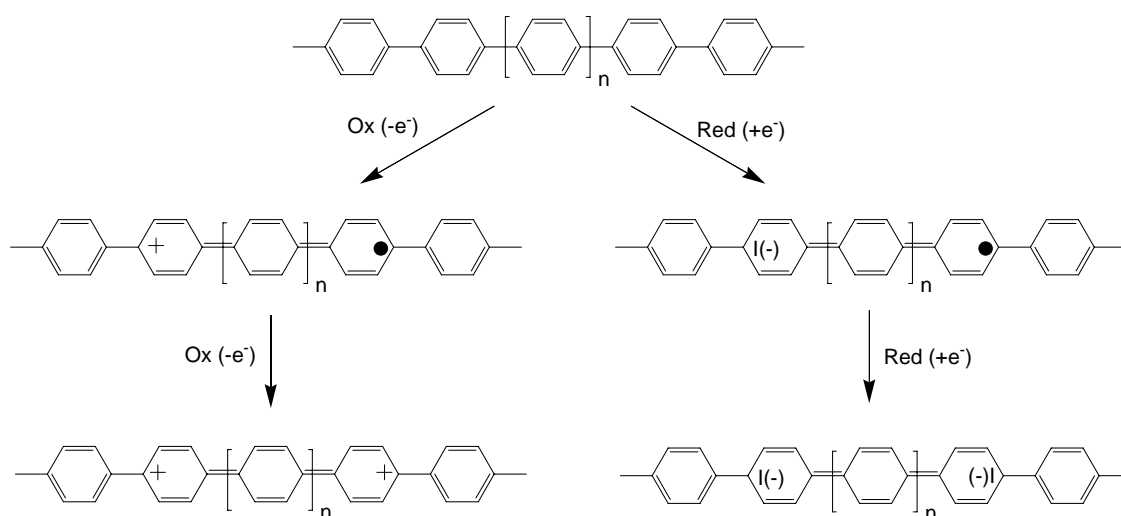
Scheme 1.13 Doping of poly-p-phenylene upon oxidation (left) or reduction (right)

The greatest challenge thing in an applicable electrochromic material is its reversibility upon the doping processes. As shown in Scheme 1.13, polarons and bipolarons determine the colour change of the materials. However, these carriers (carbanium ionsor carbanions) are very unstable and may react with the environment. Therefore the point is to increase the stability of the materials in the doped state. Most reported electrochromic materials are suitable for p-doping because carbanium ions are generally considered more stable than the carbonions. To increase the stability of carbanium ions, a low oxidation potential is preferred. Thus for lowering the oxidation potential of the polymer it is very important to decrease the reaction with the environment and increase the reversibility of the polymer upon p-doping and dedoping processes.

Of the conjugated polymers, derivatives of poly(thiophene), poly(pyrrole) and poly(aniline) are widely studied for their electrochromism. The commonly used electrochromic materials and their colour changes are reviewed in publications[48].

1.6. DPP-based conjugated polyelectrolytes

DPP-based conjugated polyelectrolytes are DPP containing conjugated polymers featured with ionic side group which render the material soluble in water and other polar organic solvent such as methanol and DMSO. Due to the solubility, these polymers are useful for special applications, e.g. for the preparation of ultrathin organized films in layer-by-layer self-assembly film processes.[49]

A photoluminescent amphiphilic 1,4-diketo-3,6-diphenylpyrrolo-[3,4-c]-pyrrole derivative and its complexes with polyelectrolytes were prepared by Behnke[35] using the method of polymer modification (Scheme 1.14). The water soluble DPP molecule was reported by Saremi et. al[50]. Self-assembled multilayers of anionic DPP bolaamphiphiles and cationic polyelectrolytes were also reported (Scheme 1.14). However, up to now, there is no report on conjugated DPP-based polyelectrolytes and the use of these polyelectrolytes for preparation of layer-by-layer assembled films.
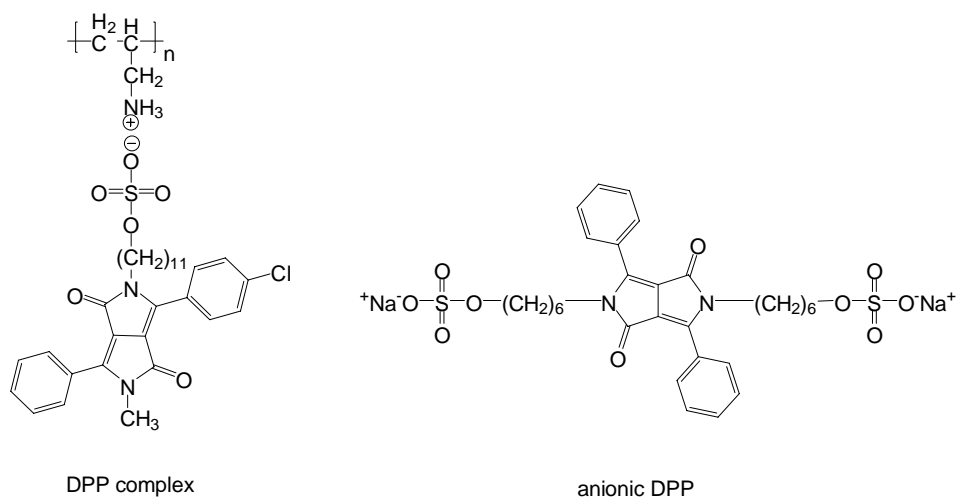
Scheme 1.14 DPP complex with polyallylamine, and an anionic DPP used for preparation of self-assembled multilayers with cationic polyelectrolytes.

1.7.   Motivation of the work

The purpose of this dissertation is to synthesize new conjugated DPP containing polymers suitable for electroluminescent or electrochromic applications. Although some reports about the synthesis of DPP containing conjugated polymers are published already, this type of conjugated polymers has not yet been explored thoroughly. Suzuki, Stille and Heck polycondensations are the only reported methods for DPP conjugated polymers and the explored building blocks are limited (only with fluorene and phenylene). There are several reasons to synthesize new DPP containing conjugated polymers.

- There are lots of newly developed polycondensation methods, which have not been applied for the preparation of the DPP containing conjugated polymers yet. Two of the most important techniques are Buchwald-Hartwig coupling and electropolymerization. Buchwald-Hartwig coupling offers the possibility to couple DPP derivatives with different arylamine compounds, which are more easily prepared than the stannanes and boron compounds. Using electropolymerization, the polymer films can be formed on the electrode *in-situ*.

- Some building blocks, which either offer high luminescence or low oxidation potential, have not been incorporated into the DPP containing polymers yet. These building-blocks should be commercial available and the corresponding dibromo derivatives can be easily prepared. The examples are carbazole, triphenylamine, benzothiodiazole, thiophene, pyrrole etc.

- A low oxidation potential of the polymer is crucial for a successful electrochromic material. The reversibility of the electrochromism is very much related with the

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stability of the doped polymer. New synthetic method and new functional groups are needed to be introduced to afford the requirements.

- New developed techniques such as layer by layer assembling need a new class of polymers, such as the conjugated DPP polyelectrolytes.

The synthetic methods and the physical chemistry properties of the polymers will be discussed in the following chapters. The applications of these polymers are also described.

2. Conjugated DPP polymers prepared upon palladium catalyzed polycondensation

One of the most important methods for preparation of conjugated polymers is chemical polycondensation. The Ni promoted coupling reactions (Yamamoto coupling[51], Kumada coupling[52], Negishi coupling[53]), Palladium catalyzed reactions (Heck coupling[54], Suzuki coupling[55], Stille coupling[30,56-58], Sonogashira coupling[59,60], Buchwald-Hartwig coupling, Kumuda coupling[52], Negishi coupling[53], Hiyama coupling[61]), Cu-catalyzed reactions (Ullmann Reaction[62], Glaser coupling[63]) and coupling reactions not involving metal catalysis (Wittig coupling[64], Knoevenagel coupling[65,66]) were applied. Up to now, the palladium catalyzed polycondensations were regarded as the best methods. Especially Suzuki coupling, Stille coupling, Heck coupling and Sonogashira coupling are widely used in the field.

In this chapter, new DPP containing conjugated polymers (and some exceptions without DPP units in the backbone) were prepared upon Suzuki, Stille and Buchwald-Hartwig polycondensation catalyzed by palladium compounds.

2.1. Suzuki coupling polycondensation

Suzuki coupling is a Pd-catalysed reaction for carbon–carbon (C–C) bond formation. The organoboron compounds serve as the active material to react with halide (Scheme 2.1).
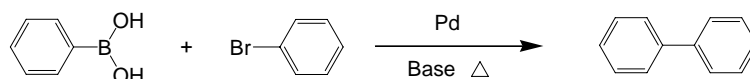
Scheme 2.1 Scheme of Suzuki coupling.

Potassium trifluoroborates and organoboranes or boronic esters may be used in place of boronic acids. Some pseudohalides (for example triflates) may also be used as coupling partners. One difference between the Suzuki mechanism and that of other cross coupling reactions (such as Stille coupling) is that the boronic acid must be activated, generally with a base. This activation of the boron atom enhances the polarization of the organic ligand, and facilitates transmetallation. The generally accepted mechanism of Suzuki coupling is shown in Figure 2.1.
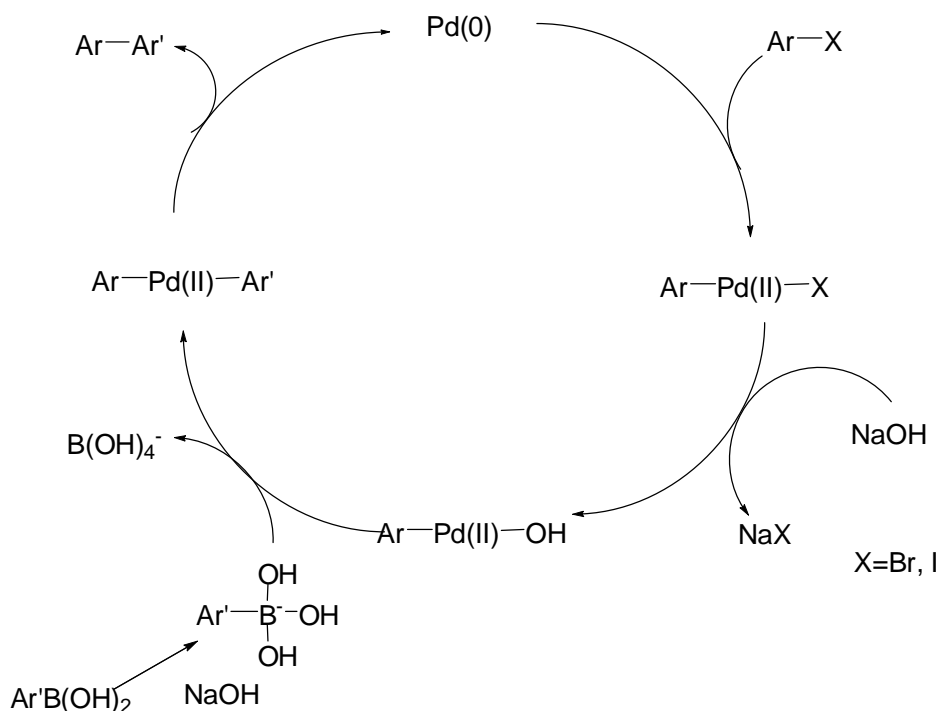
Figure 2.1 Mechanism of Suzuki coupling

The first step is the oxidative addition of palladium to the halide to form the organo-palladium species. This species reacts with a base to give intermediate Ar-Pd(II)-OH, which via transmetallation with the boronate complex forms the organopalladium species Ar-Pd(II)-Ar'. Reductive elimination of the desired product restores the original palladium catalyst.

In case of polymerization, bifunctional dibromo-compounds and diboronic acid derivatives are needed. Therefore the first step is to prepare suitable monomers to be used in the polycondensation reaction.

2.1.1. Preparation of the monomers

The dibromo-DPP derivative (see Scheme 2.2) is used as the start material. Similar to the ordinary DPP pigments, this material is insoluble in most solvents. Before the polycondensation is preceded, the monomer has to be rendered soluble upon N-alkylation. The alkylation reaction has been reported before; however, the yield is quite low (<20%). In this work, a new procedure (originally from Ciba) was investigated giving a yield of soluble monomer at around 50%. The alkylation reaction is shown in Scheme 2.2.
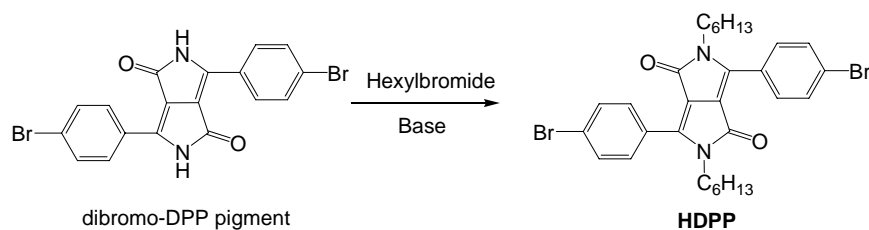
Scheme 2.2 Alkylation of dibromo-DPP pigment

In the new procedure, NMP and potassium t-butoxide replace the DMF and potassium carbonate. Therefore the reaction can be carried out at a much lower temperature (60 $^\circ$C). Because the deprotonated intermediate DPP is very reactive, the lower reaction temperature can efficiently reduce the side reaction. Then the yield of the desired N-alkylated compound can be much higher.

The diboronic acid or diboronic ester is another crucial monomer for the Suzuki coupling. Unfortunately, due to the presence of the carbonyl group, the DPP compound can not be transferred to boronic acid using the general lithiation procedure. The chromophore will be destroyed immediately after the n-butyllithium is dropped into the 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole (**HDPP**) containing THF solution even at low temperature (-70 $^\circ$C). Miyaura[67] developed another method to prepare a boronic ester via palladium catalyzed coupling reaction using bispinacolate diboron. This method is very mild and can tolerate many functional groups. The DPP diboronic ester 1,4-diketo-2,5-dihexyl-3,6-*bis*(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolo[3,4-c]pyrrole (**HDPPB**) was successfully synthesized by this reaction with a high yield (> 80%).
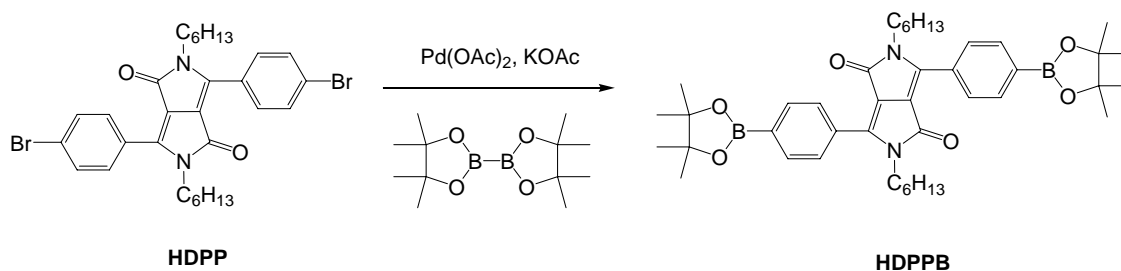
Scheme 2.3 Preparation of DPP diboronic ester **HDPPB**

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Preparation of DPP-based monomers

The resulting monomers **HDPP** and **HDPPB** are very soluble in common organic solvents such as chloroform, toluene and THF. The UV/vis absorption and photoluminescence spectra of **HDPP** and **HDPPB** in chloroform are shown in Figure 2.2.
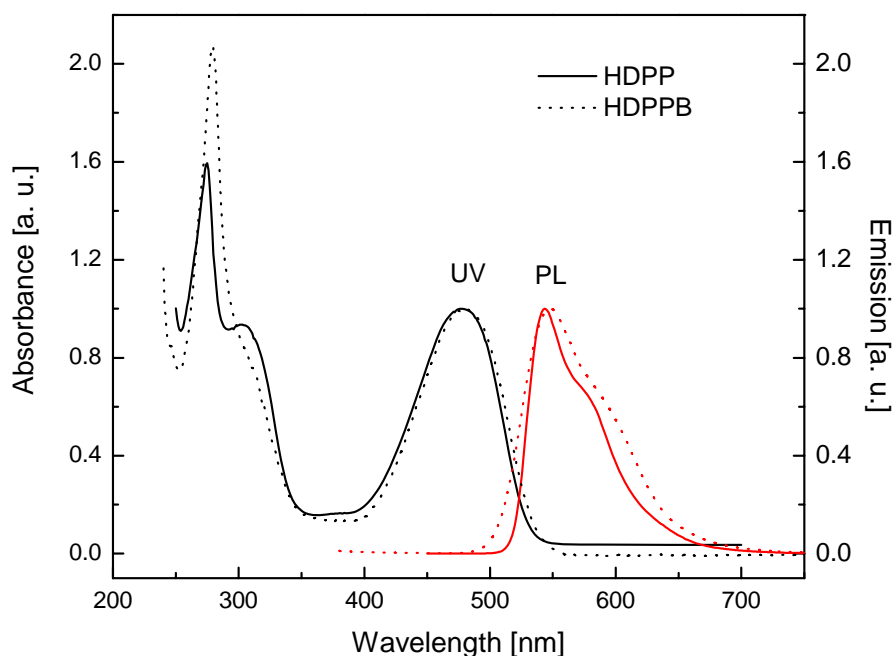
Figure 2.2 UV/vis absorbance and photoluminescence spectra of **HDPP** and **HDPPB**. Solvent: CHCl$_3$. The excitation wavelength is 350 nm.

Both monomers have an absorption maximum in the ultraviolet region, which originates from the phenylene units connected with the DPP chromophore. The absorption maxima from the DPP chromophore are at 476 nm and 479 nm for **HDPP** and **HDPPB**, respectively. The emission maxima are at 533 nm and 548 nm. The colours of these two polymers are very similar, but for the luminescence they are quite different. Monomer **HDPP** is green luminescent, **HDPPB** is yellow luminescent (Figure 2.3). The photoluminescence quantum yields for these two monomers are over 90% (compared with Rhodamine 6G 95% in ethanol).
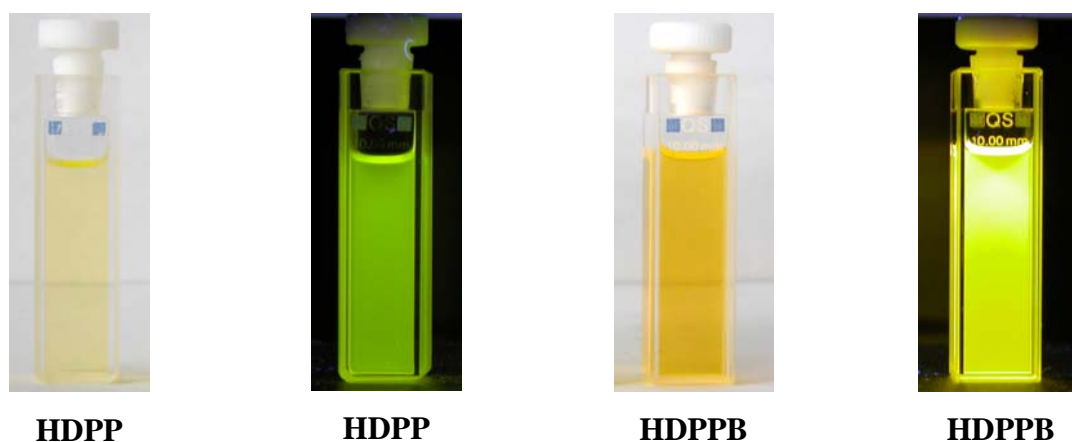
Figure 2.3 Photographs of **HDPP** and **HDPPB** in normal and luminescent state. Solvent: CHCl$_3$

The ^{1}H-NMR of **HDPP** and **HDPPB** are shown in Figure 2.4. The triplet signal at 0.85 ppm originates from the methyl group of the hexyl unit. The signal of the α-methylene unit directly attached to the N-atom of the lactam unit appears at 3.72 ppm. Signals of the other methylene unit appeared at 1.23 ppm and 1.85 ppm. The doublet signals of aromatic protons of **HDPP** are overlapped between 7.65 ppm to 7.66 ppm. For the boronic ester **HDPPB**, the additional peak at 1.38 ppm stems from the methyl group of the pinacolato boronester unit. The doublet signals of aromatic protons of **HDPPB** are found at 7.80 ppm to 7.95 ppm.
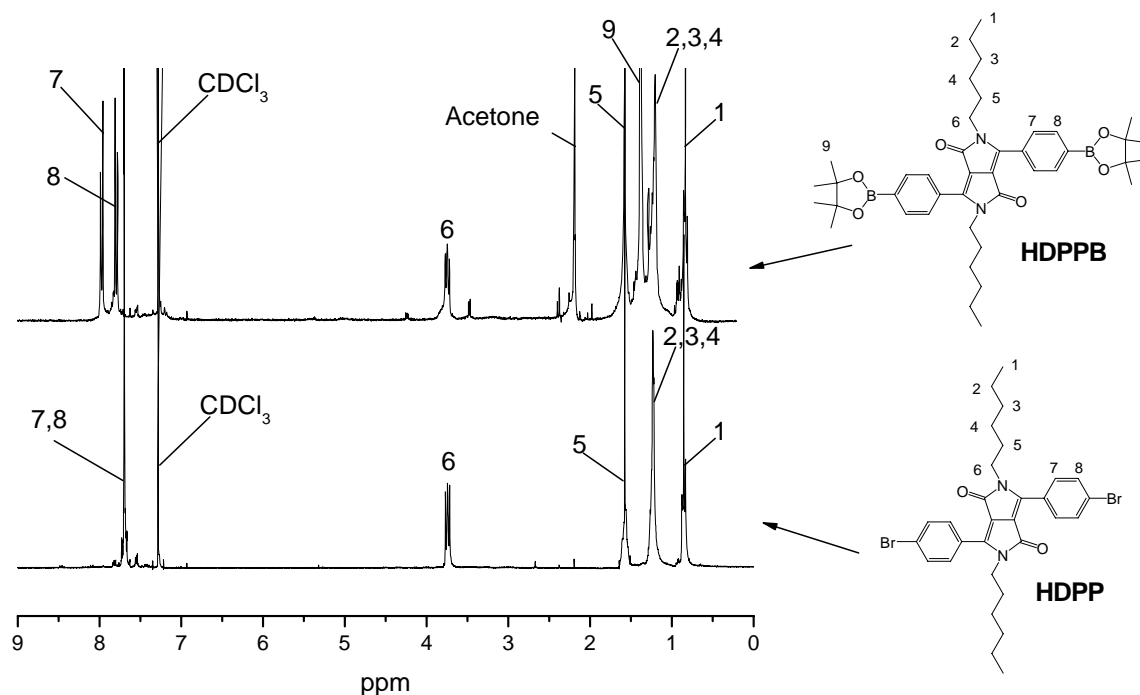
Figure 2.4 The proton NMR spectra of **HDPP** and **HDPPB**

Preparation of other monomers

The corresponding monomers were prepared as outlined in Scheme 2.4. The boronic ester of carbazole[68,69] and triphenylamine[70-73] were prepared from the corresponding dibromo derivatives upon successive treatment with n-butyllithium and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, respectively. In order to increase the solubility of the monomer and to block the active proton at the carbazole unit, the 3,6-dibromocarbazole[74,75] was alkylated with 2-ethylhexyl bromide before lithiation was carried out. The method of direct lithiation of 4,7-dibromo-2,1,3-benzothiadiazole was not applied, since 2,1,3-benzothiadiazole can not bear such a strong base as n-butyllithium. In this case, 4,7-dibromo-2,1,3-benzothiodiazole[76] was prepared and used for the polycondensation reaction.
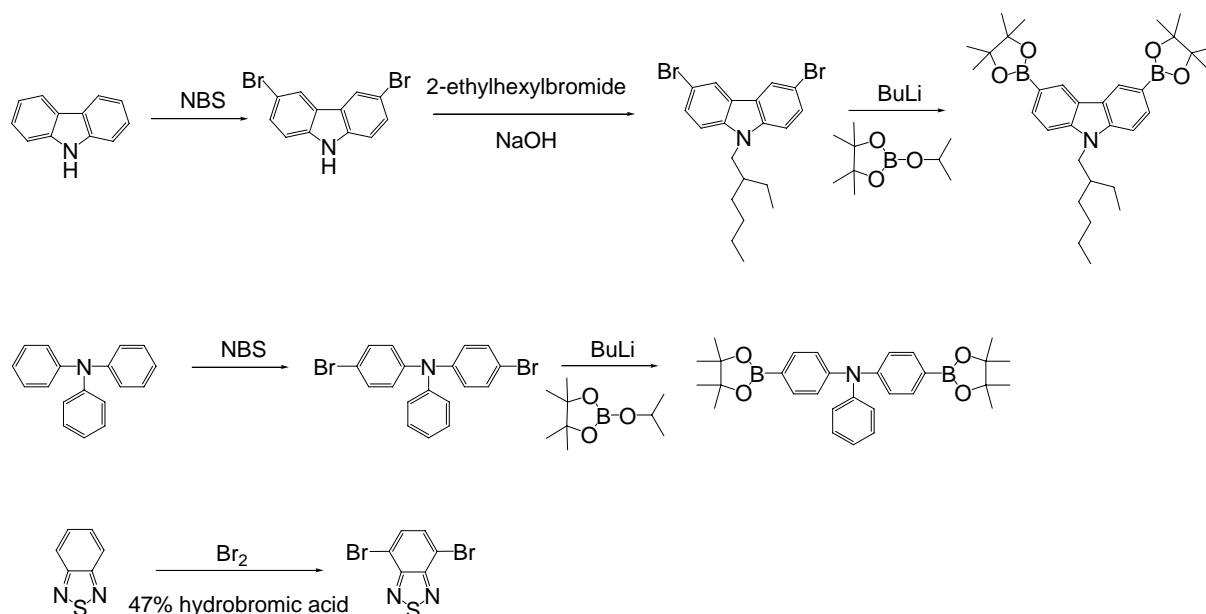
Scheme 2.4 Preparation of other Suzuki coupling monomers

2.1.2. Polymerization

The Suzuki polycondensation reactions performed in this work are shown in Scheme 2.5.
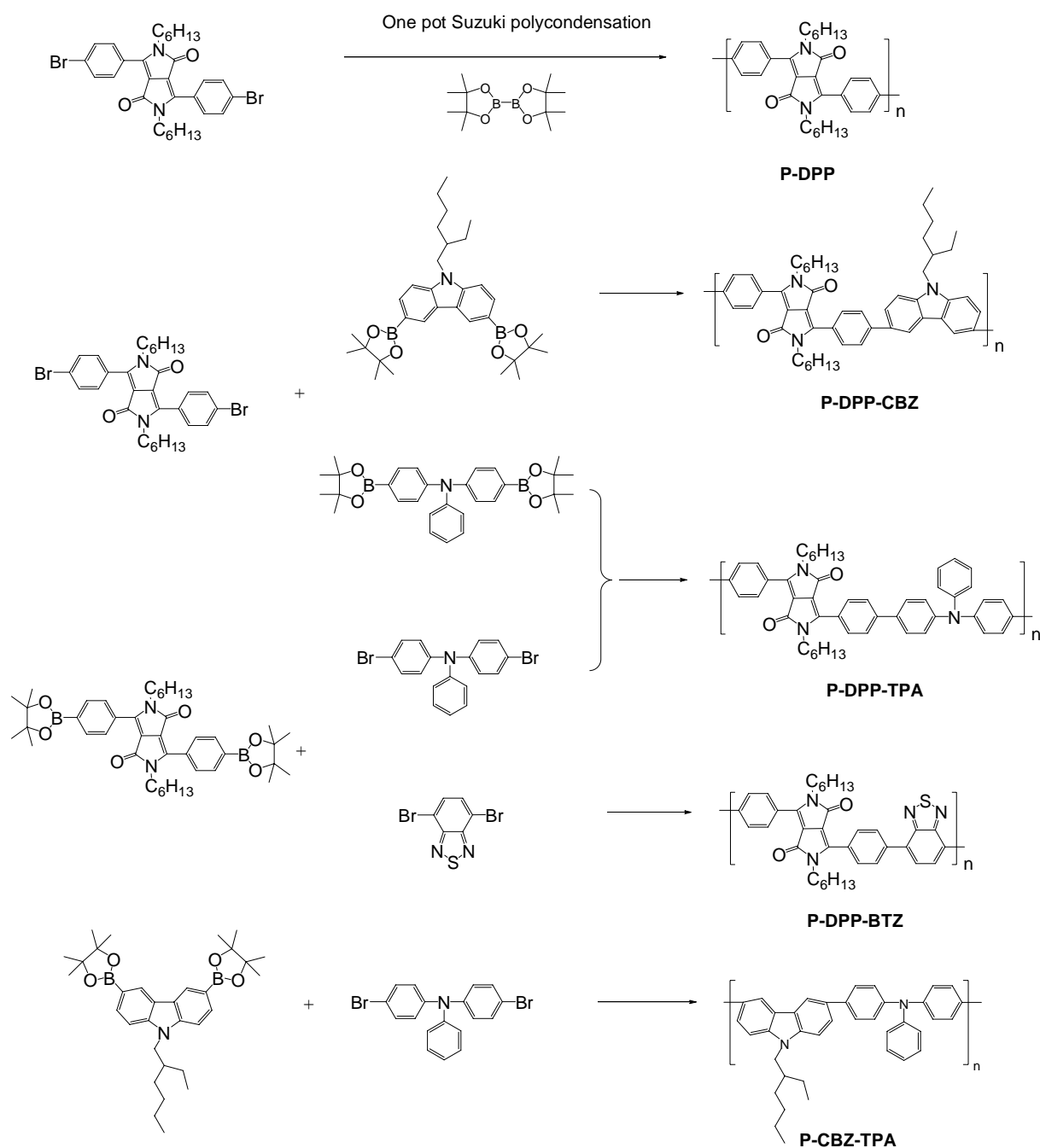
Scheme 2.5 Scheme of Suzuki polycondensation.

In this work, the new DPP-based homopolymer (**P-DPP**), which only contains the N,N'-di-alkylated DPP-chromophore as para-linked repeating unit (the so-called 'poly-DPP'), was synthesized at first. In an earlier progress report of our group[77], the **P-DPP** was synthesized by Ni-promoted Yamamoto coupling. The resulting polymer had a molecular weight up to 3 kDa. In order to avoid the use of the expensive Yamamoto reagent, another preparation route

based on Suzuki coupling was investigated. The reaction route started from the 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole and led to the polymer in one reaction step. While this kind of one-pot synthetic method is already well-known for preparation of biaryl compounds[78-80], only a single report on one-pot Suzuki polycondensation was reported so far by A. Izumi[81]. In this work, the method was optimized and successfully applied for the preparation of DPP homopolymer. The first stage of the reaction was carried out using 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole (**HDPP**) and bis(pinacolato)diboron in the presence of palladium(II) acetate (Pd(OAc)$_2$) and potassium acetate. The weak base and the non-ligand catalysis will restrain the reaction in the Ishiyama-Miyaura state[67]. During this process, the **HDPP** could be transformed to **HDPPB**. This transformation could be monitored accurately by thin layer chromatography (TLC) (silica, dichloromethane). After all the **HDPP** reacted, another equimolar amount of HDPP and the required amounts of the tetrakis(triphenylphosphine)palladium catalyst and the strong base potassium carbonate were added to the reaction mixture. The reaction condition was then changed to the standard Suzuki polycondensation reaction. Finally, **P-DPP** was obtained with a molecular weight up to 8.7 kDa.

Carbazole, triphenylamine and benzothiadiazole units are very useful building blocks for the preparation of conjugated polymers. They are widely used in light emitting polymers, electrochromic polymers and polymer field-effect transistors[68,72,74,75,82-86]. The conjugated copolymer **P-DPP-CBZ** was prepared from **HDPP** and 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexyl-carbazole. Toluene was chosen as the solvent to reach a high reaction temperature. At first, tetrakis(triphenylphosphine)palladium(0) was used as catalyst, but later on the combination of palladium(II) acetate (Pd(OAc)$_2$) and tris(o-tolyl)phosphine was found more efficient for giving high molecular weights. This is probably due to the ligand tris(o-tolyl)phosphine, which is used to prevent the incorporation of the phosphor into the polymer main chain. In all reactions, tetrabutylammonium bromide was used as the phase-transfer catalyst. Furthermore this salt also worked as the bromine source[87,88]. After the reaction, the diluted reaction solution was passed through a celite column to remove the residual catalyst and then the polymers were precipitated in acetone or ethanol to form red powders after drying.

The preparation of copolymer **P-DPP-TPA** was rather complicated. Two different strategies were applied: firstly **HDPP** and 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-triphenylamine were used. The resulting polymer exhibited a molecular weight of only 3.7 kDa. Alternatively, **HDPPB** and 4,4′-dibromotriphenylamine were reacted and a polymer

with molecular weight of 7.4 kDa was obtained. The UV absorption of the polymer from the second route was more red-shifted indicating more extended π-conjugation along the polymer main chain. The difference might be caused by the low yield of boronic ester of triphenylamine, which made the purification of the compound very difficult.

The preparation method of **P-DPP-BTZ** and **P-CBZ-TPA** was similar to that of **P-DPP-CBZ** except for the use of the different monomers. For **P-DPP-BTZ**, **HDPPB** and 4,7-dibromo-2,1,3-benzothiadiazole were used. For **P-CBZ-TPA**, 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexyl-carbazole and 4,4′-dibromotriphenylamine were used.

2.1.3. Characterization of the polymers

GPC

The polymers received are all very soluble in common organic solvents such as chloroform, toluene and THF. Molecular weights were determined upon size exclusion chromatography (SEC) using a Waters/Millipore UV detector 481 and an SEC column combination (Latek/styragel 50/1000) nm pore size). All measurements were carried out in tetrahydrofuran at 45 °C. The columns were calibrated versus commercially available polystyrene standards. The weight average molecular weight and the polydispersity of the polymers are listed in Table 2.1. The polymers exhibit molecular weights between 5.0 and 16.5 kDa.

Table 2.1 Molecular weight and polydispersity of the polymers prepared via Suzuki coupling.

	Mw (kDa)	Polydispersity
P-DPP	8.7	1.6
P-DPP-CBZ	16.5	2.2
P-DPP-TPA	7.4	1.9
P-DPP-BTZ	7.0	1.7
P-CBZ-TPA	5.0	1.3

¹H-NMR

The proton NMR spectra of monomer **HDPP** and various polymers were measured in chloroform-D. They are shown in Figure 2.5. For all DPP containing polymers, the signals of the hexylated lactam group of DPP appear in the region from 0.7 ppm to 1.8 ppm, corresponding to the signals at 0.85 ppm, 1.23 ppm and 1.85 ppm for the monomer **HDPP**.

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The signal of the α-methylene unit directly attached to the N-atom of the lactam unit appears around 3.8 ppm for all DPP containing polymers. The signal for the phenyl rings connected with the DPP chromophore is generally separated in the polymer spectra. The only exception is **P-DPP-BTZ**, in which the signals for the phenyl rings were overlapped with the signal for the benzothiadiazole group. In case of **P-DPP-CBZ**, the α-methylene unit directly attached to the N-atom of the carbazole unit appears around the position 4.2 ppm. The signal of methylidyne group appears at 2.1 ppm for **P-DPP-CBZ**. For **P-DPP-CBZ** and **P-DPP-TPA**, there are several signals overlapped in the region of the aromatic protons. Regarding **P-DPP-TPA**, the characteristic signals are the peaks between 6.9 ppm to 7.2 ppm belonging to the aromatic protons adjacent to the amine group. For polymer **P-CBZ-TPA**, there is no DPP unit in the polymer. However, compared with **P-DPP-CBZ** and **P-DPP-TPA**, the signals at 2.1 ppm (methylidyne group), 4.2 ppm (α-methylene group), 6.9 ppm to 7.2 ppm (aromatic protons adjacent to the amine group) clearly elucidate the structure of the polymer. There is a small peak around 3.9 ppm to 4.0 ppm in some polymers such as **P-DPP** and **P-DPP-BTZ**. It probably originates from the O-alkylated DPP formed during the polycondensation reaction.
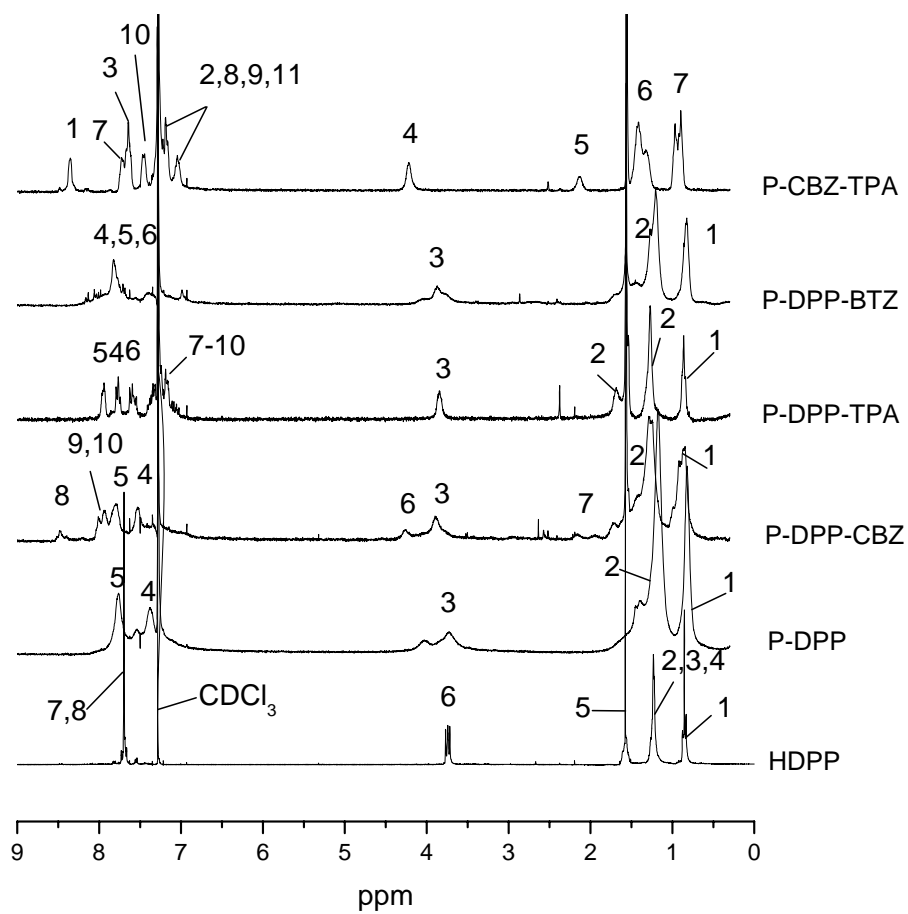
Figure 2.5 The proton NMR of **HDPP**, **P-DPP**, **P-DPP-CBZ**,

P-DPP-TPA, **P-DPP-BTZ** and **P-CBZ-TPA** in CDCl₃

(The structures of the monomer and polymer are shown in the following page)
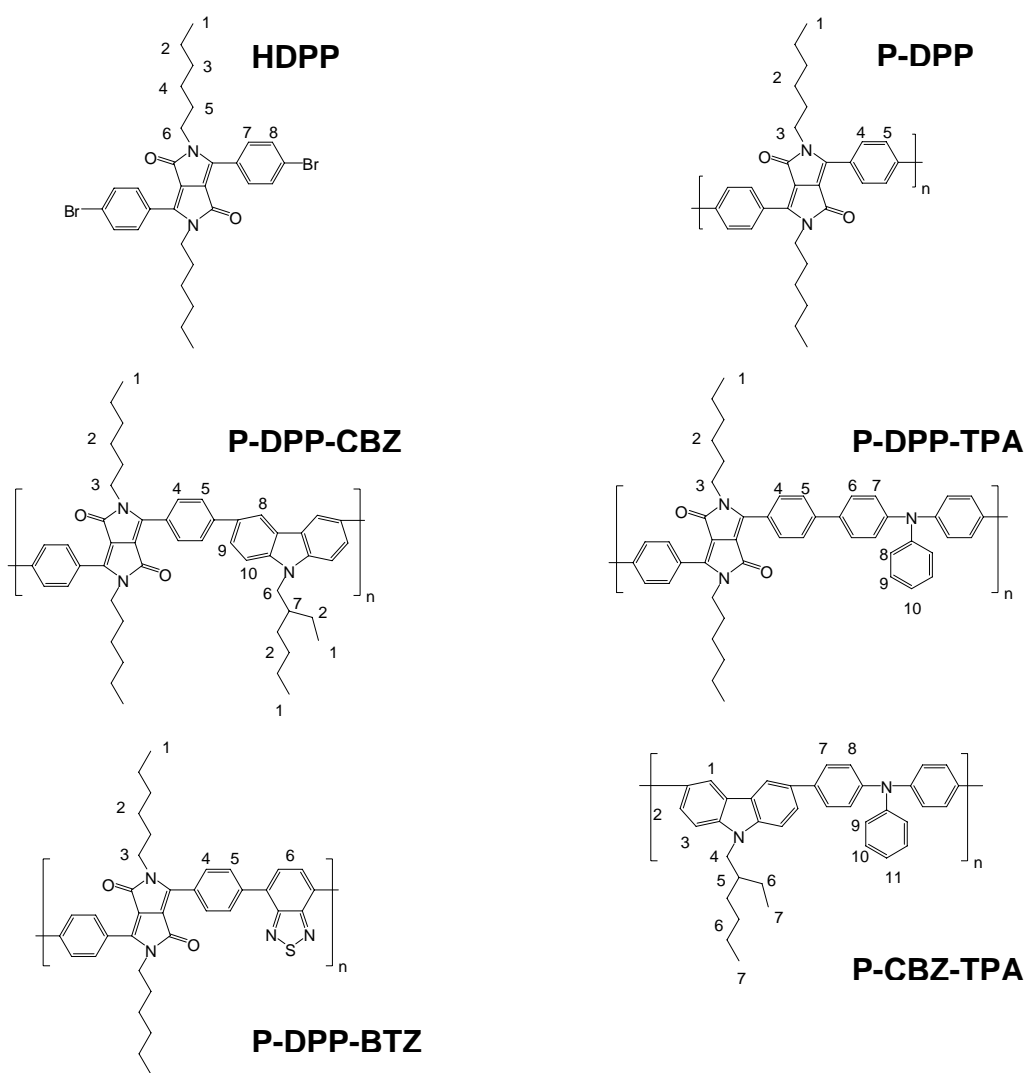
Figure 2.5 continued.

Optical properties

All the synthesized DPP containing polymers are red powders, while the non-DPP-containing polymer **P-CBZ-TPA** is a white powder. After being dissolved in chloroform or toluene, the DPP polymers form red solutions; the **P-CBZ-TPA** solution is colorless. The photographs are shown in Figure 2.6.

| **HDPP** | **P-DPP** | **P-DPP-CBZ** | **P-DPP-TPA** | **P-DPP-BTZ** | **P-CBZ-TPA** |

Figure 2.6 Photographs of **HDPP** and various polymers prepared via Suzuki polycondensation in normal (upper) and luminescent state (lower).

The UV/vis absorption spectra and fluorescence spectra of the polymers were measured in chloroform (**P-DPP**, **P-DPP-CBZ**, **P-DPP-BTZ**) or toluene (**P-DPP-TPA**, **P-CBZ-TPA**). For the DPP containing polymers, the maximum absorption peak in the visible region is found in the wavelength range from 506 to 528 nm. Compared with the monomer **HDPP**, the absorption is bathochromically shifted from 30 to 52 nm due to the extension of the π-conjugated system. The maximum emission wavelengths of DPP containing polymers range from 585 to 631 nm. The polymer **P-DPP** exhibits a Bordeaux-red emission colour, the fluorescence maximum appears at 631 nm (which is red-shifted by 87 nm compared with the monomer **HDPP**). From this behaviour a Stokes-shift of 103 nm can be derived, the largest value ever found for DPP-containing polymers prepared via Suzuki polycondensation. As for

polymer **P-CBZ-TPA**, it is a blue emitting material with the maximum emission being at 409 nm. The UV/vis absorption and photoluminescence spectra of these polymers are shown in Figure 2.7.
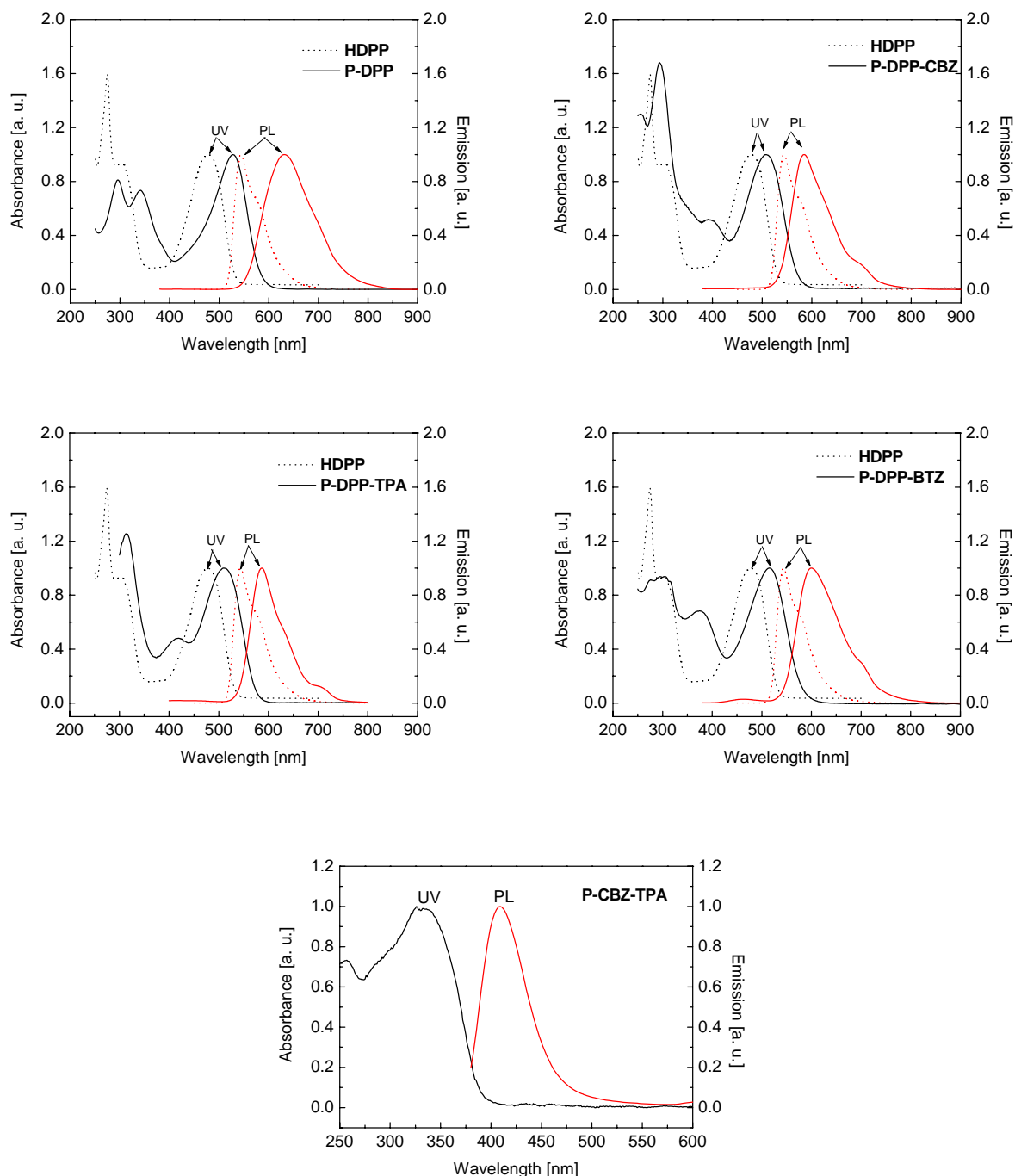
Figure 2.7 UV/vis absorbance and photoluminescence spectra of the polymers prepared via Suzuki coupling polycondensation. The excitation wavelength is 350 nm. Polymer **P-DPP-TPA** and **P-CBT-TPA** are measured in toluene. Other samples are measured in chloroform. For comparison, the spectra of the corresponding monomer HDPP are also shown.

Some DPP containing polymers were found to be highly luminescent. The photoluminescence quantum yield of **P-DPP-TPA** is 85% (excited at 400 nm in toluene, and calculated by compared with Rhodamine 6G in ethanol, Φ_f=0.95), which is the highest value among all reported DPP containing conjugated polymers. The photoluminescence quantum yield of **P-DPP-CBZ** is 46%, which is also quite a good value. The quantum yield of **P-DPP** and **P-DPP-BTZ** is only 13% and 19%, respectively. The lower quantum yields probably originate from the presence of O-alkylated DPP units in the polymer chain which was detected by proton NMR spectra. **P-CBZ-TPA** has a very high photoluminescence quantum yield of 91%. The solid film absorption and luminescence of the DPP containing polymer has also been measured and the spectra are shown in Figure 2.8.
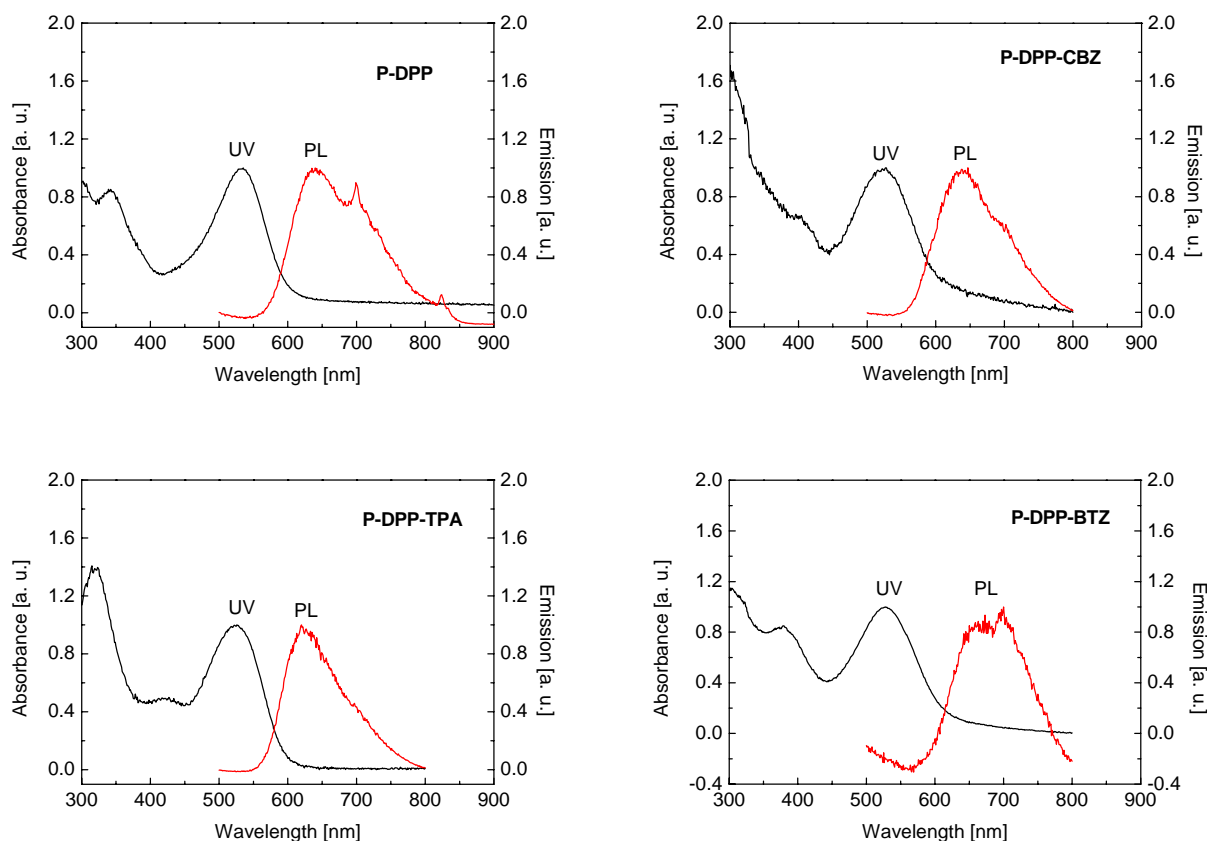
Figure 2.8 UV/vis absorbance and photoluminescence spectra of solid films of the DPP containing polymers prepared via Suzuki coupling. The excitation wavelength is 350 nm.

The optical data were collected in Table 2.2. UV and fluorescence spectra of polymer films cast from solution are very similar to the solution spectra with the exception that the absorption and emission maxima are red-shifted by 7 to 21 nm. The bathochromic shift is

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probably caused by the π-π stacking of the molecules, which was first observed in DPP pigments[15]. The absorption maximum is between 526 and 535 nm for the polymers. The maximum emission wavelength for **P-DPP**, **P-DPP-CBZ**, **P-DPP-TPA** and **P-DPP-BTZ** are 640 nm, 638 nm, 621 nm and 665 nm, respectively.

Table 2.2 Optical data of polymers prepared via Suzuki coupling in solution and solid film.

	λ_{max}(nm) solution	λ_{em}(nm) solution	λ_{max}(nm) film	λ_{em}(nm) film	Φ_f
HDPP	476	533	-	-	0.90
P-DPP	528	631	535	640	0.13
P-DPP-CBZ	506	585	527	638	0.46
P-DPP-TPA	511	587	526	621	0.85
P-DPP-BTZ	515	600	528	665	0.19
P-CBZ-TPA	326	409	-	-	0.91

*The excitation wavelength is 350 nm. Polymers **P-DPP-TPA** and **P-CBZ-TPA** were measured in toluene, others were measured in chloroform. The photoluminescence quantum yields were measured at an excitation wavelength of 400 nm (for all DPP containing compounds) or 350 nm (for **P-CBZ-TPA**), and calculated by comparing with Rhodamine 6G in ethanol (Φ_f=0.95).*

Electrochemical Characterization

Cyclic voltammograms of the polymers were recorded using a potentiostat PG390 from Heka Company. A thin film of the polymer was cast on an ITO electrode and cycled in CH_3CN containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte salt. Counter and reference electrodes were platinum. The voltage data were calculated for the standard calomel electrode (SCE), the scan rate was 25 mVs^{-1}. The measurement was carried out at room temperature.

The cyclic voltammetry (CV) data are compiled in Table 2.3. The HOMO and LUMO levels were calculated using the equations[89]

$$- E_{HOMO} = E_{onset(ox)} + 4.4 \text{ [eV]}$$

and

$$- E_{LUMO} = E_{onset(red)} + 4.4 \text{ [eV]}.$$

In Table 2.3, the HOMO and LUMO levels are listed. Based on the HOMO/LUMO calculation, the band gap can be determined.

$$- E_{electro} = E_{HOMO} - E_{LUMO} \ [eV].$$

Alternatively, the band gaps can also be calculated from the onset of the optical absorption using the equation

$$E_{opt} = 1240 \ / \ \lambda_{onset} \ [eV].$$

As shown in Table 2.3, the band gap values from the optical measurements match those from the electrochemical experiment well.

Table 2.3 Band gap data of different polymers prepared via Suzuki coupling

Polymer	Absorption of film λ_{onset}(nm)	E_{opt} (eV)/$E_{electro}$ (eV) band gap	$E_{onset(ox)}$ (V) {E_{HOMO} (eV)}	$E_{onset(red)}$ (V) {E_{LUMO} (eV)}
P-DPP	603	2.06/1.93	0.95{-5.35}	-0.98{-3.42}
P-DPP-CBZ	615	2.02/1.90	0.93{-5.33}	-0.97{-3.43}
P-DPP-TPA	596	2.08/1.82	0.97{-5.37}	-0.85{-3.55}
P-DPP-BTZ	617	2.01/1.77	0.94{-5.34}	-0.83{-3.57}
P-CBZ-TPA	-	-/-	0.54{-4.94}	-{-}

Band gap (E_{opt}) measured at the onset of electronic absorption of the polymer film (E_{opt} =1240/λ_{onset} eV). HOMO-LUMO gap according to the equation: -E_{LUMO}=$E_{onset(red)}$+4.4 eV and - E_{HOMO}=$E_{onset(ox)}$+4.4 eV, where $E_{onset(ox)}$ and $E_{onset(red)}$ are the onset potentials for the oxidation and reduction processes of polymer thin films vs. SCE.

The CV-diagrams are shown in Figure 2.9. All DPP containing polymers exhibit quasi-reversible oxidative processes with onset potential $E_{onset(ox)}$ between 0.93 V and 0.97 V(vs. SCE). The similar oxidation potentials indicate that the first oxidation step occurred at the DPP chromophore. The oxidation onset potential of polymer **P-CBZ-TPA** is only 0.54 V (vs. SCE). For all polymers, the reduction is irreversible.
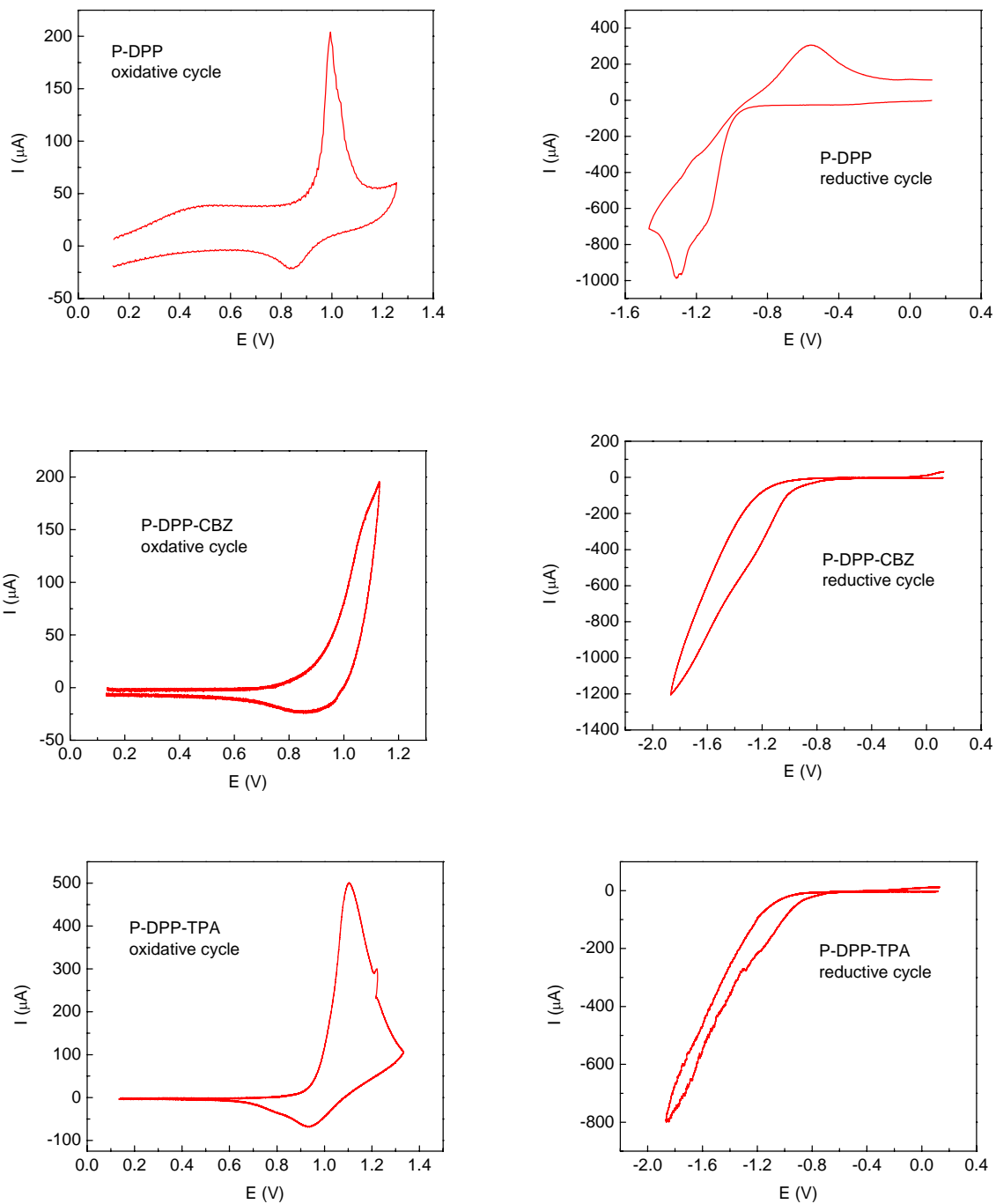
Figure 2.9 Cyclic voltammograms of **P-DPP**, **P-DPP-CBZ**, **P-DPP-TPA**, **P-DPP-BTZ** and **P-CBZ-TPA**. Scan rate: 25 mVs^{-1}, T = 20 ^{0}C. Electrolyte solution: 0,1 M TBAPF$_6$ in acetonitrile.
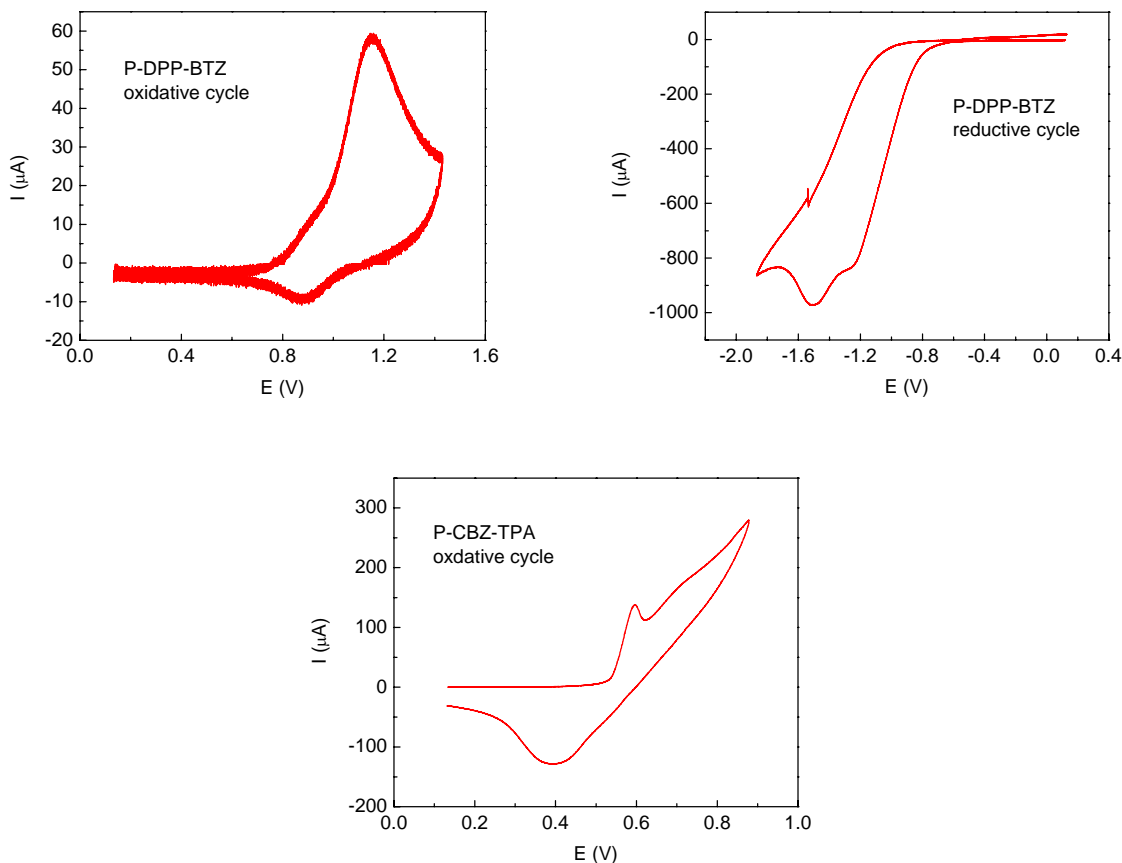
Figure 2.9 continued

The electrochromic properties of the polymers were investigated through spectroelectrochemical experiments. Unfortunately, the colours of DPP containing polymer can be changed only at very high oxidation potentials. The change is accompanied by a destruction of the DPP chromophore. As a consequence, the colour change becomes irreversible. The polymers can not be switched back to the original state upon the dedoping process. Only **P-CBZ-TPA** can change and restore its colour during the doping and dedoping processes due to its very low oxidation potential.

The spectroelectrochemical experiments of a solid film of **P-CBZ-TPA** were carried out in clean CH_3CN solution with $TBAPF_6$ as electrolyte. The UV/vis absorption at different oxidation potentials are shown in Figure 2.10. Upon oxidation, new absorption peaks originating from radical cations (polarons) and dications (bipolarons) appear at 450 nm and over 1000 nm respectively. There is a very clear colour change after the oxidation potential of 0.53 V (vs. SCE) has been reached. The colour of the polymer film changes from colorless to green (see the photographs in Figure 2.10).
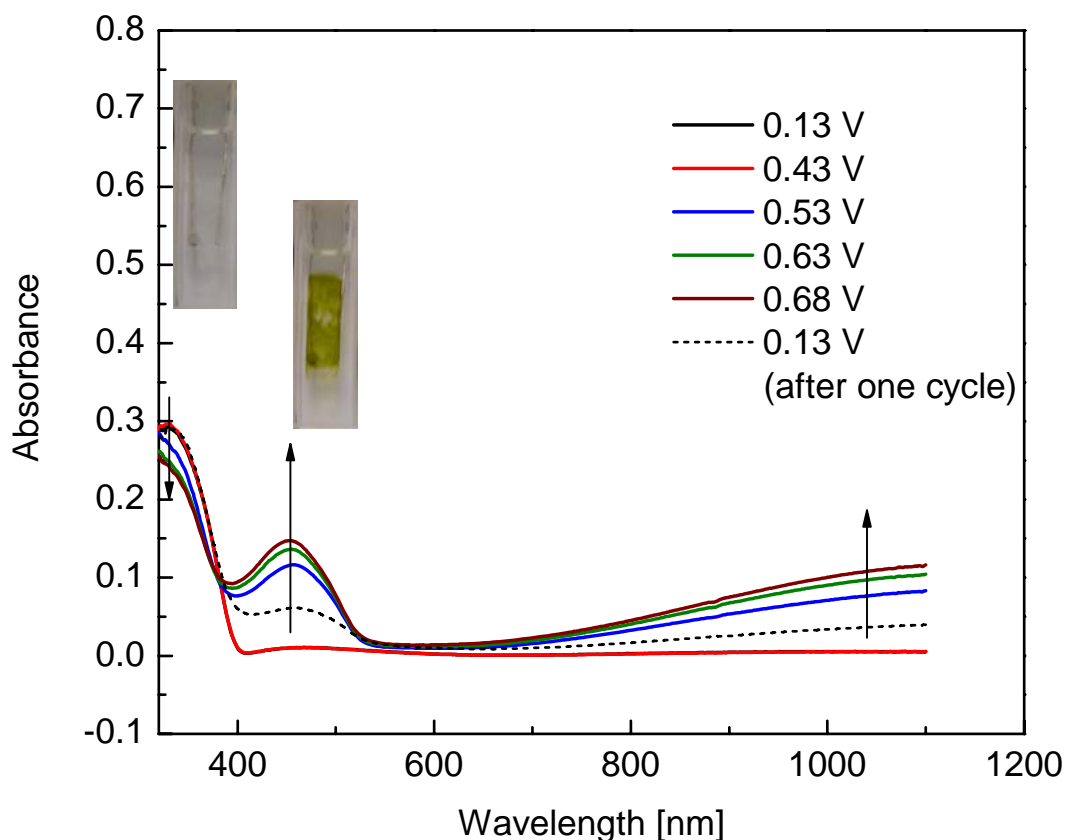
Figure 2.10 Spectroelectrochemical study of **P-CBZ-TPA** film on ITO-coated glass anode in 0.1M TBAPF$_6$ in CH$_3$CN. (Voltage calculated versus SCE).

The origin of this kind of colour change has been described in a recent publication[48]. In the neutral (insulating) state, the conjugated polymer shows semiconducting behaviour with an energy gap between the valence band (HOMO) and the conduction band (LUMO). Upon electrochemical doping ("p-doping" for oxidation and "n-doping" for reduction), the band structure of the neutral polymer is modified, generating lower energy intraband transitions and creating charged carriers (polarons and bipolarons), which are responsible for the increased conductivity and optical modulation. The electrochromic process is quite stable and can be repeated many times in air without special treatment of the solution. The absorption of the neutral film after the first cycle is shown in Figure 2.10 (dashed line). During the oxidation process, some oxidized polymer may enter the solution. This probably is the origin of the diminished absorption in the visible region.

2.2. Stille coupling polycondensation

Stille coupling is a Pd-catalysed reaction for carbon–carbon (C–C) bond formation. Aryl stannanes serve as the active materials to react with aryl halides (Scheme 2.6).

$$R'—X \quad + \quad RSnBu_3 \quad \xrightarrow{\text{Pd-Cat}} \quad R'—R \quad + \quad XSnBu_3$$
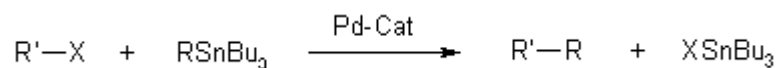
Scheme 2.6 Stille coupling reaction.

The generally accepted mechanism of Stille coupling is shown in Figure 2.11.
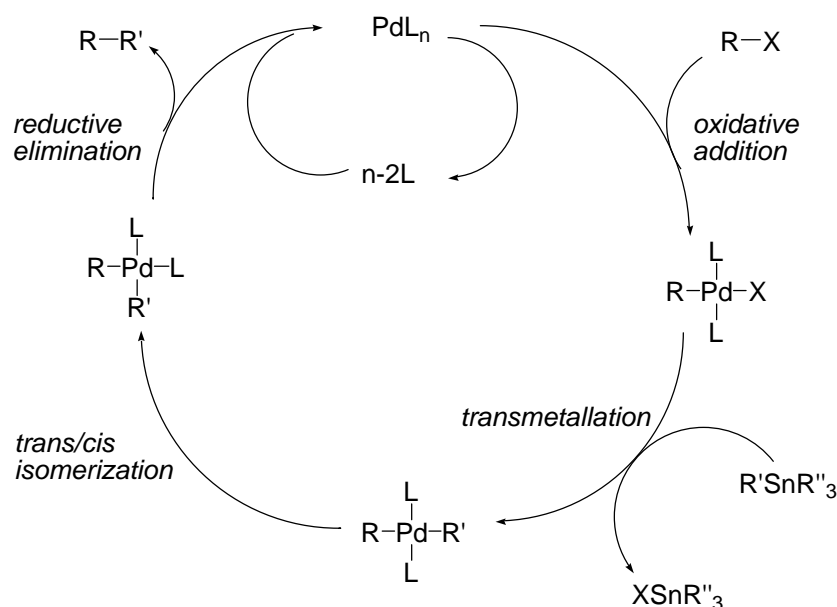
Figure 2.11 Mechanism of Stille coupling

The active catalyst is believed to be a 14-electron palladium(0) complex, which can be generated from a suitable palladium(0) precursor such as $Pd(PPh_3)_4$. Alternatively, the active palladium(0) catalyst can be formed by reduction of a suitable palladium(II) precursor such as $(Ph_2P)_2PdCl_2$. Palladium(0) complexes are nucleophilic and they react readily with organic electrophiles in an oxidative addition reaction to produce a 16-electron palladium(II) intermediate $RPdL_2X$. The electrophilic component RX in the reaction is frequently an organohalide or organotriflate compound. The next step occurring in the catalytic cycle of the Stille reaction is a transmetallation reaction. In the transmetallation step one group from the organotin reagent transfers to the palladium(II) intermediate whilst the halide or triflate group becomes associated with the tin of the organostannane. Fortunately, alkyl groups migrate from tin to palladium at the slowest rate. Mixed organostannanes that contain three spectator

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methyl or butyl groups can therefore be used so that exclusive transfer of a more chemically complex group such as a vinyl or aryl moiety can occur. The transmetallation step is the rate-determining step in the catalytic cycle. In the final step of the catalytic cycle the cross-coupled product is expelled from the palladium(II) intermediate and the active palladium(0) catalyst is regenerated.

2.2.1. Polymerization

Since Stille coupling was found in 1970s, there are several reviews discussing the reaction conditions in the synthesis of small molecules[56-58]. The polymerization process was discussed by Bao and Yu[30]. Stille coupling was found very efficient for heterocyclic aromatic compounds, especially for thiophene and its derivatives. In this work, thiophene containing stannanes were prepared.
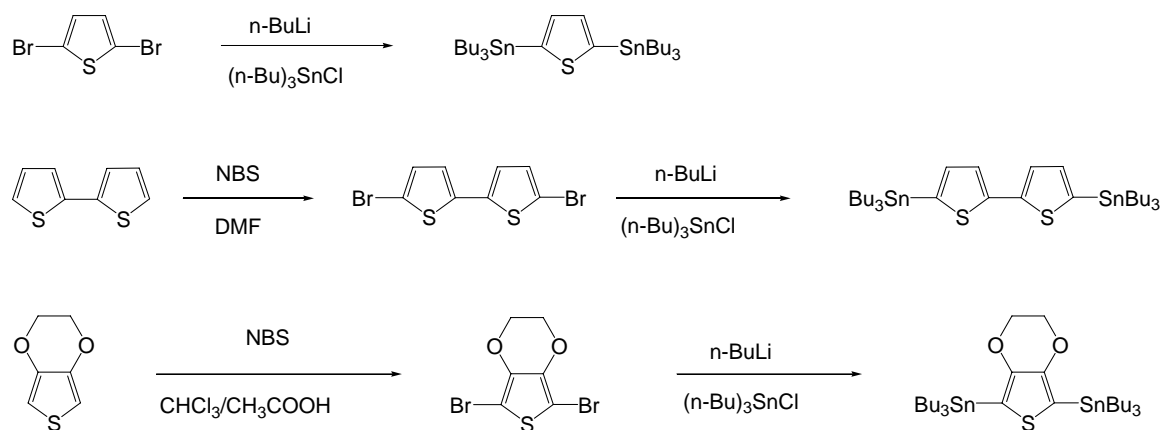
Scheme 2.7 Preapartion of monomers for Stille coupling.

The syntheses of 2,5-bis(tributylstannyl)thiophene[90,91], 5,5′-bis(tributylstannyl)bithiophene[91] and 2,5-bis(tributylstannyl)-3,4-ethylenedioxythiophene[92-95] described in Scheme 2.7 are reported in the literature. However, in this work all stannanes were prepared in a two step process: bromination of the thiophene derivative and successive treatment with butyllithium and tributyltin chloride, respectively. The method of direct lithiation of the non-brominated thiophene precursors was not applied, because in this route the separation of mono- and bis-substituted stannanes is quite difficult. The two step process assures the purity of the monomers and this is crucial for the polymerization reaction.

The Stille polycondensation reactions performed in this thesis are shown in Scheme 2.8.
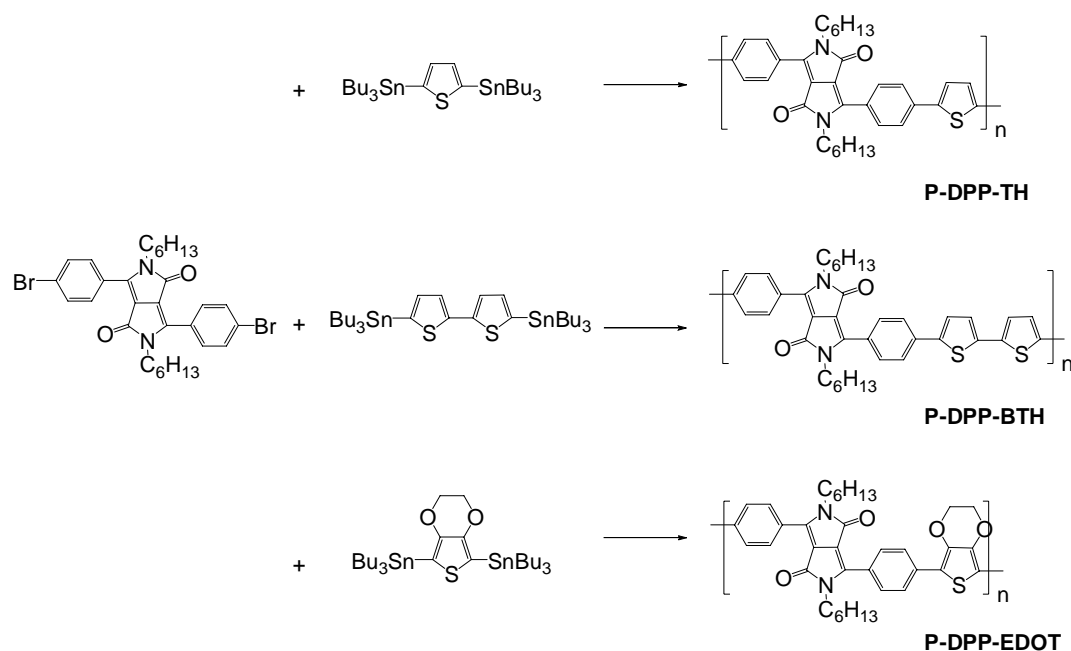
Scheme 2.8 Scheme of Stille polycondensation.

The polymers **P-DPP-TH**, **P-DPP-BTH** and **P-DPP-EDOT** were synthesized upon Stille coupling polycondensation. For the coupling, tetrahydrofuran was chosen as the solvent, because it previously turned out to be well suited for this type of reaction[30]. Tetrakis(triphenylphosphine)palladium(0) was used as catalyst, because it is stable enough to withstand the prolonged heating time of 48 h. After the reaction, the polymers were precipitated in acetone and formed dark powders after drying.

2.2.2. Characterization of the polymers

GPC

The polymers were very soluble in chloroform and toluene, and slightly less soluble in THF. However, after ultrasonic treatment, a complete dissolution in THF was possible. The weight average molecular weight and the polydispersity of the polymers are listed in Table 2.4. The polythienylenes exhibit molecular weights between 6.7 and 12 kDa.

Table 2.4 Molecular weight and polydispersity of polymers prepared via Stille coupling.

	Mw (kDa)	Polydispersity
P-DPP-TH	12.2	2.2
P-DPP-BTH	9.1	1.7
P-CBZ-BTH	6.7	1.5

¹H-NMR

The proton NMR spectra of the polymers were measured in chloroform-D and are shown in Figure 2.12.
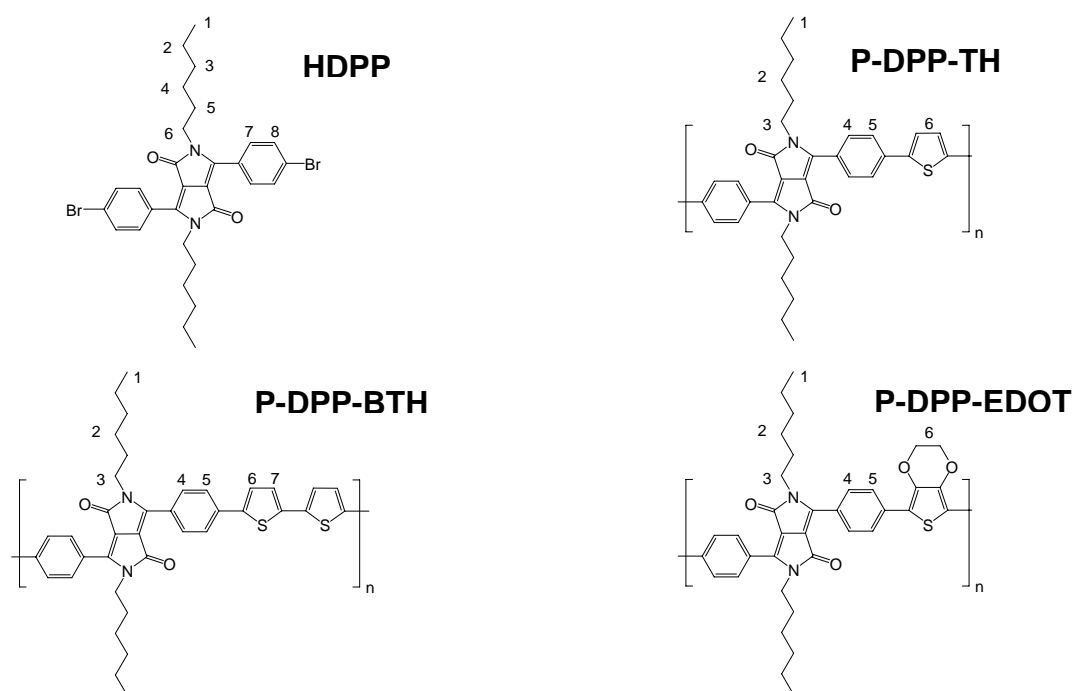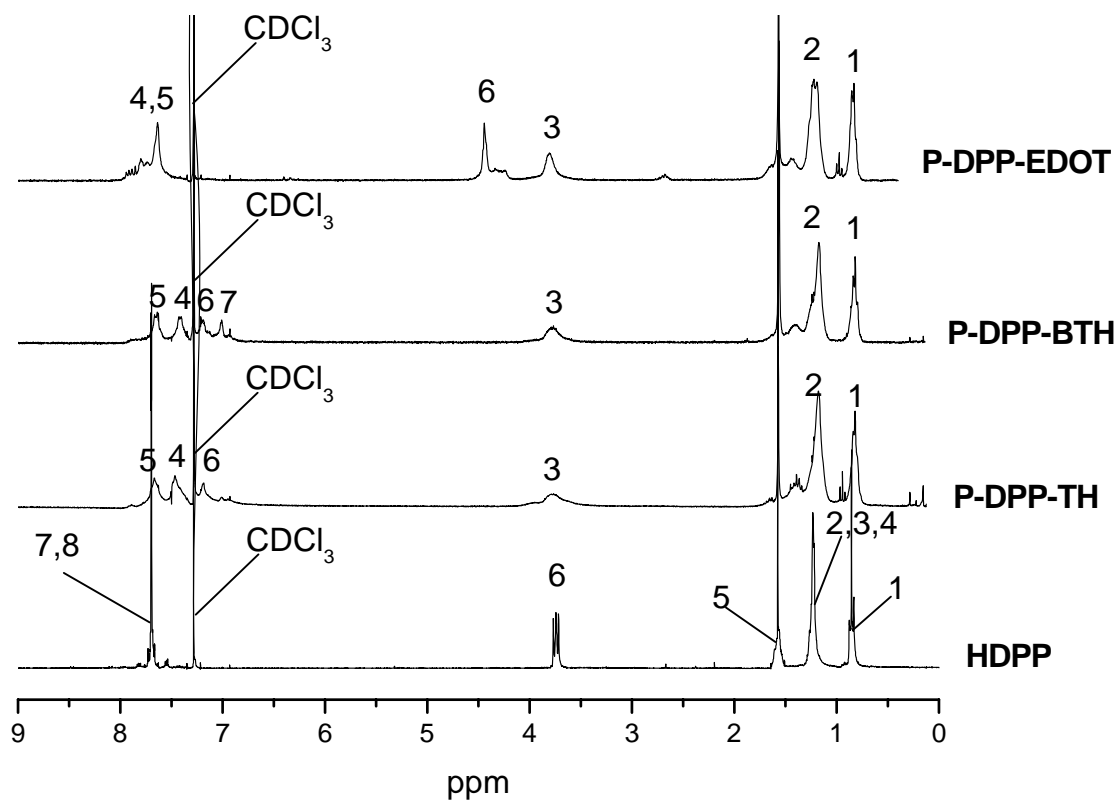
Figure 2.12 Proton NMR spectra of **HDPP**, **P-DPP-TH**, **P-DPP-BTH** and **P-DPP-EDOT**

All spectra show signals of the phenylene protons at about 7.6 ppm, and signals of the hexylated lactam group of DPP in the region from 0.7 to 1.5 ppm. The signal of the methylene group adjacent to the lactam N atom appears at 3.7 ppm. The characteristic signal of the thienylene protons of **P-DPP-TH** occurs at 7.2 ppm, and the signal of the dioxyethylene group in **P-DPP-EDOT** is observed at about 4.4 ppm.

Optical properties

The DPP-polythienylenes were obtained as black powders. After dissolution in chloroform, the polymers formed bright red purple solutions. The photographs are shown in Figure 2.13. The UV/vis absorption spectra and fluorescence spectra of the DPP-thienylene polymers were measured in chloroform. The maximum absorption peak in the visible range is found in the wavelength range from 545 to 560 nm. Compared with monomer **HDPP**, the absorption is bathochromically shifted from 75 to 90 nm due to the extension of the π-conjugated system. In addition, some charge transfer from the easily oxidizable ethylenedioxythiophene and bithiophene units to the electron accepting DPP chromophore might contribute to the shift. The maximum emission wavelength of the polymers ranges from 616 to 640 nm as indicated in Figure 2.14.

| **HDPP** | **P-DPP-TH** | **P-DPP-BTH** | **P-DPP-EDOT** |
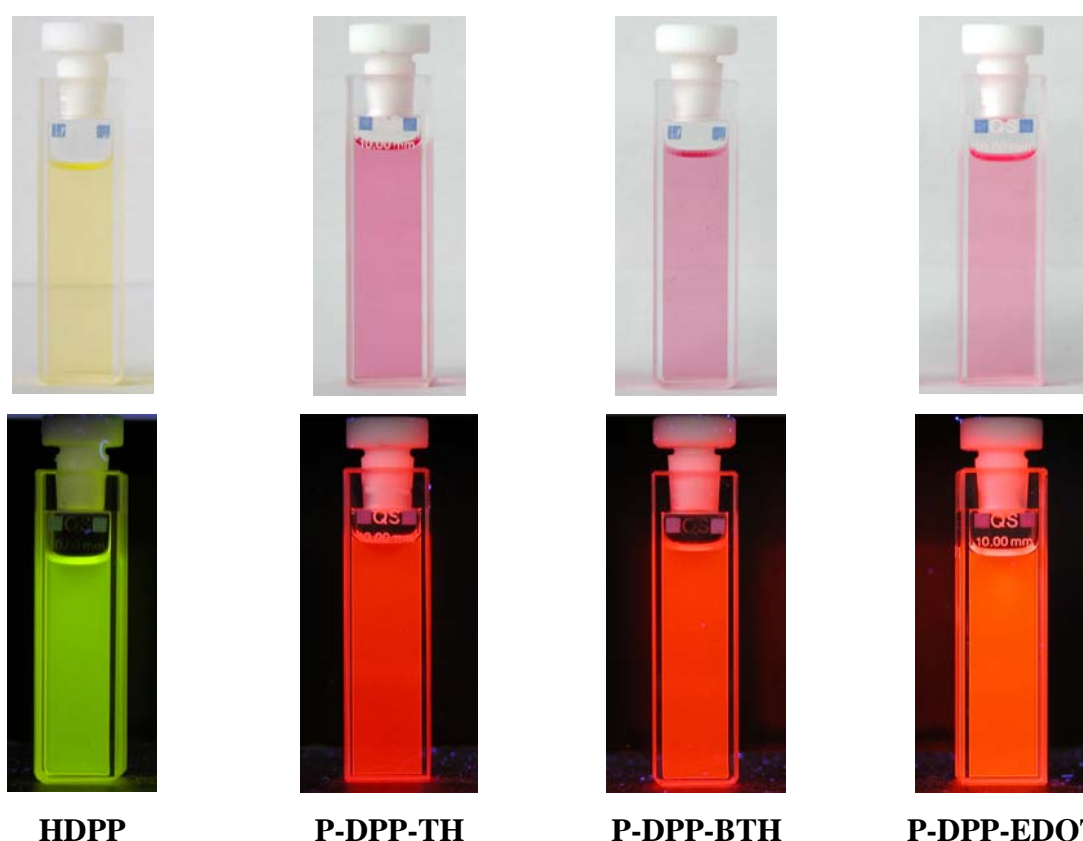
Figure 2.13 Photographs of **HDPP** monomer and corresponding polymers prepared via Stille polycondensation in normal (upper) and luminescent state (lower).
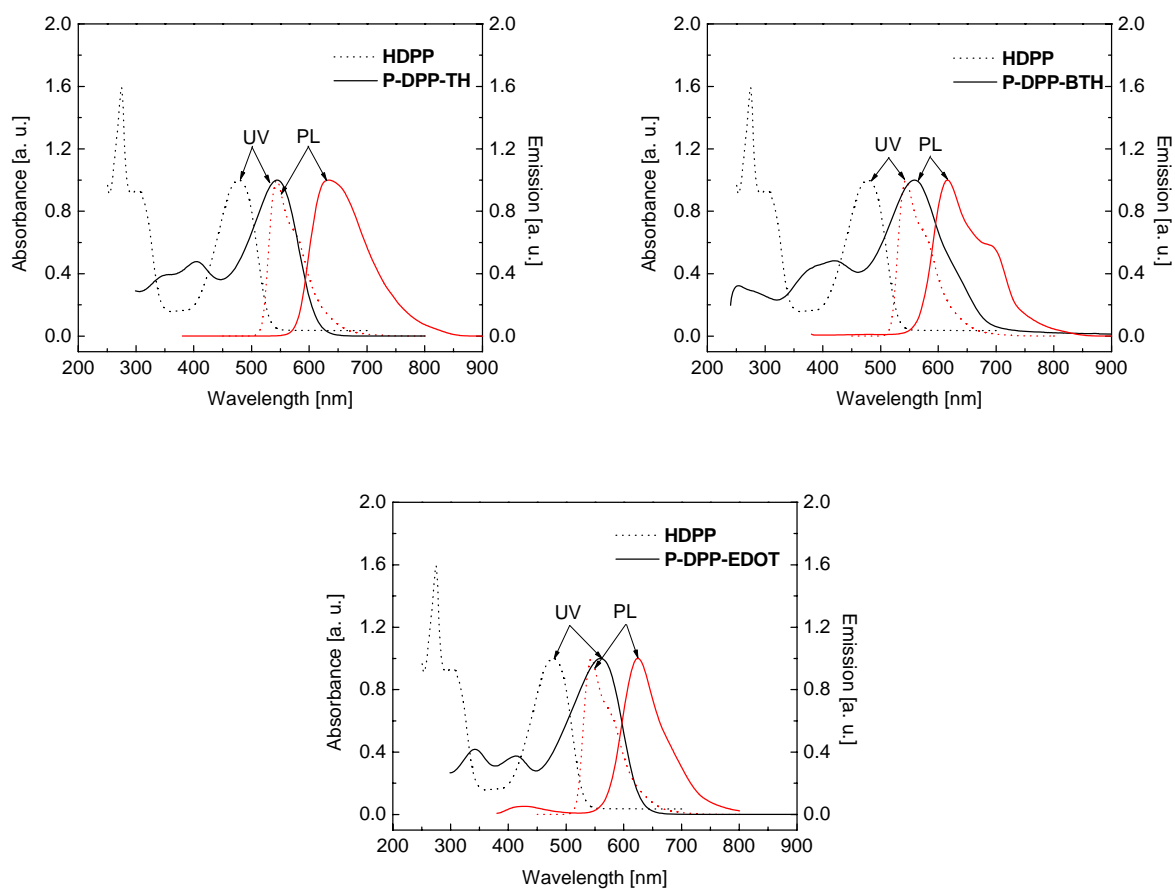
Figure 2.14 UV/vis absorbance and photoluminescence spectra of the polymers prepared via Suzuki coupling polycondensation. The excitation wavelength is 350 nm. Solvent: CHCl$_3$

Unfortunately, the DPP polythienylenes prepared upon Stille coupling were found to exhibit relatively low photoluminescence quantum yields. The highest quantum yield was found for **P-DPP-EDOT**. However, the value is only 36% (excited at 400 nm in chloroform and calculated by comparison with Rhodamine 6G in ethanol, Φ_f=0.95). The values for **P-DPP-TH** and **P-DPP-BTH** are 12% and 13%, respectively. It may also be caused by the presence of tin and residual catalyst in the polymer.
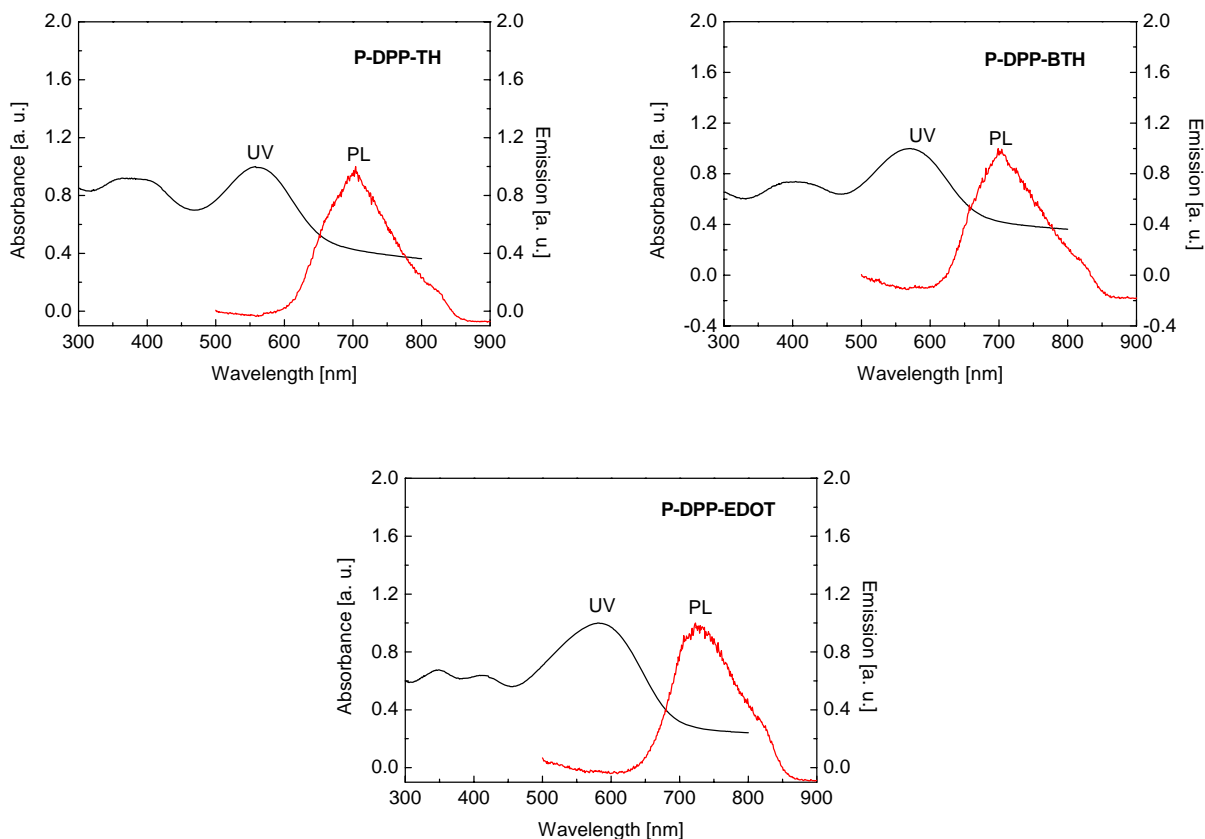
Figure 2.15 UV/vis absorbance and photoluminescence spectra of solid films of DPP-polythienylenes. The excitation wavelength is 350 nm.

Films of the polymers cast from chloroform solution are bluish purple with absorption maxima between 558 and 581 nm (Figure 2.15). Compared with the solution spectra, the maxima are red-shifted by 12 to 21 nm (see Table 2.5). The fluorescence maxima of the polymer films occur between 699 and 723 nm. They are red-shifted with regard to the fluorescence maxima in solution from 70 to 100 nm, probably due to interaction moments of nearest-neighbour molecules in the solid state[24].

Table 2.5 Optical data of polythienylenes in solution and as solid film.

	λ_{max}(nm) solution	λ_{em}(nm) solution	λ_{max}(nm) film	λ_{em}(nm) film	Φ_f
HDPP	476	533	-	-	0.90
P-DPP-TH	545	635	558	704	0.12
P-DPP-BTH	558	616	570	699	0.13
P-DPP-EDOT	560	624	581	723	0.36

Excitation wavelength is 350 nm. Polymers were measured in chloroform. The photoluminescence quantum yields were measured at an excitation wavelength of 400 nm and calculated by comparison with Rhodamine 6G in ethanol (Φ_f=0.95).

Electrochemical Characterization

Cyclic voltammograms of the polymers were carried out under the same conditions as described before in section 2.1.3. The corresponding CV-diagrams are shown in Figure 2.16. CV-data are compiled in Table 2.6. **P-DPP-TH**, **P-DPP-BTH** and **P-DPP-EDOT** exhibit quasireversible oxidative processes with onset potentials $E_{onset(ox)}$ at 0.86, 0.75 and 0.72 V (vs. SCE), respectively. For all polymers, the reduction is irreversible. The HOMO and LUMO as well as the optical band gaps are also listed in Table 2.6.
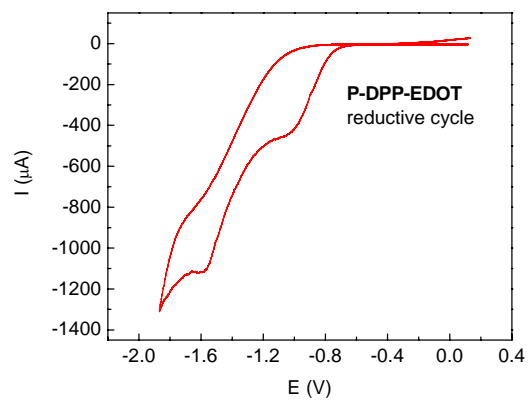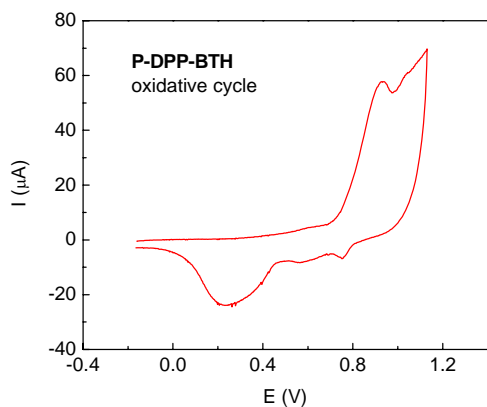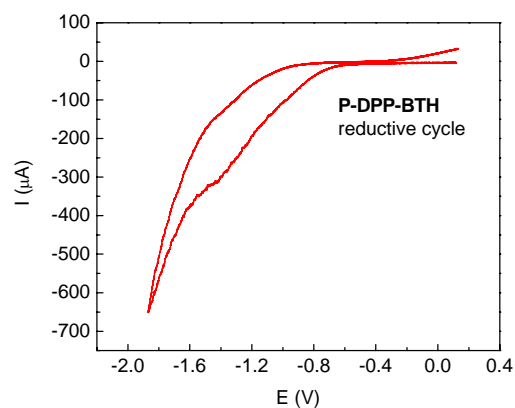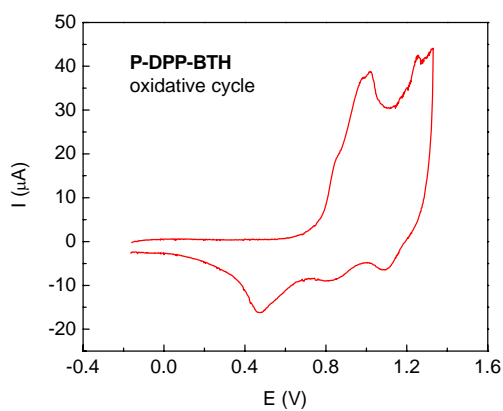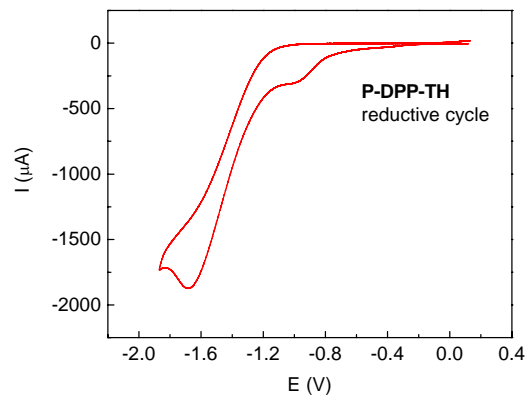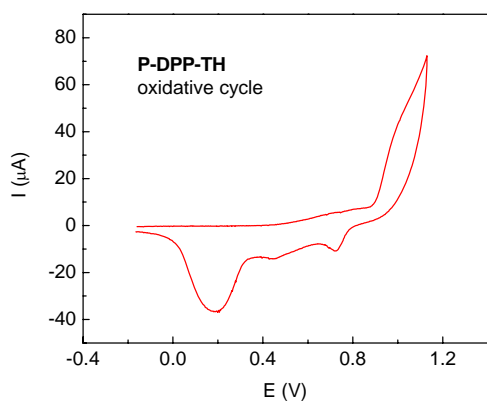
Figure 2.16 Cyclic voltammograms of **P-DPP-TH**, **P-DPP-BTH** and **P-DPP-EDOT**. Scan rate: 25 mVs^{-1}, T = 20 ^{0}C. Electrolyte solution: 0.1 M TBAPF$_6$ in acetonitrile.

Table 2.6 Band gap data of polymers prepared via Stille coupling

Polymer	Absorption of film λ_{onset}(nm)	E_{opt} (eV)/$E_{electro}$ (eV) band gap	$E_{onset(ox)}$ (V) {E_{HOMO} (eV)}	$E_{onset(red)}$ (V) {E_{LUMO} (eV)}
P-DPP-TH	711	1.74/1.57	0.86{-5.26}	-0.71{-3.69}
P-DPP-BTH	759	1.63/1.47	0.75{-5.15}	-0.72{-3.68}
P-DPP-EDOT	757	1.64/1.47	0.72{-5.11}	-0.75{-3.65}

Band gap (E_{opt}) measured at the onset of electronic absorption of the polymer film (E_{opt} =1240/λ_{onset} eV). HOMO-LUMO gap according to the equation: $-E_{LUMO}=E_{onset(red)}+4.4$ eV and $-E_{HOMO}=E_{onset(ox)}+4.4$ eV, where $E_{onset(ox)}$ and $E_{onset(red)}$ are the onset potentials for the oxidation and reduction processes of polymer thin films vs. SCE.

As shown in Table 2, the band gap values from the optical and electrochemical measurements match very well. Among the polymers, **P-DPP-BTH** and **P-DPP-EDOT** have the lowest band gap of 1.54 ± 0.09 eV. The bandgap and oxidation onset potential of the polythienylenes are significantly lower than that of the polymers synthesized via Suzuki coupling. The low oxidation potential indicates that the first oxidation step occurred at the thiophene ring of the polymers.

Although the thiophene containing DPP conjugated polymers do not exhibit a strong luminescence, their stable oxidized state and low oxidation potential render them promising for electrochromic devices. The electrochromic properties of the polymers were characterized using spectroelectrochemical studies. Among the DPP polythienylenes, the p-doping of **P-DPP-BTH** exhibits the best reversibility and stability. The colour of this polymer could be switched many times between the oxidative and neutral state.

The spectroelectrochemical studies of **P-DPP-BTH** films were carried out in clean CH$_3$CN solution with TBAPF$_6$ as electrolyte. The UV/vis absorption at several different oxidation potentials are shown in Figure 2.17.

Upon oxidation, the absorption peaks of the thiophene ($\sim$ 405 nm) and DPP chromophore ($\sim$ 580 nm) gradually decreased. Simultaneously, another absorption peak belonging to the radical cation (polaron) appeared in the infrared region. The colour of **P-DPP-BTH** changes from purple red to dark blue (see the photos in Figure 2.17). The absorption after one cycle is shown in Figure 2.17 as the dotted line. The electrochromic process is very stable and can be repeated many times in air without special treatment of the solution.
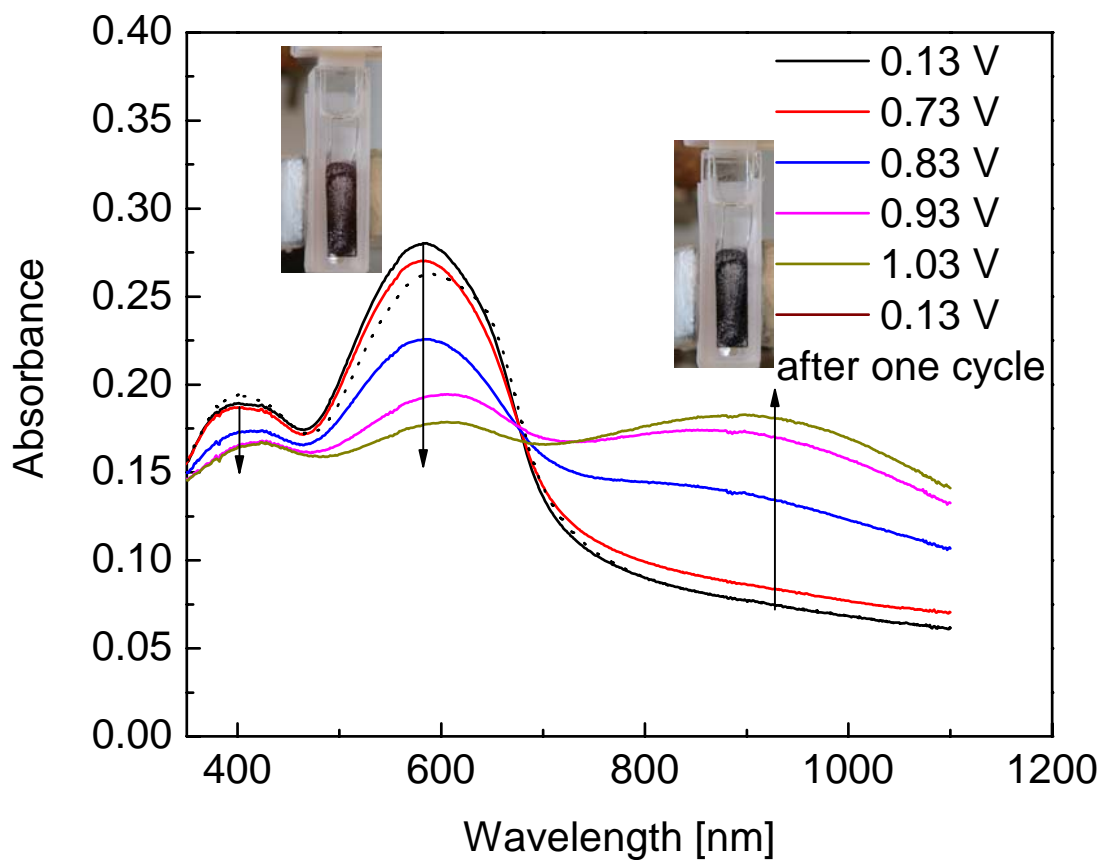
Figure 2.17 Spectroelectrochemical analysis of **P-DPP-BTH** film on ITO coated glass electrode in 0.1M TBAPF$_6$ in CH$_3$CN (Voltage calculated versus SCE).

2.3. Buchwald-Hartwig coupling polycondensation

The Buchwald-Hartwig coupling is a Pd-catalysed reaction for aryl carbon–nitrogen (C–N) bond formation. The aryl amine compounds serve as the active material to react with aryl halide (Scheme 2.1).

Scheme 2.9 Buchwald-Hartwig coupling reaction.

This reaction type was developed independently by the groups of S. Buchwald[96] and J. Hartwig[97]. The primary or secondary amine substituents can be any aryl group. The regular catalyst ligand combination is tris(dibenzylideneacetone)dipalladium(0). The base can be sodium t-butoxide. The reaction is conceptually related to the Stille and Heck reaction and its scope extends to oxygen nucleophiles like phenols and carbon nucleophiles like malonates. The generally accepted mechanism of Buchwald-Hartwig coupling is shown in Figure 2.18.
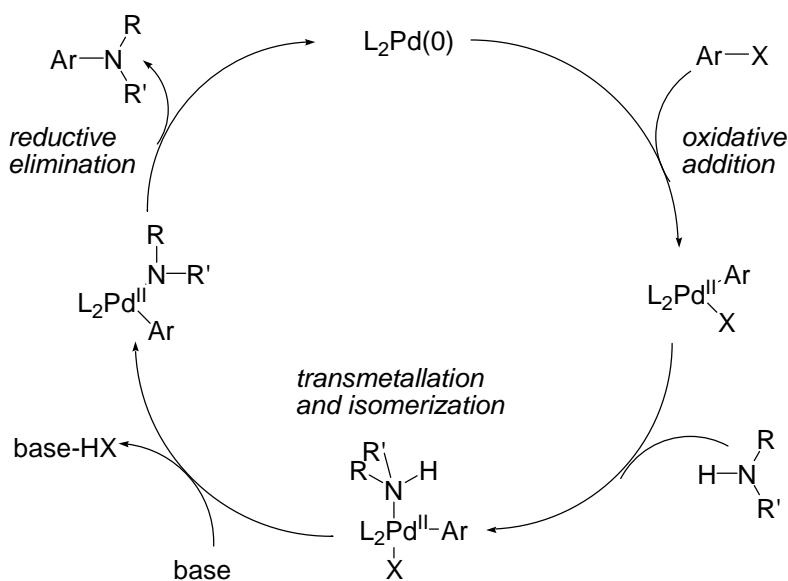
Figure 2.18 Mechanism of Buchwald-Hartwig coupling

The catalytic cycle starts with species $L_2Pd(0)$ lacking one ligand. Then the aryl halide coordinates to palladium by oxidative addition forming intermediate $L_2Pd(II)ArX$. In the next step a halide atom is replaced by the nitrogen atom of the amine. The strong base is required to abstract the proton from the amine towards $L_2Pd(II)NR(R')$. This intermediate undergoes a reductive elimination to the desired aryl amine. The liberated L_2Pd species starts a new catalytic cycle.

2.3.1. Polymerization

Buchwald-Hartwig coupling was found in 1994 and has been developed since by many researchers. Many new ligands were designed to increase the reactivity and selectivity of the reaction[98]. The polymerization technique for this reaction was also developed[99-103]. In this work, two amine compounds (one primary amine, one secondary amine) were reacted with **HDPP** to prepare conjugated polymers. Additional reactions were carried out in order to explore the use of the Buchwald-Hartwig coupling in the synthesis of pyridine containing

conjugated polymers. In Scheme 2.10, all Buchwald-Hartwig polycondensation reactions performed in this study are compiled.
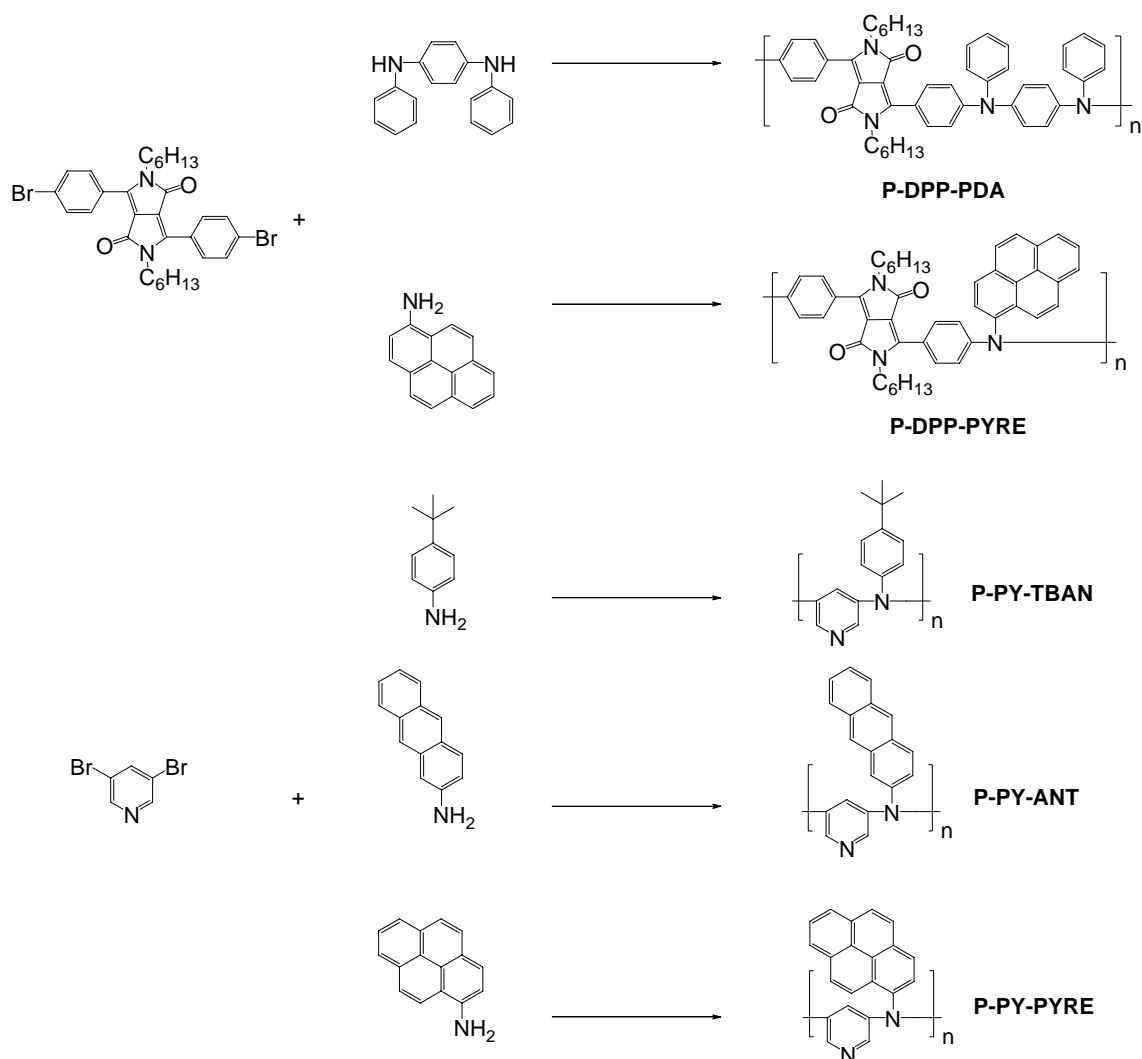
Scheme 2.10 Scheme of Buchwald-Hartwig polycondensation.

For the synthesis of two DPP-containing polymers, **P-DPP-PDA** and **P-DPP-PYRE**, the applicability of two generally used ligands (tris(t-butyl)phosphine and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos)) in Buchwald-Hartwig coupling was compared. Although the polycondensation occurred with both catalyst systems, the first system led to a higher molecular weight (for **P-DPP-PDA**, the molecular weights were 14 kDa and 9 kDa, respectively) and therefore was preferentially applied. However, Xphos was also used occasionally, because it can be handled more easily. It was very important to mix the palladium catalyst and ligand in solution for 30 min before the reaction was started. The choice of the base was also a very important factor to perform a successful polycondensation reaction. Generally used bases such as sodium butoxide or potassium butoxide were not

always effective in our reactions. In case of the preparation of **P-DPP-PYRE**, the DPP chromophore was destroyed by these strong bases. Especially when the amine was not active enough, the side reaction between the DPP chromophore and the strong base occurred. In this case, a weak base such as potassium phosphate was used to avoid the side reaction, and as the result, the polymer was obtained in sufficient yield and degree of polymerization. Organic nonpolar solvents such as toluene and dioxane were used as reaction medium in order to dissolve DPP monomers and to reach high reaction temperatures. For the pyridine containing systems, 3-amino-pyridine and 2,5-dibromopyridine were found to be not suited for the Buchwald-Hartwig polycondensation reaction. Only the 3,5-dibromopyridine could be successfully used. The reaction conditions for the pyridine containing polymers were the same as for **P-DPP-PDA**.

2.3.2. Characterization of the polymers

GPC

All polymers were very soluble in common organic solvents such as chloroform, toluene and THF. The weight average molecular weight and the polydispersity of the polymers are listed in Table 2.7. The reactivity of the secondary amine in the polymerization reaction was high. **P-DPP-PDA** exhibits a molecular weight of 14 kDa, which is comparable with the results of the other metal-catalysed polycondensation reactions. The molecular weight of **P-DPP-PYRE** is only 4.3 kDa because of a lower solubility of the pyrene compound and a relatively low reactivity of the primary amine. Due to the lower solubility, the pyridine containing polymers only exhibit molecular weights between 2.2 and 2.5 kDa.

Table 2.7 Molecular weight and polydispersity of polymers prepared via Buchwald-Hartwig coupling.

	Mw (kDa)	Polydispersity
P-DPP-PDA	14	1.9
P-DPP-PYRE	4.3	1.3
P-PY-TBAN	2.2	1.2
P-PY-ANT	2.6	1.3
P-PY-PYRE	2.3	1.1

¹H-NMR

The proton NMR spectra of the DPP-based monomer and the corresponding polymers were measured in chloroform-D.
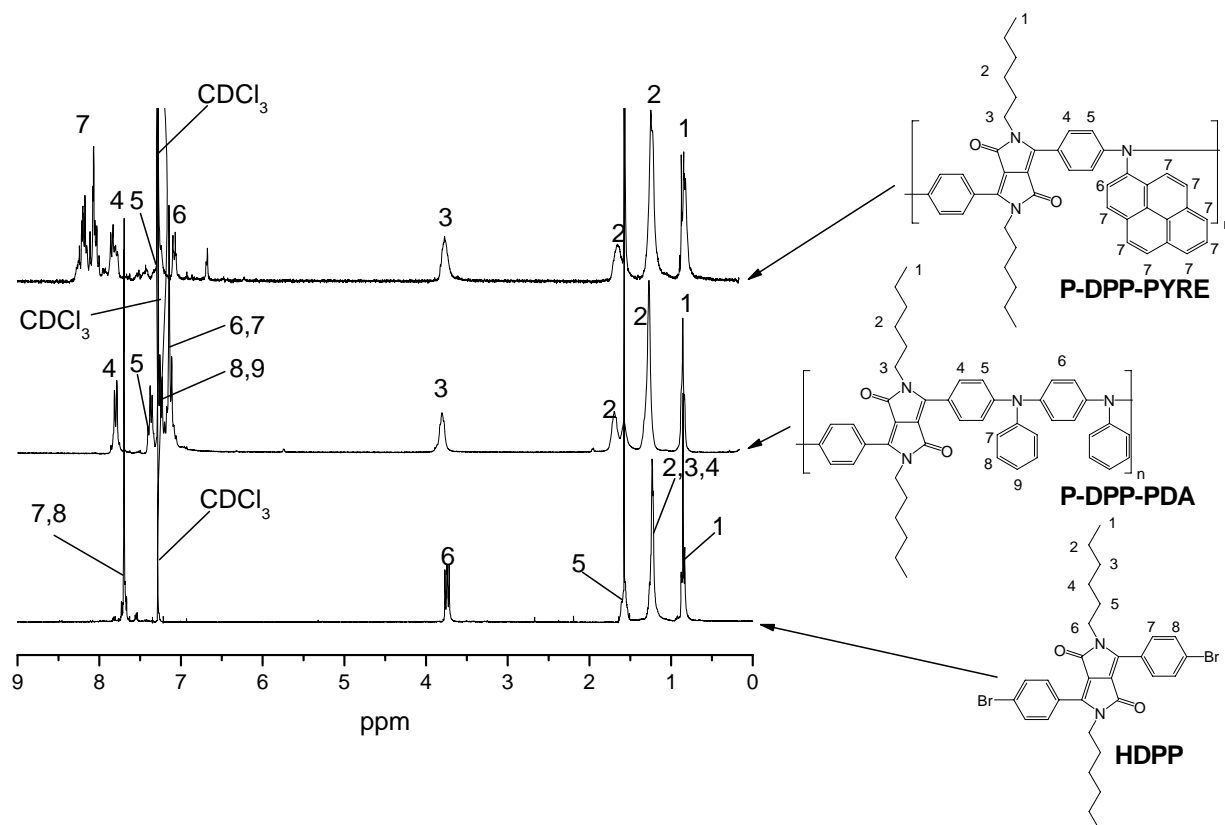
Figure 2.19 The proton NMR spectra of **HDPP**, **P-DPP-PDA** and **P-DPP-PYRE**

In Figure 2.19 the proton NMR spectra of the DPP containing polymers are compared with the spectra of **HDPP**. All spectra show signals of the DPP phenylene protons at about 7.6 ppm, and signals of the hexylated lactam group of DPP in the region from 0.7 to 1.5 ppm. The signal of the methylene group adjacent to the lactam N atom appears at 3.7 ppm. The polymer spectra mainly differ from the corresponding spectra of polymers from C-C coupling reactions by the additional presence of the characteristic signals of the aromatic protons adjacent to the imino group at about 6.6 to 7.3 ppm. For the pyridine compounds, there is a broad peak between 7 and 8 ppm, which stems from the heavily overlapping signals of the phenylene units. The proton NMR spectra of pyridine containing polymers are shown in the experimental part of this work.

50

Optical properties

The DPP containing polyiminoarylenes are obtained as black powders. After dissolution in toluene, the polymers form bright purple red solutions. The pyridine-based polymers are brown. Their solutions are colorless or slightly brown. Photographs of all polymer solutions are shown in Figure 2.20.

| HDPP | P-DPP-PDA | P-DPP-PYRE | P-PY-TBAN | P-PY-ANT | P-PY-PYRE |
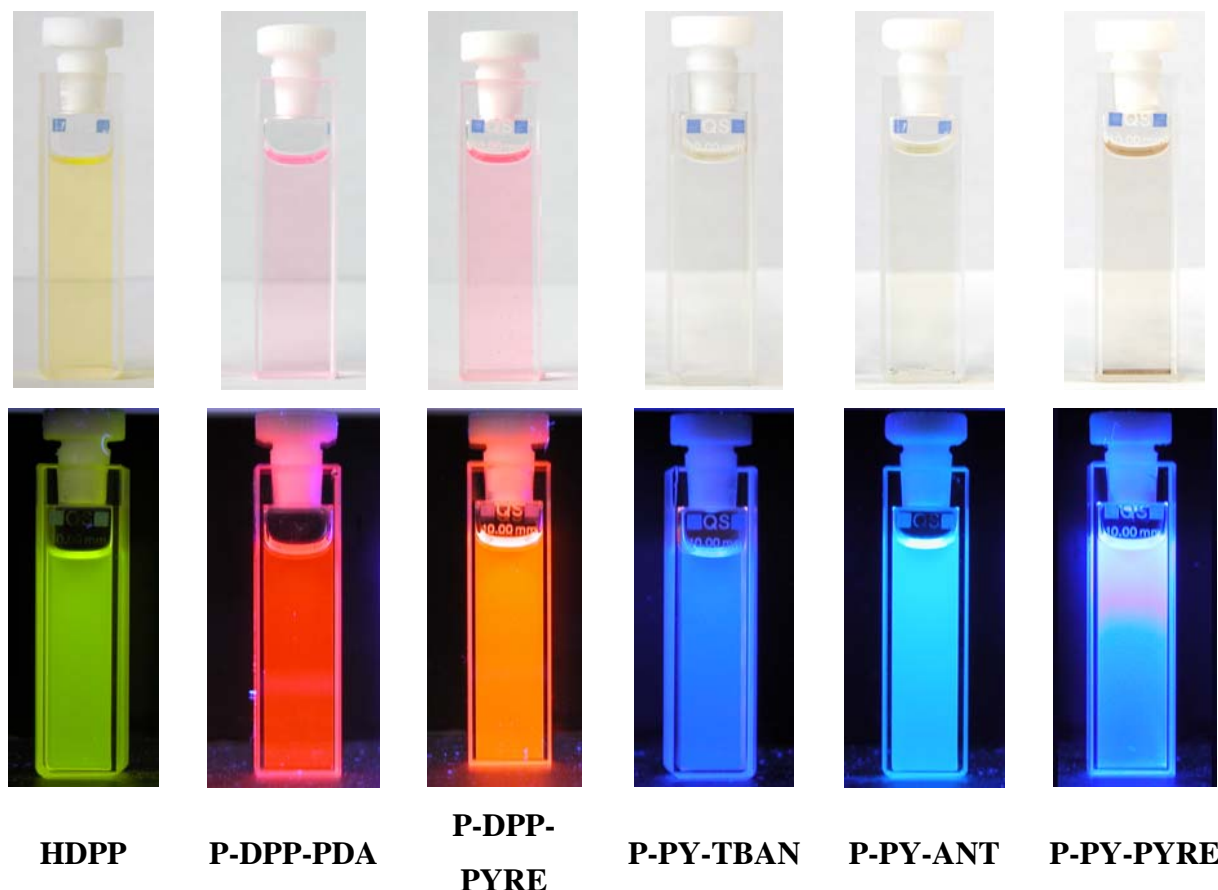
Figure 2.20 Photographs of **HDPP** monomers and various polymers prepared via Buchwald-Hartwig polycondensation in normal (upper) and luminescent state (lower).

The UV/vis absorption spectra and fluorescence spectra of the polyiminoarylenes were measured in toluene. The DPP containing polymers form bright purple red solutions with absorption maxima between 527 and 539 nm. Compared with the DPP copolymers from Suzuki coupling, the emission maxima of **P-DPP-PDA** and **P-DPP-PYRE** are clearly red shifted (Figure 2.21). They appear at 608 and 607 nm, respectively. Similar to **P-DPP-TPA**, in which an amine group is also present in the polymer main chain, the polymers exhibit much better luminescent properties in toluene than in chloroform.
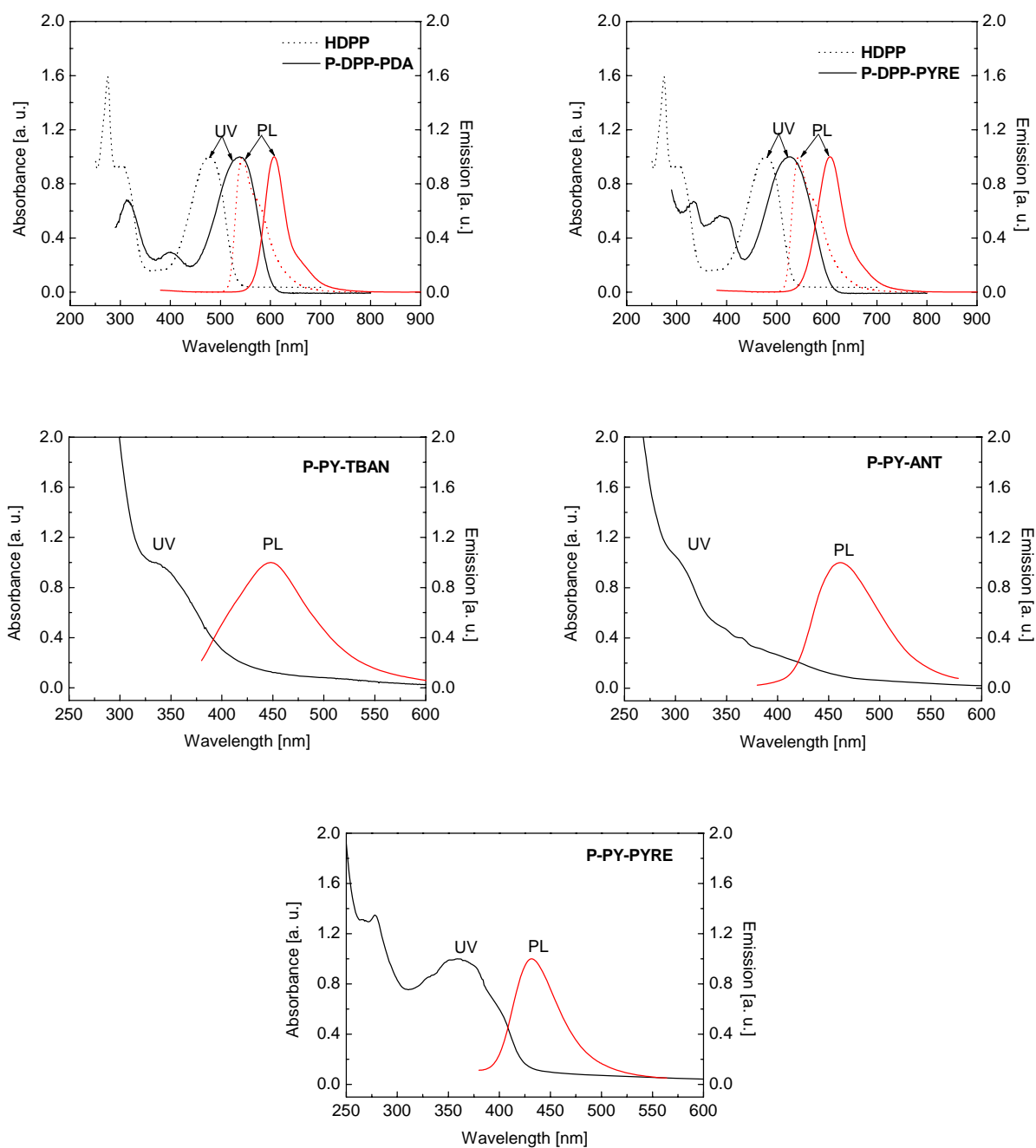
Figure 2.21 UV/vis absorbance and photoluminescence spectra of various polymers prepared via Buchwald-Hartwig coupling polycondensation. The excitation wavelength is 350 nm. Solvent: toluene

The photoluminescence quantum yields of the poly-DPP-iminoarylenes were measured in toluene. The values are 48% and 62% for **P-DPP-PDA** and **P-DPP-PYRE**, respectively. The high quantum yield of **P-DPP-PYRE** may result from the incorporation of the large aromatic pyrene group. The polymer films cast on quartz supports exhibited absorption maxima between 546 nm and 554 nm as indicated in Figure 2.22, about 16 nm to 19 nm red shifted

compared with the solution. Unfortunately, the solid films of poly-DPP-iminoarylenes were nonluminescent probably due to aggregation of the polymer chains in the solid state.
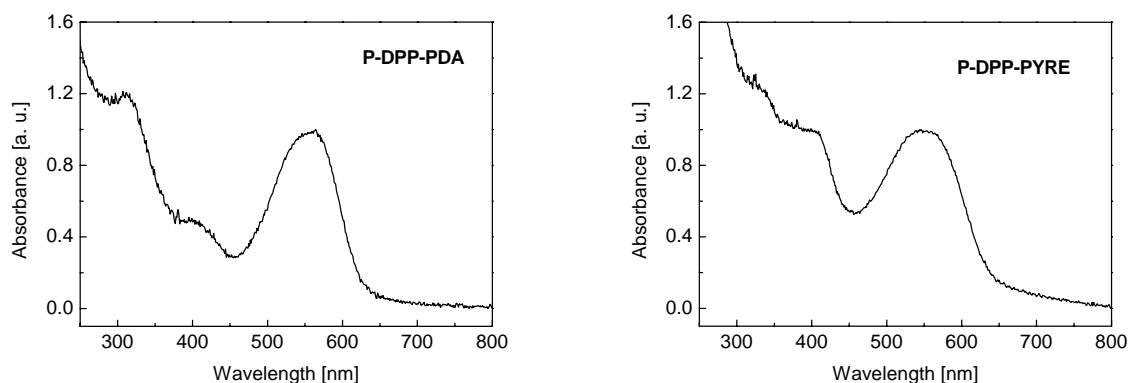
Figure 2.22 UV/vis absorbance spectra of solid films of DPP containing polyiminoarylenes. The UV/vis absorption and fluorescence spectra of the pyridine containing compounds are shown in Figure 2.21 as well. The maximum absorption of the polymers is located in the ultraviolet region. The emission maxima are 448 nm, 462 nm and 432 nm for **P-PY-TBAN**, **P-PY-ANT** and **P-PY-PYRE**, respectively. The optical data of the polymers are collected in Table 2.8.

Table 2.8 Optical data of polyiminoarylenes in toluene solution and as solid film.

	λ_{max}(nm) solution	λ_{em}(nm) solution	λ_{max}(nm) film	λ_{em}(nm) film	Φ_f
HDPP	476	533	-	-	0.90
P-DPP-PDA	539	608	544	None	0.48
P-DPP-PYRE	527	607	564	None	0.62
P-PY-TBAN	335	448	-	-	0.23
P-PY-ANT	305	462	-	-	0.34
P-PY-PYRE	359	432	-	-	0.41

The excitation wavelength is 350 nm. The photoluminescence quantum yield was measured at an excitation wavelength of 400 nm (for DPP compounds) or 350 nm (for pyridine compounds) and calculated by comparison with Rhodamine 6G in ethanol (Φ_f=0.95).

Electrochemical Characterization

Cyclic voltammograms of the polymers **P-DPP-PDA** and **P-DPP-PYRE** were determined under the same conditions as described before. The corresponding CV-diagrams are shown in Figure 2.23.
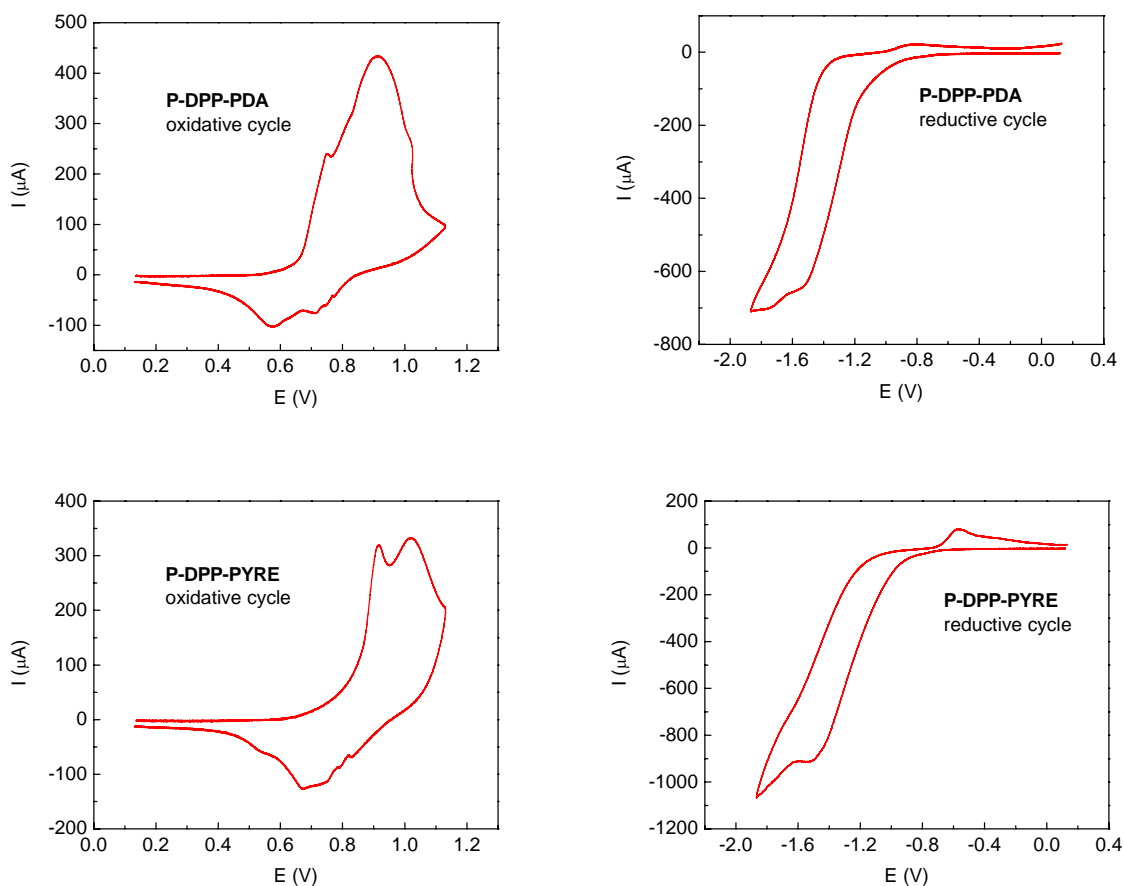
Figure 2.23 Cyclic voltammograms of **P-DPP-PDA** and **P-DPP-PYRE**. Scan rate: 25 mVs^{-1}, T = 20 ^{0}C. Electrolyte solution: 0.1 M TBAPF$_6$ in acetonitrile.

CV-data are compiled in Table 2.9. All DPP containing polymers exhibit quasi-reversible oxidative processes with onset potentials E$_{onset(ox)}$ between 0.66 and 0.84 V (vs. SCE). The oxidative onset potentials of poly-DPP-iminoarylenes (**P-DPP-PDA** and **P-DPP-PYRE**) are significantly lower than those of the poly-DPP-arylenes (**P-DPP-CBZ**, **P-DPP-TPA** and **P-DPP-BTZ**). This may result from the presence of N atom on the main chain of poly-DPP-iminoarylene, which makes the polymer easier to be oxidized. For all polymers, the reduction is irreversible. As shown in Table 2.9, the band gap values from the optical measurements and the electrochemical experiment match well. The bandgaps of the poly-DPP-iminoarylenes are between the values for poly-DPP-thienylenes and those of DPP polymers via Suzuki coupling. Among all DPP containing polymers, **P-DPP-PDA** has the lowest onset oxidation potential of 0.66 V.

Table 2.9 Band gap data of DPP-based polyiminoarylenes

Polymer	Absorption on film λ_{onset}(nm)	E_{opt} (eV)/$E_{electro}$ (eV) band gap	$E_{onset(ox)}$ (V) {E_{HOMO} (eV)}	$E_{onset(red)}$ (V) {E_{LUMO} (eV)}
P-DPP-PDA	627	1.98/1.76	0.66{-5.06}	-1.10{-3.30}
P-DPP-PYRE	647	1.92/1.84	0.84{-5.24}	-1.00{-3.40}

Band gap (E_{opt}) measured at the onset of electronic absorption of the polymer film (E_{opt} =1240/λ_{onset} eV). HOMO-LUMO gap according to the equation: -E_{LUMO}=$E_{onset(red)}$+4.4 eV and -E_{HOMO}=$E_{onset(ox)}$+4.4 eV, where $E_{onset(ox)}$ and $E_{onset(red)}$ are the onset potentials for the oxidation and reduction processes of polymer thin films vs. SCE.
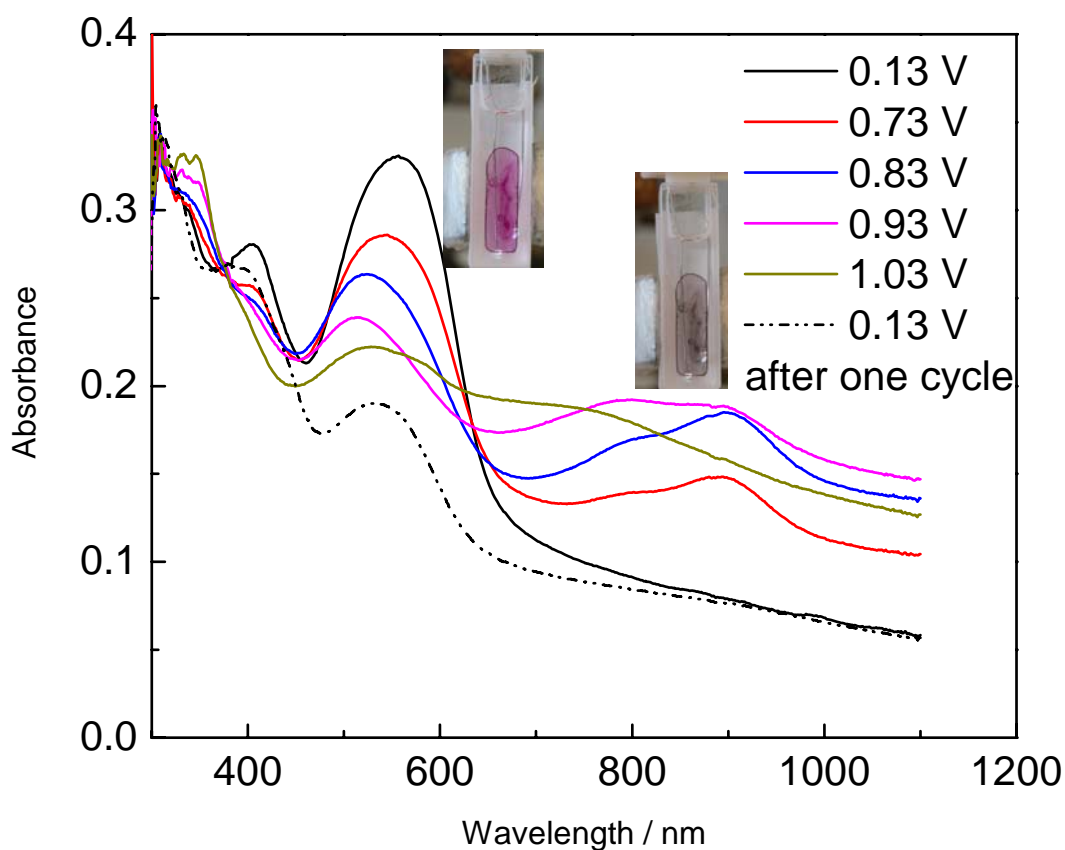
Figure 2.24 Spectroelectrochemical analysis of **P-DPP-PYRE** in 0.1M TBAPF$_6$ in CH$_3$CN. (Voltage calculated versus SCE).

The comparatively low oxidation potentials indicate that the poly-DPP-iminoarylenes are probably promising materials for electrochromic devices. The electrochromic properties of the

polymers were investigated using spectroelectrochemical analysis. It was found that **P-DPP-PDA** and **P-DPP-PYRE** exhibit very similar behaviour upon oxidative cycling. The spectroelectrochemical analysis of the **P-DPP-PYRE** film was carried out in clean CH_3CN solution with $TBAPF_6$ as electrolyte. In Figure 2.24, the UV/vis absorption at different oxidation potentials is shown. Upon oxidation, the absorption peak of the DPP chromophore (at about 560 nm) gradually decreased. Another absorption peak originating from the radical cation (polaron) appears in the infrared region. Simultaneously the colour is changed from purple to black-green (see also the photographs in Figure 2.24). The decrease of the absorbance after one cycle originates from the dissolution of parts of the polymer film at the highly oxidized state (if the oxidation potential is over 0.93 V). If the potential is clearly below 0.93 V, the electrochromism is highly reversible under ambient conditions without special treatment of the solution. The behaviour of polymer **P-DPP-PDA** is very similar to **P-DPP-PYRE**.

2.4. Conclusions

New DPP containing polymers were successfully synthesized using Suzuki, Stille and Buchwald-Hartwig coupling polycondensation with molecular weights between 5 kDa to 16.5 kDa. The polymers are readily soluble in common organic solvents, the solutions exhibit bright red colours and strong red to purple photoluminescence. **P-DPP-TPA** is especially interesting because of its high photoluminescence quantum yield of 85%. **P-DPP-CBZ** is also very promising because of its high molecular weight, excellent solubility, relatively good photoluminescence quantum yield of 46% and quasi-reversible oxidation behaviour. They are useful candidates as active materials in PLED applications. The DPP-thienylene-copolymers (**P-DPP-TH**, **P-DPP-BTH** and **P-DPP-EDOT**) are interesting because of their reversible oxidation behavior. The cyclovoltammetric and spectroelectrochemical experiments show that **P-DPP-BTH** is a promising electrochromic material. The solid state luminescence of the polymers is quenched. The poly-DPP-iminoarylenes are interesting for their significantly low oxidation potential. The spectroelectrochemical analysis shows that the polymers exhibit sharp colour changes from purple to black-green upon oxidation.

3. Electropolymerization of DPP containing molecules

3.1. Introduction

Since the first report on the electropolymerization of pyrrole was published, electropolymerization became an important method to prepare conductive polymer films [104]. Although the procedure of electropolymerization is fairly simple, the origin of this process is still unclear[105]. Despite of the many divarications, the process of electropolymerization was generally regarded as a series of oxidation reactions at the anode. For the simplest monomer pyrrole, the most popular mechanism was proposed by Diaz[106] as described in Scheme 3.1.
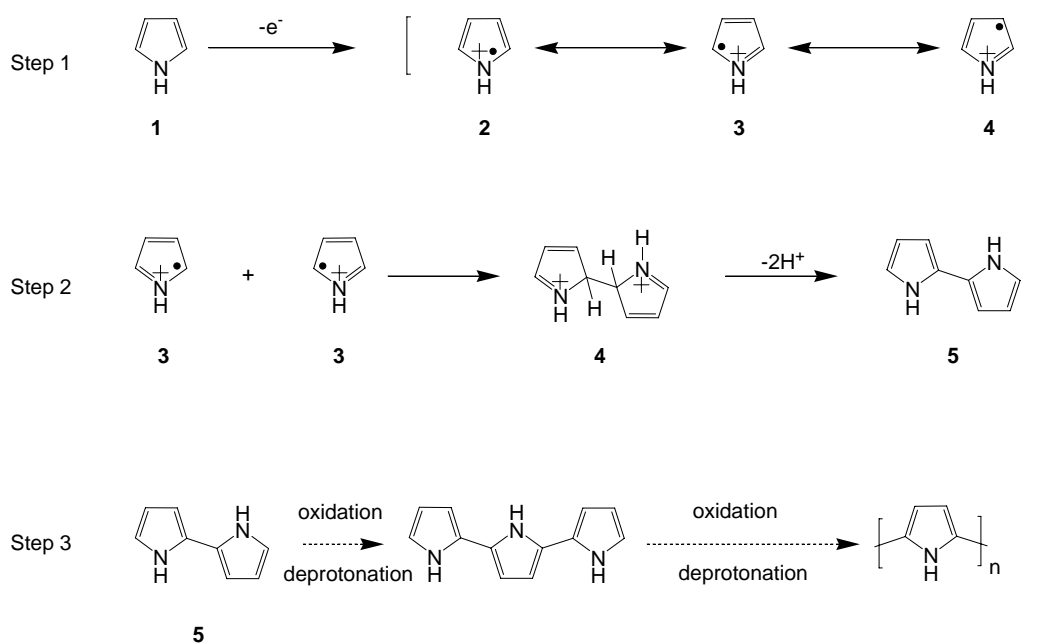
Scheme 3.1 Mechanism of electropolymerization of pyrrole

In Diaz's mechanism, the first step is the oxidation of the pyrrole monomer. The cation radical is formed, which has several resonance forms represented as 2, 3 and 4. It is clear that a high concentration of cation radicals is formed at the electrode surface. These cations may undergo the following processes depending on their reactivity:

When the cation radical is relatively stable, it can diffuse into the solution and react to form soluble products with low molecular weights.

When the cation radical is very unstable, it can rapidly react near the electrode with the solvent or the anion to also form soluble products of low molecular weight.

Between these two extremes, cation radicals can also undergo dimerization reactions. In this case, cation radicals of resonance form 3 dimerize and form the dication 4. Then the protons are released and the aromatic dimer 5 is formed.

In the following steps, the dimer is oxidized again to form a cation radical and then trimer, tetramer, pentamer etc. is formed via the same sequence: oxidation, coupling, deprotonation. Finally a polymer is obtained.

After the electropolymerization was described, Adamcova and her colleagues[104] published an excellent review on the polymer film formation by electropolymerization. This review concentrated on simple aromatic monomers, especially the five membered heterocyclic aromatic compounds such as thiophene, furan and pyrrole. The authors discussed the factors affecting the process of the film formation and regarded the monomer oxidation potential as the most important factor. The oxidation potentials of various aromatic monomers used in electropolymerzation are listed in Table 3.1 (data from reference[104]).

Table 3.1 Oxidation potentials of aromatic molecules

Compounds	Oxidation potential in voltage vs. SCE
Pyrrole	0.8
Thiophene	1.6
Furan	1.85
2,2-Bithiophene	1.32
Indole	0.9
Azulene	0.9
Pyrene	1.30-1.33
Fluorene	1.82

From the Table above, it is clear that pyrrole has the lowest oxidation potential among the various monomers. In practical, pyrrole was found the most easily oxidized monomer. Thiophene and its derivatives have a higher oxidation potential than pyrrole, the film formation process can only be achieved in some cases. For furan and other aromatic compounds, it is almost impossible to form polymer films by electropolymerization. In this dissertation, a short review of the electropolymerization is given below.

3.1.1. Electropolymerization of pyrrole and its derivatives

Pyrrole can be easily electropolymerized. However, the film-formation process can be affected by many factors.

As shown in Adamcova's review, different N-substitution changes the film-formation process dramatically. Generally non-substituted polypyrrole is regarded as a good candidate for conducting polymer films[107]. The conductivity is lowered by 2 to 3 orders of magnitude, if the proton at the nitrogen atom is replaced by a carbon atom[104]. Some researchers also detected the formation of insulating or electro-inactive polypyrrole film when a higher oxidation potential was used[108,109]. Zhou and Heinze studied the electropolymerization of pyrrole and indicated the affecting factors for this process in a series of publications[110-114].

Although pyrrole derivatives are very hard to be prepared, there are some reports on the synthesis of pyrrole derivatives and the corresponding polymers (Scheme 3.2). Thomas and Reynolds[115] synthesized 3,4-alkylenedioxypyrroles and prepared stable aqueous-compatible conducting polymers from it. The poly(3,4-ethylenedioxypyrrole) exhibits electrochromic properties[116]. Very recently, conducting polymers based on alkythiopyrroles were also reported[117].
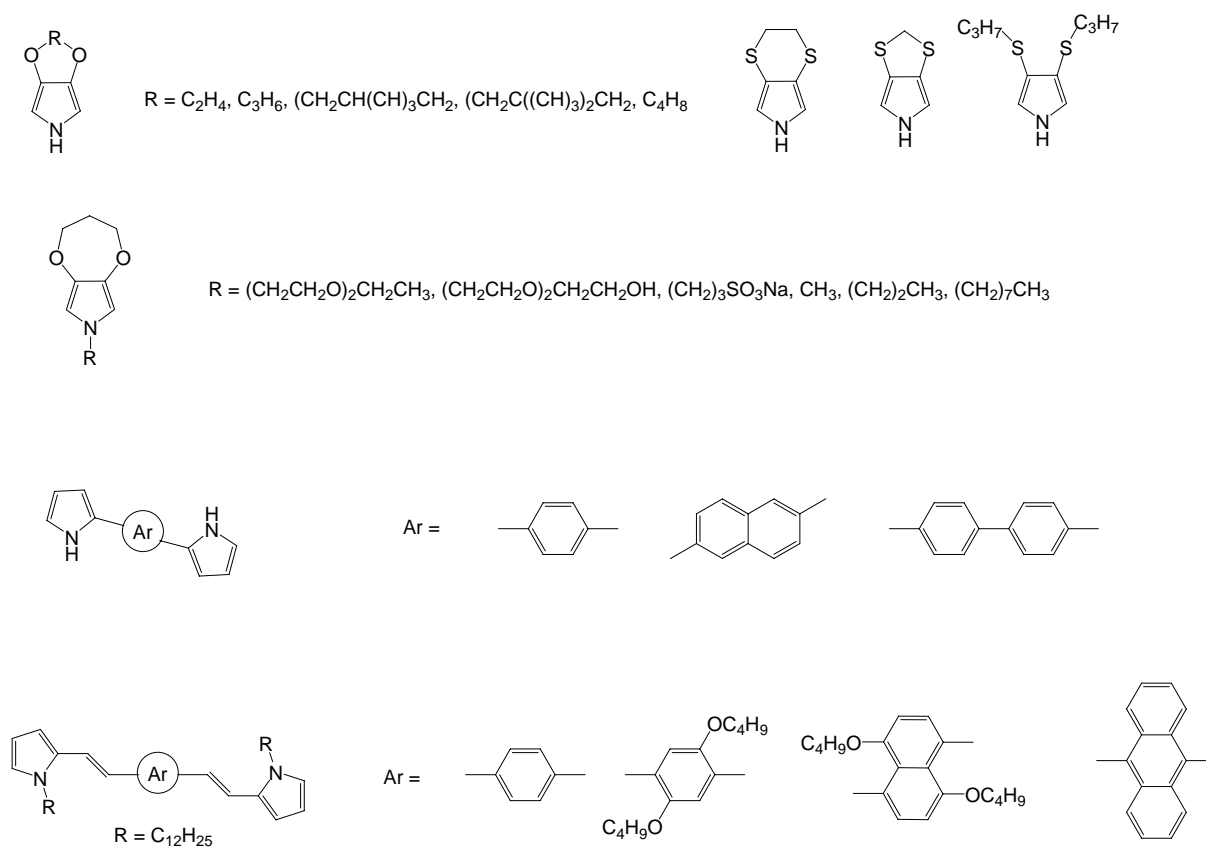
Scheme 3.2 EDOP derivatives and bispyrrole compounds suitable for electropolymerization

The unsubstituted bis-pyrrole-arylene compound is very difficult to synthesize because bromo-pyrrole is unstable[118]. Sotzing and Reynolds[119,120] prepared bis-pyrrole-arylenes from the appropriate acid chlorides using a three-step method. The arylenes involved were benzene, alkoxybenzene, naphthalene and biphenyl. The conductivity of the polymer film is up to 30 S/cm. Bueschel[121] proposed a method to prepare substituted bis-pyrrole-arylene. In his publication, the N-alkylpyrrole-2-carboxaldehydes were used in a Wittig-Horner-Emmons olefination reaction to react with benzene, alkoxybenzene, alkoxynaphthalene and anthracene. Except for divinylanthracene-bridged bispyrrole, all monomers could be successfully electropolymerized.

Besides the normal polypyrrole films, polypyrrole network films were reported by Deng and Advincula[122], who prepared the polymethacrylate functionalized with pyrrole and then electropolymerized it on ITO coated glass substrates.

3.1.2. Electropolymerization of thiophene and its derivatives (without EDOT)

Although pyrrole is the compound which can be electropolymerized most easily, it is not the most widely reported unit in electropolymerization. Thiophene is more popular in electropolymerization because it can be connected more easily with other arylenes to form electropolymerizable monomers with different conjugated length. That means, the optical properties of the thiophene derivatives can be adjusted easily.

The electropolymerization process of thiophene has been explored by many researchers. Kabasakaloglu and colleagues studied the electrochemical properties of thiophene and polythiophene using different supporting electrolytes (ammonium perchlorate, tetraethyl-ammonium tetrafluoroborate and tetrabutylammonium hexafluorophosphate) in acetonitrile[123]. The thiophene oxidation potential against Ag/Ag^+ was 1.6 V, if tetrabutylammonium hexafluorophosphate was used. It is generally accepted that the Pt working electrode adsorbs the weak acid anions such as PF_6^- and this adsorption benefits the polymer film formation process.
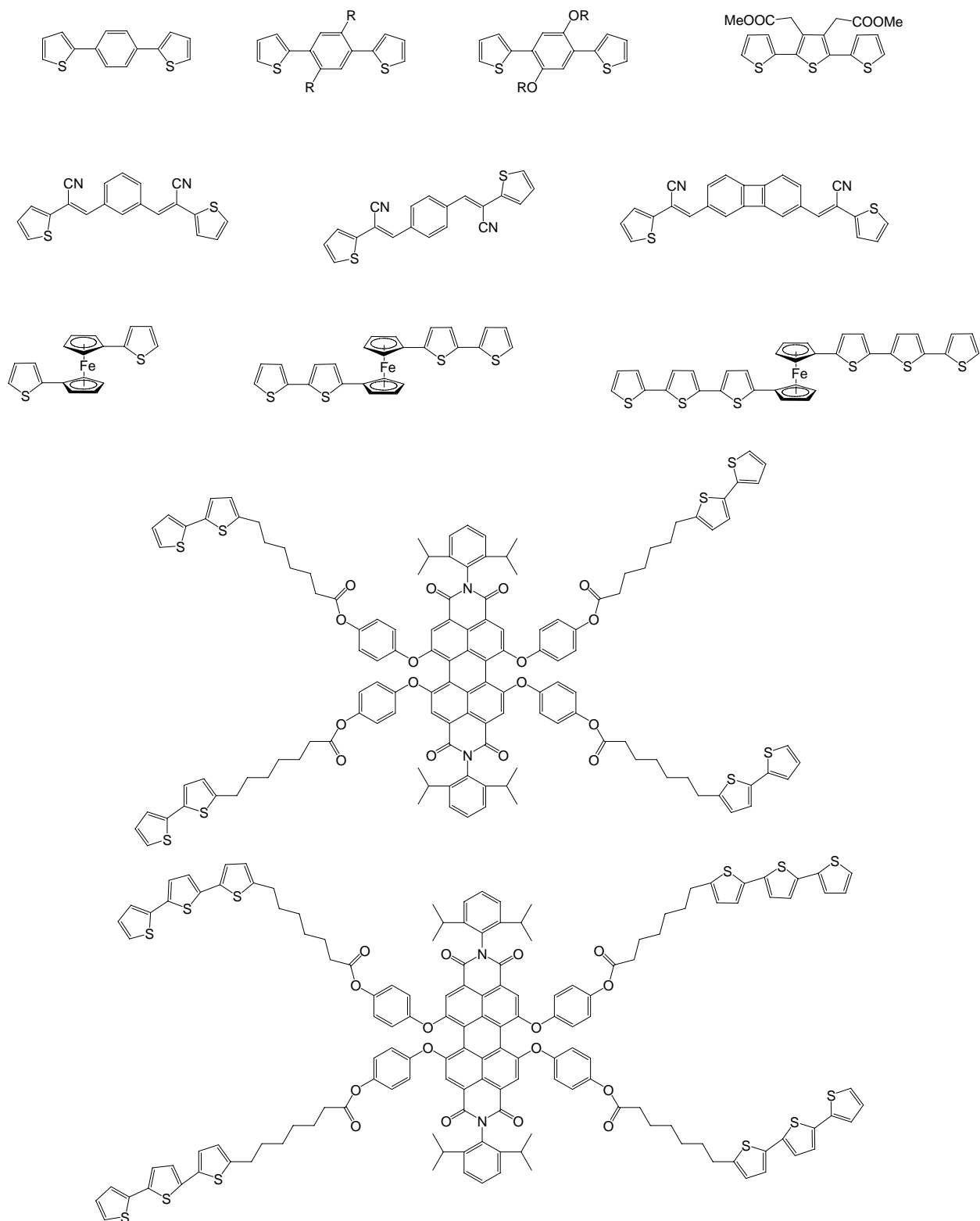
Scheme 3.3 Bis- and tetra-thiophene-arylenes reported in literature

Shi[124,125] reported high-strength conducting polythiophene prepared in boron trifluoride diethyletherate solution. The polythiophene made in this way exhibited a tensile strength even greater than that of aluminium. This method was further adopted by Alkan and Reynolds[126] and they reported the electrochromic properties of this polythiophene. Both the swiching into

the oxidized and the reduced states was fully reversible. The colour change is from transmissive blue to deep red.

Because the synthesis of the bis-thiophene-arylene compounds is quite easy, the corresponding polymers were widely reported in last ten years. The report from Reynolds group[127] disclosed the synthesis of the bis-thiophene-arylenes and bis-furan-arylenes. The arylenes include benzene, alkyl- and alkoxy- benzene (Scheme 3.3). Later, Lin and Leung[128] synthesized bis(2-cyano-2-α-thienylethenyl)arylenes.

A very simple but still not widely spread information is that the bis-bithiophene-arylenes and bis-thiophene-arylenes can be very easily oxidized and electropolymerized compared with bis-thiophene-arylenes. Destri and coworkers[129] reported thiophene derivatives, which even become luminescent after electropolymerization. The bis-thiophene-ferrocene, the bis-bithiophene-ferrocene and bis-thiophene-ferrocene were synthesized and only the latter two compounds could be electropolymerized. Perylene containing bis-bithiophene and bis-thiophene monomers[130] were also reported and the compounds could be electropolymerized using acetonitril as solvent.

3.1.3. Electropolymerization of EDOT (3,4-(ethylenedioxy)thiophene) and its derivatives

The invention of 3,4-(ethylenedioxy)thiophene (EDOT)[131] dramatically speeded up the research work of electropolymerization. EDOT is more stable than pyrrole, but is more easily oxidized than thiophene. The oxidation potential of EDOT is only 1.2 V (Ag/Ag$^+$), which is much lower than that of thiophene (1.6V vs Ag/Ag$^+$). The lower oxidation potential originates from the electron-rich ethylenedioxy group, which stabilizes the cation radical intermediates allowing the electropolymerization to proceed at low potentials and with a minimum of side reactions. The poly(3,4-(ethylenedioxy)thiophene) film is easily formed at the anode. It exhibits an oxidation potential between –0.07 V and –0.28 V (vs Ag/Ag$^+$) depending on the solvent system. The polymer films show an absorption maximum between 580 nm and 610 nm with a bandgap of 1.60 eV. After EDOT was first reported, similar compounds (3,4-(methylenedioxy)thiophene, 3,4-(propylenedioxy)thiophene, 3,4-(butylenedioxy)thiophene were prepared by several researchers [132,133]. The molecular structures are shown in Scheme 3.4.
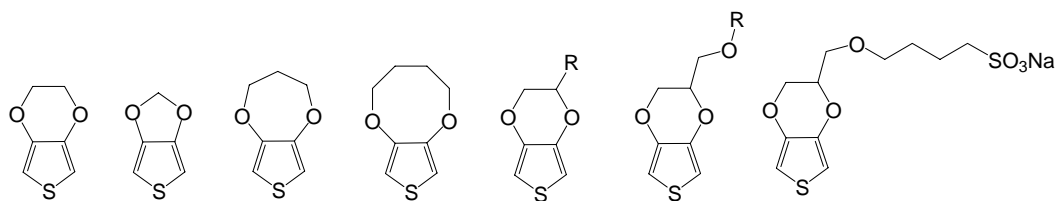
Scheme 3.4 EDOT and several derivatives

The molecular structure was varied in order to increase the solubility in different organic solvents and water. Sulfonate substituted EDOT[134,135], alkoxyl-derivatives[136] and alkyl-derivatives[137,138] have been reported. In recent research, some more sophisticated EDOT analogues have been synthesized. Roquet and his colleagues reported the synthesis of 3,4-phenylenedioxythiophene derivatives[139]. Turbiez and co-workers synthesized the 3,4-ethylenedisulfanylthiophene unit[140]. All compounds can be easily electropolymerized and the resulting films exhibit electrochromic properties.

Similar to the bisthiophene arylene compounds, a wide variety of EDOT-arylene-EDOT monomers were reported. The method to sandwich the arylene between two EDOT offers the way to change the conjugation length of the monomer and to change the optical properties of the corresponding polymers. Compared with the bisthiophene arylene compounds, the EDOT-arylene-EDOT monomers can be oxidized at a lower potential and the possibility to incorporate various arylene units in the polymer backbone is increased. In Scheme 3.5 several EDOT-arylene-EDOT compounds prepared up to now are listed.
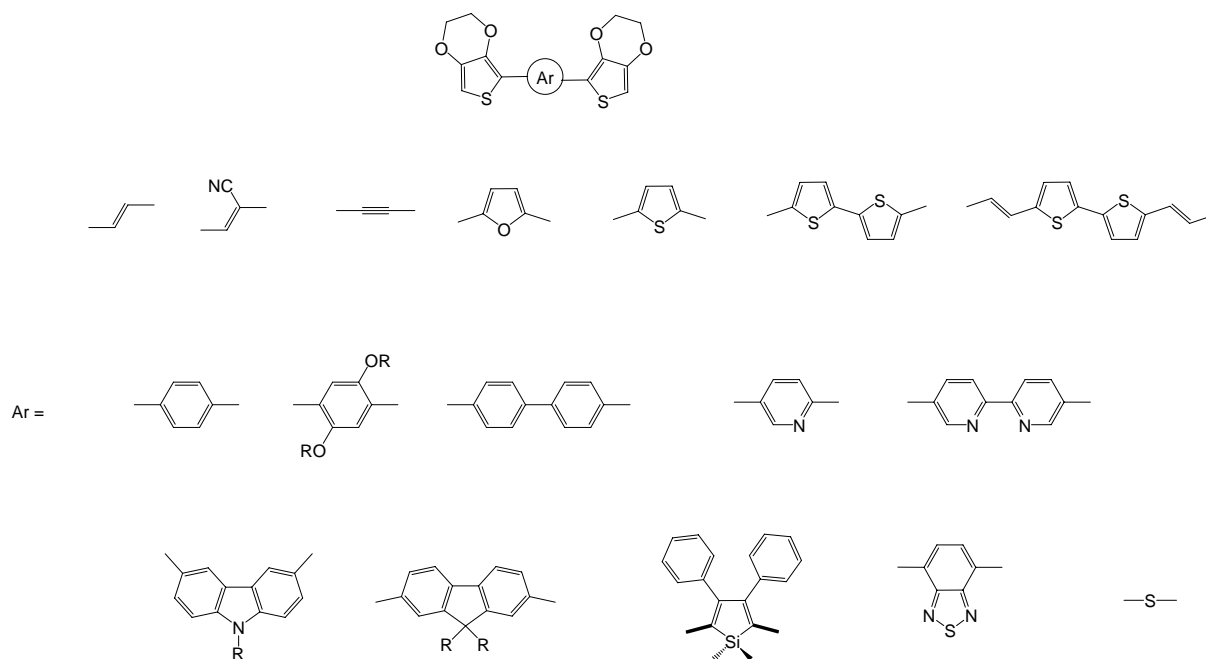
Scheme 3.5 EDOT-arylene-EDOT compounds containing various units

The reported arylenes include vinylene[119], cyanovinylene[141], ethynylene[142], furan[119], thiophene[119], bithiophene[143], 2,2'-bis(vinylene)-bithiophene[143], benzene[119], dialkoxybenzene[144], biphenyl[119], pyridine[145], bipyridine[146], N-alkylcarbazole[147], 9,9'-didecylfluorene[148], silole[149], benzothiodiazo[150] and sulphur units[151]. Recently, the electrochemistry of poly(3,4-alkylenedioxythiophene) derivatives was reviewed by Groenendaal[152].

Most of the bis-EDOT-arylene polymers exhibit electrochromic properties; the colour change in response with the potential applied is useful in many applications. The water soluble PEDOT-PSS system was introduced by Bayer as Baytron P, which was deep blue in the neutral state and transparent in the oxidized state. The polymer was used as the active material for smart windows[153]. Reynolds' group even reported a dual polymer electrochromic device which was capable to switch between a colourless neutral state and a doped gray-green state[154].

3.1.4. Electropolymerization using other building blocks
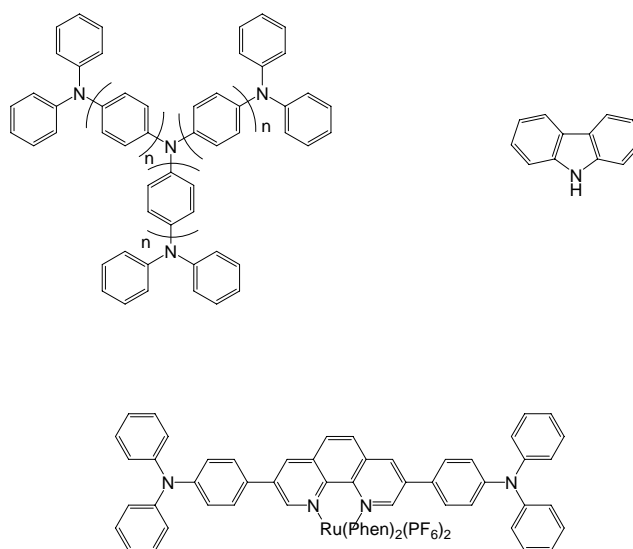
Scheme 3.6 Heterocyclic compounds suitable for electropolymerization

There are only few other units which are suitable for electropolymerization (Scheme 3.6). The most important compounds are carbazole and triphenylamine. Carbazole has been reported to be electropolymerizable at a very high potential (1.9 V vs SCE) [155]. The formation and redox behaviour of polycarbazole prepared by electropolymerization of solid carbazole crystals immobilized at an electrode surface was also reported[156]. A very recent article reported on a

luminescent polycarbazole film prepared upon electropolymerization[157], which could be quite interesting for OLED devices. Triphenylamine itself can not be electropolymerized. However, it was reported that derivatives with enlarged conjugated system can be electropolymerized[158].

3.2. Electropolymerization of DPP containing molecules

Up to now, there is no report on the electropolymerization of DPP containing compounds. The DPP monomer itself can not be electropolymerized, because the oxidation potential of the monomer is too high. In order to lower the oxidation potential and obtain electropolymerizable monomers, the following sandwich-structured monomers were synthesized (Scheme 3.7). The heterocyclic aromatic rings at both side of DPP can be thiophene, pyrrole and carbazole derivatives.
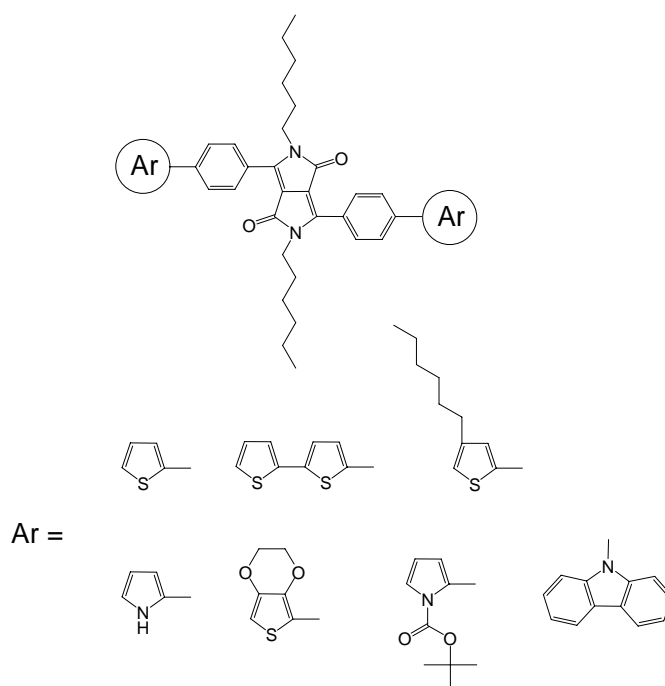
Scheme 3.7 Sandwich-structured DPP monomers

In the following sections, the monomer preparation and the process of electropolymerization will be discussed in detail.

3.2.1. Synthesis and properties of sandwich-structured DPP monomers

Thiophene containing DPP monomers

Four thiophene containing sandwich-structured DPP monomers 1,4-diketo-2,5-dihexyl-3,6-bis(4-(2-thienyl)phenyl)pyrrolo[3,4-c]pyrrole (**TH-DPP-TH**), 1,4-diketo-2,5-dihexyl-3,6-bis(4-(2-(4-hexylthienyl))phenyl)pyrrolo [3,4-c]pyrrole (**HTH-DPP-HTH**), 1,4-diketo-2,5-dihexyl-3,6-bis(4-(2,2'-bithiophen-5-yl)phenyl)pyrrolo[3,4-c]pyrrole (**BTH-DPP-BTH**) and 1,4-diketo-2,5-dihexyl-3,6-bis((2-(3',4'-ethylenedioxy)thienyl)-phenyl)pyrrolo[3,4-c]pyrrole (**EDOT-DPP-EDOT**) were prepared by Stille or Suzuki coupling. The preparation of the monomers is shown in Scheme 3.8.
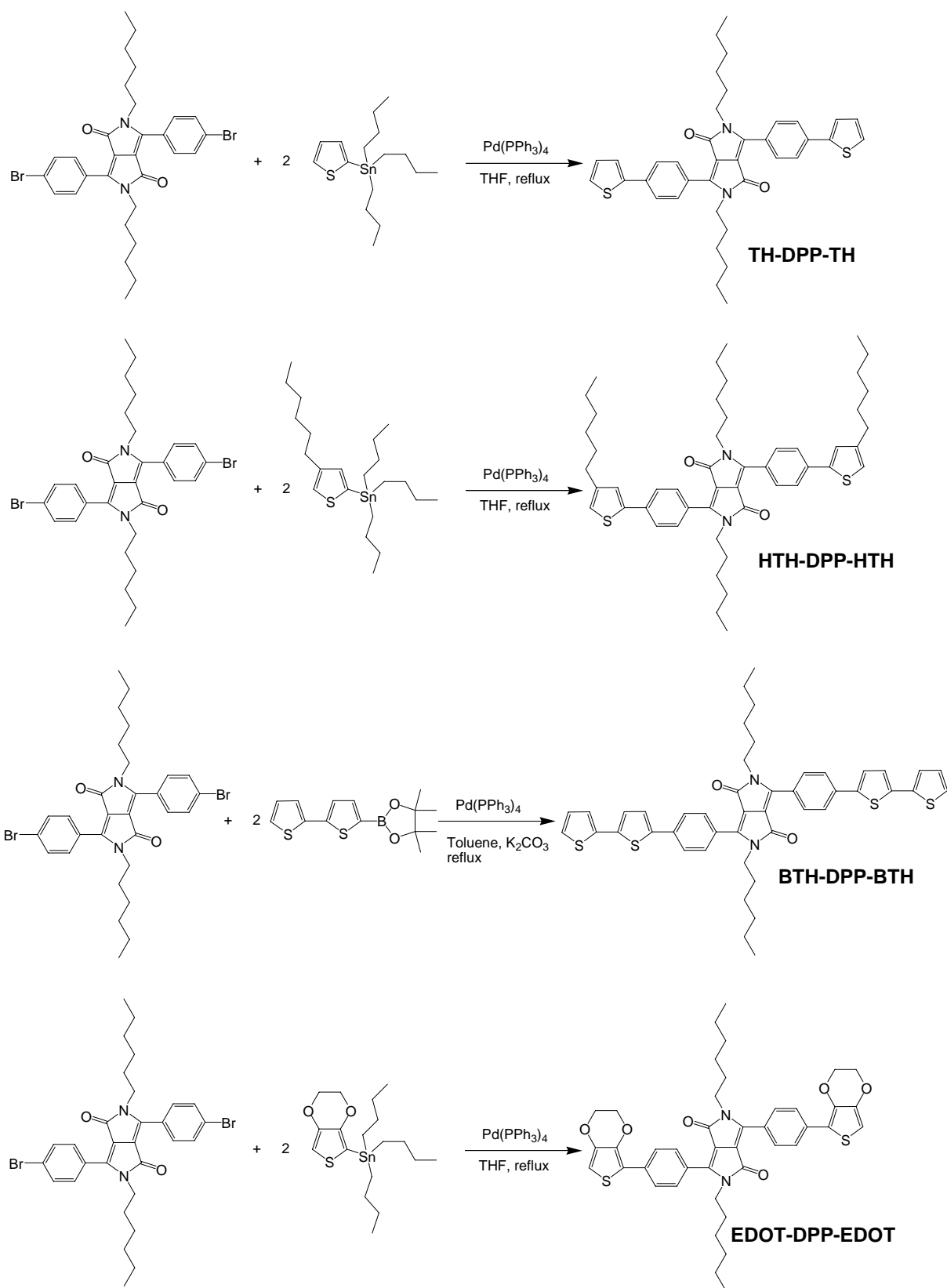
TH-DPP-TH, **HTH-DPP-HTH** and **EDOT-DPP-EDOT** are prepared upon Stille coupling. The reagent 2-(tri-n-butylstannyl)thiophene was prepared according to a general procedure[58]. The thiophene and 3,4-ethylenedioxythiophene were successively lithiated and treated with tri-n-butyltin chloride. The products were purified by chromatography using neutral alumina and petroleum ether as eluent. The precursor 2-(tri-n-butylstannyl)-4-hexyl-thiophene was synthesized by a two step reaction. In the first step, the 3-bromothiophene was alkylated in a Grignard reaction. The 3-hexylthiophene was separated by vacuum distillation and successively reacted with n-butyllithium and tributyltin chloride at low temperature. The final product was purified by chromatography using neutral alumina and petroleum ether as eluent. The Stille coupling was carried out in THF with Pd(PPh$_3$)$_4$ as catalyst. The resulting monomer was purified by column chromatography using silica and dichloromethane as solvent. **TH-DPP-TH** was collected as red powder. **HTH-DPP-HTH** and **EDOT-DPP-EDOT** were collected as red foil. They are well soluble in common organic solvents.

Different from the other thienylene DPP derivatives, **BTH-DPP-BTH** was prepared upon Suzuki coupling. The dibrominated monomer **HDPP** was reacted with an excess amount of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-(2,2'-bithiophene) as indicated in Scheme 3.8. The resulting product was purified by chromatography. The monomer **BTH-DPP-BTH** was collected as a black powder, which was different from the red powderous **TH-DPP-TH** and red foil **HTH-DPP-HTH**. The solubility of **BTH-DPP-BTH** is lower than that of **TH-DPP-TH** and **HTH-DPP-HTH**. However, it can be dissolved in chloroform, toluene and THF with the help of ultrasonic treatment.

Scheme 3.8 Preparation of **TH-DPP-TH**, **HTH-DPP-HTH**, **BTH-DPP-BTH** and **EDOT-DPP-EDOT**

The ^{1}H-NMR spectra of **TH-DPP-TH**, **HTH-DPP-HTH**, **BTH-DPP-BTH**, **EDOT-DPP-EDOT** and **HDPP** are shown in Figure 3.1.

For the spectrum of **TH-DPP-TH**, there are three signals at 7.15 ppm, 7.38 ppm and 7.45 ppm, which belong to the thiophene unit. In the spectrum of **HTH-DPP-HTH**, the signal at 2.66 ppm is typical for the alpha methylene proton of the hexyl group. The two aromatic signals of thiophene at 6.97 ppm and 7.29 ppm are both singlets, which indicate that the hexyl chain of thiophene is located at the 4-position. In the spectrum of **BTH-DPP-BTH**, the signals with chemical shift between 7.07 ppm and 7.37 ppm belong to the bithiophene unit. For **EDOT-DPP-EDOT**, the occurrence of the doublet signals with chemical shift at 4.34 ppm is typical for EDOT. The other signals in the sandwich-structured thiophene containing DPP monomers are very similar to those of **HDPP**.
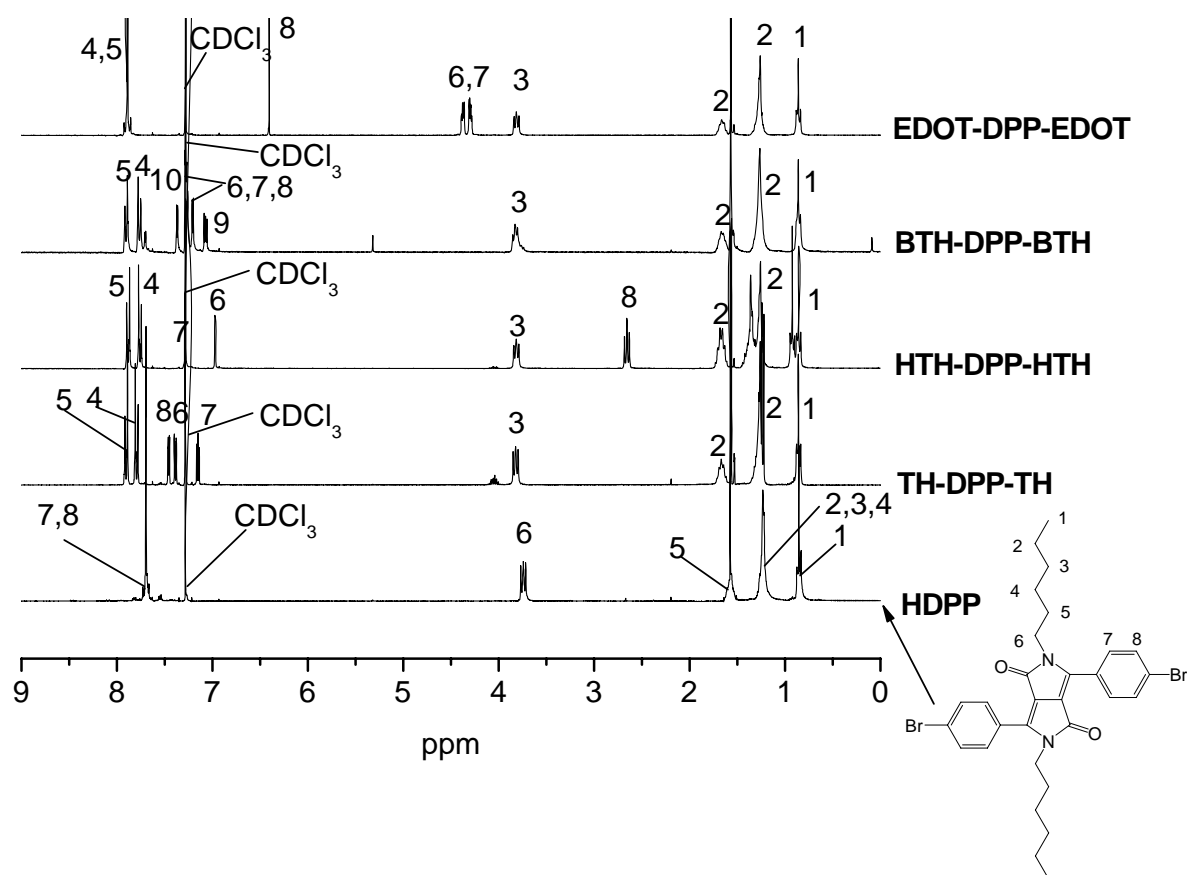
Figure 3.1 ^{1}H-NMR spectra of **TH-DPP-TH**, **HTH-DPP-HTH**, **BTH-DPP-BTH**, **EDOT-DPP-EDOT** and **HDPP** in CDCl$_3$ (for molecular structures, see next page).

TH-DPP-TH

HTH-DPP-HTH

BTH-DPP-BTH

EDOT-DPP-EDOT

Figure 3.1 Continued

The UV/vis absorption and photoluminescence spectra of **TH-DPP-TH**, **HTH-DPP-HTH**, **BTH-DPP-BTH** and **EDOT-DPP-EDOT** were measured in chloroform. The results are compared with those of **HDPP** in Figure 3.2. After the thiophene units are introduced at both ends of the DPP chromophore, a red-shift of the absorption and emission maxima can be detected. The maximum absorbance of **TH-DPP-TH** in chloroform is at 500 nm (for **HDPP**: 476 nm), the corresponding emission maximum appears at 575 nm (for **HDPP**: 533 nm). The photoluminescence quantum yield of **TH-DPP-TH** is 89%, which is almost the same as for **HDPP** (90%). The optical properties of **HTH-DPP-HTH** are very similar to that of **TH-DPP-TH**. Compared with **HDPP**, the absorption and emission maxima exhibit bathochromic shifts of 25 nm and 46 nm, respectively. The photoluminescence quantum yield is 88%. When the DPP unit is connected with the bithiophene units, the conjugation length of the molecule **BTH-DPP-BTH** is strongly extended. The absorption and emission peak now appear at 512 nm and 600 nm, respectively. Compared with **HDPP**, they exhibit a bathochromic shift of 36 nm and 67 nm, respectively. However, the photoluminescence quantum yield is lowered to

50% due to the lower solubility in common organic solvents. EDOT normally introduces a bathochromic shift and a lower bandgap in a conjugated system. However, **EDOT-DPP-EDOT** exhibits absorption and emission maxima at 510 nm and 585 nm, respectively. This means that the bathochromic shift is similar to that of **BTH-DPP-BTH**. However, the photoluminescence quantum yield is still quite high (84%). This may result from the good solubility of the EDOT unit. The UV/vis absorption of a solid monomer film was also measured and a maximum at 521 nm, 518 nm, 537 nm and 525 nm was found for **TH-DPP-TH**, **HTH-DPP-HTH**, **BTH-DPP-BTH** and **EDOT-DPP-EDOT**, respectively. This indicates a bathochromic shift compared with the absorption in chloroform solution.

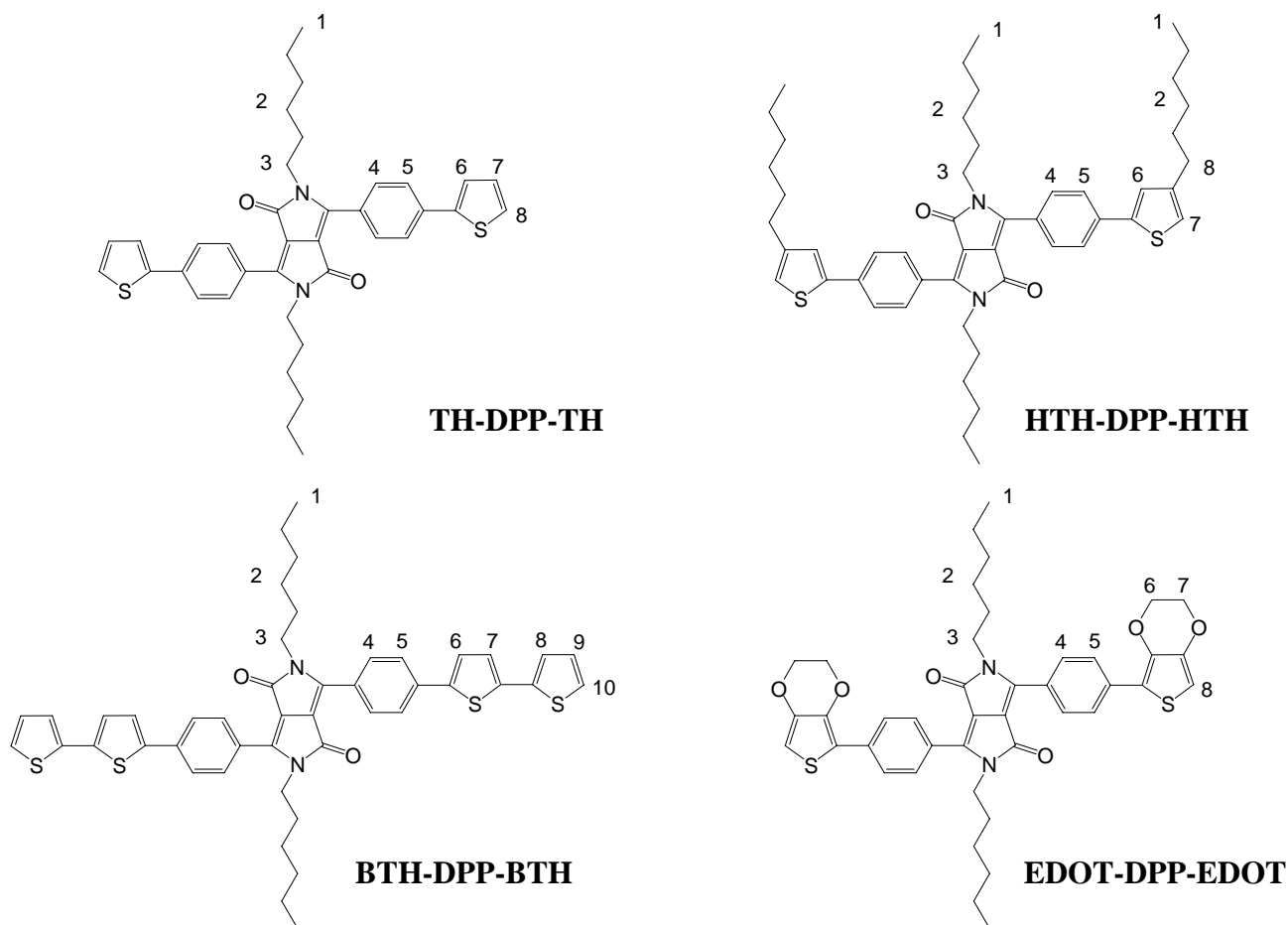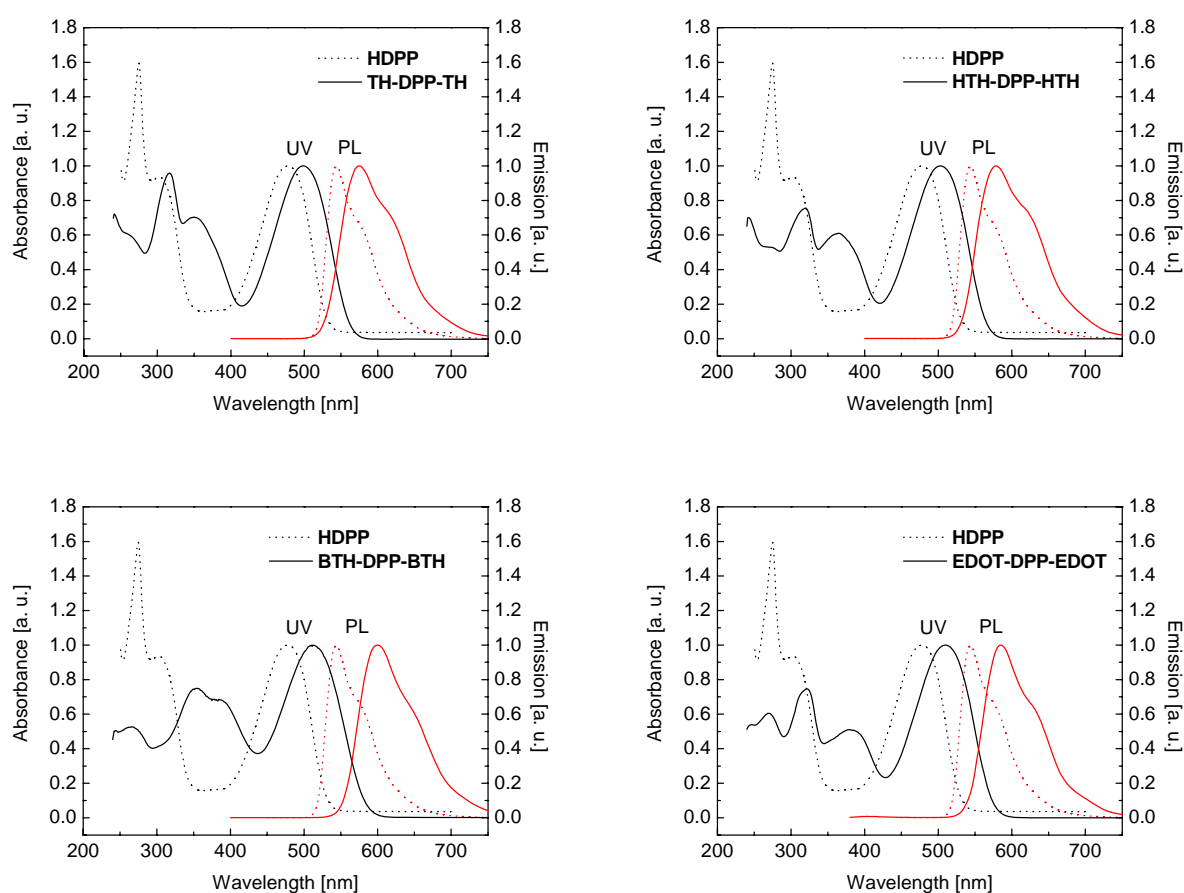Figure 3.2 UV/vis absorbance and photoluminescence spectra of **TH-DPP-TH**, **HTH-DPP-HTH**, **BTH-DPP-BTH** and **EDOT-DPP-EDOT** compared with those of **HDPP**. Solvent: CHCl$_3$. The excitation wavelength is 350 nm.

Pyrrole containing DPP monomers

Bispyrrole derivatives are very hard to be synthesized because 2-bromo-pyrrole and most N-substituted 2-bromo-pyrroles are instable[159-161]. The corresponding alkylstannyl and boronic ester derivatives are also not available. In a previous report on bis-pyrrole-arylenes[120], a complicated procedure was used to synthesize the desired compounds. Recently, t-butoxycarbonyl protected pyrrole was reported, with which the corresponding brominated derivatives[162], the boronic acid or esters[163] and the stannane[164] could be prepared. Tyrrell and Brookes discussed the preparation of the pyrrole boronic acids in a recent review[165]. The t-butoxycarbonyl protected pyrrole became popular in palladium catalyzed reactions in recent years[163,164,166-168], because it was able to bear butyl-lithium and was suitable to prepare the corresponding boronic acid, ester or stannane. Furthermore, the t-butoxycarbonyl group could be removed during the coupling reaction[166], upon treatment with a strong base[168] or heating[164,167].

The preparation of pyrrole containing DPP monomers 1,4-diketo-2,5-dihexyl-3,6-bis(4-(1-(t-butoxycarbonyl)-1H-pyrrol-2-yl)-phenyl)pyrrolo[3,4-c]pyrrole (**BPY-DPP-BPY**) and 1,4-diketo-2,5-dihexyl-3,6-bis(4-(pyrrol-2-yl)-phenyl)pyrrolo[3,4-c]pyrrole (**PY-DPP-PY**) are shown in Scheme 3.9. **PY-DPP-PY** was prepared according to a modified version of a procedure described in the literature[164,167].
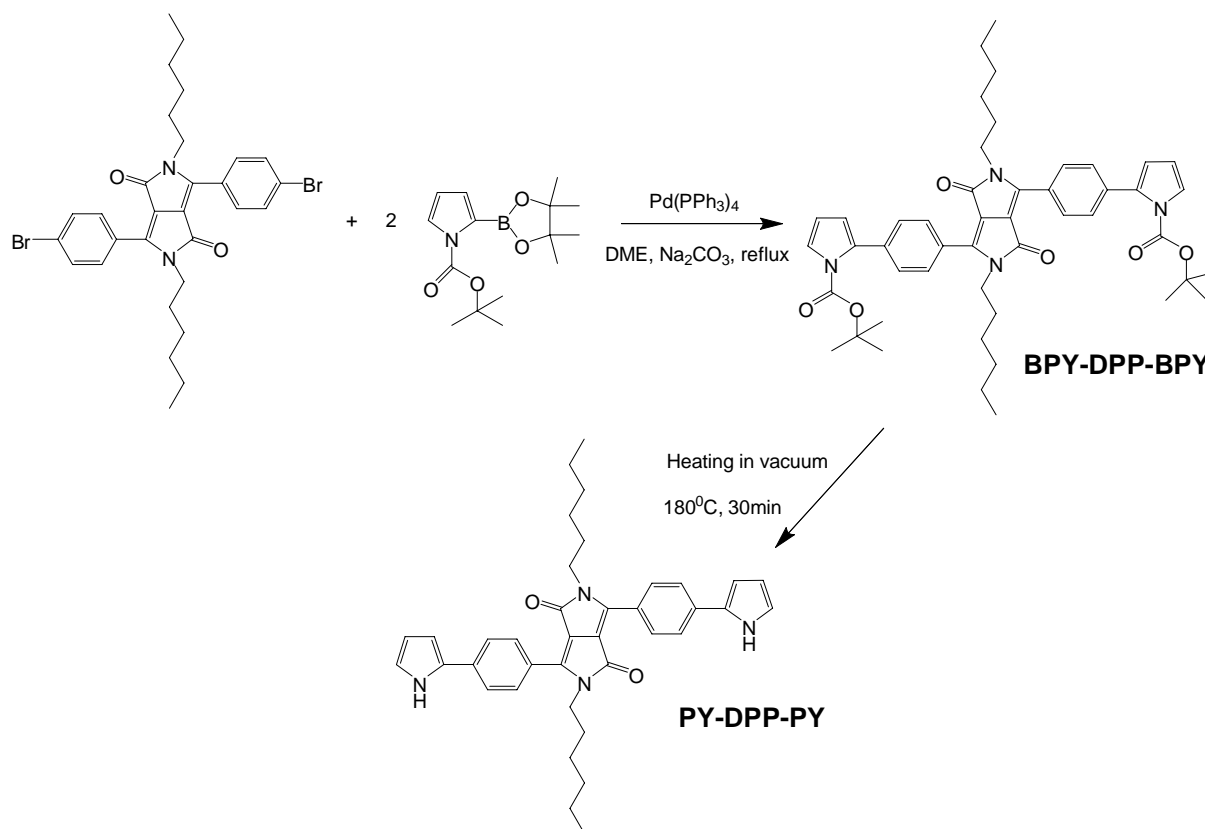
Scheme 3.9 Synthesis of **BPY-DPP-BPY** and **PY-DPP-PY**

BPY-DPP-BPY was purified by chromatography and collected as red-orange polycrystalline materials. **PY-DPP-PY** was obtained as a red powder. Both monomers are very soluble in common organic solvents such as toluene, chloroform and THF.

The proton NMR spectra of **HDPP**, **BPY-DPP-BPY** and **PY-DPP-PY** are compared in Figure 3.3. The large signal with chemical shift at 1.43 ppm indicates the presence of the t-butoxycarbonyl group. The signals of aromatic protons at the pyrrole ring appeared at 6.29, 6.31 and 7.53 ppm for **BPY-DPP-BPY**. Compared with **BPY-DPP-BPY**, the large signal at 1.43 ppm disappears in the spectrum of **PY-DPP-PY**. Another signal with chemical shift at 8.59 ppm appears. The new signal originates from the proton connected with the nitrogen atom of the pyrrole ring. The signals of the aromatic protons at the pyrrole ring are located at 6.37, 6.69 and 6.96 ppm, which are slightly smaller than those of **BPY-DPP-BPY**. The other signals in the spectra of sandwich-structured pyrrole containing DPP monomers are very similar to those of **HDPP**.
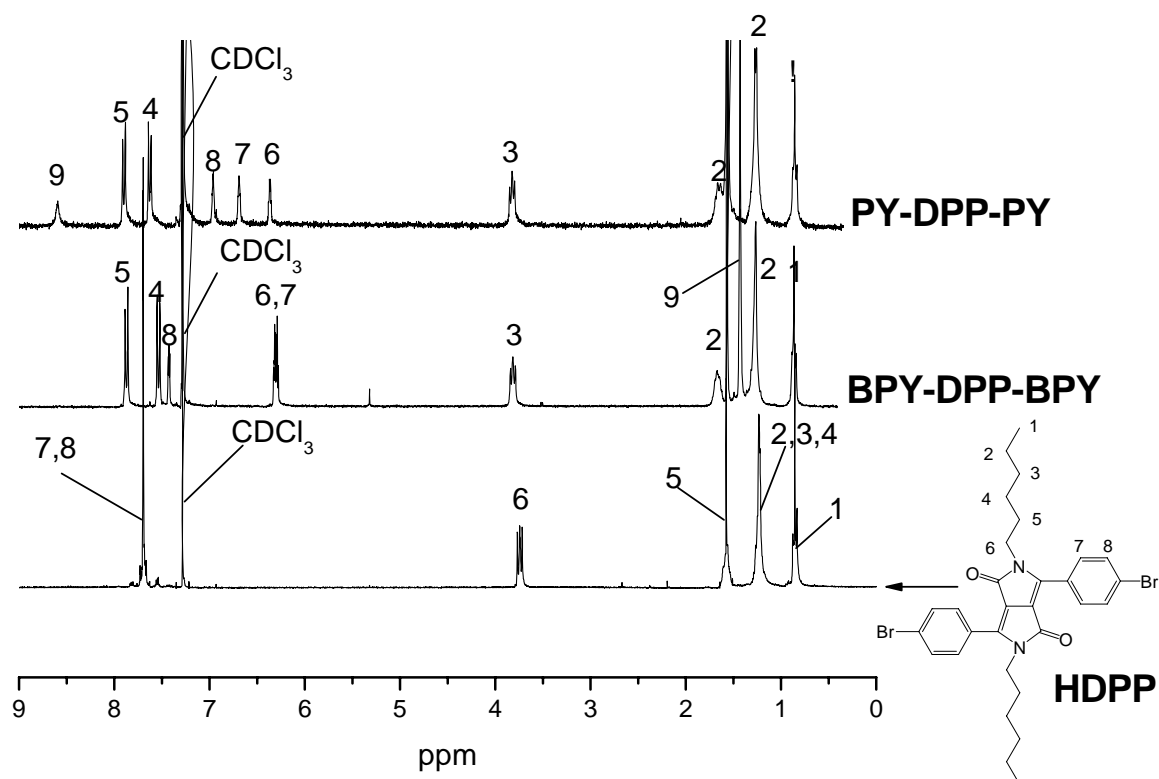

Figure 3.3 ^{1}H-NMR spectra of **BPY-DPP-BPY**, **PY-DPP-PY** and **HDPP** (for molecular structures, see next page).

Figure 3.3 Continued

The UV/vis absorption and photoluminescence spectra in chloroform are compared with those of **HDPP** in Figure 3.10. Due to the presence of the t-butoxycarbonyl group, the pyrrole can not form a co-planar structure with the DPP chromophore very well. This renders the conjugation between the pyrrole ring and the DPP chromophore significantly smaller than in the **TH-DPP-TH** monomer. As for the optical properties, the bathochromic shift of **BPY-DPP-BPY** is only 14 nm for the absorption, and 30 nm for the emission compared with **HDPP**. The photoluminescence quantum yield is still very high (85%). However, the solid monomer film exhibits an absorption maximum at 525 nm which is even larger than that of **TH-DPP-TH** indicating that a more co-planar structure formed in the solid state. If the t-butoxycarbonyl group is removed, the **PY-DPP-PY** monomer is able to form a co-planar structure. The conjugation between the pyrrole ring and the DPP chromophore becomes significantly enlarged. As a consequence, the optical absorption of **PY-DPP-PY** is bathochromically shifted by 20 nm compared with **BPY-DPP-BPY**, while the emission is shifted by 22 nm. The photoluminescence quantum yield is slightly lower (78%). The solid monomer film exhibits an absorption maximum at 544 nm, which is the largest one among all DPP containing monomers synthesized in this work.
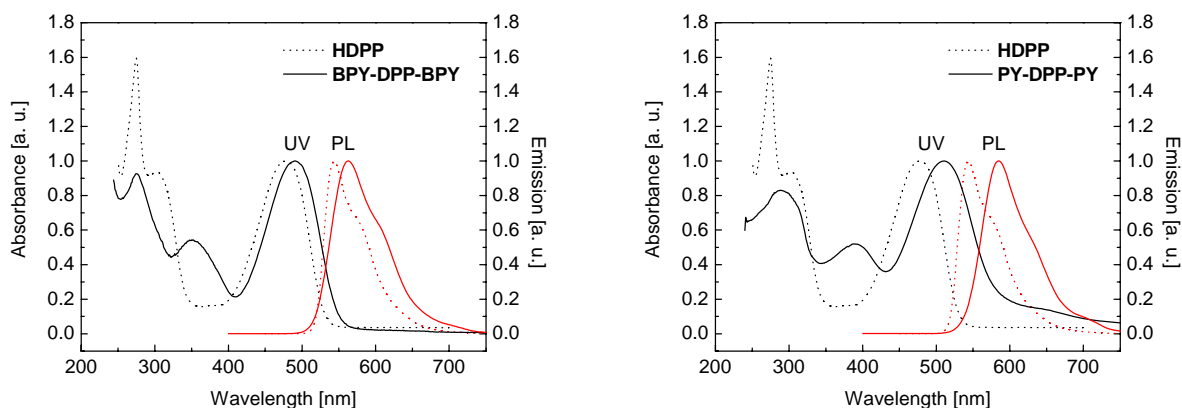
Figure 3.4 UV/vis absorbance and photoluminescence spectra of **BPY-DPP-BPY** and **PY-DPP-PY** compared with those of **HDPP**. Solvent: CHCl₃. The excitation wavelength is 350 nm.

Carbazole containing DPP monomers

The Buchwald-Hartwig coupling reaction was used to prepare 1,4-diketo-2,5-dihexyl-3,6-bis(4-N-carbazolylphenyl)pyrrolo[3,4-c]pyrrole (**CBZ-DPP-CBZ**). The synthesis is described in Scheme 3.14:
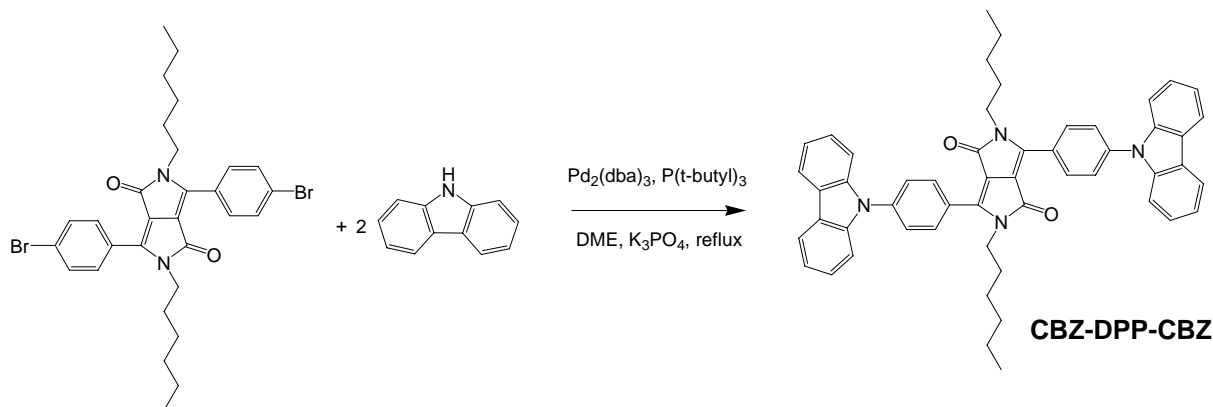
Scheme 3.10 The preparation of 1,4-diketo-2,5-dihexyl-3,6-bis(4-N-carbazolylphenyl)pyrrolo[3,4-c]pyrrole (**CBZ-DPP-CBZ**)

After purification by chromatography, the resulting monomer **CBZ-DPP-CBZ** was collected as orange foils. The compound is well soluble in common organic solvents such as toluene, chloroform and THF with the help of ultrasonic treatment. Proton NMR spectra of **CBZ-DPP-CBZ** and **HDPP** are compared in Figure 3.5.

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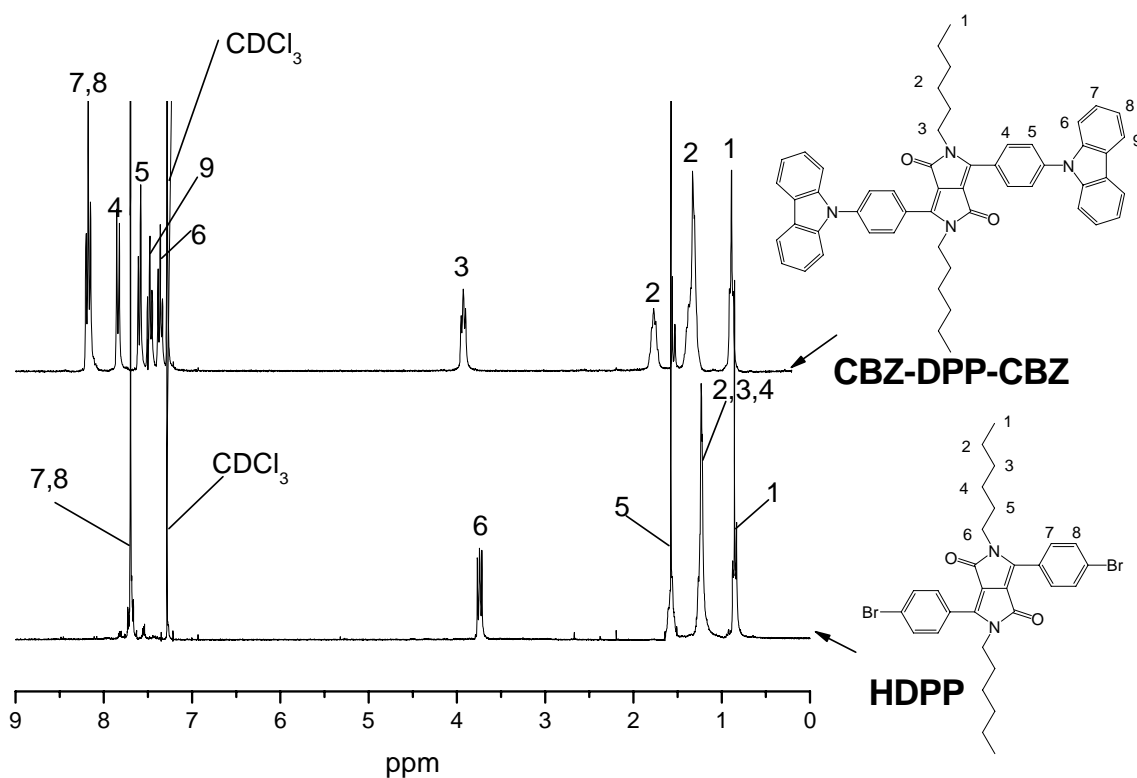
Figure 3.5, ^{1}H-NMR spectra of **CBZ-DPP-CBZ** and **HDPP** in chloroform-D

Compared with **HDPP**, additional signals at 8.2 ppm and about 7.2 ppm appear, which can be ascribed to the carbazole units. In Figure 3.6, UV/vis absorption and photoluminescence spectra in chloroform are compared with those of **HDPP**.
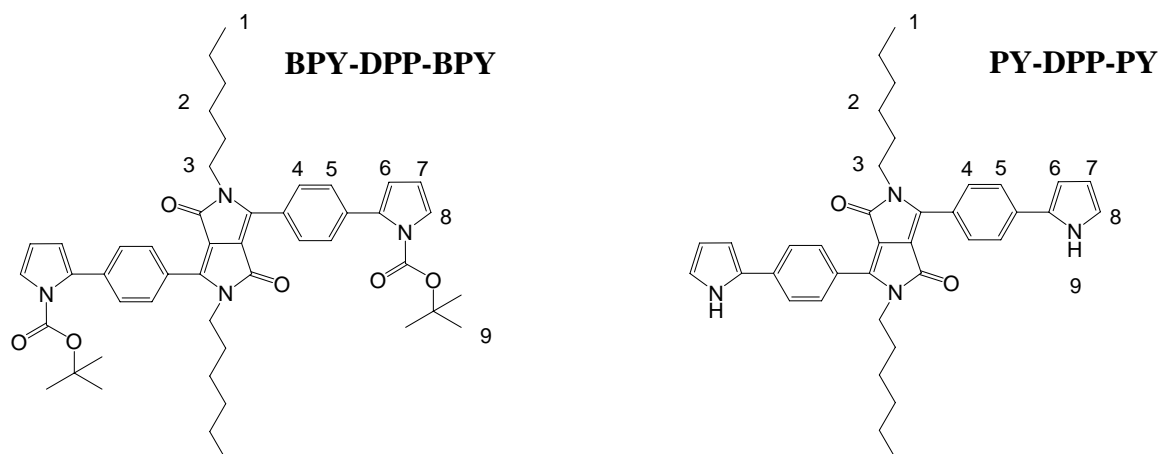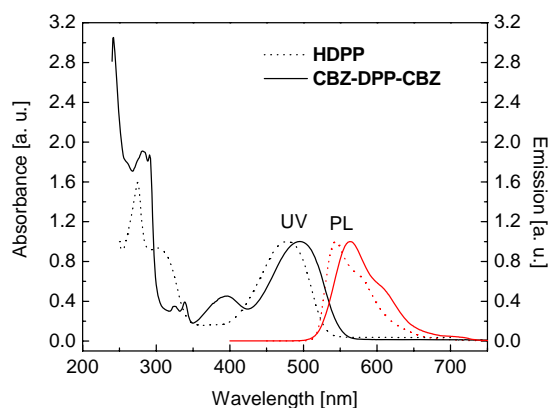

Figure 3.6, UV/vis absorbance and photoluminescence spectra of **CBZ-DPP-CBZ** and **HDPP**. Solvent: CHCl$_3$. The excitation wavelength is 350 nm.

Compared with **HDPP**, the absorption and emission maxima of **CBZ-DPP-CBZ** are bathochromically shifted by 19 and 31 nm, respectively. The small bathochromic shifts indicate that the carbazole units do not form a co-planar structure with the DPP chromophore. The photoluminescence quantum yield is very high (95%). The solid monomer film exhibits an absorption maximum at 518 nm, which is the lowest wavelength among all sandwich type DPP monomers.

3.2.2. Electrochemical polymerization

Device and method used for electrochemical polymerization
For electrochemical polymerization, a three-electrode cell was used as shown in Figure 3.7.

Figure 3.7 Three-electrode cell used for electropolymerization.

Two platinum wires are used as the counter and reference electrode. The end of the counter electrode is flattened to achieve a size of 4 mm^2. The working electrode is an ITO coated glass electrode. The cell is made of quartz and therefore can be also used for UV/vis absorption measurements at different potentials.

Unfortunately, the sandwich type DPP monomers were not soluble in acetonitrile, which is generally used as the solvent for electrochemical experiments. Therefore a mixture of acetonitrile and dichloromethane with 1:3 ratio was used. The mixture was a good solvent for most of the monomers except for **CBZ-DPP-CBZ**. For the carbazole-containing monomer, pure dichloromethane was used. In all experiments, tetrabutylammonium hexafluoro-phosphate (TBAPF$_6$) was used as the electrolyte. It was regarded as most suitable since it is

able to lower the oxidation potential of the monomers[123]. The concentration of the electrolyte was 0.1 M and the concentration of the DPP containing monomers was about 1 mg/mL.

The electropolymerization was carried out using a potentiostat PG390 from Heka Company. The anodic polymerization can be carried out at constant potential as a potentiostatic method, at constant current as a galvanostatic method, or cycling potential scanning as a potentiodynamic method. In this work, the potentiodynamic method was used for most DPP monomers except for **CBZ-DPP-CBZ**, for which the potentiostatic method was applied.

The standard potential of the platinum electrode was measured in different solvent systems using ferrocene as standard prior to the electropolymerization. The potential value can then be recalculated as versus SCE. The relationship between the platinum electrode and SCE is shown in Figure 3.8.
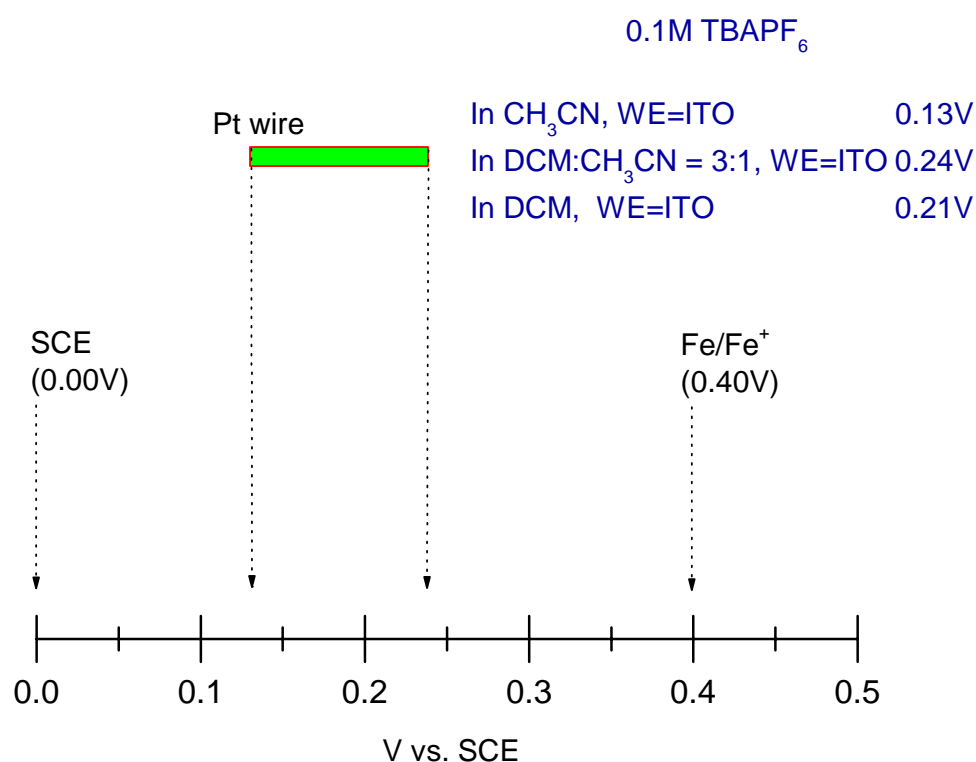

Figure 3.8 Electrode potential relationship between common reference electrodes

Using the calculation of the potential described above, the oxidation potentials of the monomers were calculated for different solvent systems versus SCE. The results are listed in Figure 3.9.

Although in all monomer molecules electropolymerizable heterocycles are attached on both sides, not all of them can be successfully electropolymerized. The electropolymerization depends on many factors, the most important one being the oxidation potential of the monomer. The monomers with the lowest oxidation potential (**PY-DPP-PY**, **EDOT-DPP-EDOT** and **BTH-DPP-BTH**) can be easily electropolymerized and the films formed on the electrode are very robust. The monomer **BPY-DPP-BPY** also has a low oxidation potential, but the polymer film formed with this monomer is electroinactive. This is probably due to the presence of the voluminous butoxycarbonyl groups, which cause that the pyrrole rings are twisted being off the plane of the DPP chromophore. As a consequence, the polymer chain becomes then twisted and the π-conjugation is interrupted after several repeated units. For **TH-DPP-TH** and **HTH-DPP-HTH**, the oxidation potentials are too high and only soluble oligomers are formed during the oxidation processes. It is unexpected that **CBZ-DPP-CBZ** can be oxidized and form polymer films although the oxidation potential is quite high. For polymerization of **CBZ-DPP-CBZ**, the potentiostatic method was used, which means that the potential was hold at 1.4 V for two minutes. The successful deposition of polymer films may be caused by the lower solubility of **CBZ-DPP-CBZ** which causes that the oligomeric intermediates deposite at the ITO glass very quickly during the oxidation process.
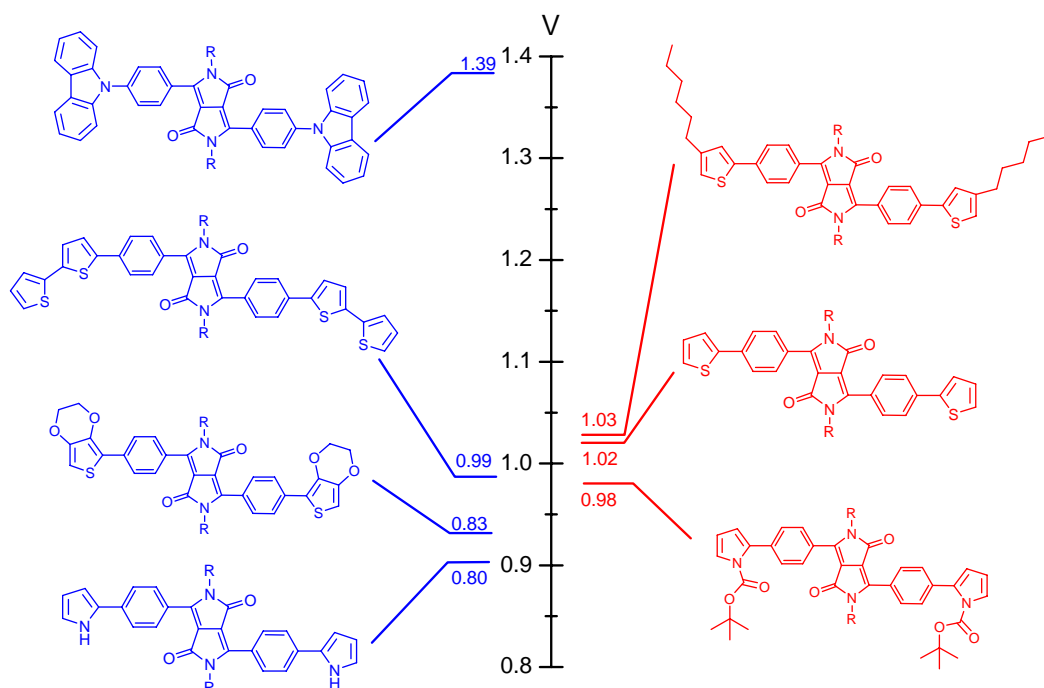
Figure 3.9 Oxidation potentials of different DPP-based monomers vs. SCE.

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Characterization of Poly(BTH-DPP-BTH) films

Poly(BTH-DPP-BTH) was prepared upon anodic electropolymerization of the monomer. For this purpose, the monomer **BTH-DPP-BTH** was dissolved in a mixture of CH_3CN/CH_2Cl_2 and 0.1 M TBAPF$_6$ as electrolyte. The ratio of CH_3CN and CH_2Cl_2 was 1:3. The potentiodynamic method was used in the potential range from -0.26 V to 1.11 V. The scan rate was 100 mV/s. The working electrode was ITO-coated glass, the counter and reference electrodes were platinum. Cyclic voltammograms monitored during the electropolymerization are shown in Figure 3.10. After several cycles, a thin polymer film was deposited on the ITO anode.

Figure 3.10 Cyclic voltammograms of electropolymerization of **BTH-DPP-BTH**. Working electrode: ITO; reference and counter electrode: Pt. Potential is vs SCE. The monomer was dissolved in 0.1 M TBAPF$_6$ in CH_3CN/CH_2Cl_2 mixture. Scan rate: 100 mV/s, T = 20 °C.

The polymer film is insoluble in common organic solvents. Therefore it is not possible to use standard characterization methods such as GPC or NMR to analyze the compound. However,

the UV/vis absorption can be measured and the in situ formed films can be directly used in many applications.

The absorption maximum of the **Poly(BTH-DPP-BTH)** film is at 356 nm and the colour is brown-red. Compared with the monomer, which has a maximum absorption at 537 nm, it is clear that the bithiophene units dominate the electronic properties of the polymer. Due to the incorporation of the counter ions in the film, the luminescence of the polymer is quenched.

The spectroelectrochemical study of the **Poly(BTH-DPP-BTH)** films was carried out in dry CH_3CN solution with $TBAPF_6$ as electrolyte salt. The cyclic voltammogram is shown in Figure 3.11-a, and the corresponding UV/vis absorption at different oxidation potentials is shown in Figure 3.11-b.
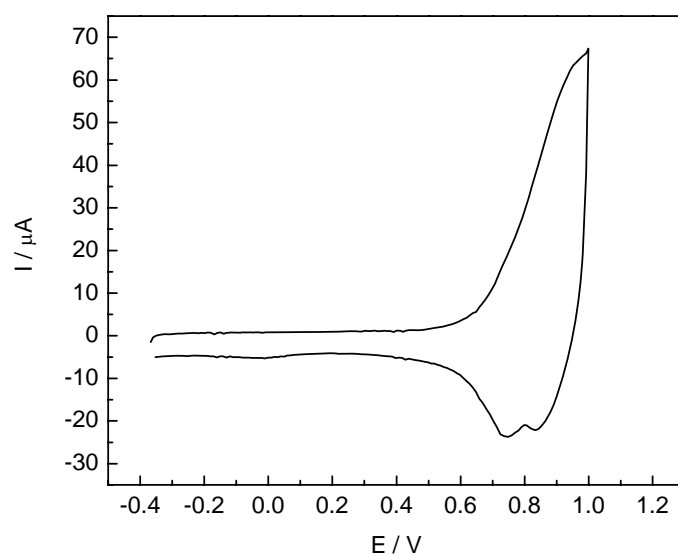
Figure 3.11-a Cyclic voltammogram of a film of **Poly(BTH-DPP-BTH)** measured in 0.1 M $TBAPF_6$ in CH_3CN (Voltage calculated versus SCE)
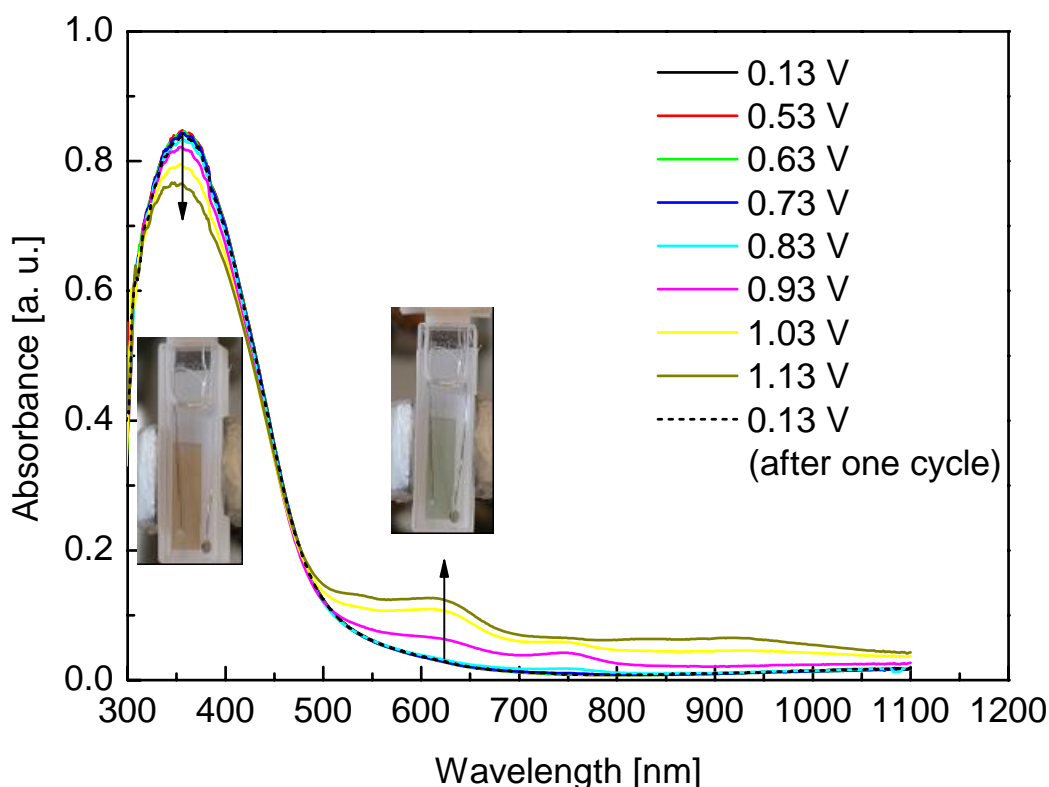
Figure 3.11-b Spectroelectrochemical analysis of **Poly(BTH-DPP-BTH)** in 0.1 M TBAPF$_6$ in CH$_3$CN (Voltage calculated versus SCE).

Upon oxidation, a new absorption peak belonging to the formation of dications (the radicals dimerize) appears at 618 nm. There is an abrupt colour change, if the oxidation potential has reached 0.93 V (vs. SCE). The colour of the polymer film changes from brown red to olive green (see the photographs in Figure 3.11-b). After the colour change, the polymer is very stable and the switching can be repeated many times without special treatment of the solution or the use of protecting gas. The origin of this kind of colour change has been described in publications[48]. In the neutral (insulating) state, the conjugated polymer shows semiconducting behaviour with an energy gap between the valence band (HOMO) and the conduction band (LUMO). Upon electrochemical doping ("p-doping" for oxidation and "n-doping" for reduction), the band structure of the neutral polymer is modified generating lower energy intraband transitions and charge carriers (polarons and bipolarons), which are responsible for the increased conductivity and optical modulation.

Characterization of Poly(EDOT-DPP-EDOT) films

Poly(EDOT-DPP-EDOT) was prepared according to the same method as described previously for **Poly(BTH-DPP-BTH)** except that another monomer **EDOT-DPP-EDOT** and a different potential range (from -0.06 V to 0.91 V) were used. The cyclic voltammograms monitored during the potential cycling are shown in Figure 3.12. After several cycles, a polymer film was deposited on the ITO electrode.
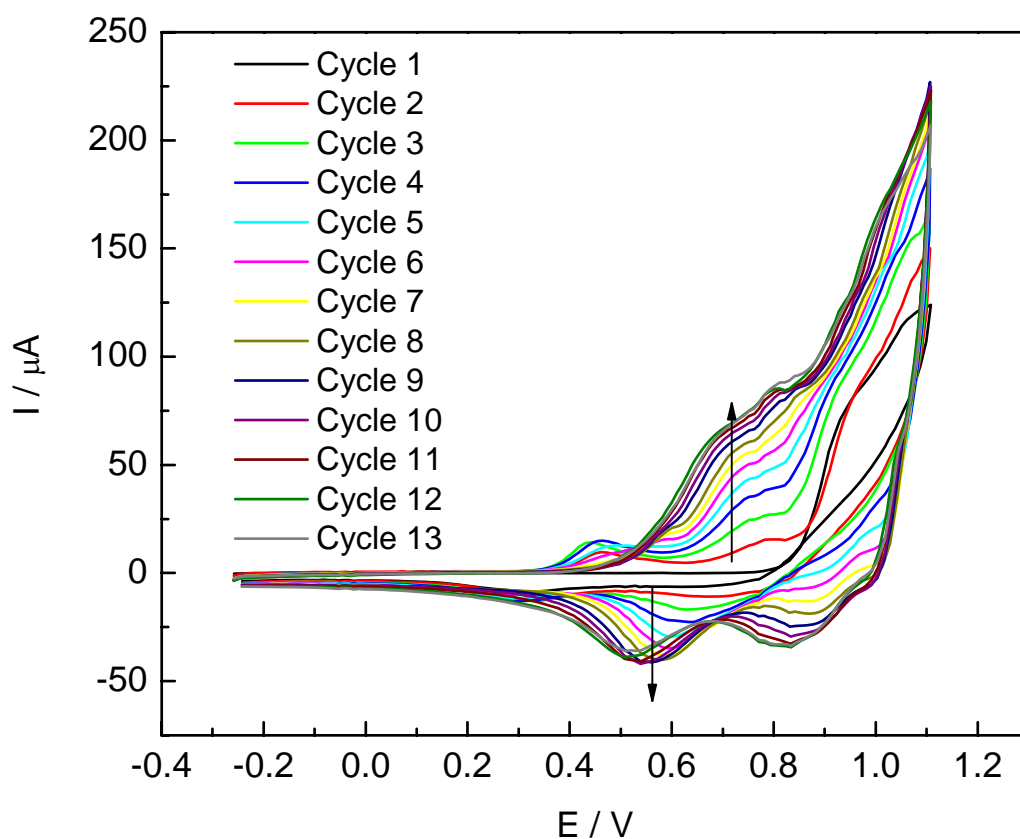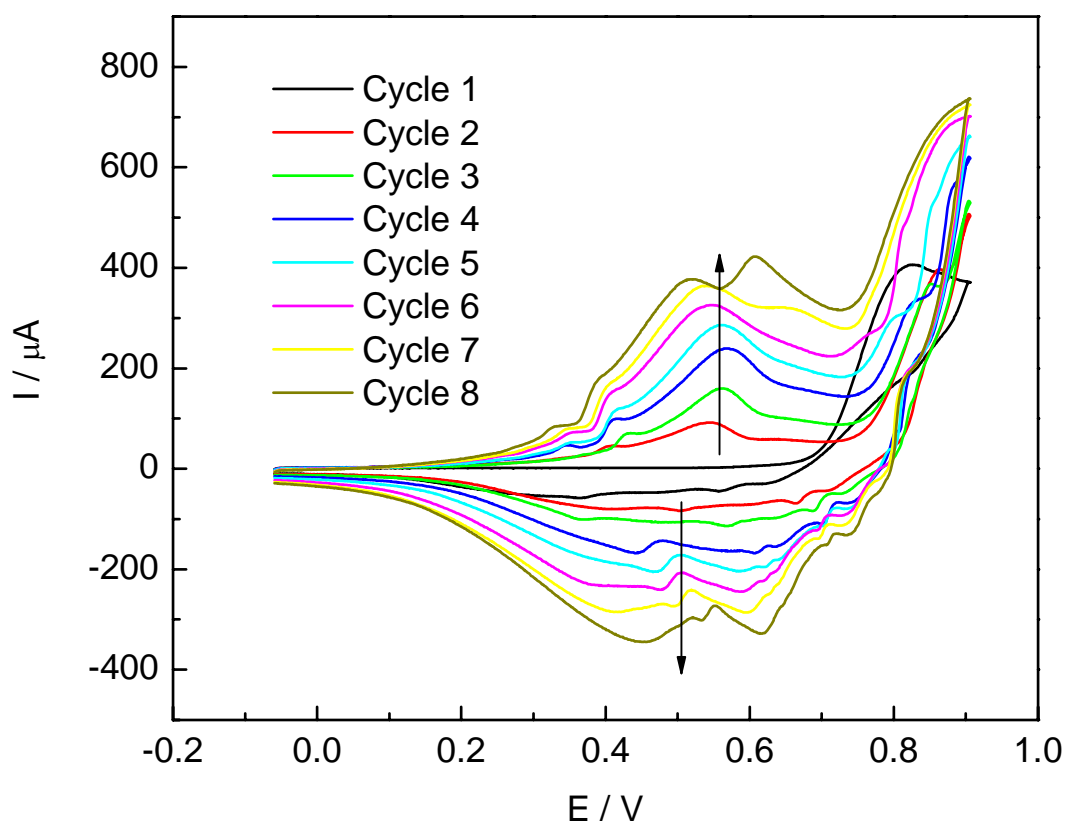

Figure 3.12 Cyclic voltammograms of electropolymerization of **EDOT-DPP-EDOT**. Working electrode: ITO; reference and counter electrode: Pt. Potential is vs SCE. The monomer was dissolved in 0.1M TBAPF$_6$ in CH$_3$CN/CH$_2$Cl$_2$ mixture, scan rate: 100 mV/s, T = 20 °C.

The **Poly(EDOT-DPP-EDOT)** polymer film is also insoluble in common organic solvents as also found for the film of **Poly(BTH-DPP-BTH)**. The absorption maximum of **Poly(EDOT-DPP-EDOT)** is at 626 nm and the colour is deep-blue, while for the monomer, the absorption maximum was only 525 nm. The red-shift of the absorption may be caused by the increase of

the conjugation length during polymerization. It may be recalled that **P-EDOT-DPP**, a polymer with similar structure prepared by Stille polycondensation (see chapter 2) exhibits an absorption maximum at 581 nm. The large bathochromic shift of the electropolymerized the film indicates that the molecular weight of the polymer is probably much higher. This may also explain the insolubility. The UV/vis absorptions of solid films of the monomers and the polymers are shown in Figure 3.13.
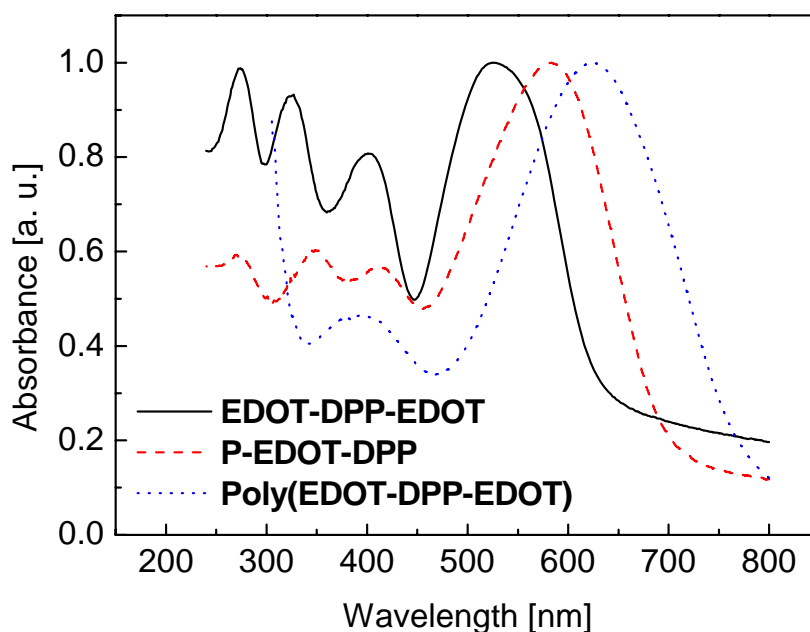
Figure 3.13 UV/vis absorption spectra of solid films of monomer **EDOT-DPP-EDOT**, polymer **P-EDOT-DPP** and **Poly(EDOT-DPP-EDOT)**.

The spectroelectrochemical analysis of the **Poly(EDOT-DPP-EDOT)** film was carried out in dry CH_3CN solution with $TBAPF_6$ as electrolyte salt. The cyclic voltammogram was performed as shown in Figure 3.14-a, and the corresponding UV/vis absorption at different oxidation potentials is shown in Figure 3.14-b.
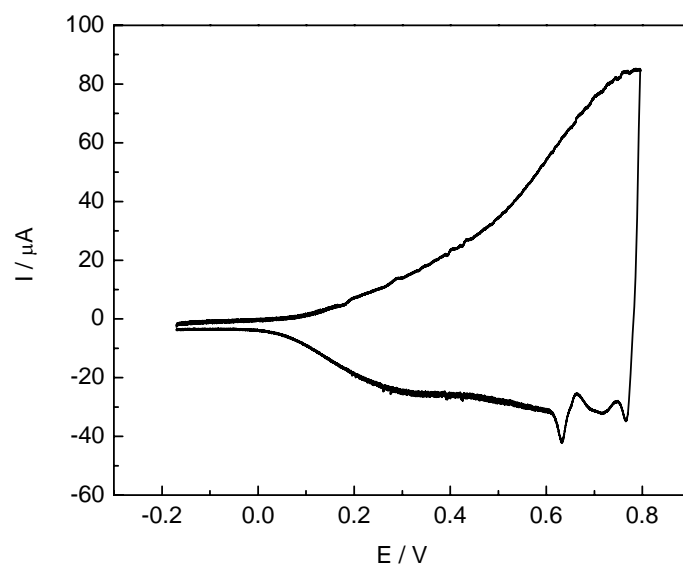
Figure 3.14-a Cyclic voltammogram of a film of **Poly(EDOT-DPP-EDOT)**. The CV was measured in 0.1 M TBAPF$_6$ in CH$_3$CN (Voltage calculated versus SCE).

Figure 3.14-b Spectroelectrochemical analysis of **Poly(EDOT-DPP-EDOT)** in 0.1 M TBAPF$_6$ in CH$_3$CN (Voltage calculated versus SCE).

Upon anodic oxidation, the original absorption peak at 626 nm decreases and another absorption peak originating from the formation cations along the conjugated backbone (polarons) appears at 900 nm. The absorption of the polymer film is shifted to the infrared region and therefore the colour changes from deep blue to nearly transparent (see the photographs in Figure 3.14-b). The colour transition is rather abrupt once the oxidation potential exceeds 0.6 V (vs. SCE). After the transition, the polymer is very stable and the switching can be repeated many times without special treatment of the solution and the use of protecting gas.

Characterization of Poly(PY-DPP-PY) films

**Poly(PY-DPP-PY)** was prepared according to the same method as described previously except that the monomer **PY-DPP-PY** and a different potential range (-0.27 V to +0.9 V) were used. The cyclic voltammograms monitored during the potential cycling are shown in Figure 3.15. After several cycles, a polymer film was deposited on the ITO electrode.

Figure 3.15 Cyclic voltammogram of electropolymerization of **PY-DPP-PY**. Working electrode: ITO; reference and counter electrode: Pt. Potential is vs SCE. The monomer was dissolved in 0.1 M TBAPF$_6$ in CH$_3$CN/CH$_2$Cl$_2$, scan rate: 100 mV/s, T = 20 °C.

PY-DPP-PY has the lowest oxidation potential and is very easily oxidized under formation of a polymer film. The polymer film is red-purple with a maximum absorption at 535 nm. It is about 11 nm hypsochromically shifted with regard to a film of the monomer. This might be an orientational effect of the chromophore units along the backbone leading to twisting of the π-conjugated polymer backbone. The polymer film is nonluminescent due to the incorporation of the counter anions.

The spectroelectrochemical analysis of **Poly(PY-DPP-PY)** films was carried out in dry CH_3CN solution with $TBAPF_6$ as electrolyte. The cyclic voltammogram of the film is shown in Figure 3.16-a, and the corresponding UV/vis absorption at different oxidation potentials is shown in Figure 3.16-b.
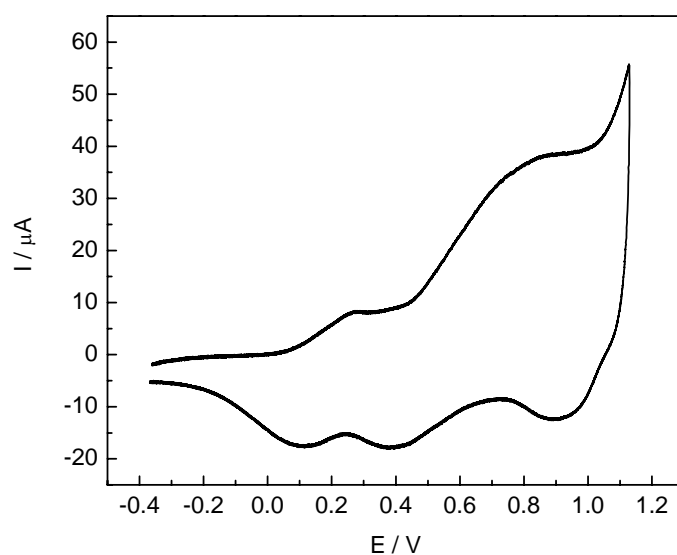
Figure 3.16-a Cyclic voltammogram of a film of **Poly(PY-DPP-PY)**. The CV was measured in 0.1 M $TBAPF_6$ in CH_3CN (Voltage calculated versus SCE).
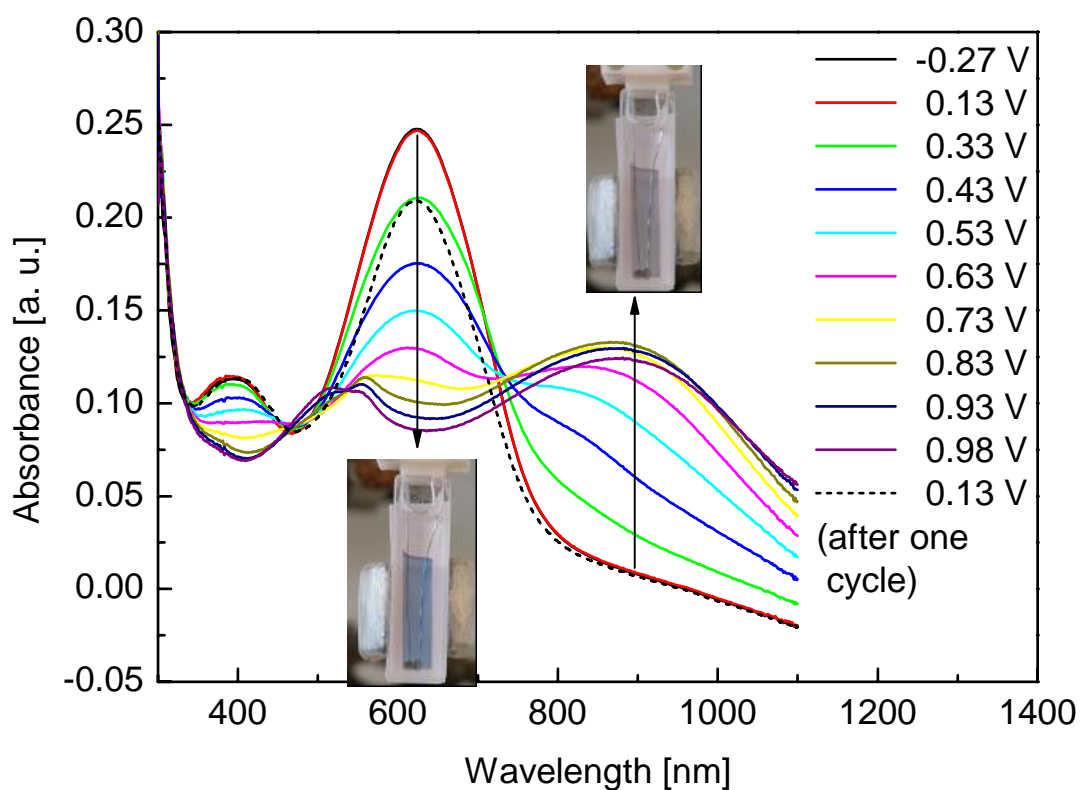
Figure 3.16-b Spectroelectrochemical analysis of **Poly(PY-DPP-PY)** in 0.1 M TBAPF$_6$ in CH$_3$CN (Voltage calculated versus SCE).

In the neutral state, the maximum absorption of the polymer film is at 535 nm. Upon oxidation the absorption peak at 535 nm decreased and the absorption at $\lambda > 700$ nm increased. The isosbestic point is around 671 nm when the potential is lower than 0.63 V. However, the colour change of the polymer film is not very pronounced because the absorption around 535 nm does not completely disappear even at a very high applied voltage (1.03 V vs. SCE). The colour turns form purple-red (in the neutral state) to brown-red (in the oxidized state).

Characterization of Poly(CBZ-DPP-CBZ) film

Poly(CBZ-DPP-CBZ) was prepared by oxidative electropolymerization of the monomer. The monomer **CBZ-DPP-CBZ** was dissolved in CH$_2$Cl$_2$ with 0.1M TBAPF$_6$ as electrolyte. The working electrode was ITO glass, the counter and reference electrodes were platinum. The cyclic voltammogram for the proceeding electropolymerization is shown in Figure 3.17. After several cycles, a very thin polymer film was obtained at the ITO coated electrode. However,

the polymer film prepared by this method is too thin for a detailed characterization. Therefore, the potentiostatic method (hold potential at 1.4 V for 2 minutes) was used. A thicker film was obtained and used for the characterization.
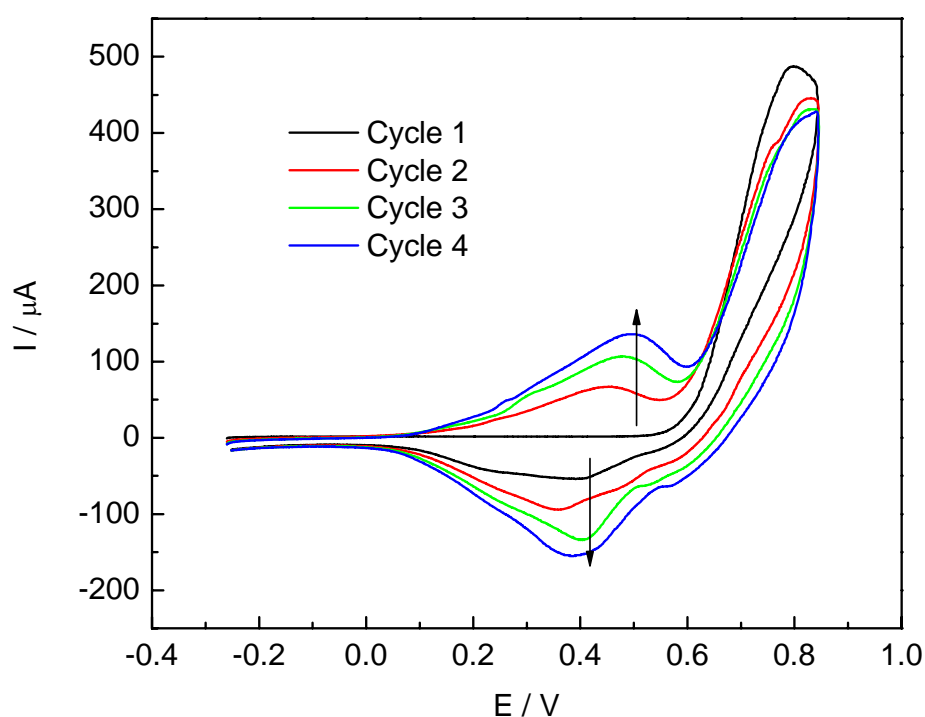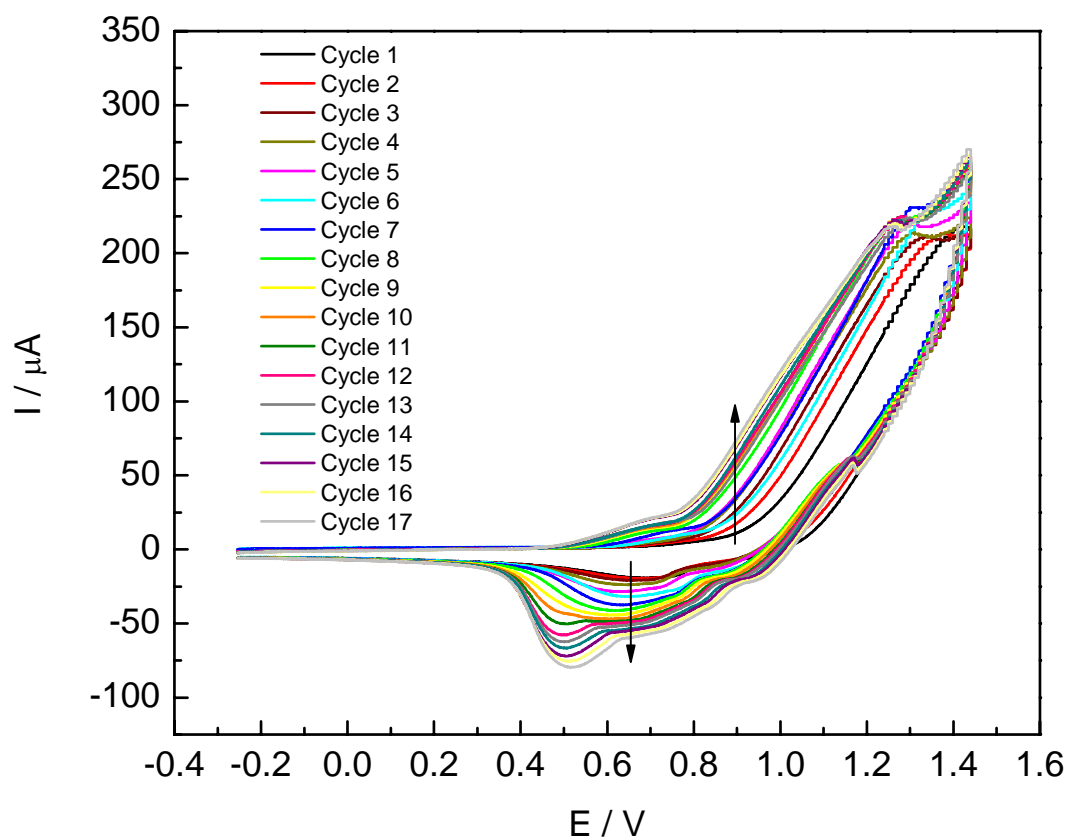

Figure 3.17 Cyclic voltammogram of electropolymerization of **CBZ-DPP-CBZ**. Working electrode: ITO; reference and counter electrode: Pt. Potential is vs SCE. The monomer was dissolved in 0.1M TBAPF$_6$ in CH$_3$CN/CH$_2$Cl$_2$ mixture, scan rate: 100 mV/s, T = 20 °C.

The potentiostatically deposited film was subjected to a spectroelectrochemical study. The results are shown in Figure 3.18-a and 3.18-b.
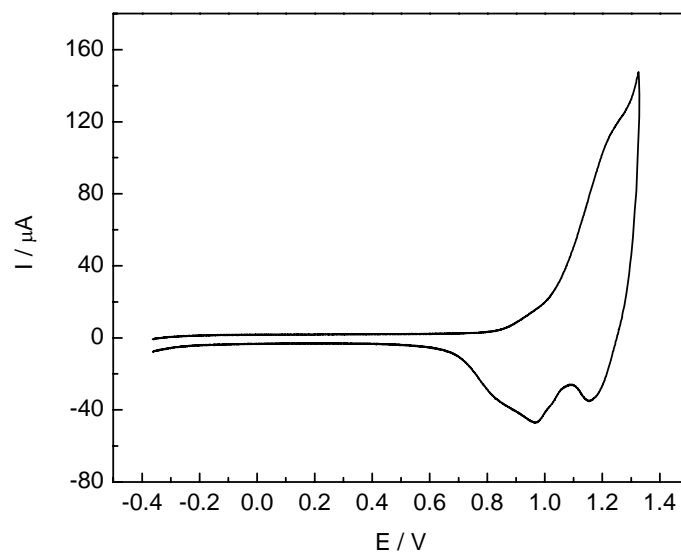
Figure 3.18-a, Cyclic voltammogram of a film of **Poly(Bis- Carbazole -DPP)**. The CV was measured in 0.1M TBAPF$_6$ in CH$_3$CN (Voltage calculated versus SCE).
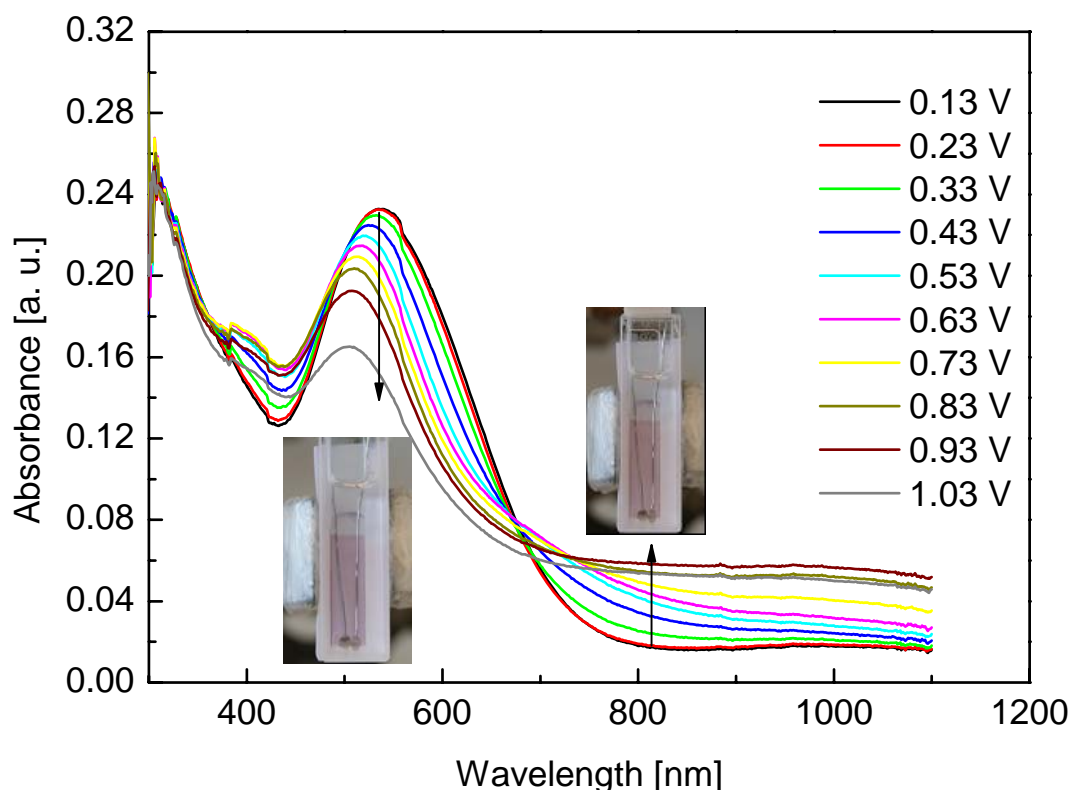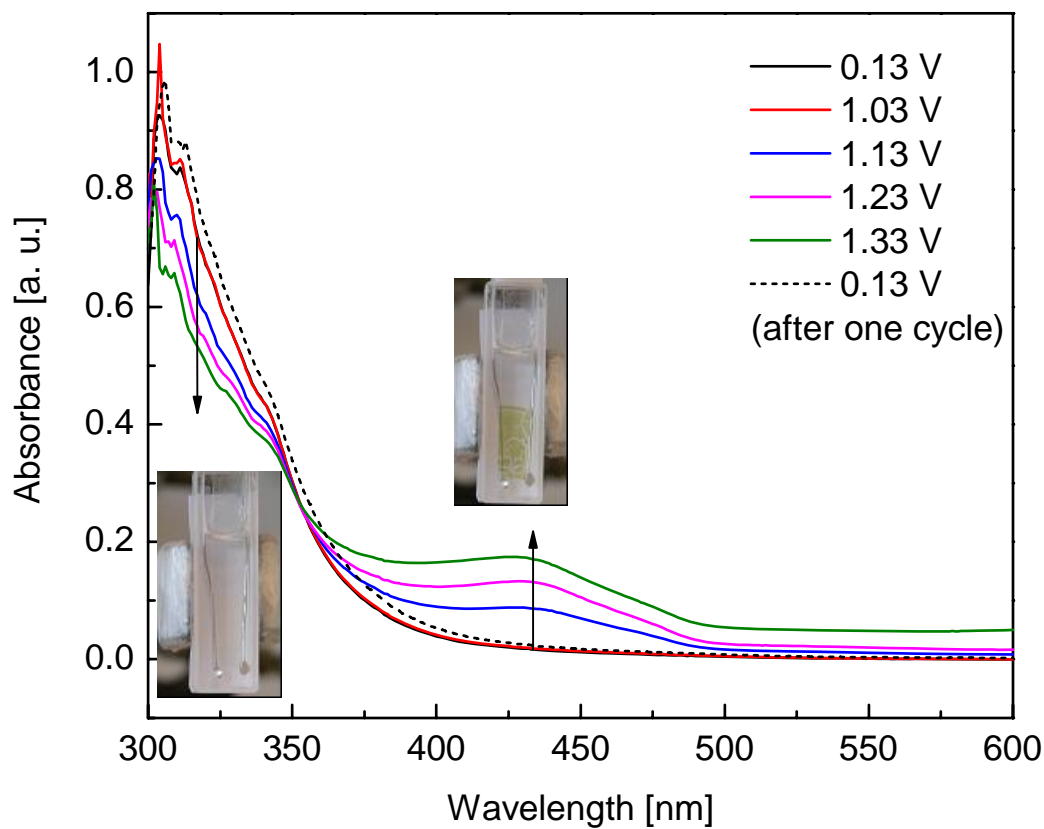

Figure 3.18-b, Spectroelectrochemical analysis of **Poly(Bis- Carbazole -DPP)** in 0.1M TBAPF$_6$ in CH$_3$CN (Voltage calculated versus SCE).

In the neutral state, the polymer film only absorbs at wavelengths shorter than 400 nm and there is almost no absorption in the visible range. This means that the DPP chromophore is probably destroyed. The destruction may originate from the very high oxidation potential applied to the **CBZ-DPP-CBZ** monomer. The polymer film is quite brittle compared with the other polymer films, which might be an indication that the molecular weight of the polymer is probably low. Upon oxidation an absorption peak at 429 nm appears and the polymer film turns to green (Figure 3.18-b). The strong colour change from colourless to green makes it very promising for electrochromic applications.

3.3. Conclusions

In this chapter, the electropolymerization of a number of DPP containing monomers was investigated and the successful preparation of four different polymer films is described. The low oxidation potential of the monomer was found to be the crucial factor for a successful electropolymerization. The reason is that there are a lot of side reactions, if a high potential is applied. Besides the oxidation potential, the solubility of the monomer also affects the deposition process. If the oligomers formed during the oxidation reaction are only little soluble, they could be easily deposited at the electrode surface, and the film formation process was considerably proved.

Compared with the polymers prepared upon chemical polycondensation reactions, the polymers from electropolymerization are generally insoluble in common organic solvents; which renders a characterization very difficult. Furthermore, the electrochemically prepared polymer is non-luminescent due to incorporation of counter anions during the polymerization process.

However, there are several advantages for the electropolymerization:

- The monomers can be purified by usual separation methods and there is no palladium and ligand from the catalyst incorporated in the polymer chain. This favours a high conductivity of the polymer film.

- The amount of monomer needed to carry out the polymerization is very small. One milligram is already sufficient to deposit several films at the anode.

- The electrochemically prepared polymer film is mechanically robust and very insoluble in most solvents. The stability is generally very good. Upon oxidative cycling (reversible p-doping and de-doping), the film is more stable and reversible than polymer film prepared by chemical polycondensation.

These properties render the electropolymerization might suitable for preparation of electroactive polymer films, which might be used as achive components in electronic devices. Upon oxidation, the polymer films reversibly change colour from brown-red to olive green (**Poly(BTH-DPP-BTH)**), deep blue to colourless (**Poly(EDOT-DPP-EDOT)**), purple-red to brown-red (**Poly(PY-DPP-PY)**) and colourless to green (**Poly(CBZ-DPP-CBZ)**).

4. Water soluble conjugated DPP polymers

4.1. Introduction

Water soluble conjugated polymers are aromatic polymers equipped with special side groups such as ionic or nonionic water soluble substituent groups. The substituents render the materials soluble in water and other polar organic solvents such as methanol or DMSO. If a water soluble conjugated polymer is dissolved in a non-aggregated state, it exhibits similar optical and electrochemical properties as the non-water soluble analogs[169]. Moreover, the solubility in water and polar solvents adds an advantage to these polymers over other materials. For example, the water soluble conjugated polymers can be used in the development of highly sensitive fluorescence-based sensors for chemical and biological targets[170].

Depending on the side chain, the water soluble conjugated polymers can be divided into the two classes of ionic conjugated polymers (conjugated polyelectrolytes) and nonionic water soluble conjugated polymers. Although there are some reports of nonionic water soluble conjugated polymers[171-173], in which oligoethylene- and sugar-substituted PPEs (poly(phenylene ethynylene)s) have been prepared, the conjugated polyelectrolytes (CPE) dominate the research area due to their better hydrophilic properties and their usefulness in the preparation of layer-by-layer assembled films. This work concentrates on the preparation of DPP containing conjugated polyelectrolytes.
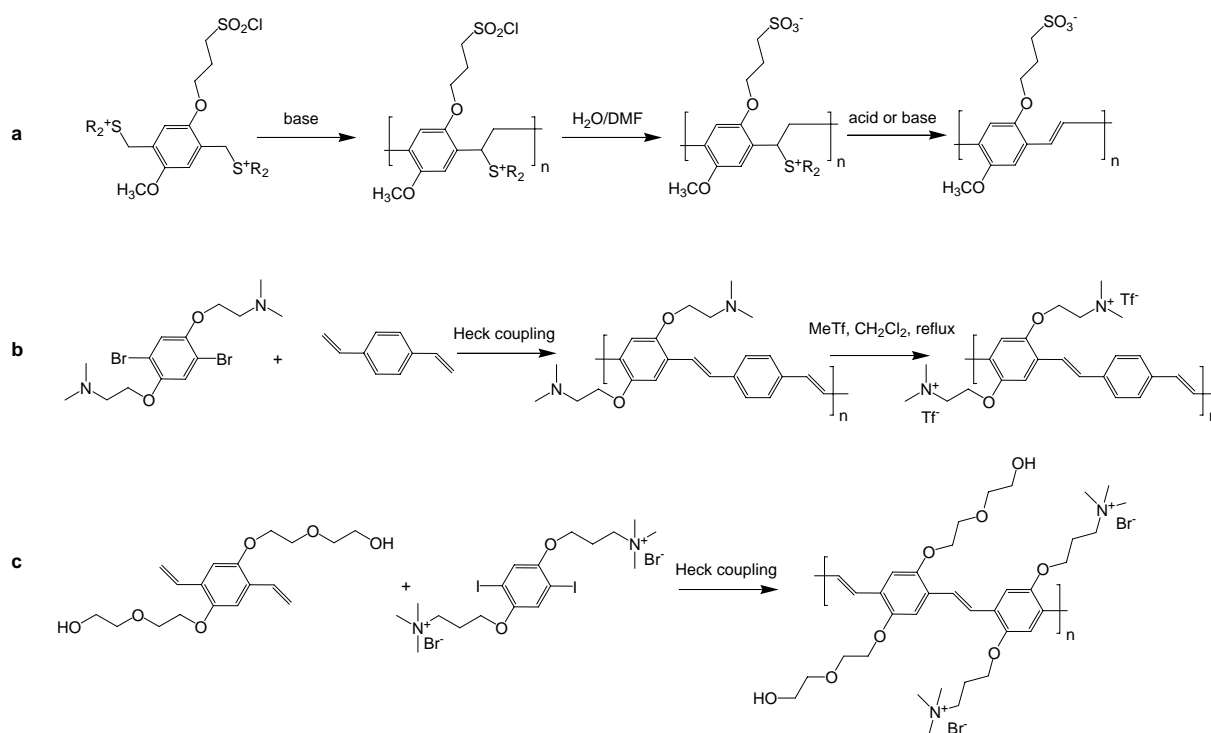
Scheme 4.1 PPV-type conjugated polyelectrolytes

The palladium catalyzed polycondensation is one of the most popular methods to prepare conjugated polymers. Among the various methods of catalytic polycondensation, the Suzuki, Sonogashira and Heck coupling are the most frequently used reactions to prepare conjugated polyelectrolytes. The first successful synthesis of a CPE is reported by Shi and Wudl[174] using the Wessling route in 1990. The reaction is described in Scheme 4.1-a. The resulting polyelectrolyte contains a PPV-type conjugated backbone. Later the Wudl group prepared a cationic poly(p-phenylene vinylene) upon Heck polycondensation[175] (Scheme 4.1-b). In a recent work[176], the cationic PPV-type CPEs (Scheme 4.1-c) were used in preparation of multilayered self-assembly films for application as solar cells.

The first PPP-type CPEs was reported by Wallow and Novak[177] in 1991. The polymer was synthesized by means of Suzuki polycondensation of biphenyl derivatives in aqueous solution catalyzed by a water-soluble catalyst-ligand system (Scheme 4.2-a). Although the boronic ester is insoluble in water, it can undergo rapid hydrolysis to afford the soluble boronic acid analog. A molecular weight of 50 kD could be determined using polyacrylamide gel electrophoretic analysis with ssDNA as a standard. The method was improved by Reynolds group using a sulfonate monomer to increase the solubility in water[178] (Scheme 4.2-b). In addition to this procedure, Rau and Rehahn developed another method to avoid the use of water soluble monomers. They synthesized a PPP-type polymer precursor containing alkyl bromide side groups and then converted it to an anionic water-soluble CPE[179,180] (Scheme 4.2-

b). Several years later, this method was adopted and revised by Ballauff and Rehahn[181] to prepare the first PPP type cationic conjugated polyelectrolyte (Scheme 4.2-c). Recently research on CPEs has been extended to fused phenyl and heterocyclic building blocks. PPP-type CPEs containing fluorene (Scheme 4.2-d)[182,183], thiophene (Scheme 4.2-e)[182,184], benzothiadiazole (Scheme 4.2-f)[182] and triphenylamine (Scheme 4.2-g)[185] have been reported.
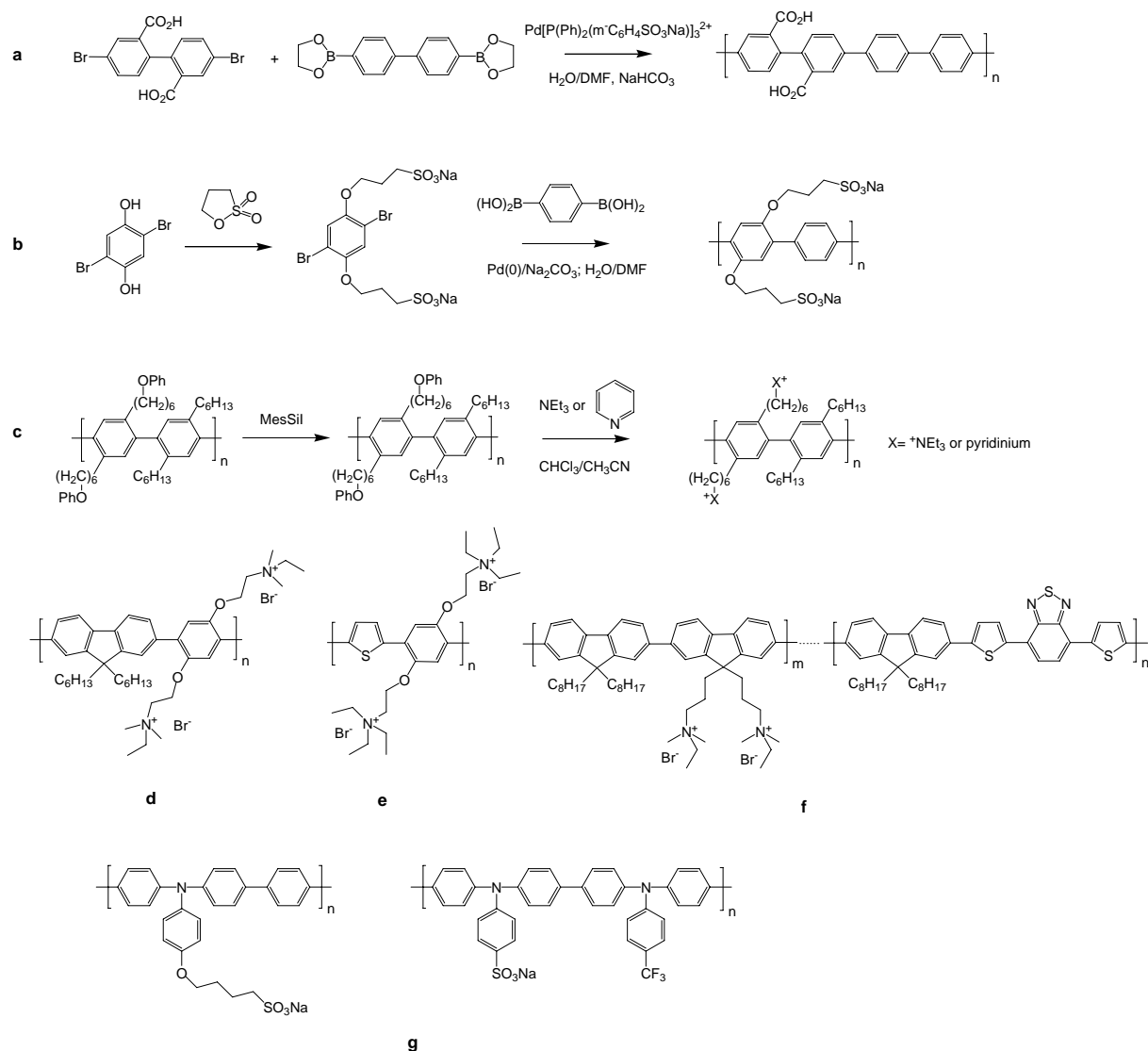
Scheme 4.2 PPP-type conjugated polyelectrolytes

The first PPE-type CPE was reported by Li[186,187]. Palladium-catalyzed copolymerization of 3,5-diiodobenzoic acid with acetylene gas in a basic aqueous medium provided a m-phenylene ethynylene polymer (Scheme 4.3-a) with a molecular weight around 60 kDa. Due to the relatively high molecular weight, this method was exploited by several other research groups soon. Swager's group[170,188] synthesized a cationic phenyleneethynylene polymer (Scheme 4.3-b) that can be used as a sensor material. Schanze's group (Scheme 4.3-c)

reported an anionic PPE type CPE with sulfonate[189] and phosphonate side chains[190] together with layer-by-layer self-assembled films. Recently, they extend this method to heterocyclic building blocks[191] such as pyridine, thiophene, benzothiadiazole and ethylenedioxythiophene (EDOT).
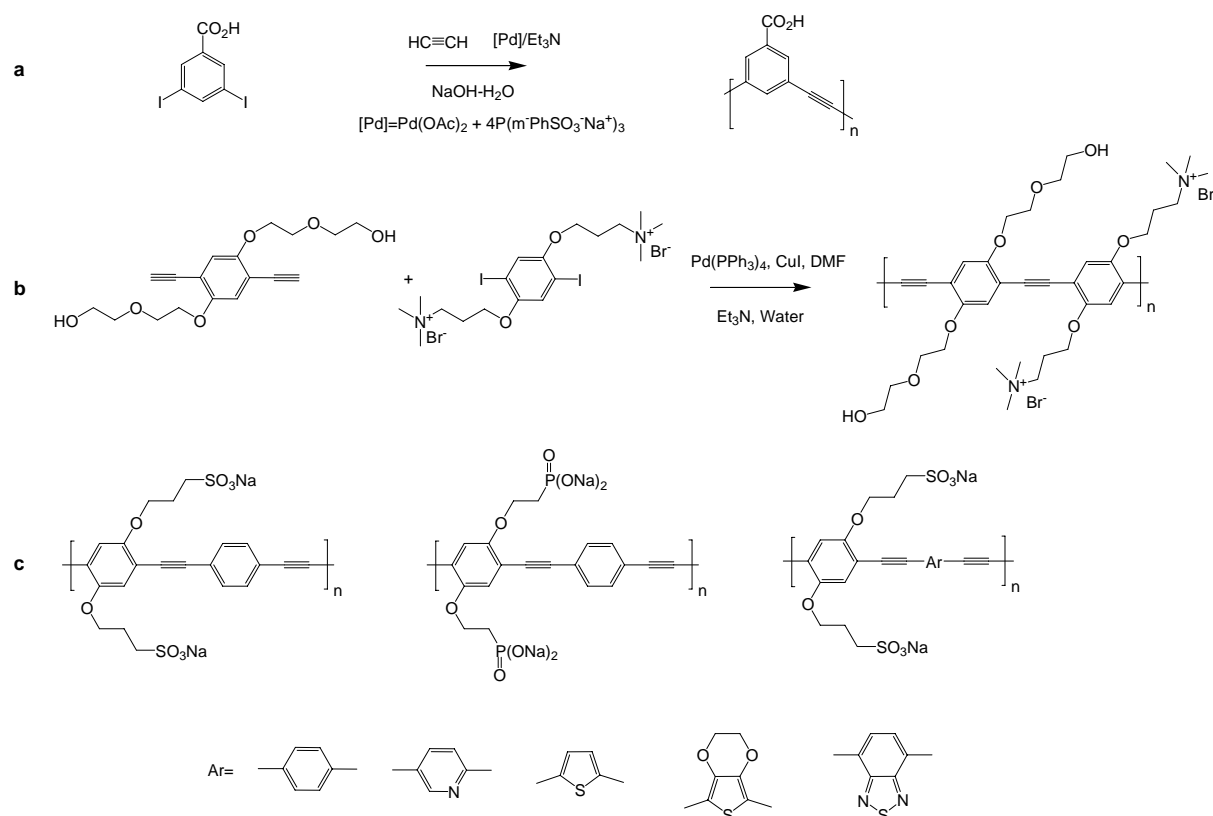
Scheme 4.3 PPE type conjugated polyelectrolytes

The first water soluble DPP compound was reported in a patent[192]. Treated with sulfonic acid, DPP pigments can undergo a sulfonation reaction and turn to water soluble DPP derivatives. However, the DPP derivatives are non-luminescent and not suitable for the polycondensation reaction. Another water soluble DPP derivative was reported from our group[35,50] several years ago. The water soluble DPP derivative was prepared in a two-step reaction: First the hydroxyhexyl alkylated DPP was prepared, and then it was reacted with the pyridine-SO3-complex to yield the desired anionic DPP disulfate. This work is aimed at preparing cationic and anionic conjugated DPP polyelectrolytes, which can be used for the preparation of layer-by-layer assembled films.

4.2. Cationic DPP containing conjugated polyelectrolytes

4.2.1. Preparation of the monomers

There are two popular methods to introduce cationic alkyl chains into conjugated polymers. The first method was reported by Swager[188] and Li[176], in which a bis-halogenated cationic monomer was prepared and the polycondensation was carried out subsequently under heterogeneous conditions. Another method adopted by most of the researchers was to prepare a neutral precursor polymer and then to quaternize the polymer in order to render it soluble in water and polar organic solvents. The latter method was used in this work, because the polycondensation could be carried out in a homogeneous system and the precursor polymer could be isolated and characterized by common procedures. Furthermore, cationic boronic esters, stannanes, ethynylenes and vinylenes can not be synthesized, and therefore the first method always involves hydrophobic groups upon polycondensation.

In the first attempt, the dibromo DPP pigment was reacted with dimethylaminohexylchloride under similar conditions as described in Cao's paper[193] (Scheme 4.4).
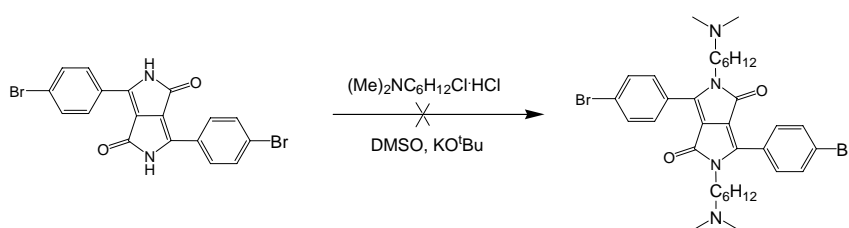
Scheme 4.4 Possible method to prepare ω-aminoalkyl substituted DPP

However, after the reaction only an oil-like non-luminescent red material is obtained, which is hard to be purified and characterized. In a second attempt, the 1,4-diketo-2,5-bis(1-bromohexyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole (**BrHDPP**) could be successfully synthesized using dibromo DPP pigment and 1,6-dibromohexane as starting reagents (Scheme 4.5).
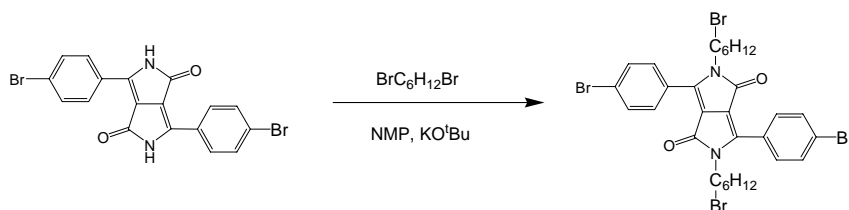
Scheme 4.5 Preparation of **BrHDPP**.

The alkylation reaction was carried out under the same conditions as for **HDPP**. However, the yield (13%) was much lower than for the hexyl alkylated analog (~ 50%). The ^{1}H-NMR spectra of **BrHDPP** and **HDPP** are compared in Figure 4.1. The characteristic triplet signal of the Br-CH$_2$ unit at 3.37 ppm is very clear. It is the strongest difference between the spectra of the two monomers. Since no methyl group is present in **BrHDPP**, the corresponding signal between 0.5 and 1.0 ppm is missing.
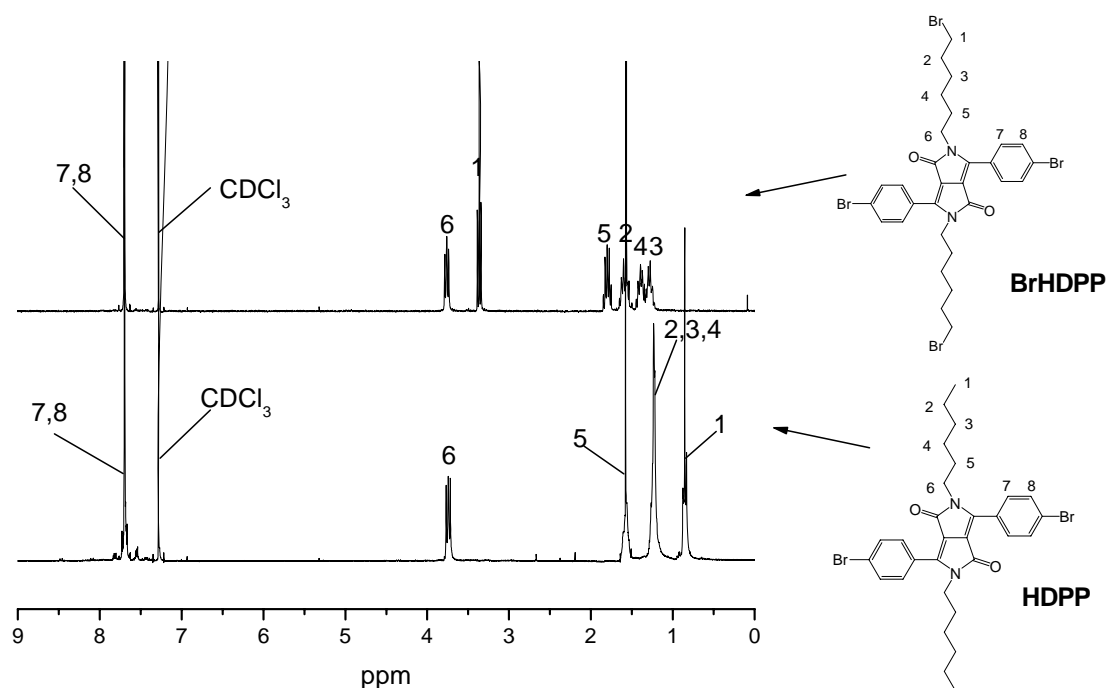
Figure 4.1 ^{1}H-NMR of **BrHDPP** and **HDPP** in CDCl$_3$.

The physical and optical properties of **BrHDPP** and **HDPP** are very similar (Figure 4.2). **BrHDPP** is very soluble in chloroform, toluene and THF, but insoluble in water and methanol. Figure 4.2 shows the absorption and emission spectra for the two monomers. The maximum UV/vis absorbance of **BrHDPP** is 477 nm. Compared with **HDPP**, there is a bathochromic shift of only 1 nm. The emission maxima of **BrHDPP** and **HDPP** are 539 nm and 533 nm, respectively. The photoluminescence quantum yield of **BrHDPP** is 95%, which is similar to that of **HDPP** (90 %).
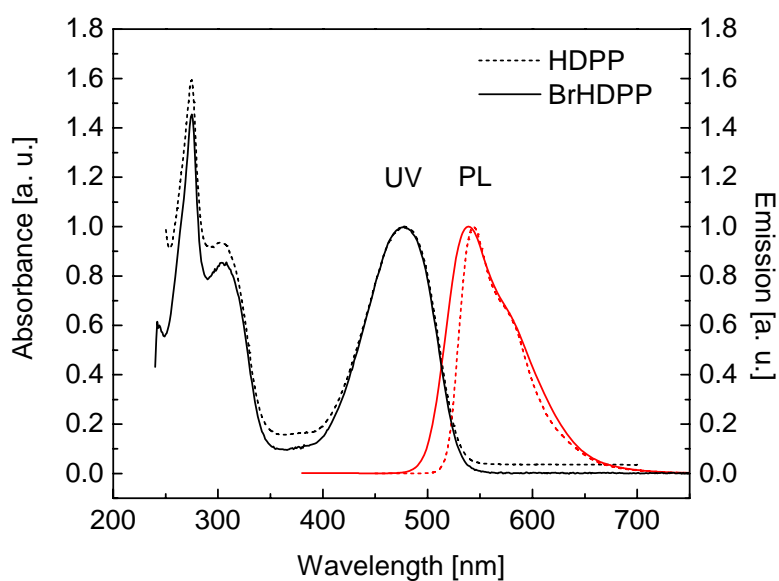
Figure 4.2 UV/vis absorbance and photoluminescence spectra of **BrHDPP** and **HDPP** in CHCl$_3$. The excitation wavelength is 350 nm.

To increase the solubility of the polymers, it is necessary to synthesize the ω-bromoalkylated phenylene diboronic ester. The synthesis of the diboronic ester 1,4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dibromohexyloxybenzene is shown in Scheme 4.6.
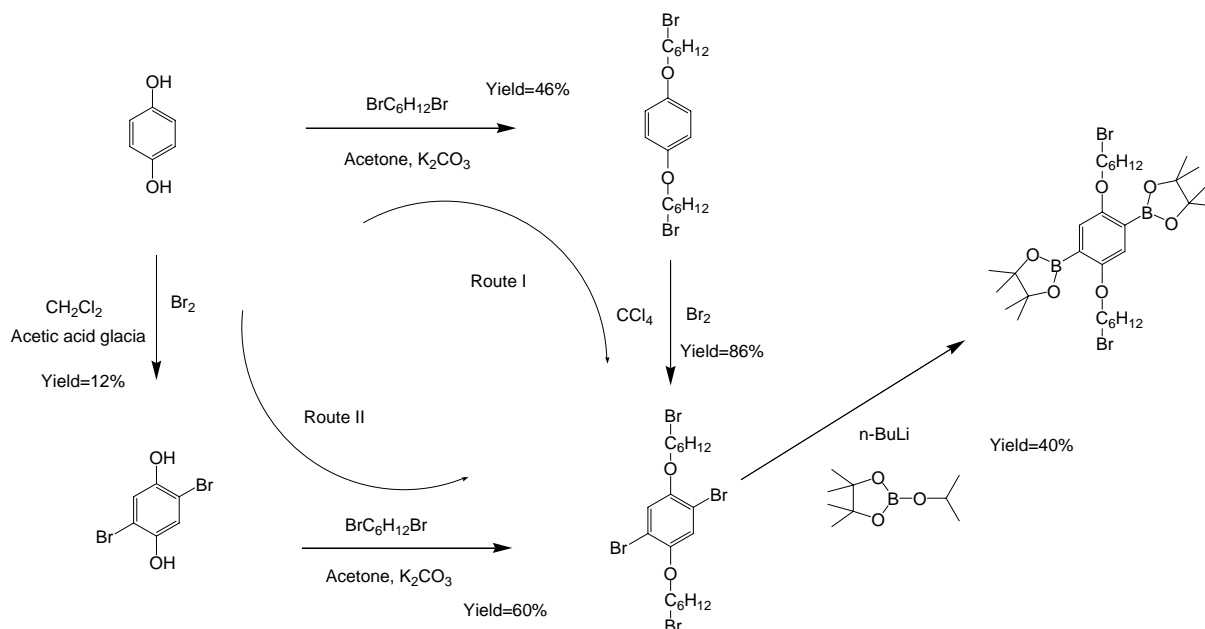
Scheme 4.6 Synthesis of 1,4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dibromohexyloxybenzene.

Hydroquinone was used as the starting material. There are two routes to prepare the desired boronic ester and both routes were tried in this work. As indicated in Scheme 4.6, route I of alkylation-bromination is more favourable than the bromination-alkylation procedure of route II. The alkylation procedure is a modification of the procedure used by Yan[194]. The yield of 1,4-dibromohexyloxybenzene is 46%. The bromination of 1,4-dibromohexyloxybenzene followed a revised procedure of Whiteside[195], the yield was 86%. The diboronic ester 1,4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dibromohexyloxybenzene was prepared from the corresponding dibromo compound upon successive treatment with n-butyllithium and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane at low temperature. The ^{1}H-NMR spectra of 1,4-dibromohexyloxybenzene, 1,4-dibromo-2,5-dibromohexyloxybenzene and 1,4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dibromohexyloxybenzene are shown in Figure 4.3.
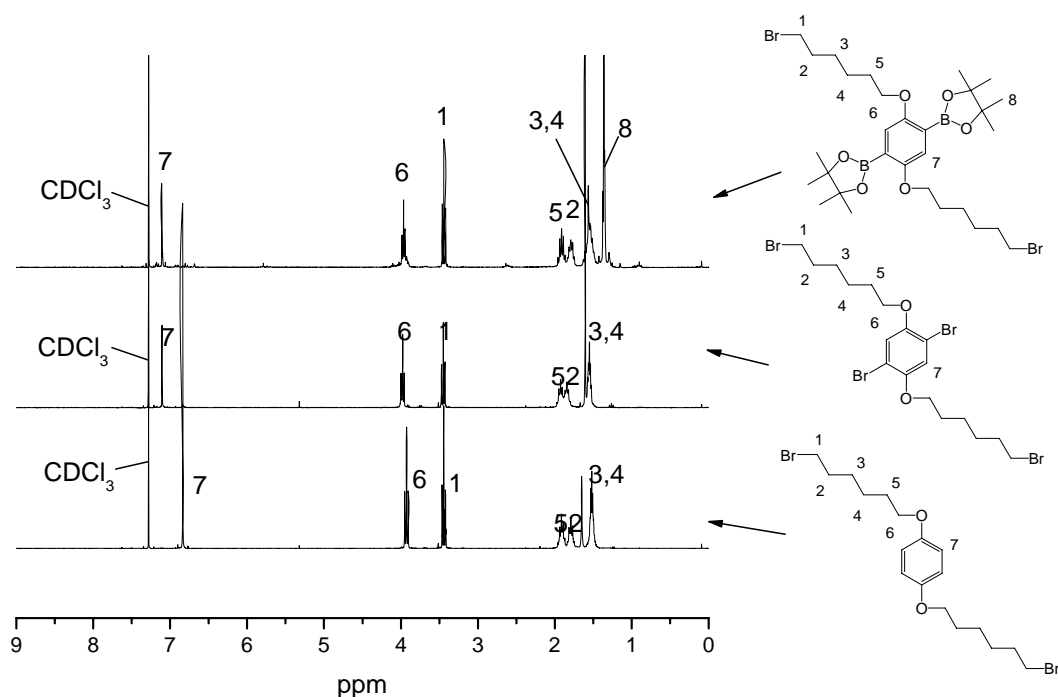
Figure 4.3 ^{1}H-NMR spectra of 1,4-dibromohexyloxybenzene, 1,4-dibromo-2,5-dibromohexyloxybenzene and 1,4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dibromohexyloxybenzene in CDCl$_3$.

The typical signals of the three monomers are the triplet signal of Br-CH$_2$ at 3.45 ppm and the triplet signal O-CH$_2$ at 3.95 ppm. The signals of the other alkyl protons are located at 1.55, 1.8 and 1.9 ppm. 1,4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dibromohexyloxy-

benzene has an additional signal at 1.36 ppm originating from its methyl groups. The aromatic protons of 1,4-dibromohexyloxybenzene are located at 6.84 ppm, which is lower than the values of the other two compounds at 7.11 ppm.

4.2.2. Preparation of the neutral precursor polymers

The Suzuki polycondensation of **BrHDPP** and 1,4-phenylenediboronic acid was carried out under conventional conditions using $Pd(PPh_3)_4$ as catalyst, K_2CO_3 as base and toluene/water as solvent system, but the molecular weight of the resulting polymers never exceeded 2500 Dalton. This is probably caused by the low solubility of oligomeric products, which prevent the further coupling. Using 1,4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dibromohexyloxybenzene in order to replace the 1,4-phenylenediboronic acid increased the degree of polymerization strongly (Scheme 4.7).
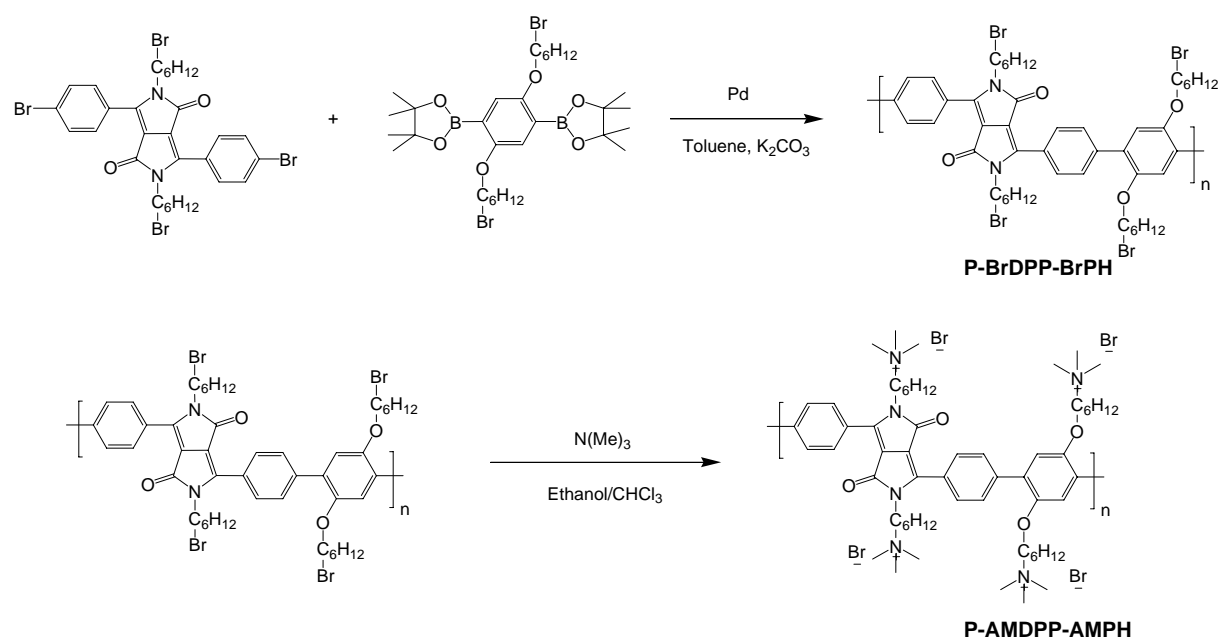
Scheme 4.7 Preparation of polymers **P-BrDPP-BrPH** and **P-AMDPP-AMPH**.

The resulting polymer **P-BrDPP-BrPH** exhibits a molecular weight up to 16 kDa with a polydispersity of 2.1. Polymer **P-BrDPP-BrPH** is very soluble in toluene, chloroform and THF. Compared with the monomer **BrHDPP**, the polymer shows a bathochromic shift of 27 nm of the maximum UV/vis absorbance (504 nm). The photoluminescence maximum is at 568 nm, about 29 nm red-shifted compared with the monomer. The photoluminescence quantum yield is 44%. The spectra are shown in Figure 4.4.

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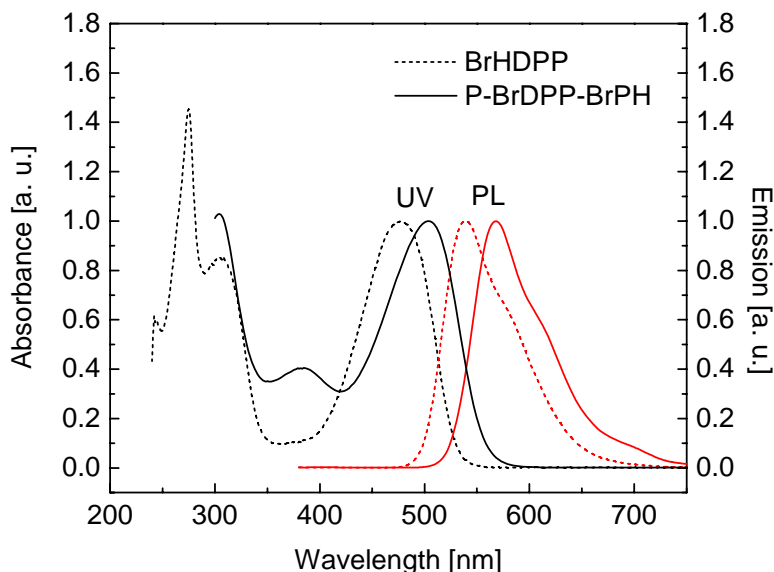
Figure 4.4. UV/vis absorbance and photoluminescence spectra of **BrHDPP** and **P-BrDPP-BrPH** in CHCl$_3$. The excitation wavelength is 350 nm.

4.2.3. Preparation of the cationic polymer

The precursor polymer was dissolved in chloroform and treated with an ethanolic trimethylamine for 24 hours. Subsequently the solvent was removed in vacuum and a red solid product was received. The resulting solid was soluble in water and DMSO with a maximum absorbance at 506 nm and 502 nm, respectively (Figure 4.5). The cationic polymer was non-luminescent in water, but luminescent in DMSO. The photoluminescence spectrum exhibits two emission peaks at 432 and 565 nm. The emission peak at 565 nm can be ascribed to the DPP chromophore, while the other one probably originates from the phenylene units in between. The emission peak of phenylene is even bigger than that of the DPP chromophore, which is very unusual for DPP polymers. It points to a partial destruction of the DPP chromophore during the quaternization reaction. As a consequence, the π-conjugation of the backbone is interrupted and emission mainly occurs from the residual phenylene units. From the NMR spectra in the experimental part, it is very clear that the percentage of the signals from aromatic protons is decreased after quaternization.
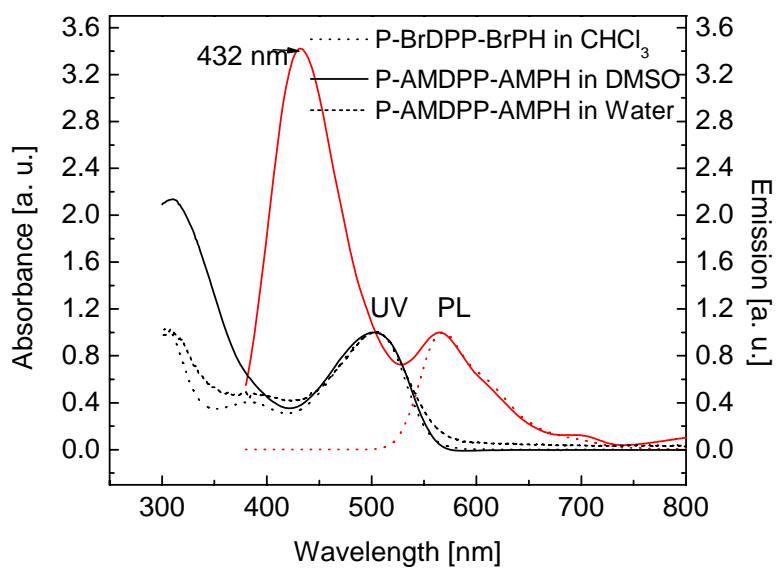
Figure 4.5 UV/vis absorbance and photoluminescence spectra of **P-BrDPP-BrPH** (CHCl$_3$) and **P-AMDPP-AMPH** (DMSO or H$_2$O). The excitation wavelength is 350 nm.

4.3. Anionic DPP containing conjugated polyelectrolytes

4.3.1. Preparation of the monomers

An anionic DPP derivative was already prepared by Saremi, Lange and Tieke[50] (Scheme 4.8-a). However, in the present work a more convenient method has been developed (Scheme 4.8-b).
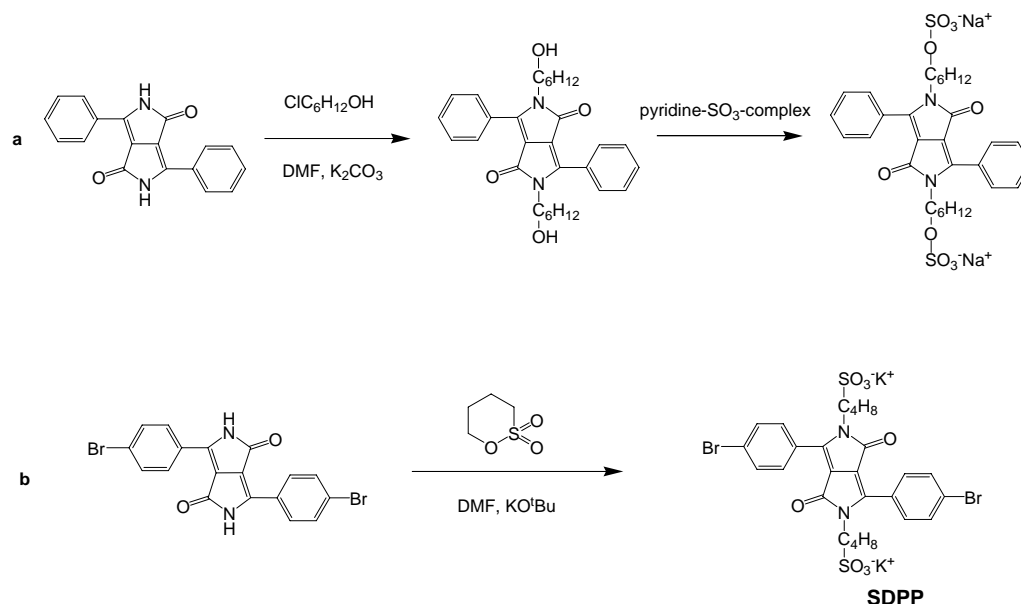
Scheme 4.8 Preparation of anionic DPP containing compounds.

Dibrominated DPP was reacted with butane sultone in the presence of a strong base such as potassium t-butoxide. The reaction was carried out in DMF for 24 hours. The resulting DPP-based monomer 1,4-diketo-2,5-bis(sulfonylbutyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]-pyrrole (**SDPP)** was obtained in a very high yield (> 95%). The monomer is very soluble in water, soluble in methanol and DMSO, but insoluble in toluene, chloroform or THF. The purification of the monomer is tedious: it has to be dissolved in water, precipitated in acetone and the dissolution/precipitation has to be repeated several times. There is always a trace amount of water inside the product even after drying in vacuum for several days. The water probably exists as crystal water. However, from the ^{1}H-NMR spectrum (Figure 4.6), it is very clear that the desired product has been formed. The typical signals at 3.59 ppm for N-CH$_2$ and 2.61 ppm for S-CH$_2$ are very clear and well in the expected 1:1 ratio. The signals of the aromatic protons are located at 7.34 and 7.50 ppm. The other methylene protons appear at 1.41 ppm.
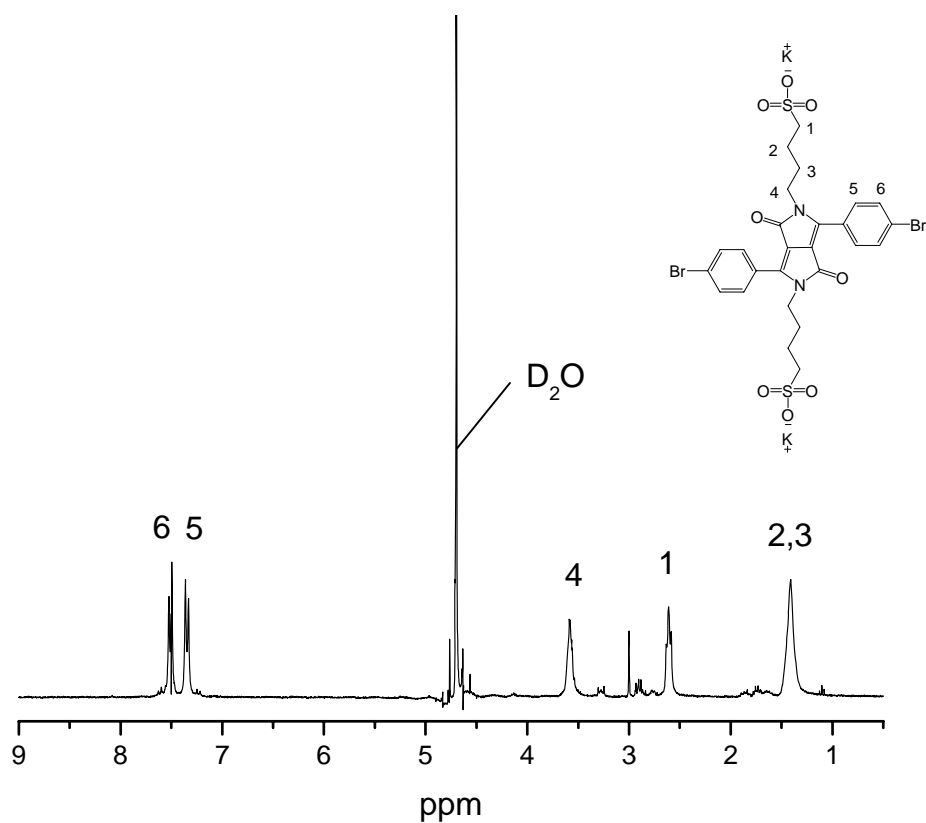
Figure 4.6 ^{1}H-NMR spectrum of **SDPP** in D$_2$O.

The monomer **SDPP** exhibits very interesting optical properties. Compared with the ordinary **HDPP**, the UV/vis absorbance maximum is hypsochromically shifted by 6 nm (Figure 4.7). The aqueous solution shows a strong photoluminescence with a quantum yield of 88%. The maximum emission is at 533 nm, which is identical with **HDPP**.
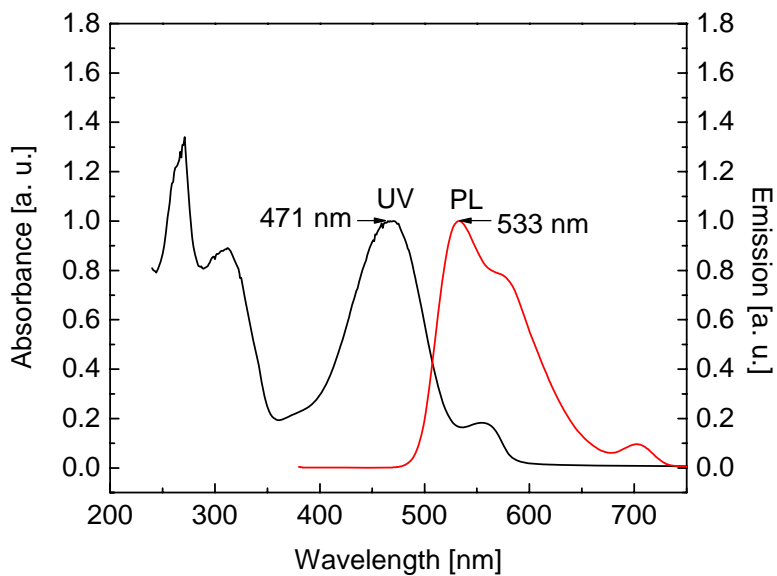
Figure 4.7 UV/vis absorbance and photoluminescence spectra of **SDPP** in water.
The excitation wavelength is 350 nm.

4.3.2. Synthesis of the anionic polymer

Suzuki polycondensation

The anionic DPP containing polymer **P-SDPP-PH** was synthesized upon Suzuki polycondensation using equal amounts of **SDPP** and 1,4-phenylenediboronic acid (Scheme 4.9). The reaction was carried out in a mixture of DMSO/water and Pd(PPh$_3$)$_4$ was used as catalyst. Potassium carbonate was dissolved in water and added to the reaction after the reactants and the catalyst were totally dissolved. Then the temperature was raised and the mixture was refluxed under nitrogen for 24 hours. After the reaction, the mixture was precipitated in ethanol while it was still hot. The precipitate was successively washed with chloroform and acetone. The solid product was collected and dried under vacuum at 100 ^{o}C for 24 hours.
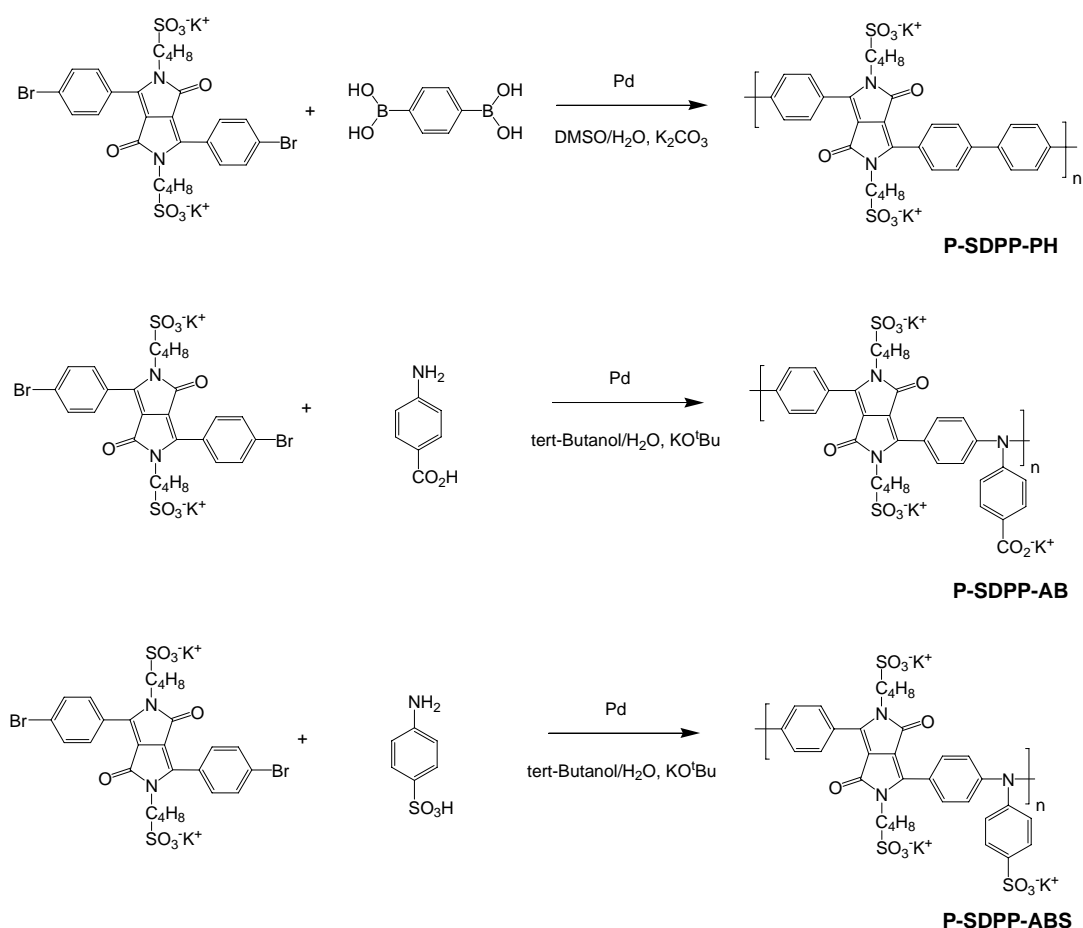
Scheme 4.9 Preparation of polymers **P-SDPP-PH**, **P-SDPP-AB** and **P-SDPP-ABS**.

Polymer **P-SDPP-PH** is soluble in water, methanol and DMSO. Although the molecular weight of the polymer was not determined because of the insolubility in THF, the large bathochromic shift of 63 nm indicates that the conjugation length of the polymer must have

been extended strongly. Unfortunately, the polymer is non-luminescent in water and only slightly luminescent in DMSO. The quenching of the fluorescence might be caused by a strong aggregation of the polymer molecules in aqueous solution[196]. The photoluminescence quantum yield in DMSO is only 6.2%. Figure 4.8 shows the UV/vis absorption spectra in water and DMSO, and the photoluminescence spectrum in DMSO. For comparison, the spectra of the monomer **SDPP** in water are also shown.

Figure 4.8 UV/vis absorbance and photoluminescence spectra of **S-DPP** and **P-SDPP-PH** in water and DMSO. The excitation wavelength is 350 nm.

Buchwald-Hartwig polycondensation

In a previous publication[77], it was pointed out that under the condition of Suzuki polycondensation the N-alkylated DPP may be transferred into the O-alkylated form, which is accompanied by a decrease of the photoluminescence quantum yield. The transformation is generally favoured by a low reactivity of the monomers in the coupling reaction. The previous Suzuki coupling in Scheme 4.9 may bear this situation because the two monomers are very different in their solubility. The preparation of the precursor for cationic polyelectrolytes (chapter 4.2.2.) also indicates this problem. Therefore it seemed useful to look for monomers which enable the polycondensation reaction in a homogeneous phase. Unfortunately, no water-soluble aryl boronic acid or boronic ester are available. Therefore the alternative method of Buchwald-Hartwig coupling was adopted to synthesize anionic DPP containing conjugated polyelectrolytes.

The first Buchwald-Hartwig C-N coupling involving a water-soluble compound was reported by Buchwald[197]. Although only a coupling reaction between aminobenzoic acid and a dibromo arylene compound was reported, it was tried to adopt this reaction for a polymerization process.

The first water soluble polymer **P-SDPP-AB** was obtained by reacting equal amounts of **SDPP** and 4-aminobenzoic acid using tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) and tris-t-butylphosphine as catalyst. The catalyst was dissolved t-butanol and stirred for 30 minutes. Subsequently the monomers, a strong base (sodium ethoxide) and more t-butanol were added. The mixture was degassed and then was stirred at 100 °C under nitrogen for 24 hours. After the reaction, the mixture was precipitated in ethanol while it was still hot. The precipitate was successively washed with chloroform and acetone. The solid product was collected and dried under vacuum at 100 °C for 24 hours. The resulting polymer was very soluble in water and exhibited a strong bathochromic shift of 57 nm compared with the monomer **SDPP** in water. The polymer was non-luminescent in water but strongly luminescent in DMSO. The absorption maximum in water and DMSO was at 528 nm and 560 nm, respectively (Figure 4.9). The maximum photoluminescence in DMSO was at 594 nm, the quantum yield was 45 %.
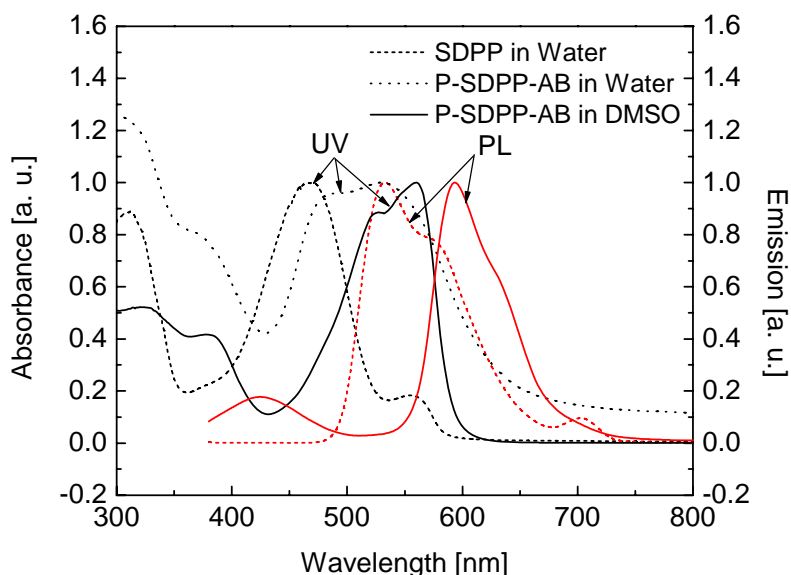
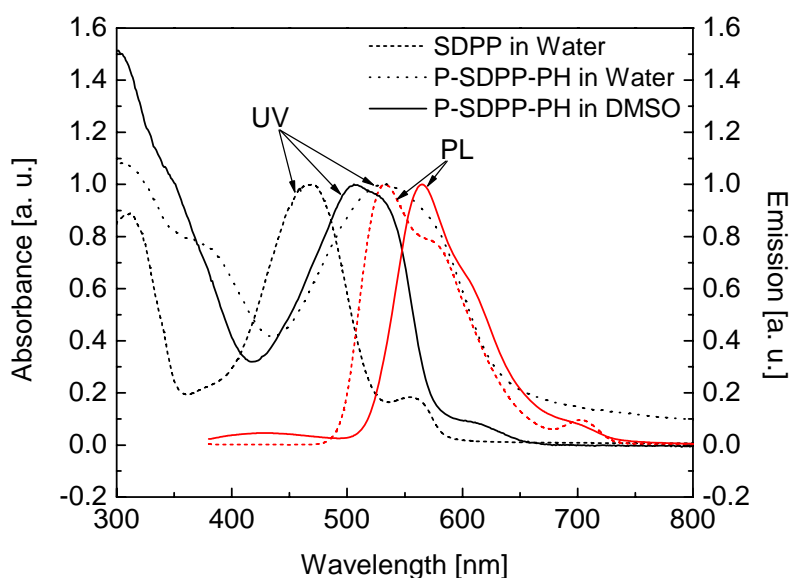
Figure 4.9 UV/vis absorbance and photoluminescence spectra of **S-DPP** and **P-SDPP-AB** in water and DMSO. The excitation wavelength is 350 nm.

In order to increase the solubility of the polymer in water, another DPP containing conjugated polyelectrolyte **P-SDPP-ABS** was prepared. The polycondensation procedure was the same as the one for **P-SDPP-AB** except that another ligand and base were used. For the new polymer, Xphos and potassium t-butoxide were used. The resulting polymer **P-SDPP-ABS** shows excellent solubility in water and DMSO, but is totally insoluble in toluene, chloroform and THF. The ^{1}H-NMR spectrum of the polymer **P-SDPP-ABS** is shown below (Figure 4.10) together with the NMR spectrum of monomer **SDPP**. For the polymer, the signals of the S-CH_2 and N-CH_2 protons occur at 2.8 ppm and 3.5 ppm, respectively. The corresponding signals of the monomer appear at 2.61 ppm and 3.59 ppm. The signals of the aromatic protons are between 6.8 ppm and 7.9 ppm for the polymer, and at 7.34 ppm and 7.50 ppm, respectively, for the monomer. The signal at 6.8 ppm is a typical signal of aromatic protons adjacent to an aromatic amine group.

Figure 4.10 ^{1}H-NMR spectra of **P-SDPP-ABS** and **SDPP** in D_2O.

The optical properties of polymer **P-SDPP-ABS** are shown in Figure 4.11.The polymer is non-luminescent in water, but strongly luminescent in DMSO, the quantum yield is 49 %. The maximum absorption maximum of the polymer in water is at 524 nm. It is red shifted by 53

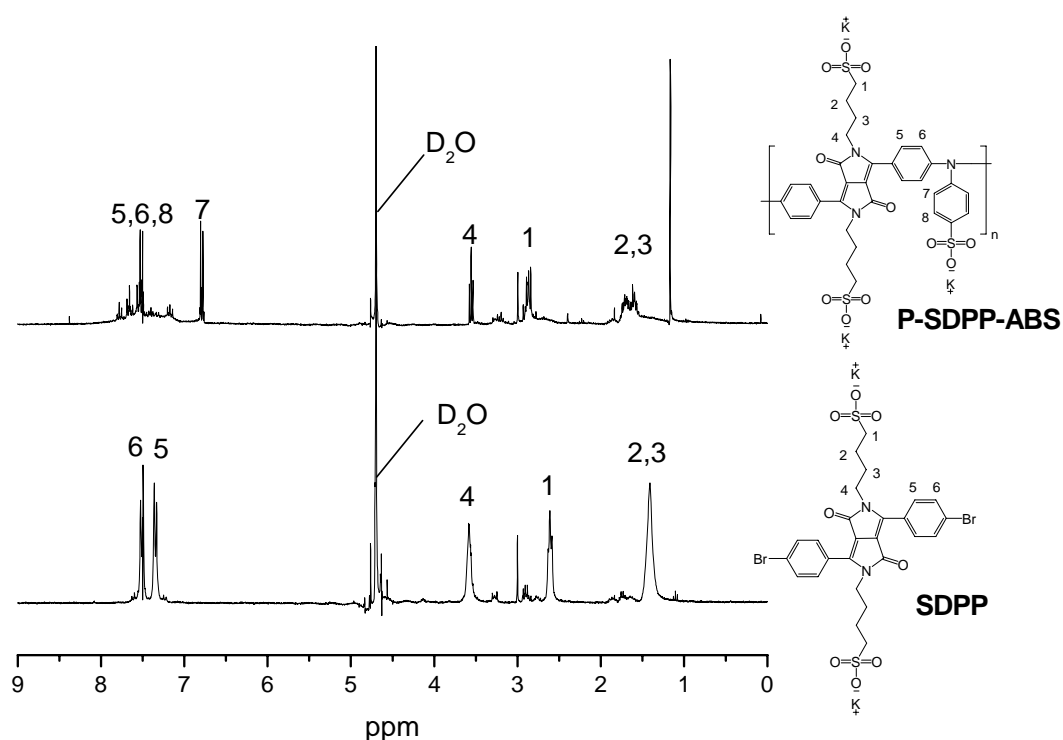nm compared with the monomer. The maximum absorption maximum of the polymer in DMSO is at 554 nm.
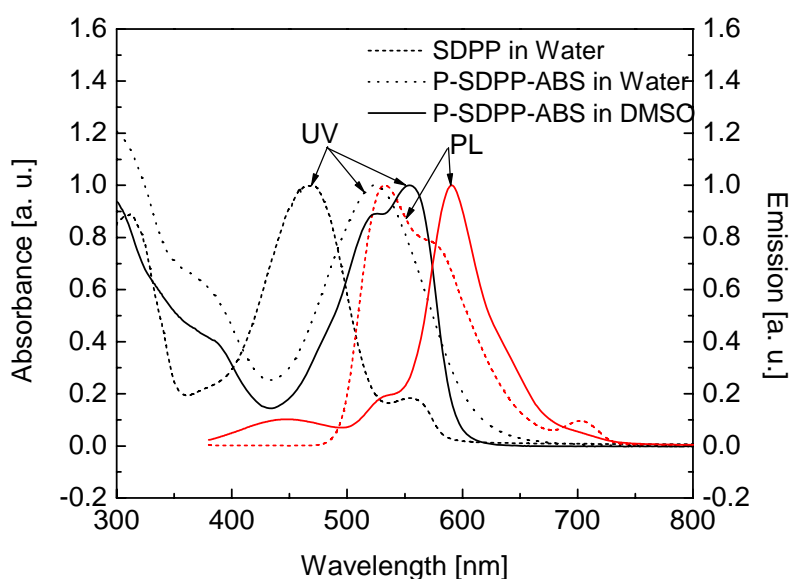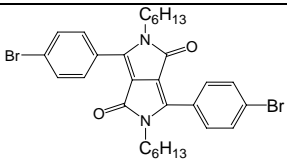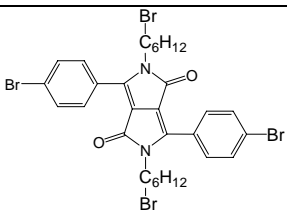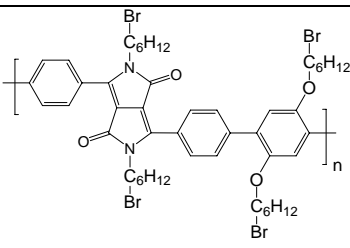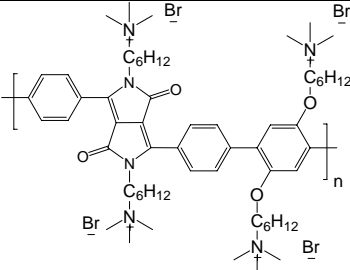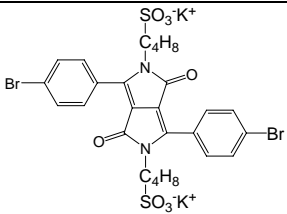
Figure 4.11 UV/vis absorbance and photoluminescence spectra of **S-DPP** and **P-SDPP-ABS** in water and DMSO. The excitation wavelength is 350 nm.

4.4.   Conclusion

The water-soluble DPP containing polyelectrolytes were successfully prepared upon Suzuki and Buchwald-Hartwig coupling polycondensation. The process for the preparation of the cationic polymer was to synthesize the neutral precursor polymer and then to quaternize the polymer. The neutral precursor could be successfully prepared and characterized. Quaternation of the neutral polymer indeed enabled the preparation of a cationic conjugated polyelectrolyte, but the emission spectrum indicated that the DPP chromophore must have been destroyed partially. The cationic polyelectrolyte is soluble in water, methanol and DMSO, but it is only luminescent in the two non-aqueous solvents. The anionic DPP monomer could successfully be synthesized and exhibited a strong photoluminescence in water and DMSO. The anionic monomer was used in the Suzuki and Buchwald-Hartwig polycondensation to synthesize three DPP containing anionic conjugated polyelectrolytes. The polymers from Buchwald-Hartwig polycondensation exhibit a stronger photoluminescence and better solubility, because an additional ionizing group is present in the aryl-amine units. However, the anionic polymers are non-luminescent in aqueous environment although the corresponding monomer is very luminescent in water. This may be

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caused by a strong aggregation of the polymers in aqueous solution. At the end of this chapter, the optical properties of all the DPP containing monomers and polymers are compiled.

Table 4.1 The optical properties of DPP containing polymer and monomers in Chapter IV

Structure	λ_{max} (nm)	λ_{em} (nm)	Φ_f
HDPP	476 (in CHCl$_3$)	533 (in CHCl$_3$)	0.90 (in CHCl$_3$)
BrHDPP	477 (in CHCl$_3$)	539 (in CHCl$_3$)	0.95 (in CHCl$_3$)
P-BrDPP-Br-PH	504 (in CHCl$_3$)	564 (in CHCl$_3$)	0.44 (in CHCl$_3$)
P-AMDPP-AMPH	506 (in H$_2$O) 502 (in DMSO)	432, 565 (in DMSO)	-
SDPP	471 (in H$_2$O)	533 (in H$_2$O)	0.88(in H$_2$O)

P-SDPP-PH	534 (in H$_2$O) 506 (in DMSO)	565 (in DMSO)	0.062 (in DMSO)
P-SDPP-AB	528 (in H$_2$O) 560 (in DMSO)	594 (in DMSO)	0.45 (in DMSO)
P-SDPP-ABS	524 (in H$_2$O) 554 (in DMSO)	591 (in DMSO)	0.49 (in DMSO)
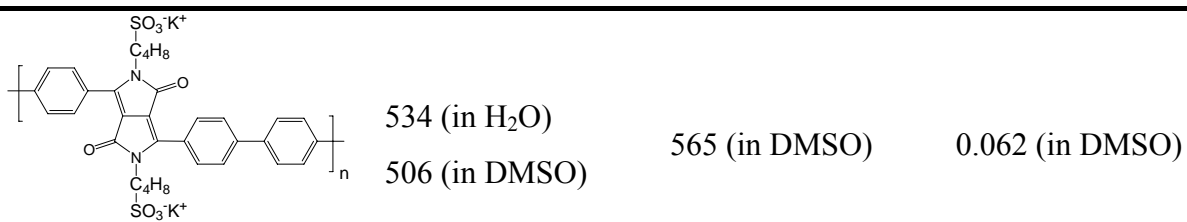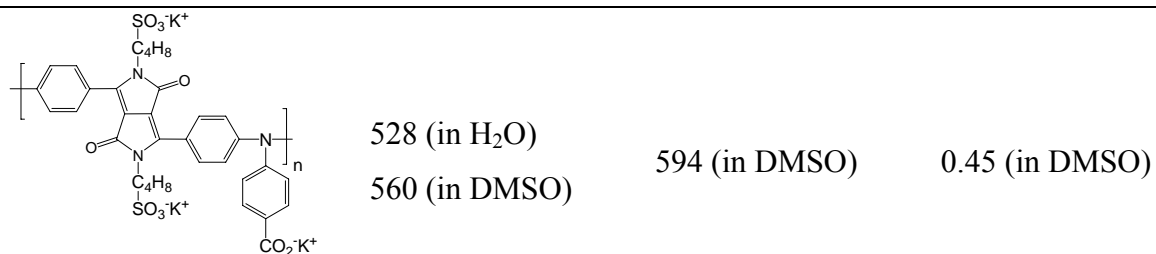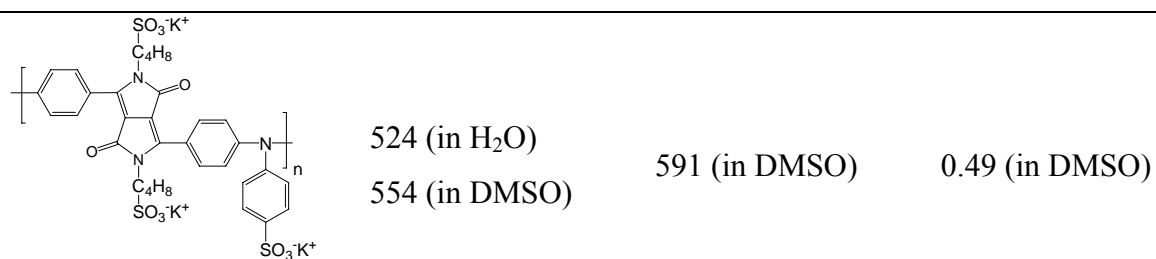
5. Experimental part

5.1. Materials, instruments and general procedures

5.1.1. Materials

Tetrahydrofuran (THF) was distilled over sodium hydride under nitrogen. N-Methyl-2-pyrrolidon (NMP) and N,N-dimethylformamide (DMF) were distilled over CaH_2. Chromatographic separations were carried out using Acros silica gel 60 (0.060 – 0.200 mm). 1,4-Diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole was kindly supplied by Dr. M. Dueggeli and Dr. R. Lenz from Ciba Specialty Chemicals, Basle, Switzerland. Bis(pinacolato)diboron was purchased from Combi-Blocks Inc. Other materials were obtained from Acros, Fluka and Aldrich and used without further purification.

5.1.2. Instruments

^{1}H NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300 MHz for ^{1}H experiments. UV/vis absorption spectra were recorded on a Perkin-Elmer Lambda 14 spectrometer. Photoluminescence spectra were recorded on a Perkin-Elmer LS50B spectrometer. Molecular weights were determined upon size exclusion chromatography (SEC) using a Waters/Millipore UV detector 481 and an SEC column combination (Latek/styragel 50/1000 nm pore size). All measurements were carried out in tetrahydrofuran at 45 °C. The columns were calibrated versus commercially available polystyrene standards. Cyclic voltammograms were recorded using a potentiostat PG390 from Heka Company. A thin film of the polymer was cast on an ITO electrode and cycled in CH_3CN containing 0.1 M tetrabutylammoniumhexafluorophosphate. Counter electrode: Pt; reference: Pt; scan rate: 25 mVs^{-1}; temperature: 20 ^{o}C.

5.1.3. Electropolymerization

The oxidative electropolymerization of the monomer was carried out in a mixture of CH_3CN/CH_2Cl_2 with 0.1M $TBAPF_6$ as electrolyte. The ratio of CH_3CN and CH_2Cl_2 was 1:3. The scan rate was 100 mV/s. The monomer was dissolved in the mixture. The working electrode was ITO coated glass, the counter and reference electrodes were platinum. The potentiostatic or potentiodynamic (cyclic voltammetry) method were performed. After polymerization, the polymer film was deposited on the ITO electrode.

5.2. DPP conjugated polymers via polycondensation reactions

5.2.1. Suzuki coupling

1,4-Diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole

8.92 g (20 mmol) 1,4-Diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 4.94 g (44 mmol) potassium *t*-butoxide and 150 mL dry NMP were heated to 60 °C. 16.9 mL (120 mmol) 1-bromohexane was slowly added and the mixture was stirred at 60 °C for 18 h. After cooling to room temperature, 250 mL toluene were added and the reaction mixture was washed with water to remove the NMP. The organic solution was concentrated using a rotary evaporator. The raw material was purified by column chromatography on silica using dichloromethane as the solvent. 5.1 g (42 %) of an orange, polycrystalline powder were obtained. The melting point was 183 °C.

^{1}H NMR (CDCl$_3$, 300 MHz): δ (ppm) 0.85 (t, 6H), 1.23 (m, 12H), 1.56 (m, 4H) 3.74 (t, 4H, N-CH$_2$), 7.65 (d, 4H), 7.66 (d, 4H);

λ_{max}(CHCl$_3$):	476 nm
λ_{em}(CHCl$_3$):	533 nm
Φ_f(CHCl$_3$):	90 %
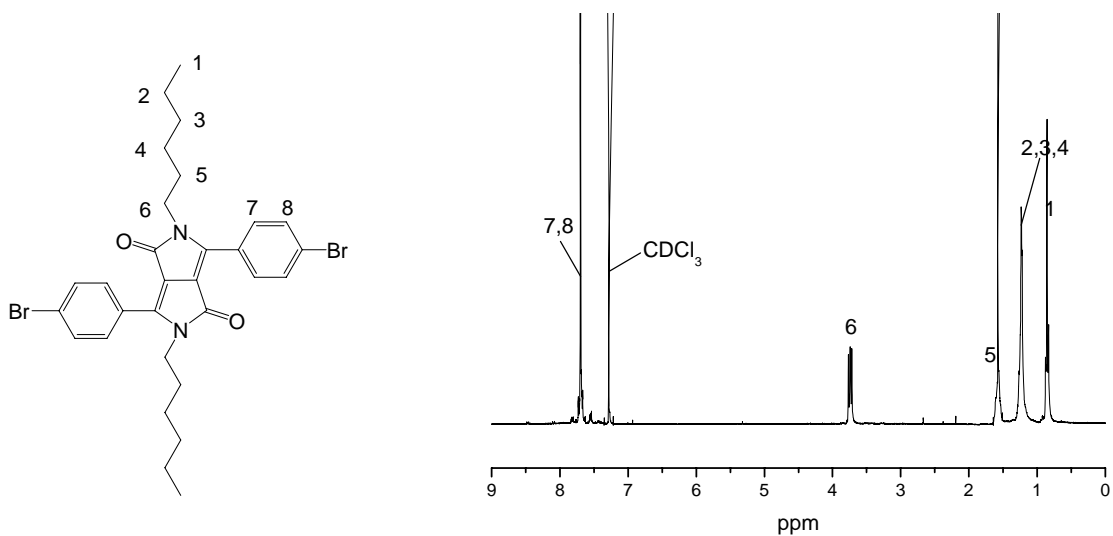
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

1,4-Diketo-2,5-dihexylpyrrolo[3,4-c]pyrrole-3,6-diphenyl-4-pinacolato boronester

1 g (1.63 mmol) 1,4-Diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, and 0.91 g (3.59 mmol) bis(pinacolato)diboron were dissolved in 60 ml degassed DMF followed by the addition of 0.022 g (6 mol%) palladium(II) acetate and 0.9593 g (9.80 mmol) potassium acetate. The reaction mixture was vigorously stirred under nitrogen at 80 °C for 2 h. During this period, the progress of the reaction was monitored by thin layer chromatography (TLC) (silica, dichlormethane/MeOH, 10:1). After completion, the reaction mixture was poured into distilled water to induce the precipitation of the crude product. A red solid was formed which was filtered off, rinsed with water and dried under ambient conditions. The crude product was dissolved in a minimum amount of dichloromethane and poured into ethanol to precipitate polymeric side products. After filtration, the mother solution was concentrated using a rotary evaporator. Upon cooling, 0.7 g (61 %) of the pure product was obtained as bright red flakes. The melting point was 235 ^{0}C.

^{1}H NMR (CDCl$_3$, 300 MHz): δ(ppm) 0.84 (t, 6H), 1.21 (m, 12H), 1.38 (s, 24H), 1.58 (m, 4H), 3.75 (t, 4H, N-CH$_2$), 7.80 (d, 4H), 7.95 (d, 4H).

λ$_{max}$(CHCl$_3$):	479 nm
λ$_{em}$(CHCl$_3$):	548 nm
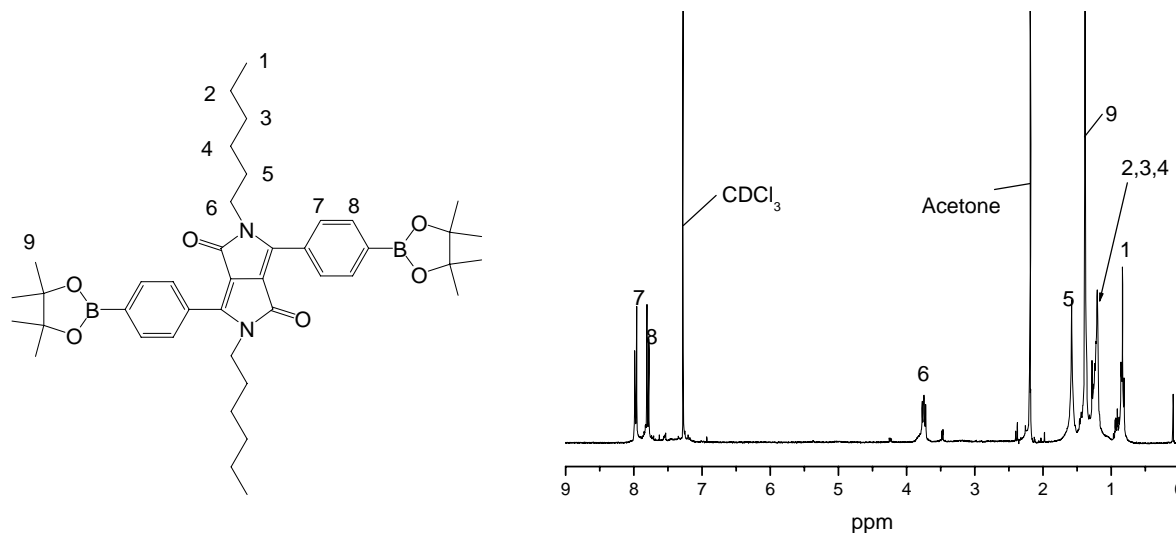
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

3,6-Dibromocarbazole

Carbazole (35.65 g, 213 mmol) was dissolved in *N,N*-dimethylformamide (DMF) (300 mL) at 0°C with stirring. To this was dropped 200 mL NBS (75.89 g, 426 mmol) DMF solution. After stirring at room temperature for 2 h, the solution was poured into 2000 mL of water, filtered, washed with 2000 mL water. The filter white residue was recrystallized in ethanol and gave 3,6-dibromocarbazole as colorless crystals (58.9 g, 85 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 7.32 (d, 2H), 7.54 (d, 2H), 8. 1(s, 1H), 8.15 (s, 2H). MP: 215-216°C.
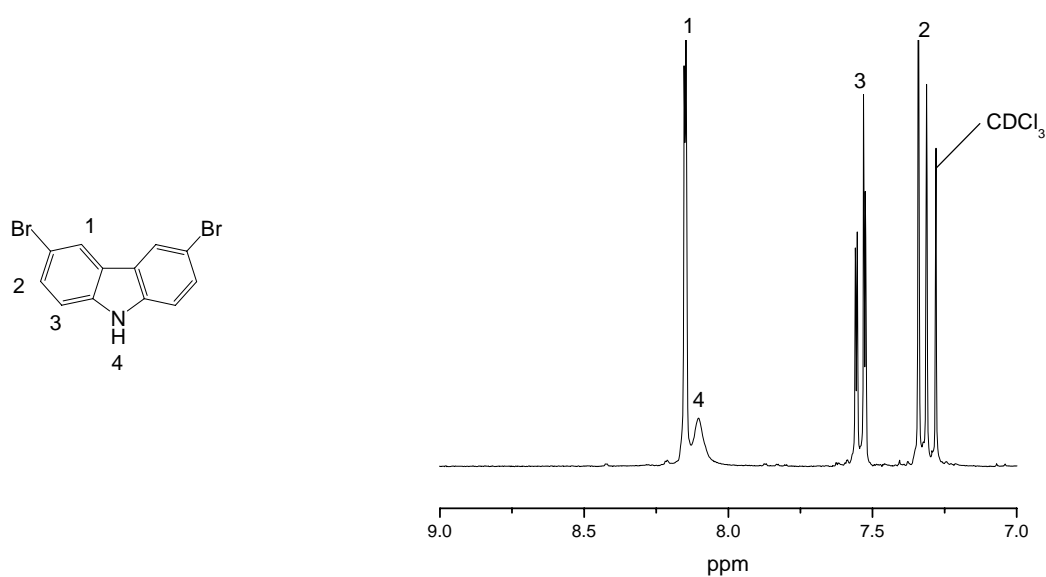
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

3,6-Dibromo-9-ethylhexylcarbazole

A revised method from Paliulis[69] was used. 3,6-dibromocarbazole (6.5 g, 20 mmol) was dissolved in 50 mL acetone. The phase-transfer catalyst $[(C_4H_9)_4N]HSO_4$ (0.41g, 1.21 mmol), 2-ethylhexylbromide (5.79 g, 30 mmol) and NaOH (1.6g, 40mmol) were added. The reaction mixture was stirred and refluxed for 4 hours. The solvent was removed and 300 mL toluene was added. Then the mixture was washed with brine (3×200 mL) and dried over anhydrous magnesium sulfate. The solvents were concentrated using a rotary evaporator. Column chromatography of the residue over silicon gel with petrol ether as eluent gave 3,6-dibromo-9-ethylhexylcarbazole as a colorless liquid (7.1g, 81%).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.92 (t, 6H), 1.31 (m, 8H), 2.01 (m, 1H), 4.12 (d, 2H), 7.24 (d, 2H), 7. 56(d, 2H), 8.15 (s, 2H).
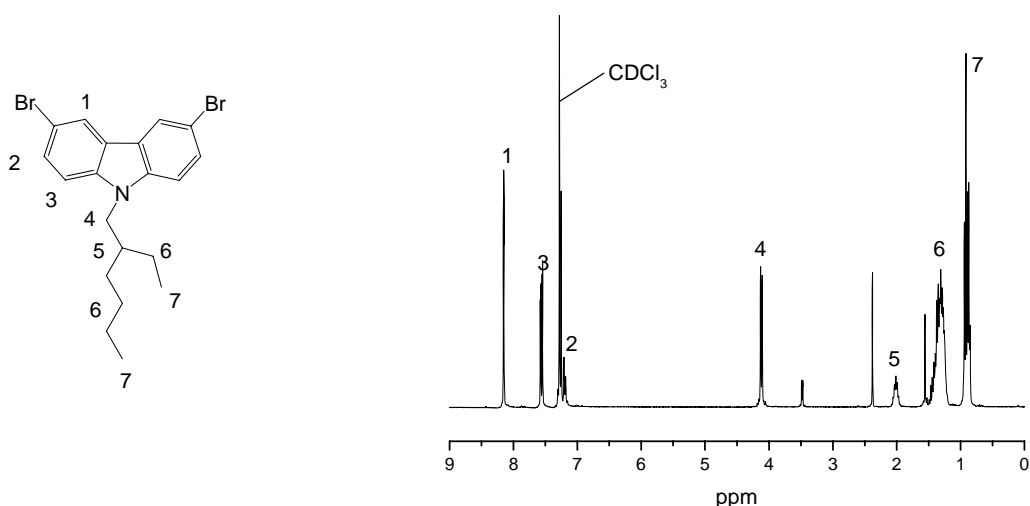
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

3,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole

Using a syringe, 2.5 M n-BuLi (8.62 mL, 20.2 mmol) were added to a solution of 3,6-dibromo-9-ethylhexylcarbazole (2.73 g, 6.23 mmol) in THF (160 mL) at -78 °C with stirring. After stirring for one hour at this temperature, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.2 mL, 20.4 mmol) was added. The reaction mixture was stirred at -78 °C for additional 1 h and then was gradually warmed to room temperature and stirred overnight. After the reaction, 100 mL water and 100 mL ether were added to the solution. Then the mixture was washed with brine (3×40 mL) and the organic layer was dried over MgSO$_4$. The solvents were evaporated using a rotary evaporator. Column chromatography of the residue over silicon gel with hexane and ethyl acetate mixture (hexane: ethyl acetate, 10:1; R$_f$≈ 0.6) as eluent gave 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole as a white solid (0.98 g, 30 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.90 (t, 6H), 1.30 (m, 8H), 1.41 (m, 24H) 2.01 (m, 1H), 4.19 (d, 2H), 7.39 (d, 2H), 7. 91(d, 2H), 8.68 (s, 2H).

300 MHz-^{1}H-NMR spectrum in CDCl$_3$

4,4′-Dibromotriphenylamine

Triphenylamine (3.65 g, 15 mmol) was dissolved in DMF (75 mL) with stirring. To this mixture, solid NBS (5.34 g, 30 mmol) was added in small portions. The color of the solution changed from colorless to clear green and then back to light yellow gradually. After stirring at room temperature for 24 h, 160 mL dichloromethane was added to the solution. Then the reaction mixture was washed with water (1×80 mL, 4×40 mL) and the organic layer was dried over MgSO$_4$. The solvents were evaporated below 40 °C using a rotary evaporator. Column chromatography of the residue over silicon gel with hexane and dichloromethane mixture (hexane: dichloromethane, 5:1; $R_f \approx 0.7$) as eluent gave 4,4′-dibromotriphenylamine as a white solid (0.98 g, 30 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 6.95 (d, 4H), 7.08 (d, 2H), 7.10 (m, 1H), 7.29 (m, 2H), 7.36 (d, 4H).

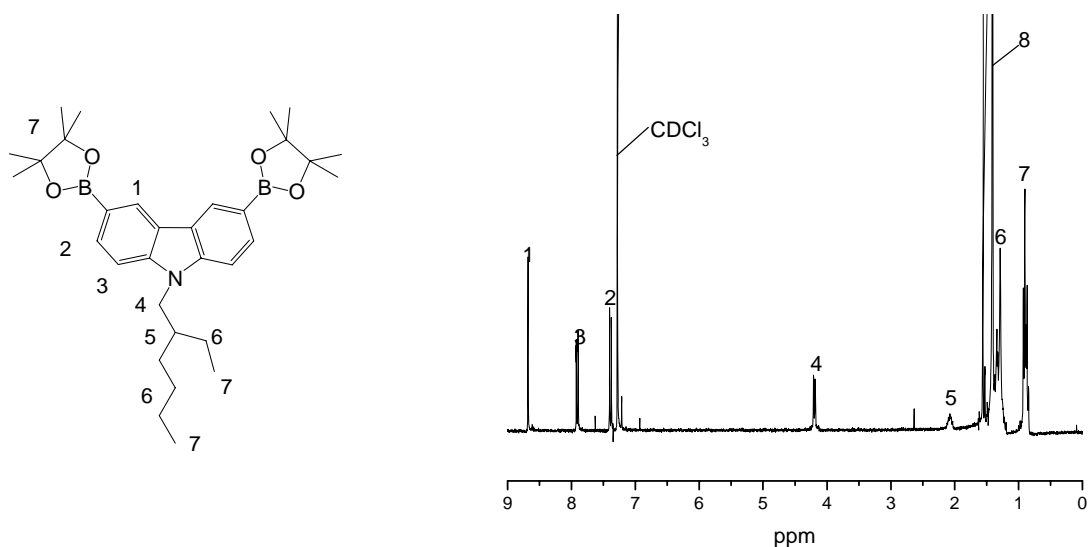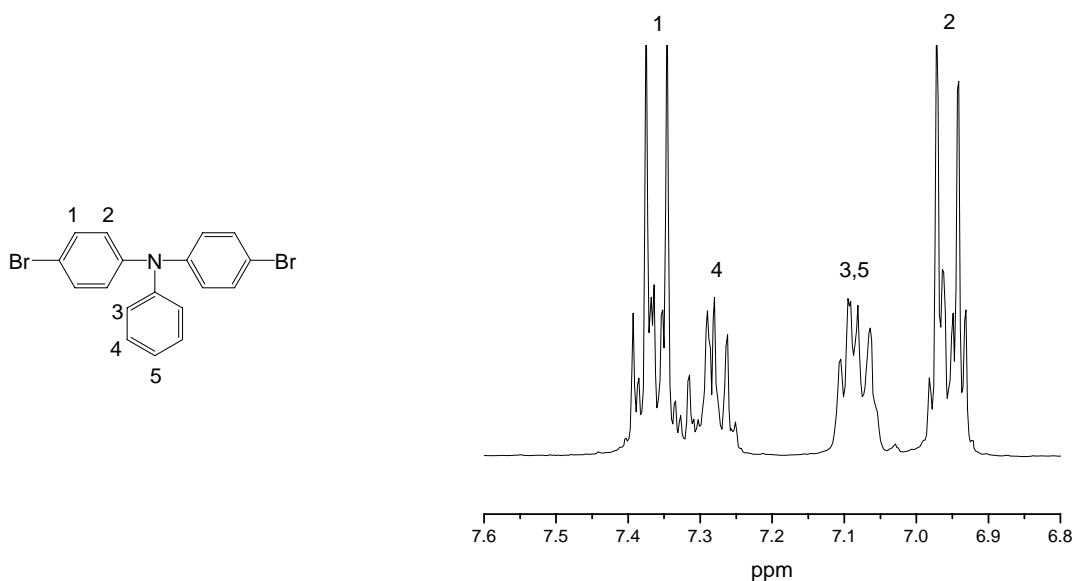300 MHz-^{1}H-NMR spectrum in CDCl$_3$

4,4´-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-triphenylamine

Using a syringe, 2.5 M n-BuLi (8.3 mL, 19.35 mmol) were added to a solution of 4,4´-dibromotriphenylamine (2.6 g, 6.45 mmol) in THF (50 mL) at -78 °C with stirring. The color of the solution turned to red-purple first and then turned to light yellow gradually. The mixture was stirred at -78 °C for one hour. Then the temperature was allowed to increase to room temperature. After that the mixture was cooled to -78 °C again, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.94 mL, 19.35 mmol) was added by syringe. The reaction mixture was stirred at -78 °C for an additional two hours and then was gradually warmed to room temperature and stirred overnight. The clear solution was diluted with ether (100 mL) and washed with water (3×50 mL). The organic layer was dried over MgSO$_4$, and the solvents were concentrated below 40 °C using a rotary evaporator. Flash column chromatography of the residue over silicon gel with hexane and ethyl acetate mixture (hexane: ethyl acetate, 100:5; R$_f$ ≈ 0.3) as eluent gave 4,4´-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-triphenylamine as a white solid (0.48 g, 15 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 1.35 (s, 24H), 7.02 (d, 4H), 7.08 (d, 2H), 7.10 (m, 1H), 7.26 (m, 2H), 7.66 (d, 4H).
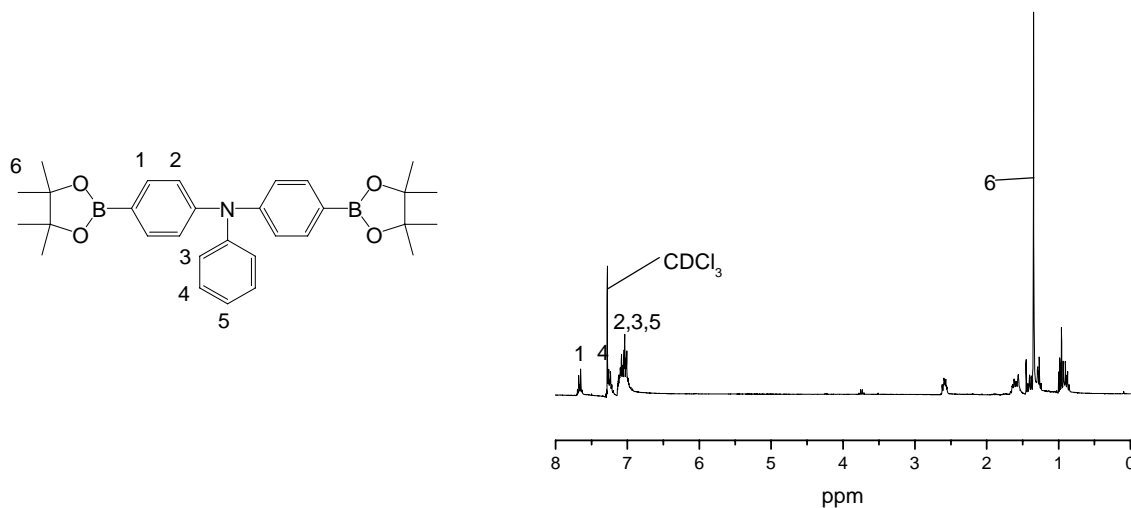
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

4,7-Dibromo-2,1,3-benzothiadiazole

The revised method form Pilgram[76] was used. 2,1,3-benzothiadiazole (2.72 g, 20 mmol) and 15 mL 47% hydrobromic acid were mixed and heated under reflux with stirring, while bromine (9.6 g, 60 mmol) was dropped slowly in within one hour. To facilitate stirring, 10 ml of 47% hydrobromic acid was added and the mixture was heated under reflux for two hours after completion of bromine addition. The mixture was filtered while hot, cooled, filtered again, washed well with water and recrystallized with 40 mL ethanol to give 4,7-dibromo-2,1,3-benzothiadiazole as white needles. (4.15 g, 71 %). m.p.: 188-189 °C.
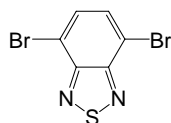
P-DPP

Under nitrogen atmosphere, 0.1224 g (0.2 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.122 g (0.48 mmol) bis(pinacolato)diboron, 0.180 g (0.6 mmol) potassium acetate, 1.5 mg (3 mol%) palladium(II) chloride and 9 mg dppf were dissolved in 30 mL DMF. The mixture was heated to 80 °C for 100 minutes until no start material could be detected anymore. After that, 5 mg (2 mol%) tetrakis(triphenylphosphine)palladium, 0.1224 g (0.2 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole and 0.089 g (0.6 mmol) potassium carbonate in aqueous solution were added to the mixture. Simultaneously 30 mL toluene were added to dissolve all solids. The reaction mixture was heated to 95 °C for 12 h. After the mixture was cooled, 200 mL toluene were added and the mixture was extracted with water to remove DMF and salts. The organic solution was dried in vacuum, redissolved in a minimum amount of chloroform, and precipitated in ethanol. The whole procedure was carried out twice. The polymer was collected and dried in vacuum to give 0.147g (82 %) of a black powder. The polymer did not melt or decompose up to 295 °C. Molecular weight: 8.7 kDa, polydispersity: 1.6.

^{1}H NMR (CDCl$_3$, 300 MHz): δ(ppm) 0.70-1.80 (Alkyl-H); 3.73 (N-CH$_2$); 7.38 (aromatic CH); 7.76 (aromatic CH).

λ_{max}(CHCl$_3$):	528 nm
λ_{em}(CHCl$_3$):	631 nm
Φ_f(CHCl$_3$):	13%
λ_{max}(film):	535 nm
λ_{em}(film):	640 nm
HOMO:	-5.35 eV
LUMO:	-3.42 eV
Bandgap:	1.93 eV

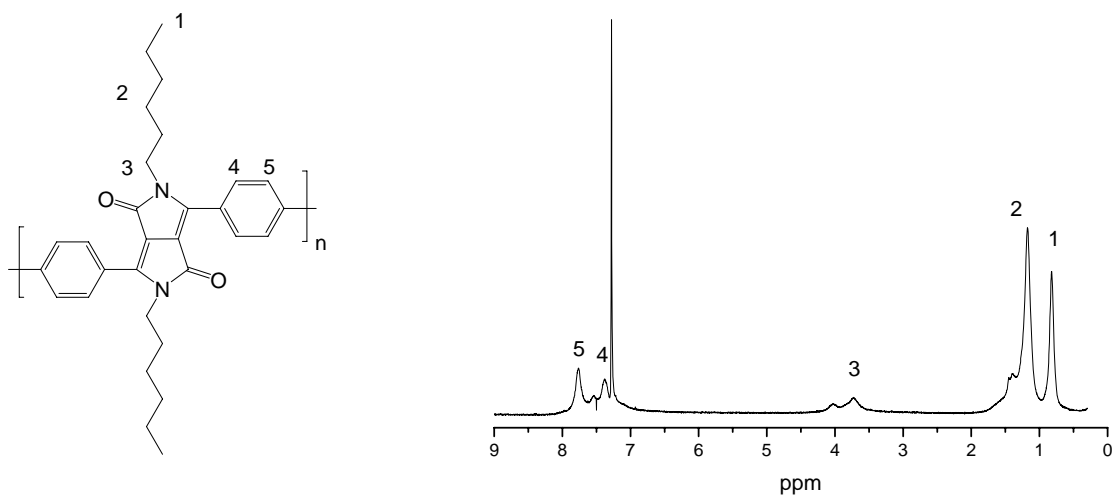300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-DPP-CBZ
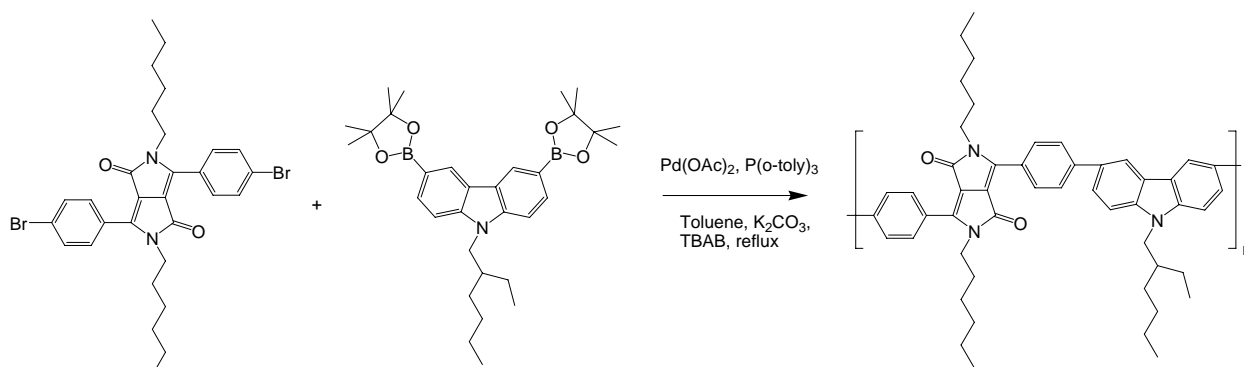
Under nitrogen atmosphere, 0.2 g (0.326 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.173 g (0.326 mmol) 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexyl-carbazole, 5 mg (3 mol%) palladium(II) acetate (Pd(OAc)$_2$) and 35 mg tris(o-tolyl)phosphine were dissolved in 5 mL toluene and stirred under room temperature for 30 minutes. After that, 226 mg K$_2$CO$_3$ (1.63 mmol) and 10 mg tetrabutylamonium bromide were dissolved in 2 mL water and added to the reaction mixture under the inert gas atmosphere. Then the reaction mixture was allowed to raise the temperature and refluxed under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered through celite to remove the residue palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24h. m.w.: 16,500, polydispersity: 2.2, yield: 61 %.

1H NMR (CDCl$_3$): δ (ppm) 0.7-1.8 (C-CH2,CH3), 2.1(CH), 3.90 (DPP N-CH2), 4.25 (carbazole N-CH2), 7.52, 7.79 (phenyl H), 7.92, 8.02, 8.48 (carbazole aromatic H).

λ$_{max}$(CHCl$_3$):	506 nm
λ$_{em}$(CHCl$_3$):	585 nm
Φ$_f$(CHCl$_3$):	46 %
λ$_{max}$(film):	527 nm
λ$_{em}$(film):	638 nm
HOMO:	-5.33 eV
LUMO:	-3.43 eV
Bandgap:	1.90 eV

300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-DPP-TPA
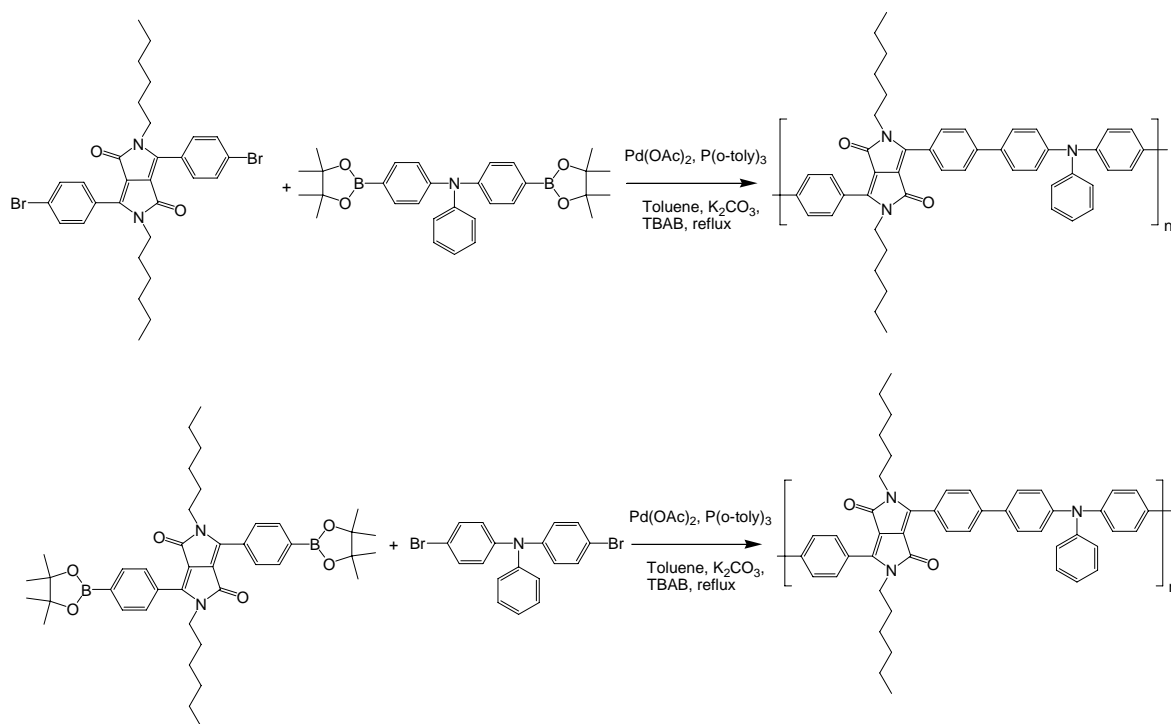
Method 1: Under nitrogen atmosphere, 0.217 g (0.355 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.177 g (0.355 mmol) 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-triphenylamine, 5 mg (3 mol%) palladium(II) acetate (P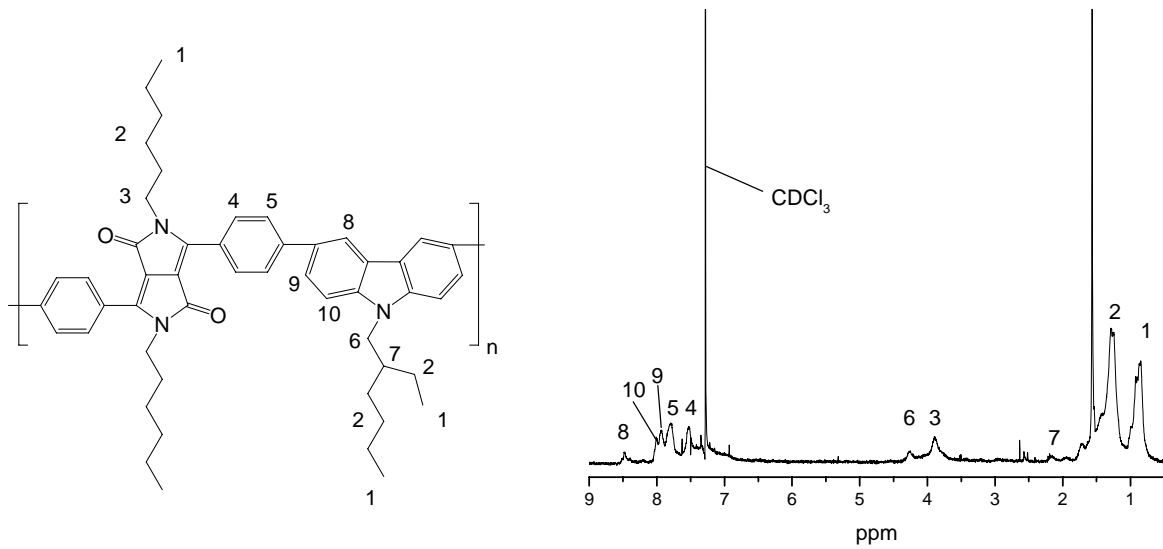d(OAc)$_2$) and 35 mg tris(o-tolyl)phosphine were dissolved in 5 mL toluene and stirred under room temperature for 30 minutes. After that, 294 mg K$_2$CO$_3$ (2.13 mmol) and 10 mg tetrabutylamonium bromide were dissolved in 2 mL water and added to the reaction mixture under the inert gas atmosphere. Then the reaction mixture was allowed to raise the temperature and refluxed under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered through celite to remove the residue palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in ethanol. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. m.w.: 3,700, polydispersity: 1.5, yield: 40 %.

Method 2: Under nitrogen atmosphere, 0.084 g (0.119 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolo[3,4-c]pyrrole, 0.048 g (0.119 mmol) 4,4′-Dibromotriphenylamine, 4.1 mg (3% mol) Pd(PPh$_3$)$_4$ were dissolved in 5 mL toluene and stirred under room temperature for 30 minutes. After that, 0.098 g K$_2$CO$_3$ (0.72 mmol) and 10 mg tetrabutylamonium bromide were dissolved in 2 mL water and added to the reaction mixture under the inert gas atmosphere. Then the reaction mixture was allowed to raise the temperature and refluxed under nitrogen for 24 h. After cooling, 50 mL of

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chloroform were added and the mixture was filtered through celite to remove the residue palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in ethanol. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. m.w.: 7,400, polydispersity: 1.9, yield: 30 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 0.7-1.8 (C-CH$_2$,CH$_3$), 3.850 (DPP N-CH$_2$), 7.0-7.4(TPA-H) 7.59 (TPA-H), 7.77, 7.93 (phenyl-H).

λ$_{max}$(toluene):	511 nm
λ$_{em}$(toluene):	587 nm
Φ$_f$(toluene):	85 %
λ$_{max}$(film):	526 nm
λ$_{em}$(film):	621 nm
HOMO:	-5.37 eV
LUMO:	-3.55 eV
Bandgap:	1.82 eV
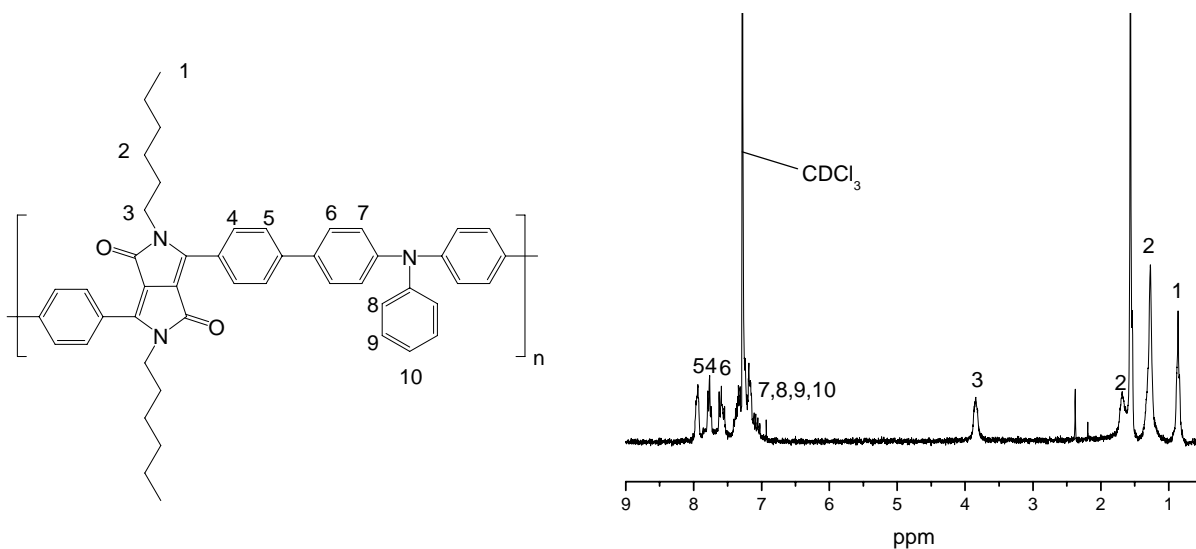
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-DPP-BTZ
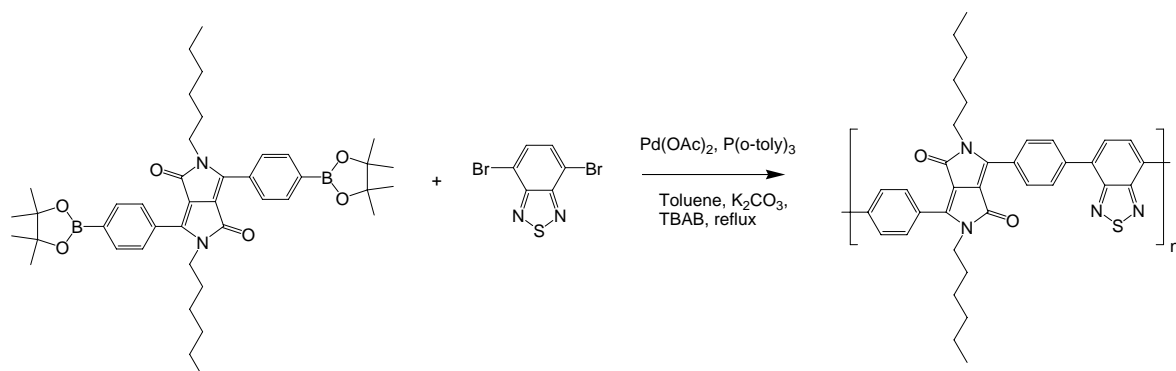
Under nitrogen atmosphere, 0.120 g (0.170 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolo[3,4-c]pyrrole, 0.050 g (0.170 mmol) 4,7-dibromo-2,1,3-benzothiodiazole, 2.2 mg (3 mol%) palladium(II) acetate (Pd(OAc)$_2$) and 6.1 mg tris(o-tolyl)phosphine were dissolved in 5 mL toluene and stirred under room temperature for 30 minutes. After that, 0.141 g K$_2$CO$_3$ (1.02 mmol) and 10 mg tetrabutylamonium bromide were dissolved in 2 mL water and added to the reaction mixture under the inert gas atmosphere. Then the reaction mixture was allowed to raise the temperature and refluxed under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered through celite to remove the residue palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. m.w.: 7,000, polydispersity: 1.3, yield: 75 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 0.7-1.5 (C-CH$_2$,CH$_3$), 3.9 (DPP N-CH$_2$), 7.17 (thiophene-H), 7.44, 7.65 (phenyl-H). m.w.: 7,000, polydispersity: 1.70, yield: 70 %, ^{1}H NMR (CDCl$_3$): δ (ppm) 0.7-1.8 (alkyl-H), 3.87 (N-CH$_2$), 7.82 (aromatic H).

λ$_{max}$(CHCl$_3$):	515 nm;
λ$_{em}$(CHCl$_3$):	600 nm.
Φ$_f$(CHCl$_3$):	19%
λ$_{max}$(film):	528 nm.
λ$_{em}$(film):	665 nm.
HOMO:	-5.34 eV
LUMO:	-3.57 eV
Bandgap:	1.77 eV
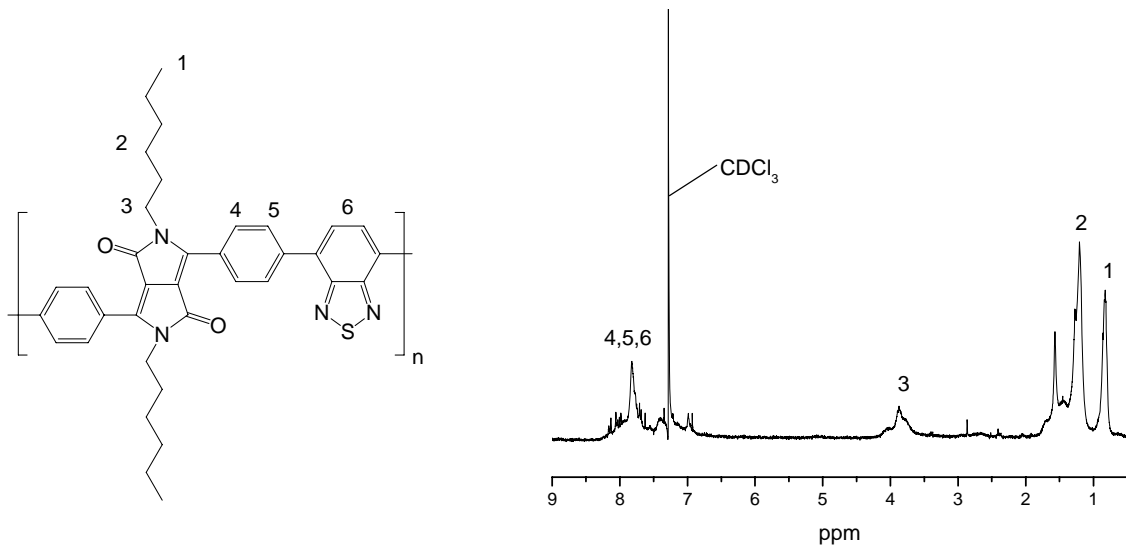
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-CBZ-TPA
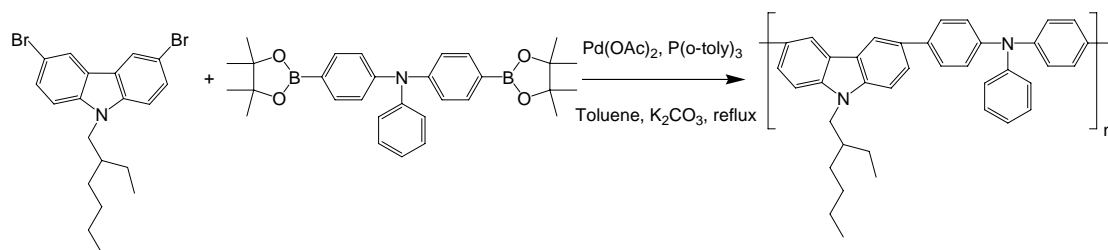
Under nitrogen atmosphere, 0.084 g (0.21 mmol) 4,4′-dibromotriphenylamine, 0.111 g (0.21 mmol) 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole, 3 mg (3 mol%) Pd(OAc)$_2$ and 12 mg tris(o-tolyl)phosphine were dissolved in 5 mL toluene and stirred under room temperature for 30 minutes. After that, 0.174 g K$_2$CO$_3$ (1.26 mmol) were dissolved in 2 mL water and added to the reaction mixture under the inert gas atmosphere. Then the reaction mixture was allowed to raise the temperature and refluxed under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered through celite to remove the residue palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. m.w.: 5,000, polydispersity: 1.3, yield: 61 %. ^{1}H NMR (CDCl$_3$): δ (ppm) 0.8-1.0 (CH$_3$), 1.2-1.5 (C-CH$_2$), 2.1 (-CH), 4.2 (N-CH$_2$), 6.9-7.3 (TPA and CBZ aromatic H), 7.45 (TPA aromatic H), 7.64 (CBZ aromatic H), 7.71 (TPA aromatic H), 8.35 (CBZ aromatic H).

λ$_{max}$(toluene):   326 nm

λ$_{em}$(toluene):   409 nm

Φ$_f$(toluene):   91 %

300 MHz-^{1}H-NMR spectrum in CDCl$_3$

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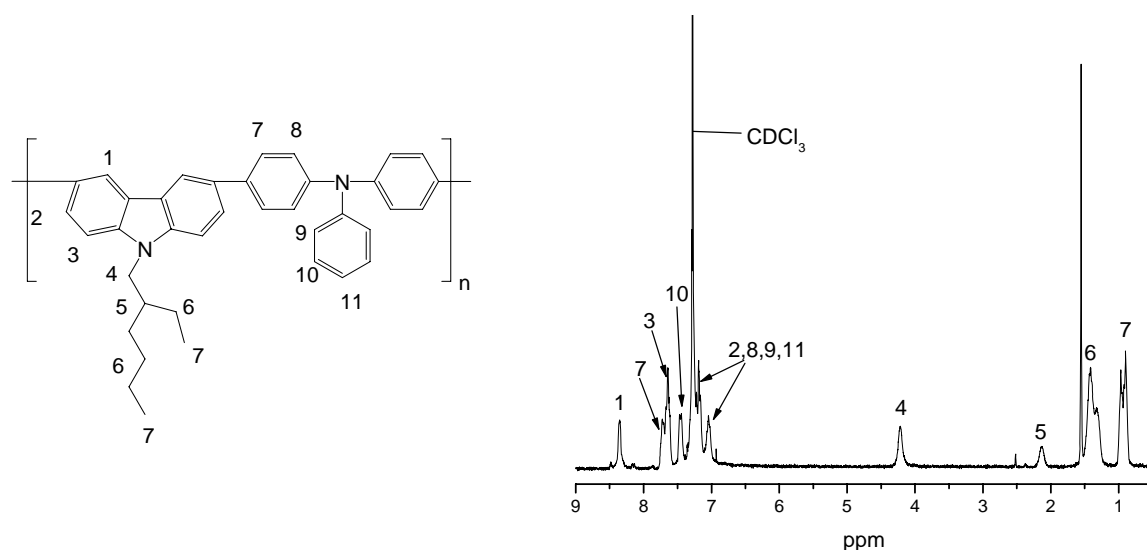
5.2.2. Stille coupling

2,5-Bis(tri-n-butylstannyl)thiophene

Using a syringe, 1.6 M n-BuLi (2.6 mL, 4 mmol) were added to a solution of 2,5-dibromothiophene (0.24 mL, 2 mmol) in THF (40 mL) at -78 °C with stirring. A thick, white precipitation was formed. Then the temperature was allowed to increase to 0 °C in one hour. After that the mixture was cooled to -78 °C again, tri-n-butyltin chloride (1.2 mL, 4 mmol) was added. The reaction mixture was stirred at -78 °C for additional 1 h, and then was gradually warmed to room temperature and stirred overnight. The clear solution was diluted with n-hexane (200 mL) and washed with aqueous sodium bicarbonate solution (5%, 20 mL), and water (20 mL). The organic layer was dried over MgSO$_4$, and the solvents were concentrated using a rotary evaporator. Column chromatography of the residue over grade I neutral alumina with petrol ether as eluent gave title compound as a colorless liquid (0.93 g, 70 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.92 (t, 18H), 1.13 (m, 12H), 1.37 (m, 12H), 1.60 (t, 12H), 7.39 (s, 2H).
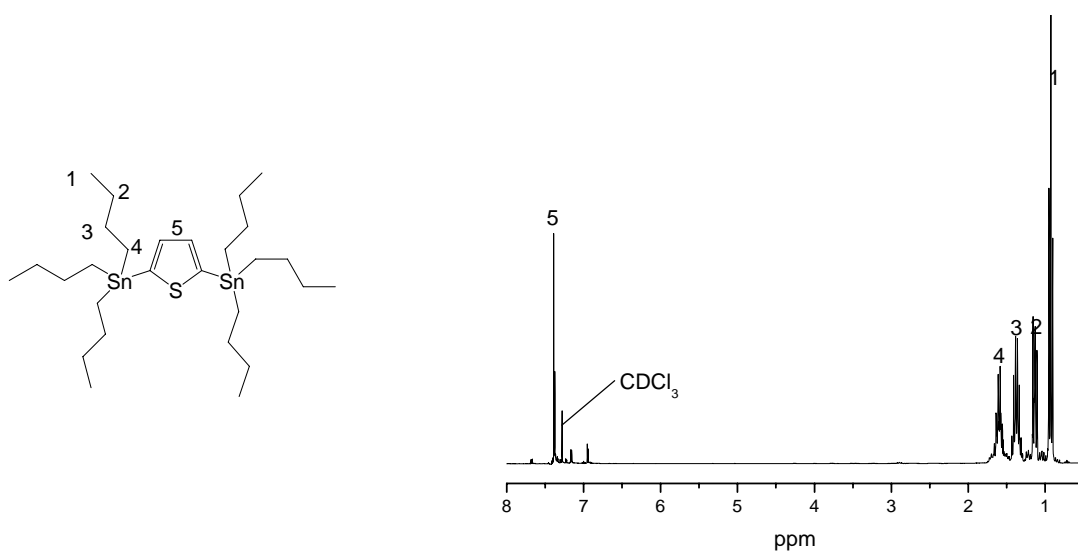
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

5,5'-Dibromo-2,2'-bithiophene

2,2'-Bithiophene (1.66 g, 10 mmol) was dissolved in *N,N*-dimethylformamide (DMF) (50 mL). To this was added solid *N*-Bromosuccinimide (3.6 g, 20 mmol) in small portions. After stirring at 50°C for 3 h, the solution was poured into 100 mL of water, filtered, washed with 100 mL water and aqueous sodium bicarbonate solution until no bubbles appeared anymore. The filter residue was recrystallized in ethanol and gave 5,5'-bis(bromo)-2,2'-bithiophene as white crystals (1.95 g, 60 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 6.87 (d, 2H), 6.98 (d, 2H).

300 MHz-^{1}H-NMR spectrum in CDCl$_3$

5,5'-Bis(tri-n-butylstannyl)-2,2'-bithiophene

Using a syringe, 2.5 M n-BuLi (1.23 mL, 3.08 mmol) were added to a solution of 5,5'-bis(bromo)-2,2'-bithiophene (0.5 g, 1.54 mmol) in THF (40 mL) at -78 °C with stirring. A thick, white precipitate was formed. Then the temperature was allowed to increase to 0 °C in one hour. After that the mixture was cooled to -78 °C again and tri-n-butyltin chloride (0.925 mL, 3.08 mmol) was added. The reaction mixture was stirred at -78 °C for additional 1 h and then was gradually warmed to room temperature and stirred overnight. The clear solution was diluted with n-hexane (200 mL) and washed with aqueous sodium bicarbonate solution (5 %, 20 mL), and water (20 mL). The organic layer was dried over MgSO$_4$, and the solvents were evaporated using a rotary evaporator. Column chromatography of the residue over grade I neutral alumina with petrol ether as eluent gave the title compound as a colorless liquid (1.15 g, 70 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.92 (t, 18H), 1.13 (m, 12H), 1.36 (m, 12H), 1.60 (t, 12H), 7.07 (d, 2H), 7.30 (d, 2H).
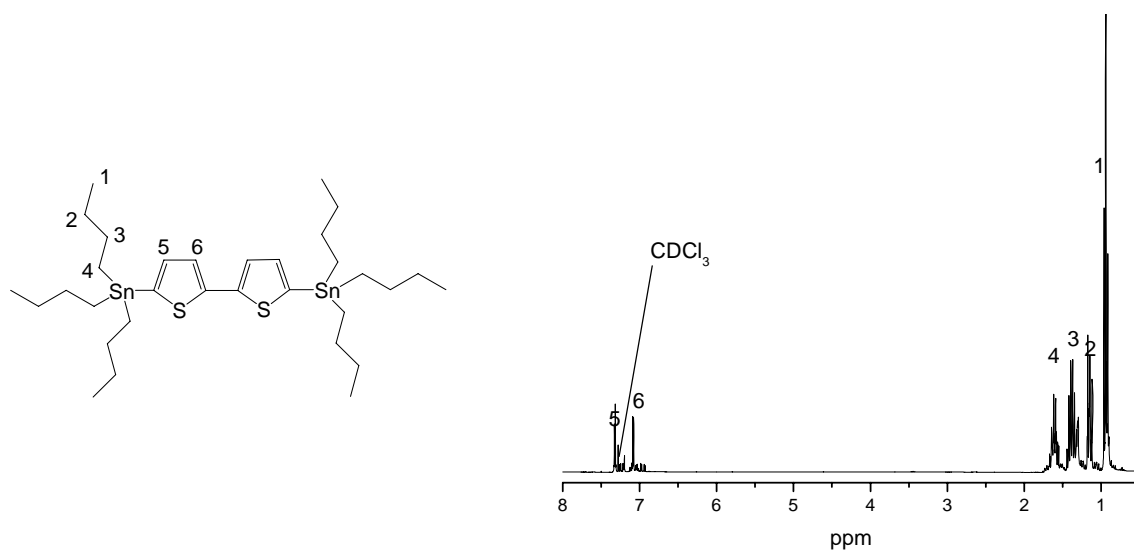
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

2,5-Dibromo-3,4-ethylenedioxythiophene.

EDOT (2.668 g, 18.77 mmol) was dissolved in a mixture of chloroform (50 mL) and glacial acetic acid (50 mL). To this mixture, solid *N*-Bromosuccinimide (7.1 g, 38.7 mmol) was added in small portions. The color of the solution changed from colorless to clear yellow. After stirring at room temperature for 2.5 h, the solution was poured into 200 mL of water, filtered and washed with 100 mL of water and aqueous sodium bicarbonate solution, until no bubble appeared anymore. The filter residue was recrystallized in ethanol and gave 2,5-dibromo-3,4-ethylenedioxythiophene as white crystals (1.71 g, 30 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 4.28 (s, 4H)
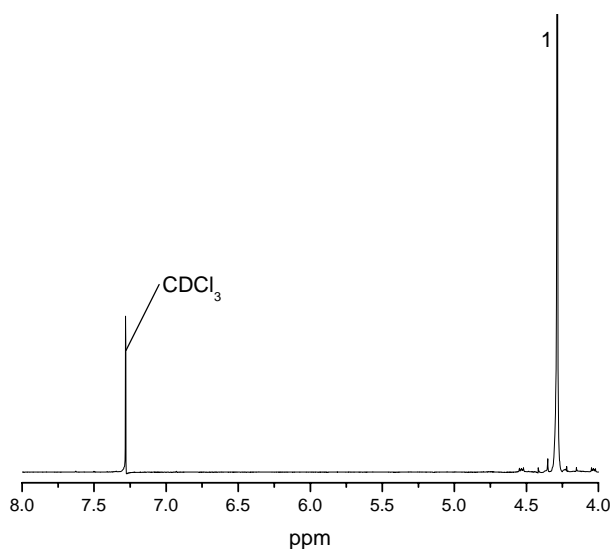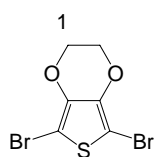
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

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2,5-Bis(tri-n-butylstannyl)-3,4-ethylenedioxythiophene.

Using a syringe, 1.6 M n-BuLi (2.6 mL, 4 mmol) were added to a solution of 2,5-dibromo-3,4-ethylenedioxythiophene (0.6 g, 2 mmol) in THF (40 mL) at -78 °C with stirring. Then the temperature was allowed to increase to 0 °C in one hour. After that the mixture was cooled to -78 °C again, tri-n-butyltin chloride (1.2 mL, 4 mmol) was added. The reaction mixture was stirred at -78 °C for an additional hour and then was gradually warmed to room temperature and stirred overnight. The clear solution was diluted with n-hexane (200 mL) and washed with aqueous sodium bicarbonate solution (5 %, 20 mL), and water (20 mL). The organic layer was dried over MgSO$_4$, and the solvents were concentrated using a rotary evaporator. Column chromatography of the residue over grade I neutral alumina with petrol ether as eluent gave the title compound as a colorless liquid (1.04 g, 72 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.89 (t, 18H), 1.09 (m, 12H), 1.32 (m, 12H), 1.57 (t, 12H), 4.11 (s, 4H).
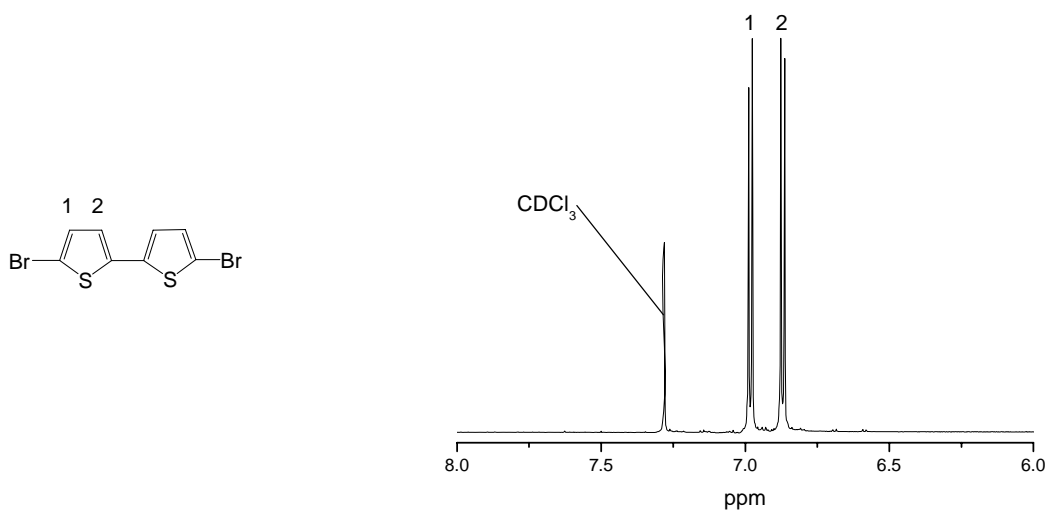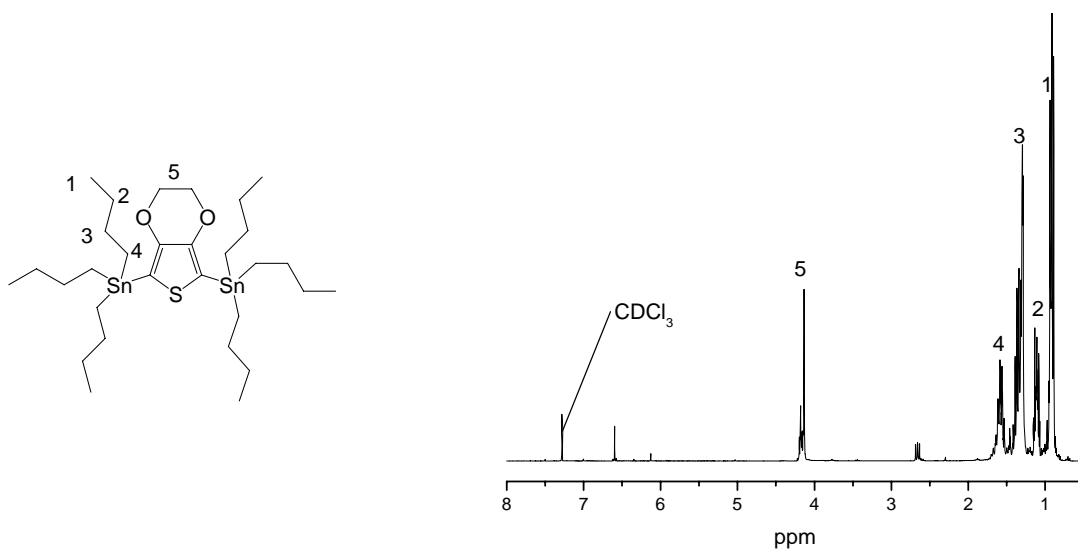

300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-DPP-TH
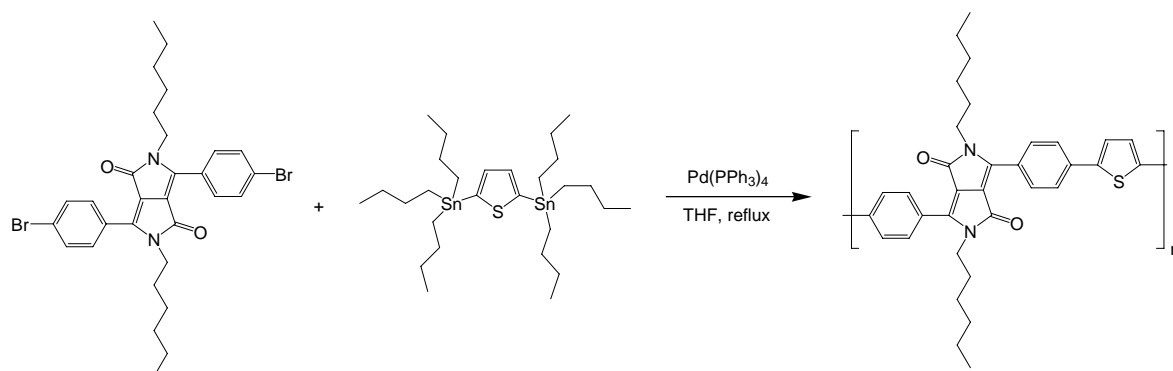
In a 100 mL flask, 0.1 g (0.163 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.108 g (0.163 mmol) 2,5-bis(tri-n-butylstannyl)thiophene and 5.5 mg (2 mol%) $Pd(PPh_3)_4$ were dissolved in 20 mL THF and refluxed under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and reprecipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum at 100 °C for 24 h. m.w.: 12,200, polydispersity: 2.15, yield: 71 %,

^{1}H NMR (CDCl$_3$): δ (ppm) 0.7-1.5 (alkyl-H), 3.75 (N-CH$_2$), 7.17 (thiophene-H), 7.44, 7.65 (phenyl-H).

λ_{max}(CHCl$_3$):	545 nm
λ_{em}(CHCl$_3$):	635 nm
Φ_f(CHCl$_3$):	12 %
λ_{max}(film):	558 nm
λ_{em}(film):	704 nm
HOMO:	-5.26 eV
LUMO:	-3.69 eV
Bandgap:	1.57 eV
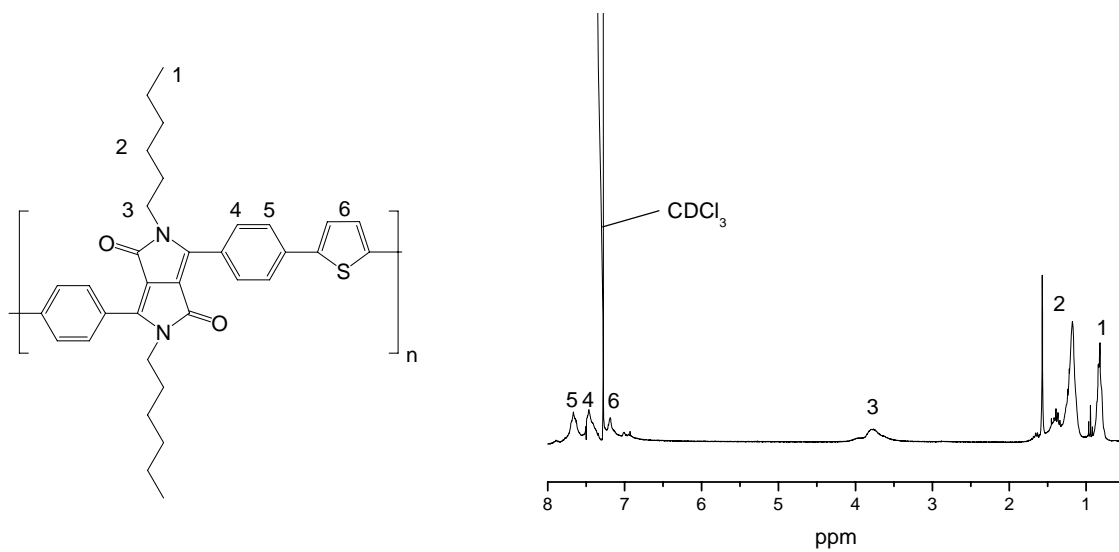
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-DPP-BTH
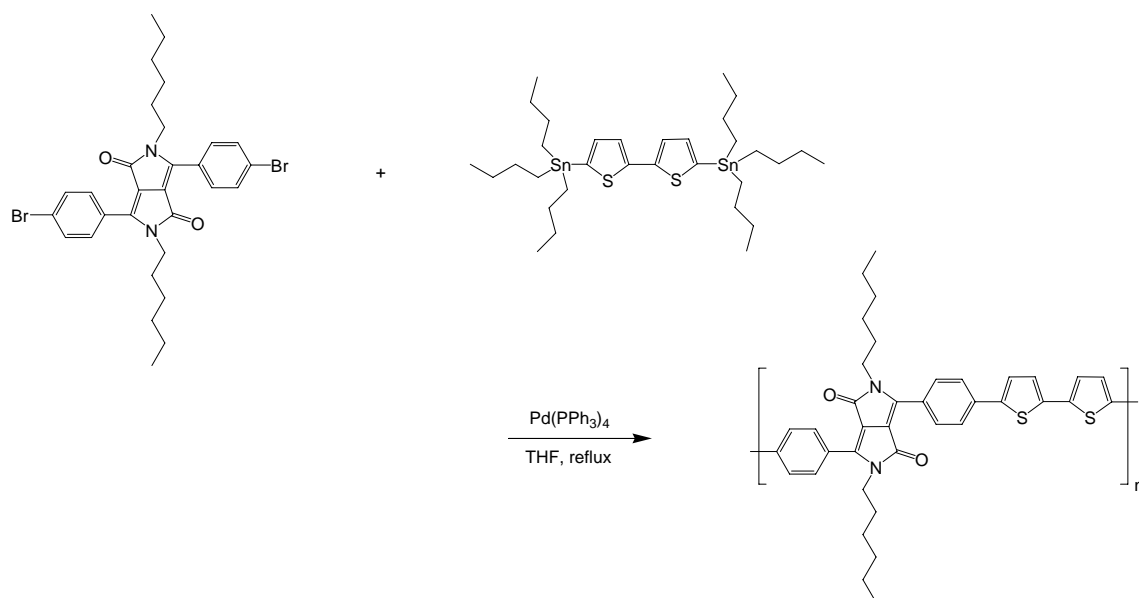
In a 100 mL flask, 0.1 g (0.163 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.121 g (0.163 mmol) 5,5'-bis(tri-n-butylstannyl)-2,2'-bithiophene and 5.5 mg (2% mol) Pd(PPh$_3$)$_4$ were dissolved in 20 mL THF and refluxed under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and reprecipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum at 100 °C for 24 h. m.w.: 9,100, polydispersity: 1.70, yield: 70 %,

^{1}H NMR (CDCl$_3$): δ (ppm) 0.7-1.5 (alkyl-H), 3.75 (N-CH$_2$), 6.99, 7.17 (bithiophene-H), 7.40, 7.59 (phenyl-H).

|	
λ$_{max}$(CHCl$_3$):	558 nm
λ$_{em}$(CHCl$_3$):	616 nm
Φ$_f$(CHCl$_3$):	13 %
λ$_{max}$(film):	570 nm
λ$_{em}$(film):	699 nm
HOMO:	-5.15 eV
LUMO:	-3.68 eV
Bandgap:	1.47 eV
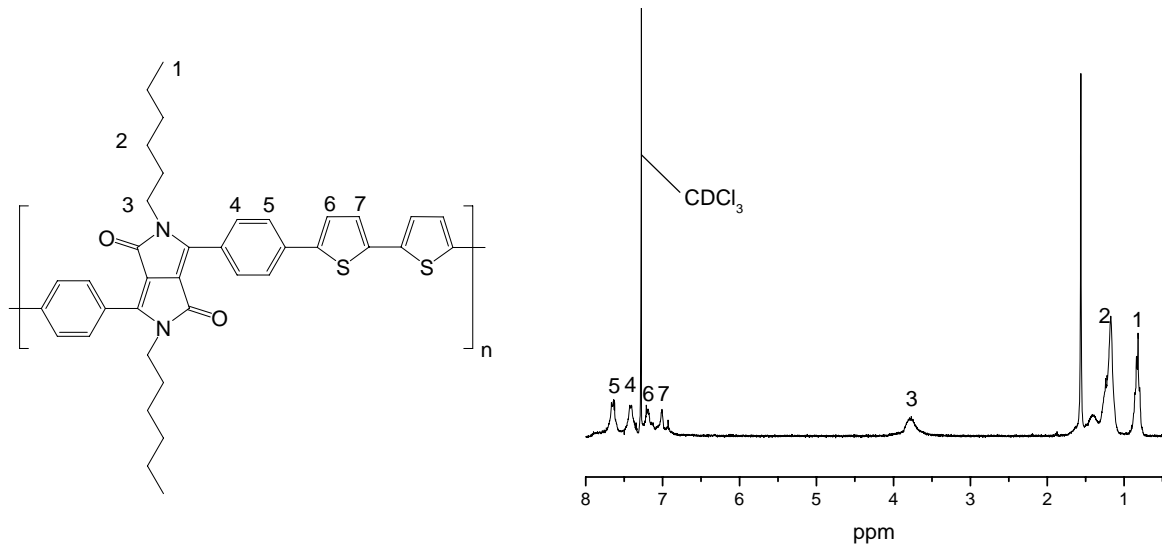
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-DPP-EDOT
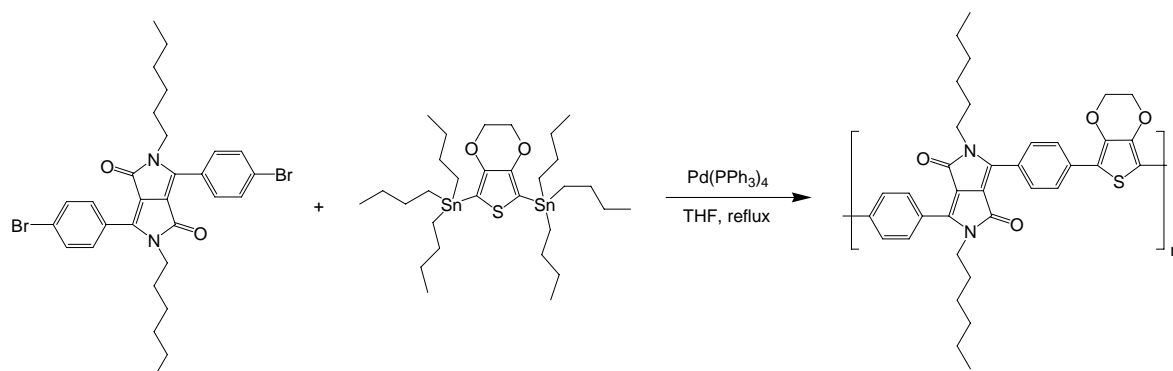
In a 100 mL flask, 0.1 g (0.163 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.117 g (0.163 mmol) 2,5-Bis(tri-n-butylstannyl)-3,4-ethylenedioxythiophene and 5.5 mg (2 mol%) Pd(PPh$_3$)$_4$ were dissolved in 20 mL THF and refluxed under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and reprecipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum at 100 °C for 24 h. m.w.: 6700, polydispersity: 1.47, yield: 40 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 0.7-1.5 (alkyl-H), 3.79 (N-CH$_2$), 4.42 (O-CH$_2$), 7.62, 7.78 (phenyl-H).

λ$_{max}$(CHCl$_3$):	560 nm
λ$_{em}$(CHCl$_3$):	624 nm
Φ$_f$(CHCl$_3$):	36 %
λ$_{max}$(film):	581 nm
λ$_{em}$(film):	723 nm
HOMO:	-5.11 eV
LUMO:	-3.65 eV
Bandgap:	1.47 eV
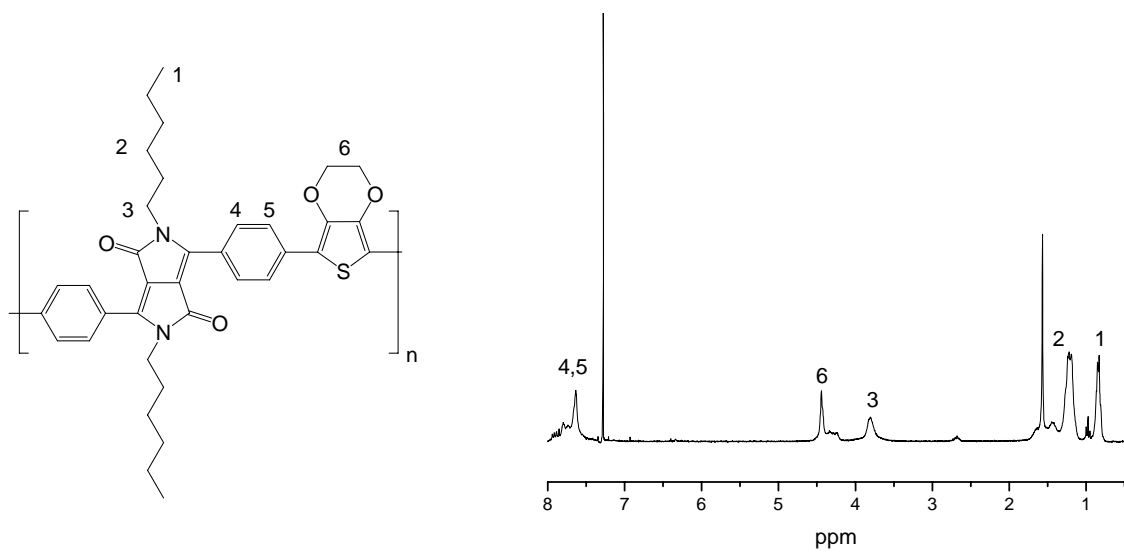
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

5.2.3. Buchwald-Hartwig coupling

P-DPP-PDA
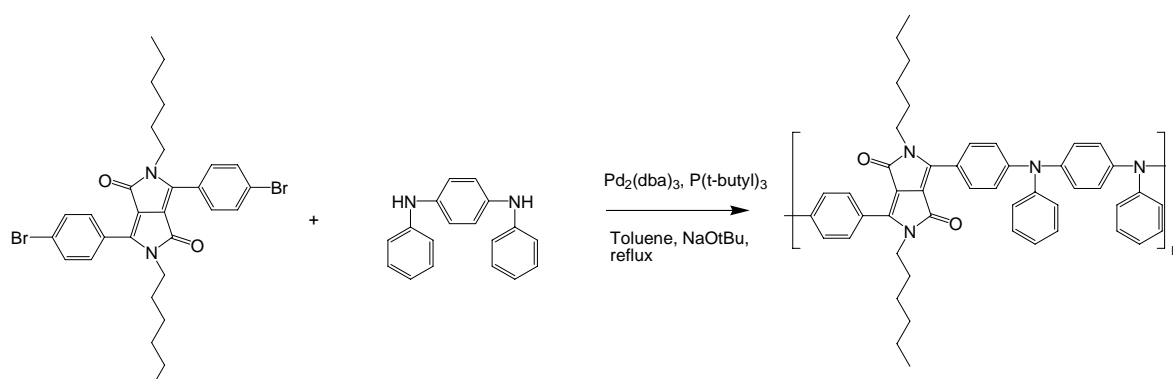
Under nitrogen atmosphere, 6 mg (2 mol%) tris(dibenzylideneacetone) dipalladium(0) (Pd$_2$(dba)$_3$) and 2.7 mg tris-t-butylphosphine were dissolved in 2 mL toluene and stirred under room temperature for 30 minutes. Another Schlenk tube was charged with 0.1224 g (0.200 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.0521 g (0.200 mmol) *N,N'*-diphenyl-*p*-phenylenediamine and 0.041 g (0.600 mmol) sodium t-butylate and 8 ml of dry toluene. The mixture was degassed. Then the solution of the palladium complex was added and the reaction mixture was stirred at 100 °C under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered through celite to remove the residue palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. m.w.: 14,000, polydispersity: 1.9, yield: 80 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 0.7-1.8 (alkyl-H), 3.81 (N-CH$_2$), 7.15, 7.25 (PDA aromatic H), 7.37, 7.80 (DPP phenyl H).

λ$_{max}$(toluene):	539 nm
λ$_{em}$(toluene):	608 nm
Φ$_f$(toluene):	42 %
λ$_{max}$(film):	544 nm
λ$_{em}$(film):	none
HOMO:	-5.06 eV
LUMO:	-3.30 eV
Bandgap:	1.76 eV
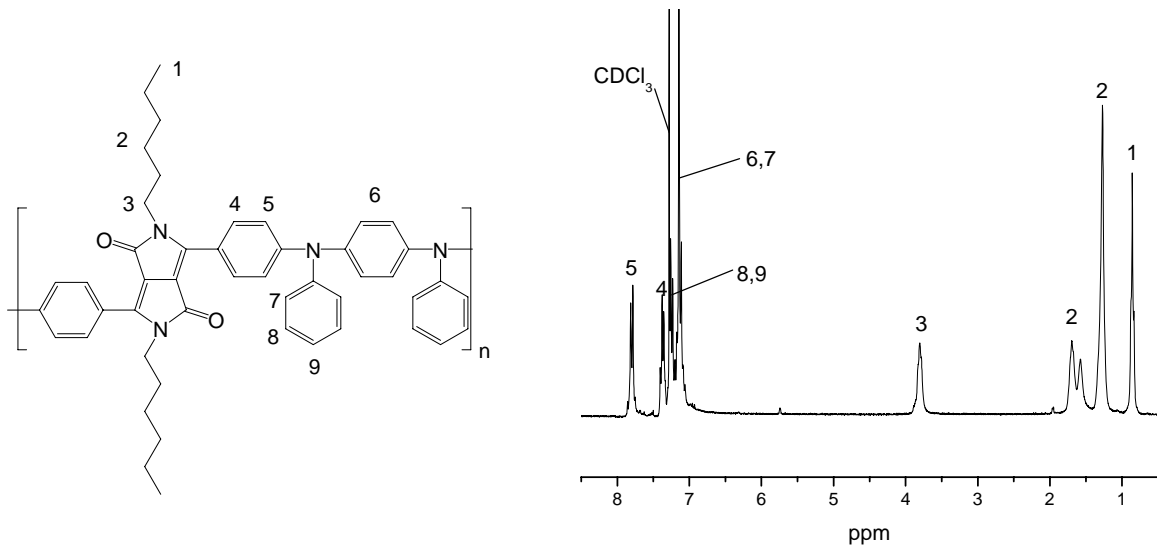
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-DPP-PYRE
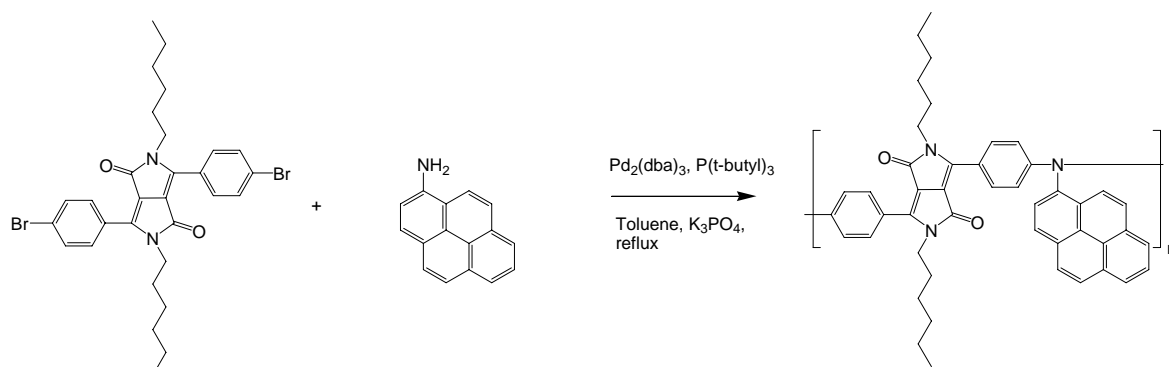
Under nitrogen atmosphere, 6 mg (2% mol) tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) and 2.7 mg tris-t-butylphosphine were dissolved in 2 mL toluene and stirred under room temperature for 30 minutes. A Schlenk tube was charged with 0.1224 g (0.200 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.0434 g (0.200 mmol) 1-aminopyrene and 0.17 g (0.800 mmol) potassium phosphate and 8 ml of dry toluene. The mixture was degassed. Then the solution of the palladium complex was added and the reaction mixture was stirred at 100 °C under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered through celite to remove the residue palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. m.w.: 4,300, polydispersity: 1.3, yield: 81 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 0.7-1.8 (alkyl-H), 3.7 (N-CH$_2$), 7.08 (Pyrene-H), 7.3, 7.8 (DPP phenyl-H), 7.9-8.3 (Pyrene-H).

λ$_{max}$(toluene):	527 nm
λ$_{em}$(toluene):	607 nm
Φ$_f$(toluene):	62 %
λ$_{max}$(film):	564 nm
λ$_{em}$(film):	none
HOMO:	-5.24 eV
LUMO:	-3.40 eV
Bandgap:	1.84 eV

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300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-PY-TBAN
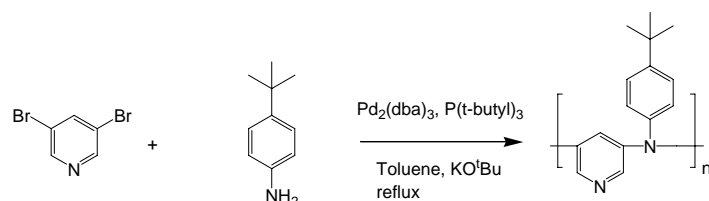
Under nitrogen atmosphere, 55 mg (3% mol) tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) and 49 mg tris-t-butylphosphine were dissolved in 5 mL toluene and stirred under room temperature for 120 minutes. A Schlenk tube was charged with 474 mg (2 mmol) 3,5-dibromopyridine, 298 mg (2 mmol) 4-t-butylanilin and 337 mg (6 mmol) potassium t-butoxide and 8 ml of dry toluene. The mixture was degassed. Then the solution of the palladium complex was added and the reaction mixture was stirred at 100 °C under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered through celite to remove the residual palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in petroleum ether. The polymer was collected and dried under vacuum for 24 h. m.w.: 2200, polydispersity: 1.2, yield: 65 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 1.35 (*t*-butyl H), 7.0 (aromatic H), 7.3 (aromatic H), 7.9 (aromatic H).

λ$_{max}$(toluene):	335 nm
λ$_{em}$(toluene):	448 nm
Φ$_f$(toluene):	23 %
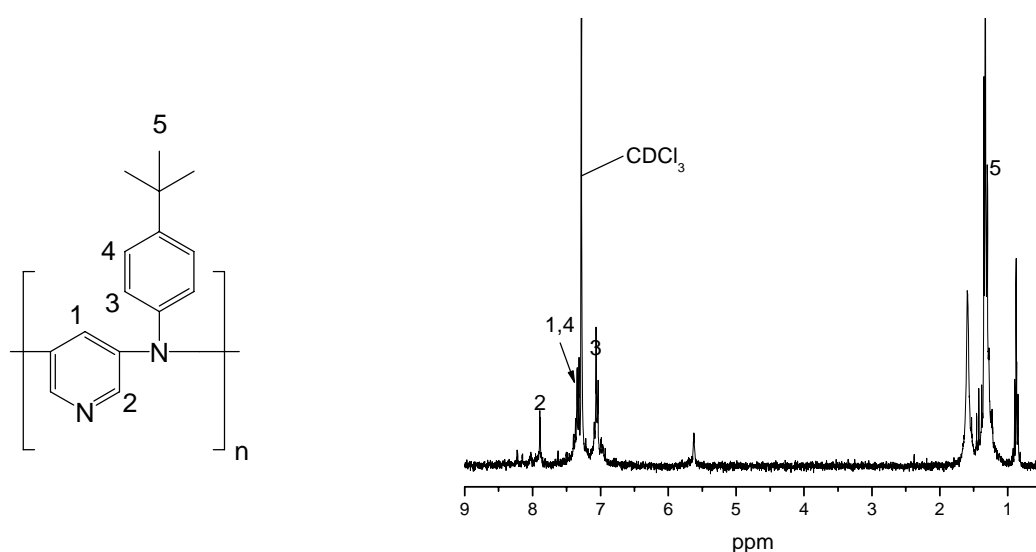
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-PY-ANT
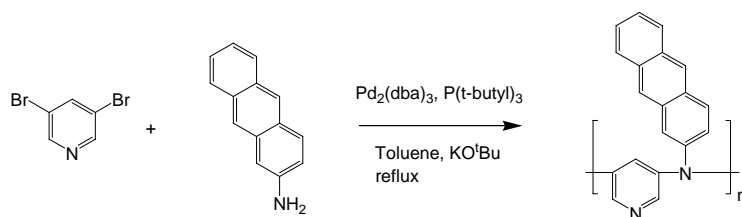
Under nitrogen atmosphere, 15 mg (3% mol) tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) and 13 mg tris-t-butylphosphine were dissolved in 5 mL toluene and stirred under room temperature for 120 minutes. A Schlenk tube was charged with 123 mg (0.52 mmol) 3,5-dibromopyridine, 100 mg (0.52 mmol) 2-aminoanthracene and 175 mg (1.56 mmol) potassium t-butoxide and 8 ml of dry toluene. The mixture was degassed. Then the solution of the palladium complex was added and the reaction mixture was stirred at 100 °C under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered through celite to remove the residual palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in petroleum ether. The polymer was collected and dried under vacuum for 24 h. m.w.: 2600, polydispersity: 1.3, yield: 30 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 7.1-8.4 (aromatic H).

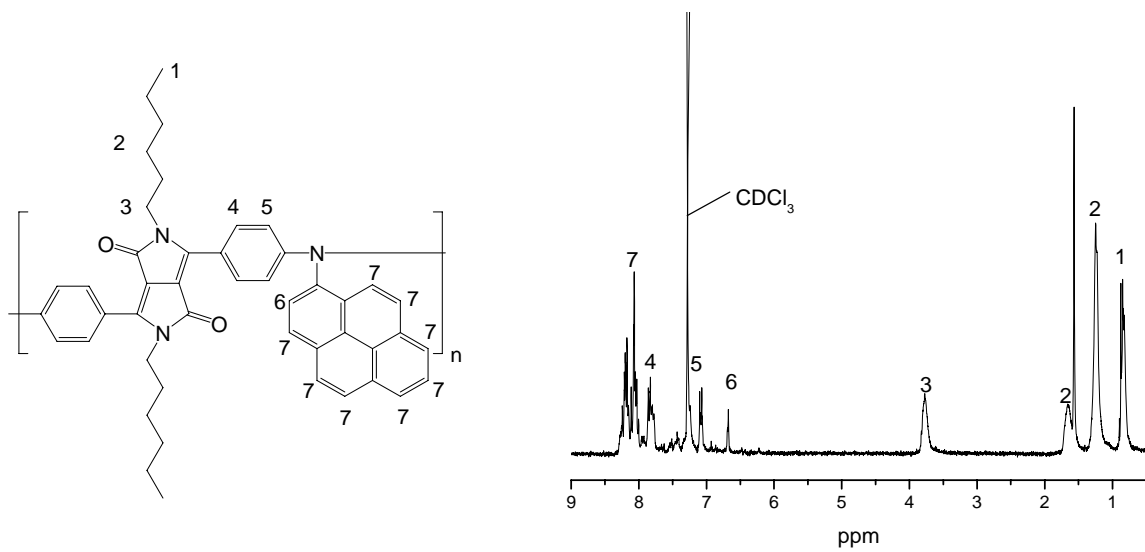|	
λ$_{max}$(toluene):	305 nm
λ$_{em}$(toluene):	462 nm
Φ$_f$(toluene):	34 %
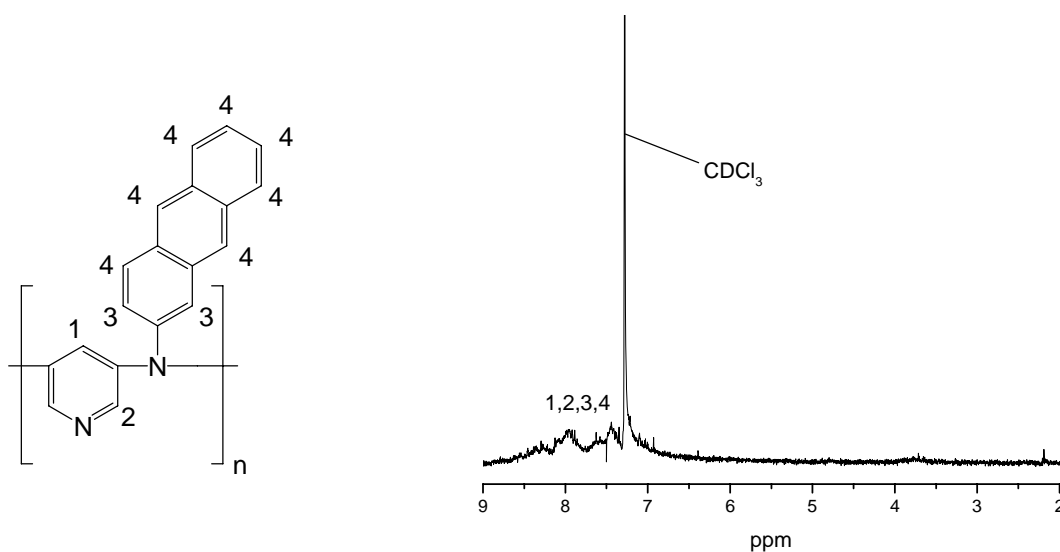
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-PY-PYRE
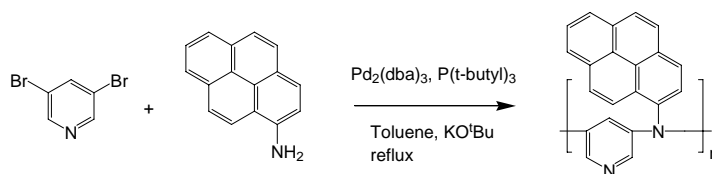
Under nitrogen atmosphere, 14 mg (3% mol) tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) and 12 mg tris-t-butylphosphine were dissolved in 5 mL toluene and stirred under room temperature for 120 minutes. A Schlenk tube was charged with 119 mg (0.5 mmol) 3,5-dibromopyridine, 109 mg (0.5 mmol) 1-aminopyrene and 168 mg (1.5 mmol) potassium t-butoxide and 8 ml of dry toluene. The mixture was degassed. Then the solution of the palladium complex was added and the reaction mixture was stirred at 100 °C under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered through celite to remove the residual palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in petroleum ether. The polymer was collected and dried under vacuum for 24 h. m.w.: 2300, polydispersity: 1.1, yield: 40 %.

1H NMR (CDCl3): δ (ppm) 7.5-8.3 (aromatic H).

λ$_{max}$(toluene):	359 nm
λ$_{em}$(toluene):	432 nm
Φ$_f$(toluene):	41 %

300 MHz-^{1}H-NMR spectrum in CDCl$_3$

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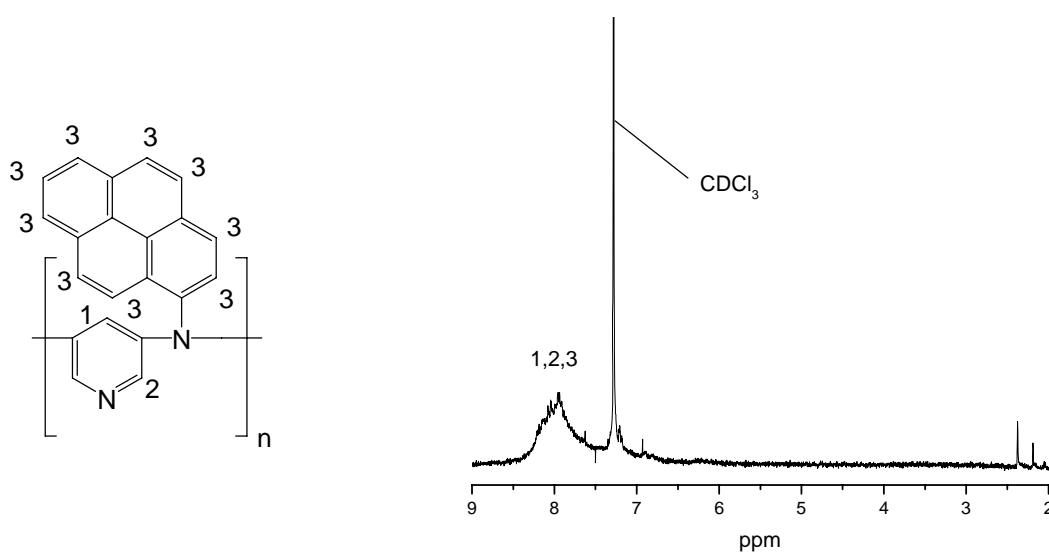
5.3. DPP conjugated polymers via electropolymerization

5.3.1. Synthesis of the Precursors

2-(tri-n-butylstannyl)thiophene

Using a syringe, 1.5 M n-BuLi (22 mL, 33 mmol) were added to a solution of thiophene (4.8 mL, 60 mmol) in THF (50 mL) at -78 °C with stirring. A thick, white precipitation was formed. Then the temperature was allowed to increase to 0 °C in one hour. After that the mixture was cooled to -78 °C again, tri-n-butyltin chloride (8.8 mL, 30 mmol) was added. The reaction mixture was stirred at -78 °C for additional 1 h, and then was gradually warmed to room temperature and stirred overnight. The clear solution was diluted with n-hexane (200 mL) and washed with aqueous sodium bicarbonate solution (5%, 50 mL), and brine (50 mL). The organic layer was dried over MgSO$_4$, and the solvents were concentrated using a rotary evaporator. Column chromatography of the residue over grade I neutral alumina with petroleum ether as eluent gave title compound as a colorless liquid (7.8 g, 70 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.92 (t, 9H), 1.13 (m, 6H), 1.37 (m, 6H), 1.60 (t, 6H), 7.26 (d, 1H), 7.32 (t, 1H), 7.69 (d, 1H).
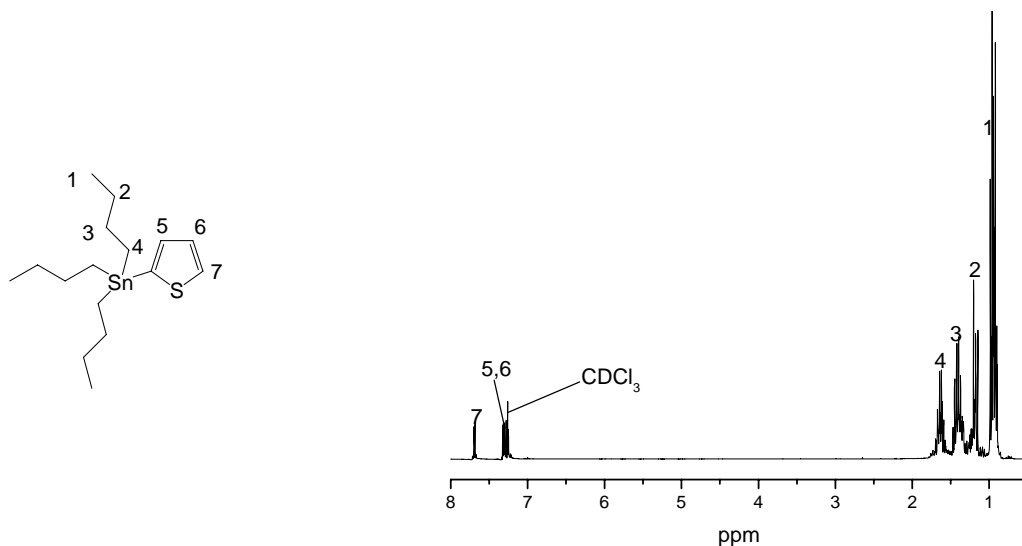
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

3-hexyl-thiophene

Step 1: Preparation of the Grignard reagent

A three neck flask was charged with 3 g (0.12 mmol) magnesium, 1 piece of iodine and 30 mL of absolute diethyl ether. 14.1 mL hexylbromide was dissolved in 40 mL absolute diethyl ether and was poured in a dropping funnel. Under nitrogen atmosphere, 1/8 of the hexylbromide solution was dropped in the flask to initiate the reaction. The remaining hexylbromide was dropped slowly to hold the reaction statues. After the addition was finished, the mixture was heated to reflux for 30 min until all magnesium disappeared.

Step 2: Preparation of 3-hexyl-thiophene

A three neck flask was charged with 10 mL (103.3 mmol) 3-bromothiophene, 40 mg (10%) NiCl$_2$(dppp) and 60 mL absolute diethyl ether. 4-5 mL Grignard reagent was dropped into the flask and the mixture was stirred for 15 min at a temperature between 15 to 20 °C. Then the remaining Grignard reagent was dropped slowly keeping the temperature between 25 to 30 °C. After the addition, the mixture was heated to reflux for 30 min. The reaction mixture was cooled and filtered. The filtrate was distilled in vacuum and the title compound was received as colorless oil at 65 °C, 0.45 mmHg (11.8 g, 70 %).
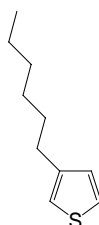
2-(tri-n-butylstannyl)-4-hexyl-thiophene

Using a syringe, 1.6 M n-BuLi (3.84 mL, 6 mmol) were added to a solution of 3-hexyl-thiophene (1.0 g, 5.94 mmol) in THF (50 mL) at -78 °C with stirring. A thick, white precipitation was formed. Then the temperature was allowed to increase to 0 °C in one hour. After that the mixture was cooled to -78 °C again, tri-n-butyltin chloride (1.8 mL, 6 mmol) was added. The reaction mixture was stirred at -78 °C for additional 1 h, and then was gradually warmed to room temperature and stirred overnight. The clear solution was diluted with n-hexane (200 mL) and washed with aqueous sodium bicarbonate solution (5 %, 50 mL), and brine (50 mL). The organic layer was dried over MgSO$_4$, and the solvents were concentrated using a rotary evaporator. Column chromatography of the residue over grade I neutral alumina with petroleum ether as eluent gave title compound as a colorless liquid (2.0 g, 71 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.90 (t, 12H), 1.09 (m, 8H), 1.33 (m, 10H), 1.57 (m, 8H), 2.66 (t, 2H), 6.97 (s, 1H), 7.20 (s, 1H).
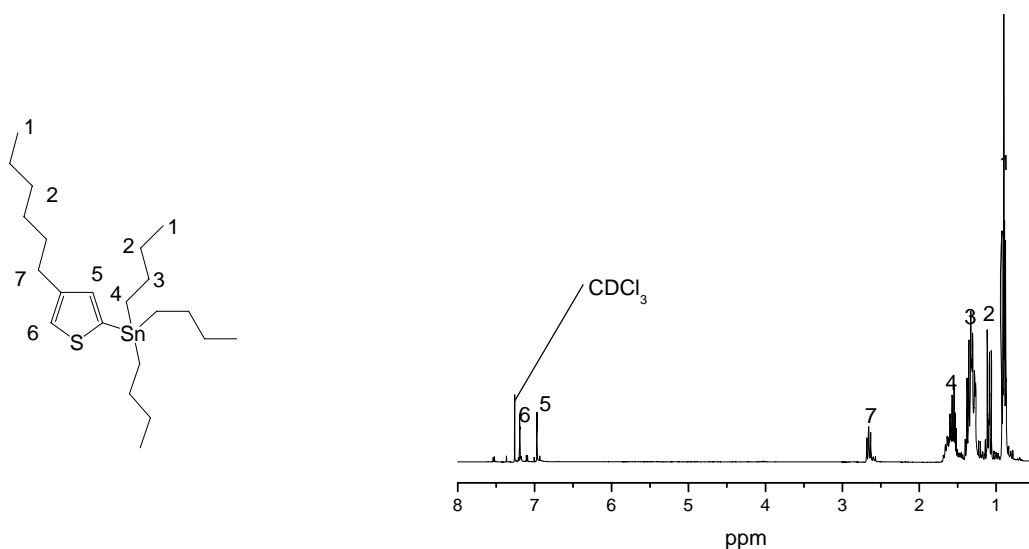
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

2-(tri-n-butylstannyl)-3,4-ethylenedioxythiophene.

Using a syringe, 1.6 M n-BuLi (6.1 mL, 9.5 mmol) were added to a solution of 3,4-ethylenedioxythiophene (0.667 g, 4.7 mmol) in THF (40 mL) at -78 °C with stirring. Then the temperature was allowed to increase to 0 °C in one hour. After that the mixture was cooled to -78 °C again, tri-n-butyltin chloride (2.85 mL, 9.5 mmol) was added. The reaction mixture was stirred at -78 °C for an additional hour and then was gradually warmed to room temperature and stirred overnight. The clear solution was diluted with n-hexane (200 mL) and washed with aqueous sodium bicarbonate solution (5 %, 20 mL), and water (20 mL). The organic layer was dried over MgSO$_4$, and the solvents were concentrated using a rotary evaporator. Column chromatography of the residue over grade I neutral alumina with petrol ether as eluent gave the title compound as a colorless liquid (1.04 g, 72 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.89 (t, 9H), 1.09 (m, 6H), 1.32 (m, 6H), 1.57 (t, 6H), 4.11 (s, 4H), 6.66 (s, 1H).
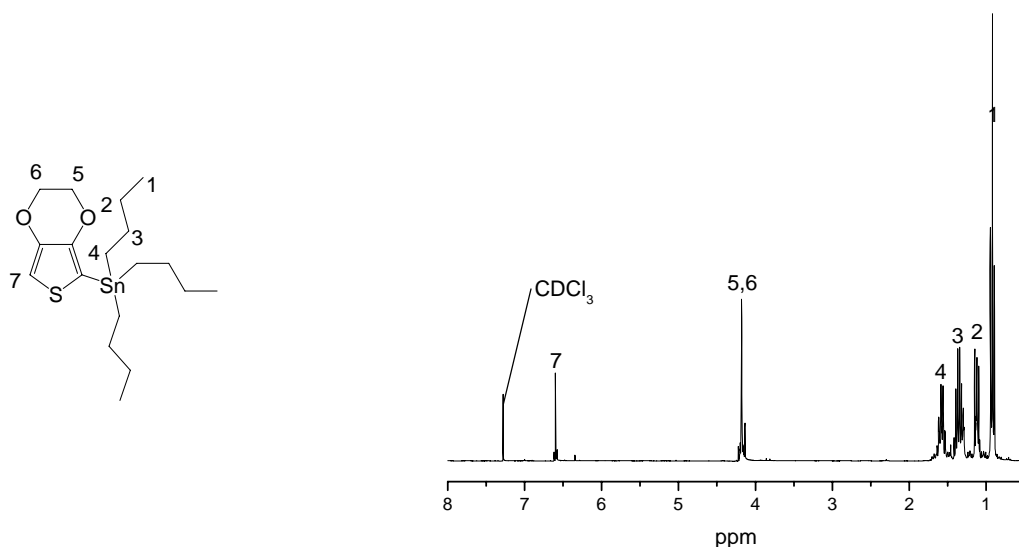
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

5.3.2. Synthesis of the monomers and electropolymerization

1,4-Diketo-2,5-dihexyl-3,6-bis(4-(2-thienyl)phenyl)pyrrolo[3,4-c]pyrrole
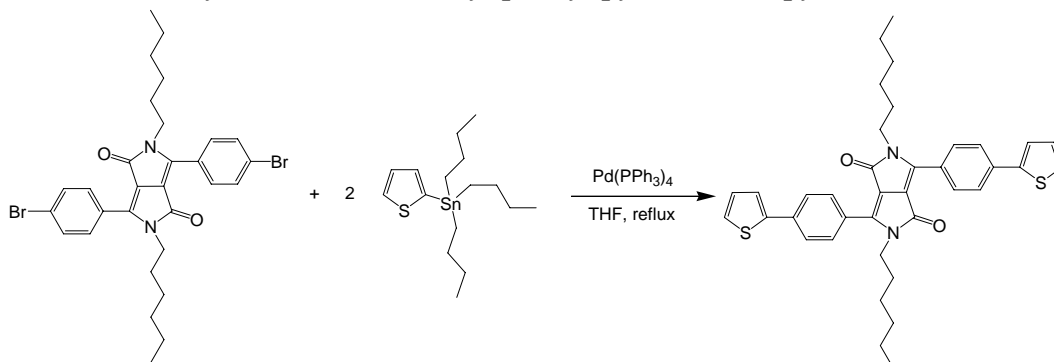
In a 100 mL flask, 0.234 g (0.4 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.5 g (1.34 mmol) 2-(tri-n-butylstannyl)thiophene and 9.2 mg (2 mol%) Pd(PPh$_3$)$_4$ were dissolved in 20 mL THF and refluxed under nitrogen for 24 h. After cooling, 50 mL of dichloromethane were added and the mixture was filtered. Then the mixture was washed with brine (3×40mL) and the organic layer was dried over anhydrous MgSO$_4$. The solvents were evaporated using a rotary evaporator. Column chromatography of the residue over silicon gel with dichloromethane as eluent gave the title compound as a red solid (1.98 g, 75 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.86 (t, 6H), 1.26 (m, 12H), 1.68 (m, 4H), 3.82 (t, N-CH$_2$, 4H), 7.15 (t, thiophene-H, 2H), 7.38 (d, thiophene-H, 2H), 7.45 (d, thiophene-H, 2H), 7.79 (d, 4H), 7.90 (d, 4H).

λ$_{max}$(CHCl$_3$):	500 nm
λ$_{em}$(CHCl$_3$):	575 nm
λ$_{max}$(film):	521 nm
Φ$_f$(CHCl$_3$):	89 %
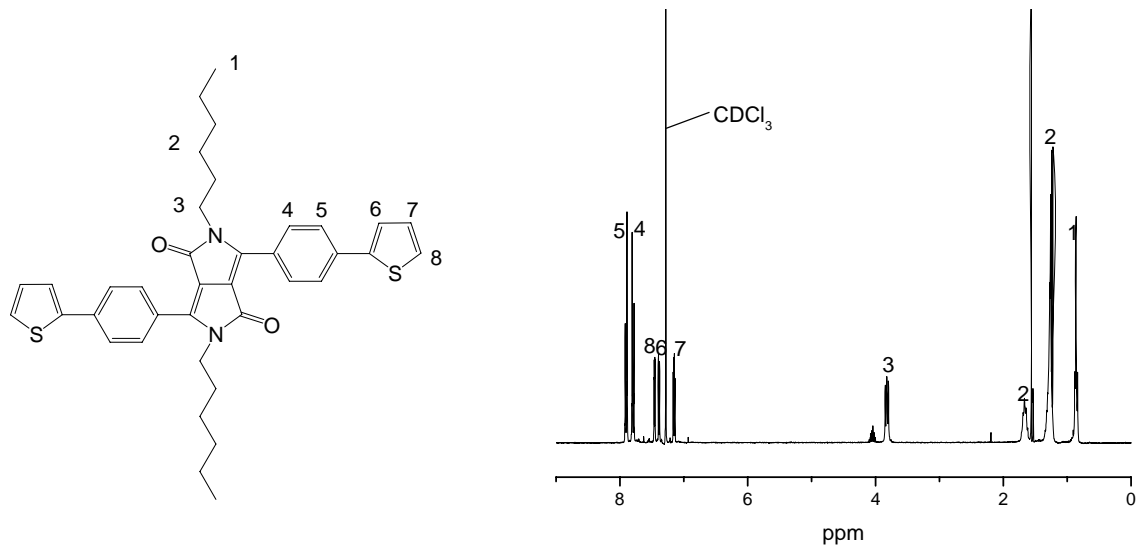
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

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1,4-Diketo-2,5-dihexyl-3,6-bis(4-(2-(4-hexylthienyl))phenyl)pyrrolo [3,4-c]pyrrole
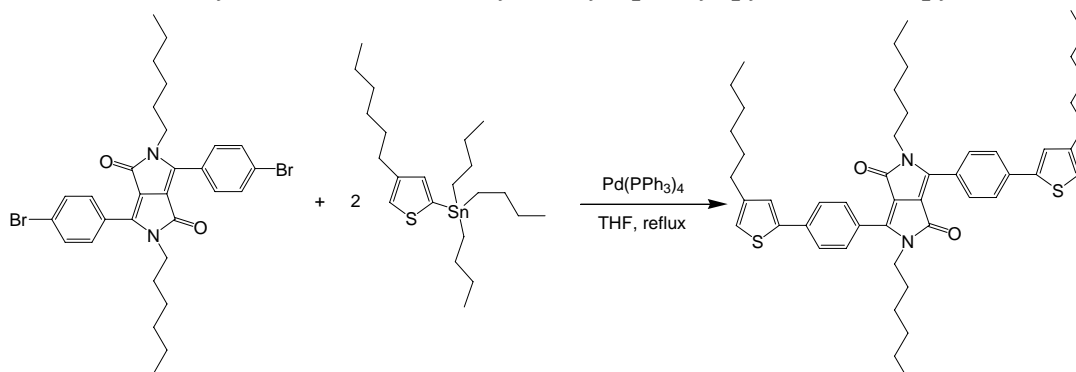
In a 100 mL flask, 0.072 g (0.117 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.21 g (0.467 mmol) 2-(tri-n-butylstannyl)-4-hexyl-thiophene and 2.2 mg (2 mol%) Pd(PPh$_3$)$_4$ were dissolved in 20 mL THF and refluxed under nitrogen for 24 h. After cooling, 50 mL of dichloromethane were added and the mixture was filtered. Then the mixture was washed with brine (3×40mL) and the organic layer was dried over anhydrous MgSO$_4$. The solvents were evaporated using a rotary evaporator. Column chromatography of the residue over silicon gel with dichloromethane as eluent gave the title compound as a red foil (0.053 g, 58 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.86 (t, 6H), 0.92 (t, 6H), 1.25 (m, 12H), 1.36 (m, 12H), 1.66 (m, 4H), 1.68 (m, 4H), 2.66 (t, 4H), 3.82 (t, N-CH$_2$, 4H), 6.97 (d, thiophene-H, 2H), 7.29 (d, thiophene-H, 2H), 7.76 (d, 4H), 7.87 (d, 4H).

λ$_{max}$(CHCl$_3$):	501 nm
λ$_{em}$(CHCl$_3$):	579 nm
λ$_{max}$(film):	518 nm
Φ$_f$(CHCl$_3$):	88 %
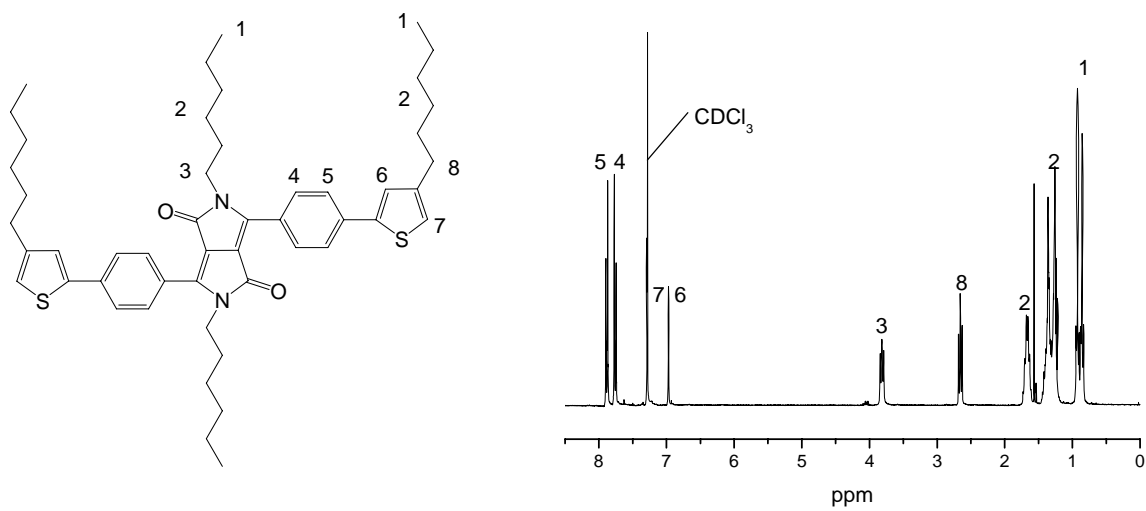
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

1,4-Diketo-2,5-dihexyl-3,6-bis(4-(2,2'-bithiophen-5-yl)phenyl)pyrrolo[3,4-c]pyrrole
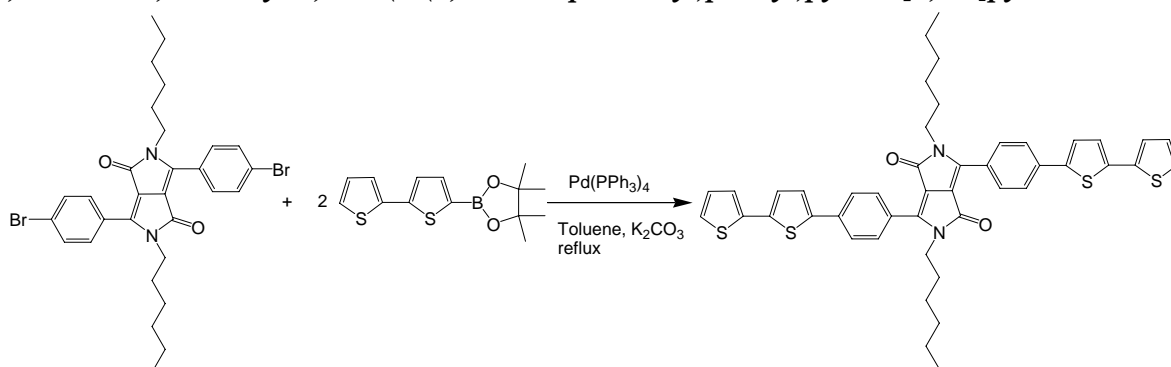
In a 100 mL flask, 0.234 g (0.4 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.350 g (1.2 mmol) 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-(2,2'-bithiophene) and 28 mg (3 mol%) $Pd(PPh_3)_4$ were dissolved in 20 mL toluene and stirred for 30 min. After that, 331 mg K_2CO_3 (2.4 mmol) were dissolved in 5 mL water and added to the reaction mixture under the inert gas atmosphere. Then the reaction mixture was allowed to raise the temperature and refluxed under nitrogen for 12 h. After cooling, 50 mL of dichloromethane were added and the mixture was filtered. Then the mixture was washed with brine (3×40mL) and the organic layer was dried over anhydrous $MgSO_4$. The solvents were evaporated using a rotary evaporator. Column chromatography of the residue over silicon gel with dichloromethane as eluent gave the title compound as a black purple powder (0.21 g, 70 %).

^{1}H NMR (CDCl₃): δ (ppm) 0.86 (t, 6H), 1.27 (m, 12H), 1.67 (m, 4H), 3.83 (t, N-CH₂, 4H), 7.08 (t, thiophene-H, 2H), 7.21 (d, thiophene-H, 2H), 7.27 (d, thiophene-H, 4H), 7.37 (d, thiophene-H, 2H), 7.77 (d, 4H), 7.91 (d, 4H).
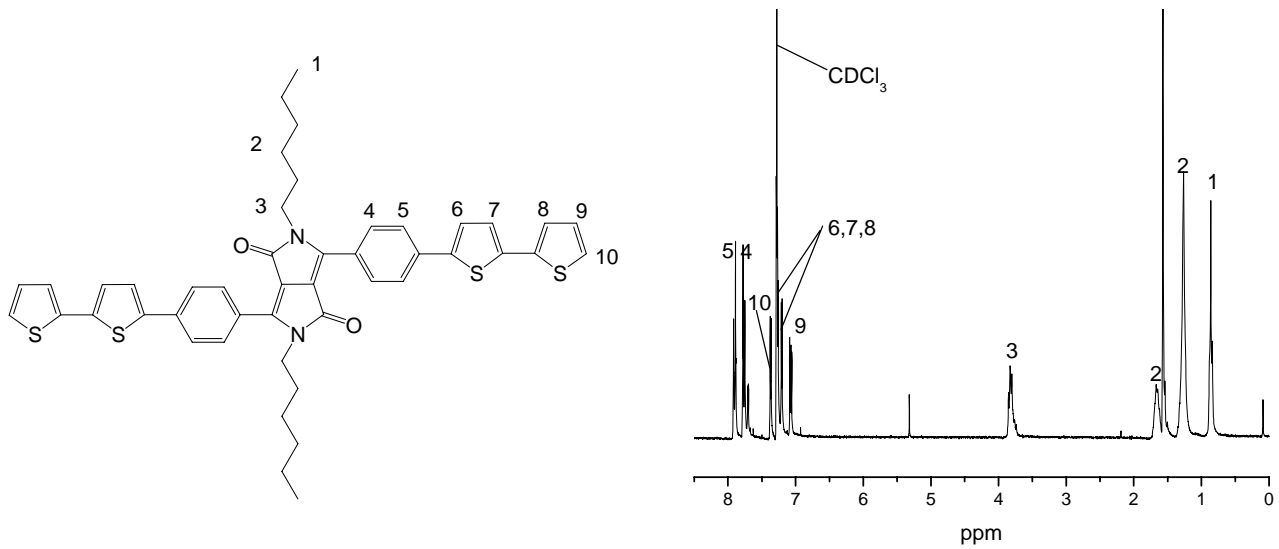
$\lambda_{max}(CHCl_3)$:	512 nm
$\lambda_{em}(CHCl_3)$:	600 nm
$\lambda_{max}(film)$:	537 nm
$\Phi_f(CHCl_3)$:	50 %

300 MHz-^{1}H-NMR spectrum in CDCl$_3$

1,4-Diketo-2,5-dihexyl-3,6-bis((2-(3',4'-ethylenedioxy)thienyl)-phenyl)pyrrolo[3,4-c]pyrrole
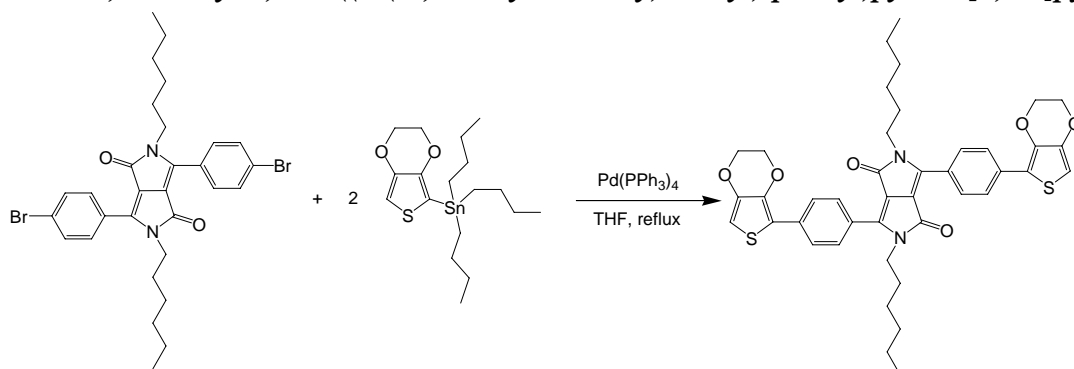
In a 100 mL flask, 0.39 g (0.63 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo [3,4-c]pyrrole, 0.82 g (1.9 mmol) 2-(tri-n-butylstannyl)-3,4-ethylenedioxythiophene and 22 mg (3 mol%) Pd(PPh$_3$)$_4$ were dissolved in 20 mL toluene and heated at 85°C under nitrogen for 24 h. After cooling, 50 mL of dichloromethane were added and the mixture was filtered. Then the mixture was washed with brine (3×40mL) and the organic layer was dried over anhydrous MgSO$_4$. The solvents were evaporated using a rotary evaporator. Column chromatography of the residue over silicon gel with dichloromethane as eluent gave the title compound as a dark red foil (0.25 g, 52 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.86 (t, 6H), 1.26 (m, 12H), 1.67 (m, 4H), 3.82 (t, N-CH$_2$, 4H), 4.34 (d, EDOT-CH$_2$, 8H), 6.4 (t, EDOT aromatic H, 2H), 7.89 (d, DPP aromatic H, 8H).
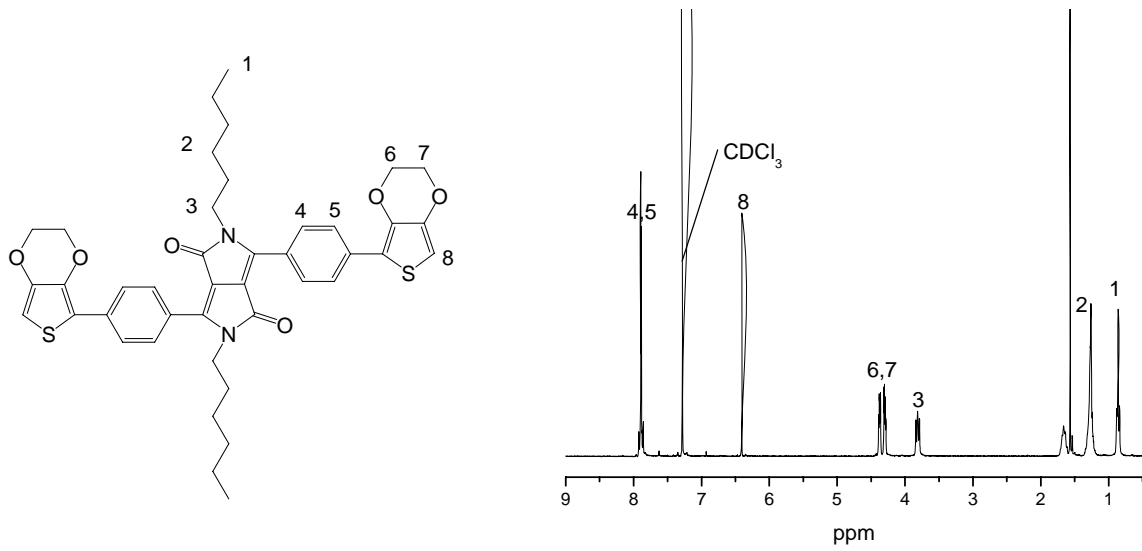
λ$_{max}$(CHCl$_3$):	510 nm
λ$_{em}$(CHCl$_3$):	585 nm
λ$_{max}$(film):	525 nm
Φ$_f$(CHCl$_3$):	84 %

300 MHz-^{1}H-NMR spectrum in CDCl$_3$

1,4-Diketo-2,5-dihexyl-3,6-bis(4-(1-(t-butoxycarbonyl)-1H-pyrrol-2-yl)-phenyl)pyrrolo[3,4-c]pyrrole
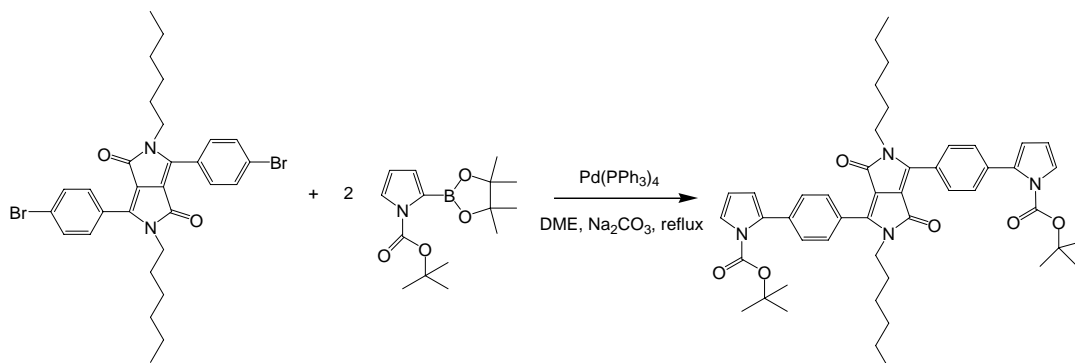
In a 100 mL flask, 0.123 g (0.2 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo [3,4-c]pyrrole, 0.250 g (1.18 mmol) 1-(t-butoxycarbonyl)-1H-pyrrol-2-ylboronic acid and 68 mg (5 mol%) Pd(PPh$_3$)$_4$ were dissolved in 20 mL DME and stirred for 30 min. After that, 375 mg Na$_2$CO$_3$ (3.54 mmol) were dissolved in 5 mL water and added to the reaction mixture under the inert gas atmosphere. Then the reaction mixture was allowed to raise the temperature and refluxed under nitrogen for 12 h. After cooling, 50 mL of dichloromethane were added and the mixture was filtered. Then the mixture was washed with brine (3×40mL) and the organic layer was dried over anhydrous MgSO$_4$. The solvents were evaporated using a rotary evaporator. Flash column chromatography of the residue over silicon gel with toluene as eluent gave the title compound as dark orange powder (0.096 g, 61 %).

^{1}H NMR (CDCl$_3$): δ (ppm). 0.86 (t, 6H), 1.26 (m, 12H), 1.43 (*t*-butyl, 18H), 1.67 (m, 4H), 3.82 (t, N-CH$_2$, 4H), 6.29 (d, pyrrol-H, 2H), 6.31 (t, pyrrole-H, 2H), 7.43 (d, pyrrol-H, 2H), 7.53 (d, DPP aromatic H, 4H), 7.87 (d, DPP aromatic H, 4H).
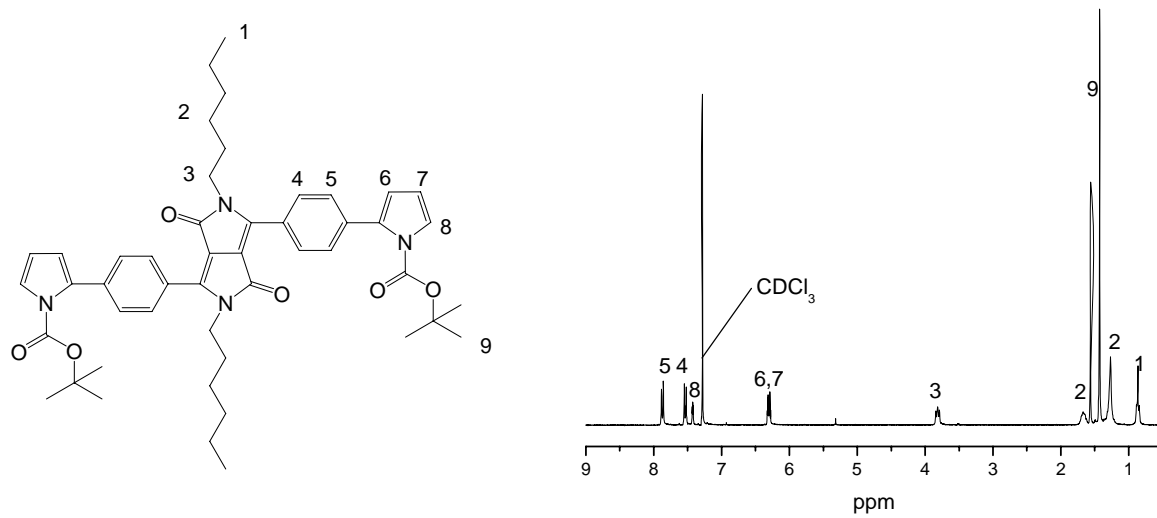
λ_{max}(CHCl$_3$):	490 nm
λ_{em}(CHCl$_3$):	563 nm
λ_{max}(film):	525 nm
Φ_f(CHCl$_3$):	85 %

300 MHz-^{1}H-NMR spectrum in CDCl$_3$

1,4-Diketo-2,5-dihexyl-3,6-bis(4-(pyrrol-2-yl)-phenyl)pyrrolo[3,4-c]pyrrole
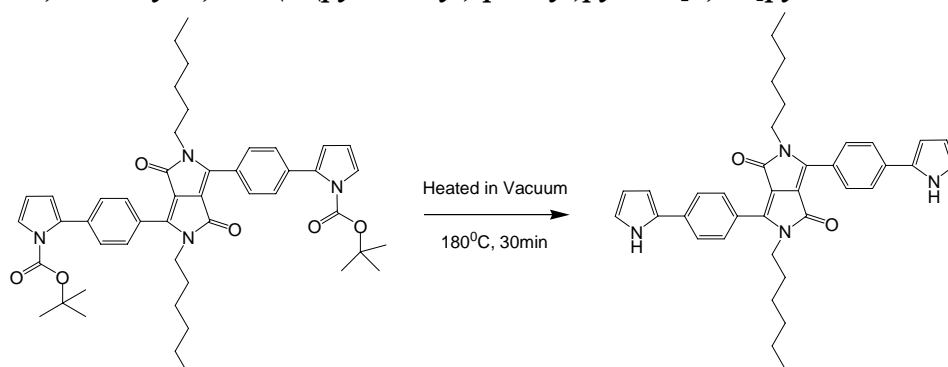
1,4-Diketo-2,5-dihexyl-3,6-bis(4-(1-(t-butoxycarbonyl)-1H-pyrrol-2-yl)-phenyl)pyrrolo[3,4-c]pyrrole was heated in vacuum at 180 ^{o}C for 30 min. The title compound was received as red powder.

^{1}H NMR (CDCl$_3$): δ (ppm). 0.86 (t, 6H), 1.26 (m, 12H), 1.67 (m, 4H), 3.82 (t, N-CH$_2$, 4H), 6.37 (d, pyrrol-H, 2H), 6.69 (t, pyrrol-H, 2H), 6.96 (d, pyrrol-H, 2H), 7.63 (d, DPP aromatic H, 4H), 7.90 (d, DPP aromatic H, 4H), 8.59 (s, pyrrol-H, 1H).
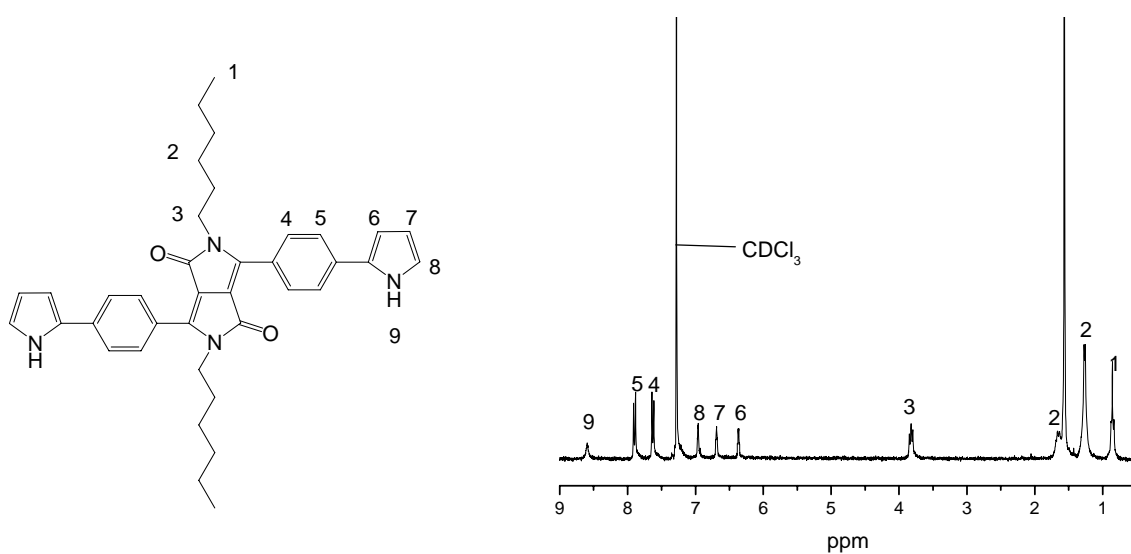
λ$_{max}$(CHCl$_3$):	510 nm
λ$_{em}$(CHCl$_3$):	585 nm
λ$_{max}$(film):	544 nm
Φ$_f$(CHCl$_3$):	78 %

300 MHz-^{1}H-NMR spectrum in CDCl$_3$

1,4-Diketo-2,5-dihexyl-3,6-bis(4-N-carbazolylphenyl)pyrrolo[3,4-c]pyrrole
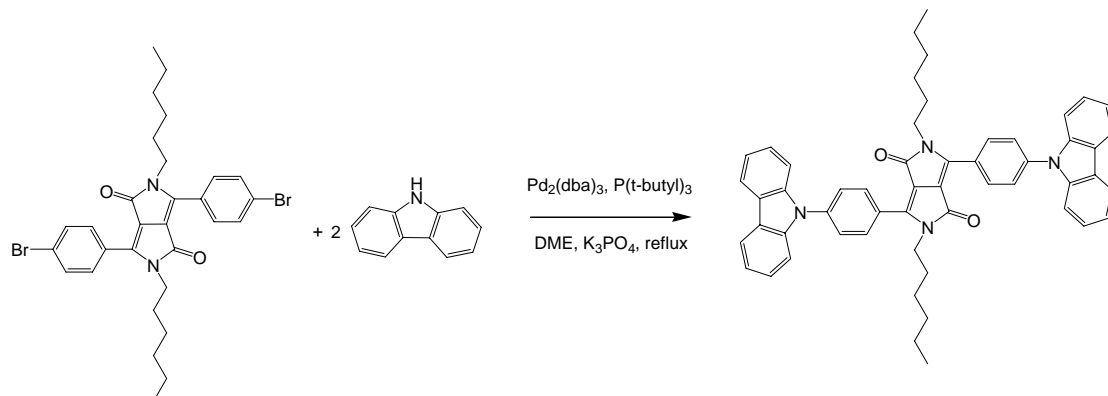
Under nitrogen atmosphere, 6 mg (3% mol) tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) and 5.1 mg tris-t-butylphosphine were dissolved in 10 mL DME and stirred under room temperature for 30 minutes. 0.123 g (0.2 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.08 g (0.48 mmol) carbazole, 0.17 g (0.8 mmol) K$_3$PO$_4$ were added to the reaction mixture under the inert gas atmosphere. Then the reaction mixture was allowed to raise the temperature and refluxed under nitrogen for 48 h. After cooling, 50 mL of dichloromethane were added and the mixture was filtered. Then the mixture was washed with brine (3×40mL) and the organic layer was dried over anhydrous MgSO$_4$. The solvents were evaporated using a rotary evaporator. Column chromatography of the residue over silicon gel with dichloromethane as eluent gave the title compound as a bright orange foil (0.095 g, 60 %).

^{1}H NMR (CDCl$_3$): δ (ppm) 0.86 (t, 6H), 1.26 (m, 12H), 1.67 (m, 4H), 3.82 (t, N-CH$_2$, 4H).

λ$_{max}$(CHCl$_3$):	495 nm
λ$_{em}$(CHCl$_3$):	564 nm
λ$_{max}$(film):	518 nm
Φ$_f$(CHCl$_3$):	95 %
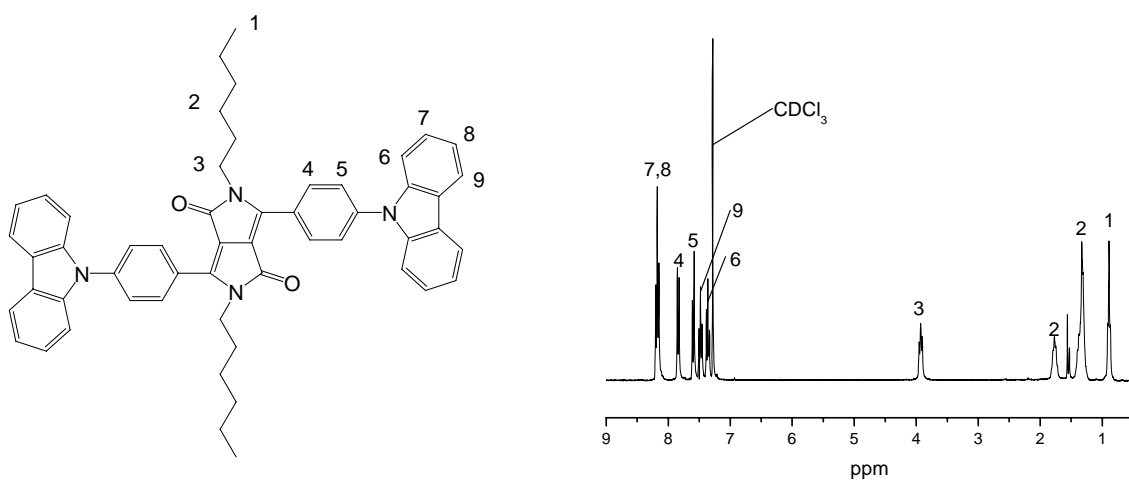
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

5.4. Water-soluble DPP containing conjugated polyelectrolytes

5.4.1. Synthesis of the monomers

1,4-Diketo-2,5-bis(1-bromohexyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-c] pyrrole

2.23 g (5 mmol) 1,4-Diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 1.68 g (15 mmol) potassium t-butoxide and 60 mL dry NMP were heated to 60 °C. 2.36 mL (15 mmol) 1,6-dibromohexane was slowly added and the mixture was stirred at 50 °C for 14 h. After cooling to room temperature, 100 mL toluene was added and the reaction mixture was washed with water to remove the NMP. The organic solution was concentrated using a rotary evaporator. The raw material was purified by column chromatography on silica using dichloromethane as the solvent. 0.47 g (13 %) of an orange, polycrystalline powder was obtained.

^{1}H NMR (CDCl$_3$, 300 MHz): δ (ppm) 1.28 (m, 4H), 1.39 (m, 4H), 1.60 (m, 4H), 1.8 (m, 4H), 3.37 (t, Br-CH$_2$, 4H), 3.77 (t, N-CH$_2$, 4H), 6.37 (d, pyrrol-H, 2H), 6.69 (t, pyrrol-H, 2H), 6.96 (d, pyrrol-H, 2H), 7.70 (s, DPP aromatic H, 8H);

λ$_{max}$(CHCl$_3$):	477 nm
λ$_{em}$(CHCl$_3$):	539 nm
Φ$_f$(CHCl$_3$):	95%
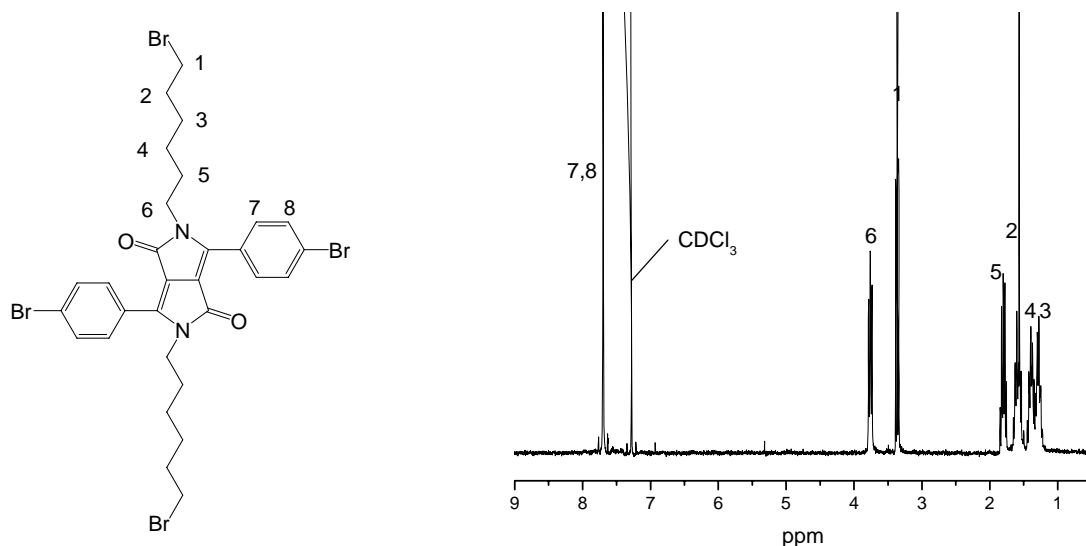
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

1,4-diketo-2,5-bis(sulfonylbutyl)-3,6-bis(4-bromophenyl) pyrrolo [3,4-c] pyrrole

4.46 g (10 mmol) 1,4-Diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 1.76 g (22 mmol) lithium t-butoxide and 150 mL dry DMF were heated to 60 °C. 3.1 mL (30 mmol) Butane sultone was slowly added and the mixture was stirred at 90 °C for 12 h. The mixture was precipitated in 1 L ethanol when it was still hot. The precipitates were collected and washed with acetone. The dark red powder 5.9 g (95 %) was obtained after dried in vacuum for 24h at 120 °C.

^{1}H NMR (D$_2$O, 300 MHz): δ (ppm) 1.41 (m, 8H), 2.61 (t, S-CH$_2$, 4H), 3.59 (t, N-CH$_2$, 4H), 7.34 (d, DPP aromatic H, 4H), 7.50 (d, DPP aromatic H, 4H);

λ$_{max}$(H$_2$O):	471 nm
λ$_{em}$(H$_2$O):	533 nm
Φ$_f$(H$_2$O):	88 %
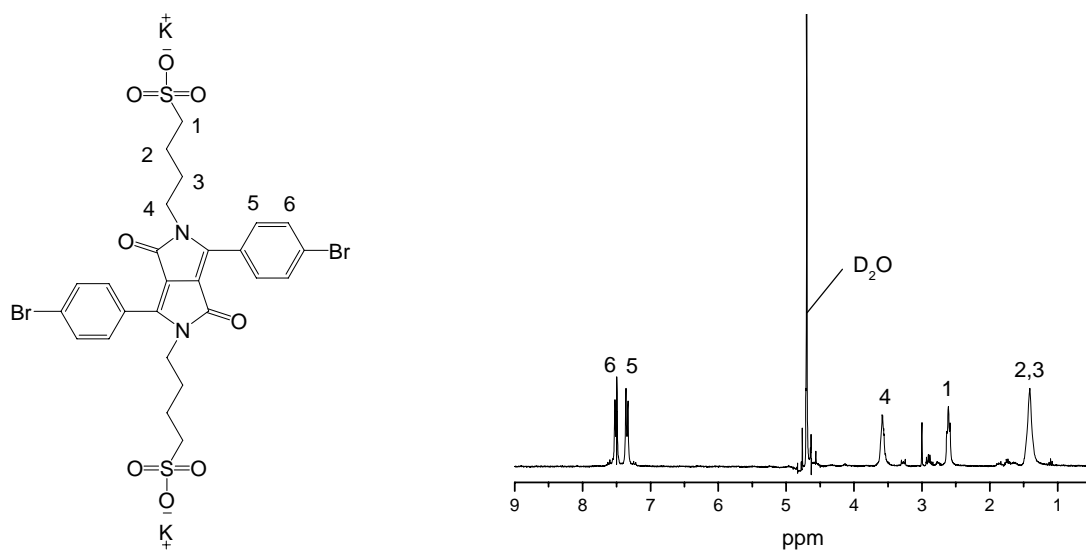
300 MHz-^{1}H-NMR spectrum in D$_2$O

1,4-Dibromohexyloxybenzene

4.4 g (40 mmol) Hydroquinone, 24 g (172 mmol) potassium carbonate and 200 mL dry acetone were mixed. 38 mL (240 mmol) 1,6-dibromohexane was slowly added and the mixture was heated to reflux for 24 h. The mixture was filtered when it was hot. After cooling to room temperature, the solid was obtained form the filtrate and was recrystallized in acetone. The solid was further purified by silica gel chromatography with ether to give the white powder 8.02 g (46 %). m.p.: 98 °C.

^{1}H NMR (CDCl3, 300 MHz): δ (ppm) 1.52 (m, 8H), 1.79 (m, 4H), 1.91 (m, 4H), 3.44 (t, Br-CH$_2$, 4H), 3.92 (t, O-CH$_2$, 4H), 6.84 (s, phenyl-H, 4H);
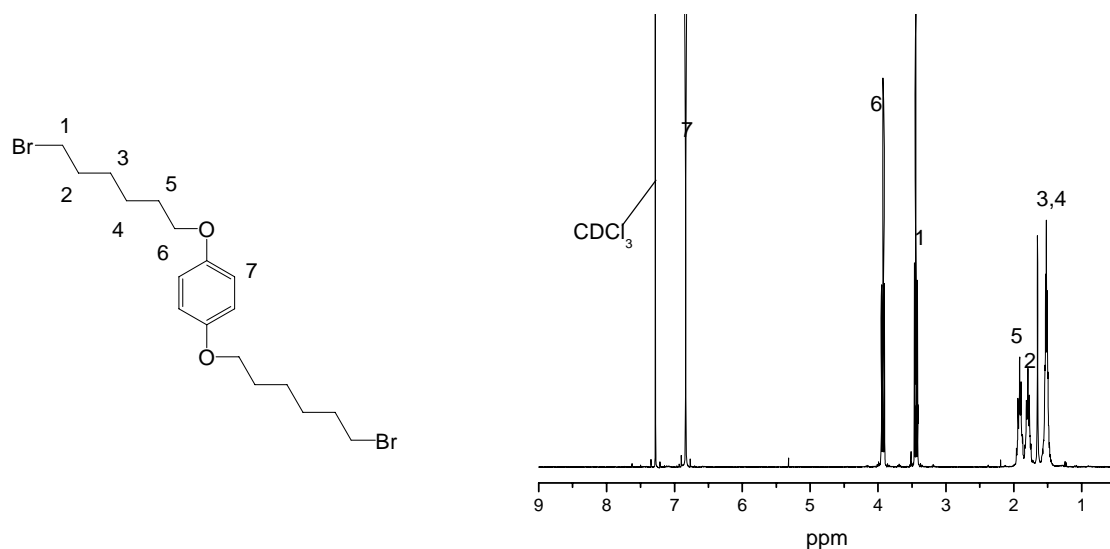
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

1,4-Dibromo-2,5-dibromohexyloxybenzene

2 g (4.58 mmol) 1,4-Dibromohexyloxybenzene was dissolved in 75 mL carbon tetrachloride. 0.52 mL (10 mmol) bromine was dissolved in 20 mL carbon tetrachloride and was slowly added under the nitrogen atmosphere at a temperature lower than 5 °C. After stirring for 2 h at a temperature lower than 5 °C, the mixture was poured into a separatory funnel and washed with 5% $Na_2S_2O_4$ (2×30 mL) and brine (3×30 mL). The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed and the solid was recrystallized in ethyl acetate to give title compound as white powder 1.82 g (67 %).

^{1}H NMR (CDCl3, 300 MHz): δ (ppm) 1.55 (m, 8H), 1.84 (m, 4H), 1.93 (m, 4H), 3.45 (t, Br-CH_2, 4H), 3.98 (t, O-CH_2, 4H), 7.11 (s, phenyl-H, 2H);
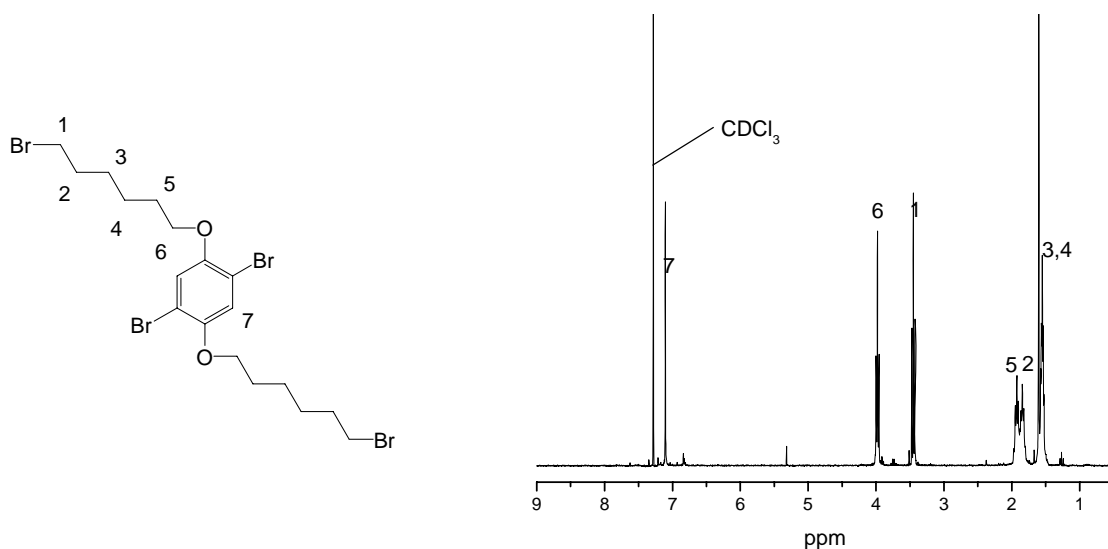
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

1,4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dibromohexyloxybenzene

Using a syringe, 2.5 M n-BuLi (1.8 mL, 4.2 mmol) were added to a solution of 1,4-dibromo-2,5-dibromohexyloxybenzene (1.2 g, 2 mmol) in THF (50 mL) at -78 °C with stirring. After stirring for one hour at this temperature, the temperature of the solution was allowed to increase to room temperature. Then the mixture was cooled to -78 °C again and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.9 mL, 4.4 mmol) was added. The reaction mixture was stirred at -78 °C for additional 1 h and then was gradually warmed to room temperature and stirred overnight. After the reaction, 100 mL water and 100 mL ether were added to the solution. Then the mixture was washed with brine (3×40mL) and the organic layer was dried over MgSO$_4$. The solvents were evaporated using a rotary evaporator. Column chromatography of the residue over silicon gel with hexane and ethyl acetate mixture as eluent gave the title compound as a white solid (0.54 g, 40 %).

^{1}H NMR (CDCl3, 300 MHz): δ (ppm) 1.36 (s, 24H),1.56 (m, 8H), 1.79 (m, 4H), 1.91 (m, 4H), 3.44 (t, Br-CH$_2$, 4H), 3.97 (t, O-CH$_2$, 4H), 7.11 (s, phenyl-H, 2H);
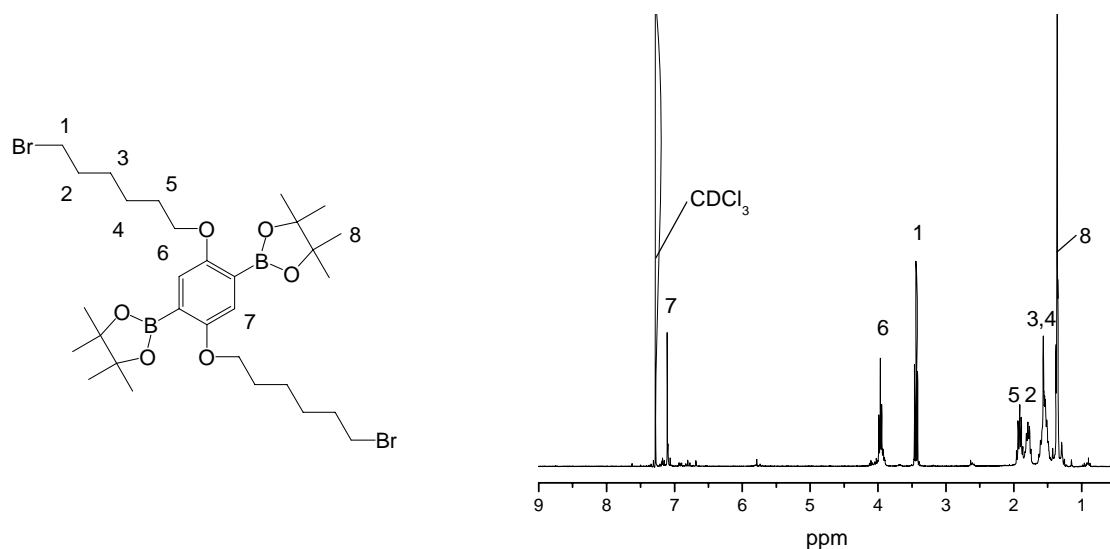
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

5.4.2. Synthesis of the polymers

P-BrDPP-BrPH
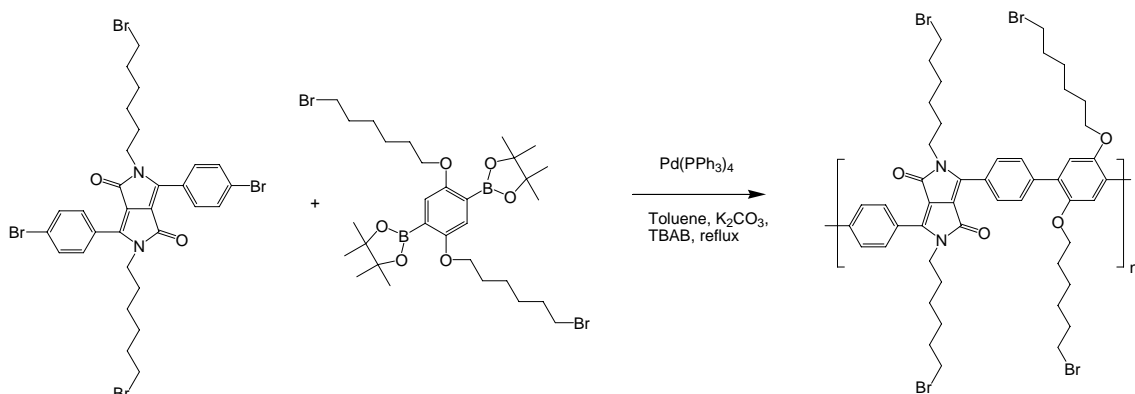
Under nitrogen atmosphere, 0.096 g (0.1242 mmol) 1,4-diketo-2,5-bis(1-bromohexyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.0855 g (0.1242 mmol) 1,4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dibromohexyloxybenzene and 7 mg (5 mol%) Pd(PPh$_3$)$_4$ were dissolved in 5 mL toluene and stirred under room temperature for 30 minutes. After that, 0.103 g K$_2$CO$_3$ (0.75 mmol) were dissolved in 2 mL water and added to the reaction mixture under the inert gas atmosphere. Then the reaction mixture was allowed to raise the temperature and refluxed under nitrogen for 24 h. After cooling, 50 mL of chloroform were added and the mixture was filtered through celite to remove the residue palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. m.w.: 16,000, polydispersity: 2.1, yield: 61 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 1.0-2.1 (C-CH$_2$), 3.38 (Br-CH$_2$), 3.87 (N-CH$_2$), 4.07 (O-CH$_2$), 7.46 (aromatic H at o-alkylated phenylene), 7.67 (DPP aromatic H), 7.89 (DPP aromatic H).

λ$_{max}$(CHCl$_3$):	504 nm
λ$_{em}$(CHCl$_3$):	568 nm
Φ$_f$(CHCl$_3$):	44 %
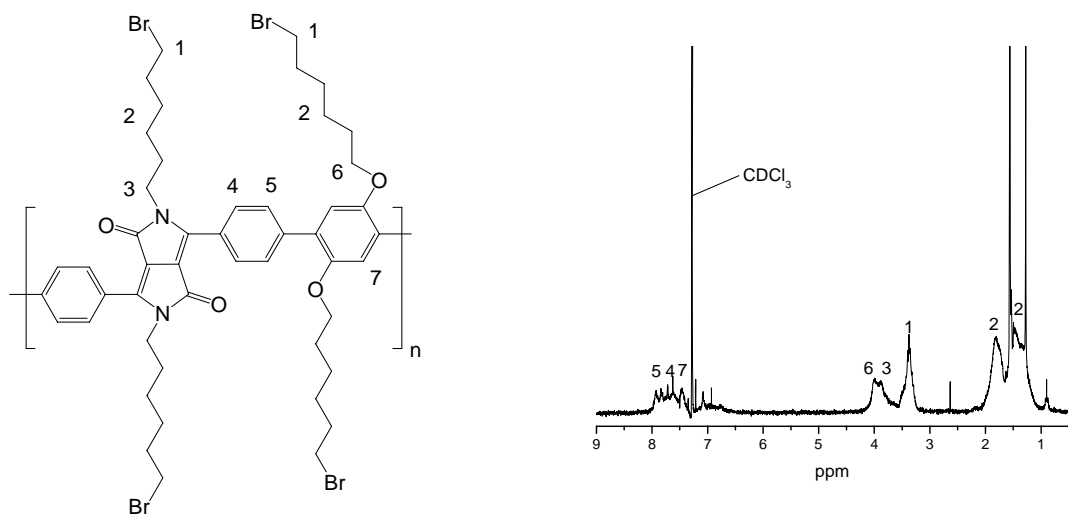
300 MHz-^{1}H-NMR spectrum in CDCl$_3$

P-AMDPP-AMPH
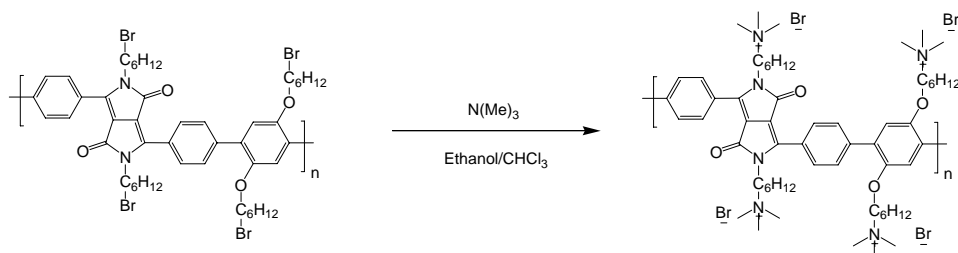
Trimethylamine ethanol solution (2 mL) was added to a solution of the neutral polymer **P-BrDPP-BrPH** (50 mg) in CHCl$_3$ (10 mL) at low temperature (-70 ^{o}C). The mixture was allowed to warm up to room temperature. The precipitate was redissolved by the addition of water (10 mL). After the mixture was cooled down to 0 ^{o}C, extra trimehtylamine ethanol solution (mL) was added and the mixture was stirred for 24 h at room temperature. After removing most of solvent, acetone was added to precipitate **P-AMDPP-AMPH** (35 mg) as red powder, yield: 65 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 1.0-2.0 (C-CH$_2$), 2.5-3.5 (N-CH$_2$, O-CH$_2$), 7.2-7.9 (aromatic H).

λ$_{max}$(H$_2$O):   506 nm

λ$_{max}$(DMSO):   502 nm

λ$_{em}$(DMSO):   432, 565 nm
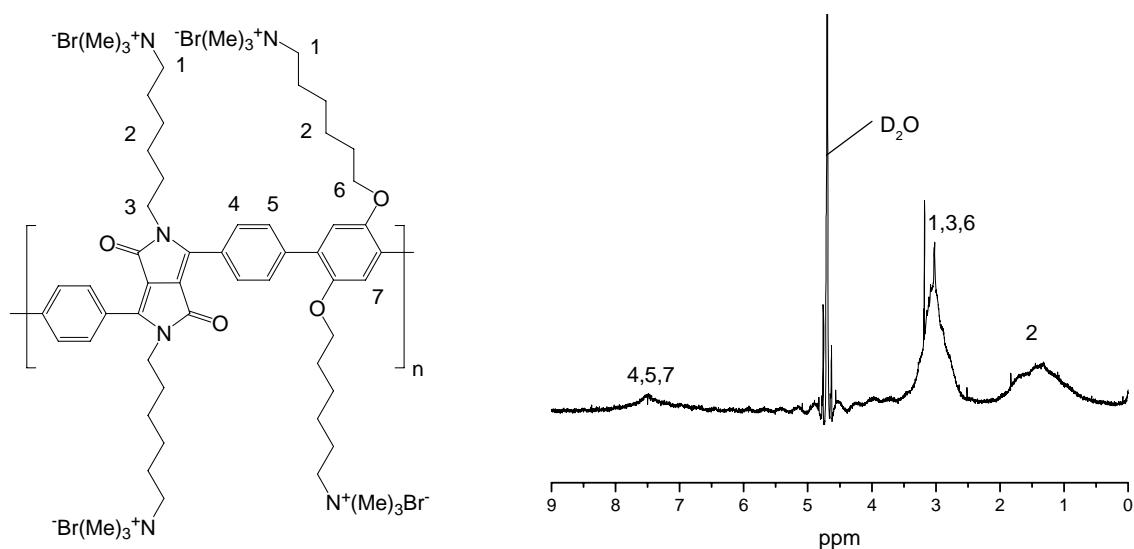
300 MHz-^{1}H-NMR spectrum in D$_2$O

P-SDPP-PH
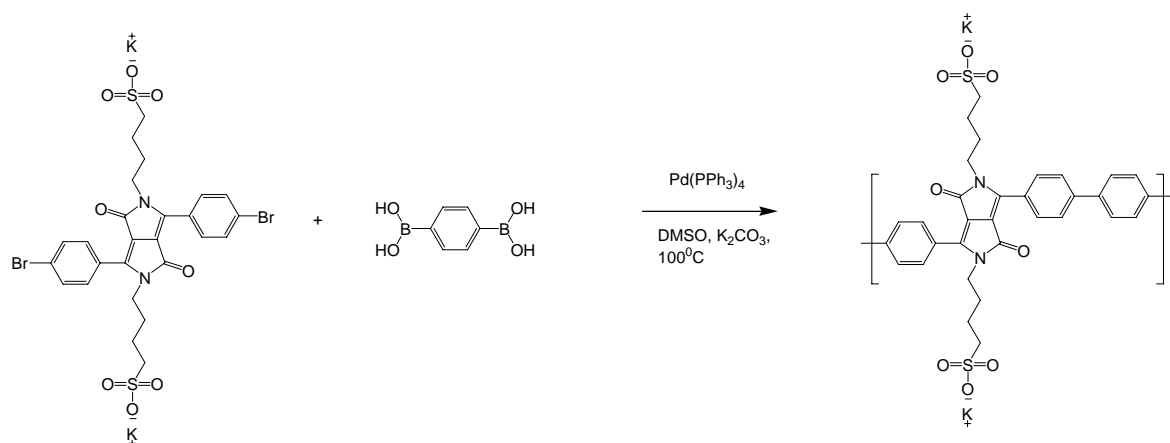
Under nitrogen atmosphere, 0.73 g (1 mmol) 1,4-diketo-2,5-bis(sulfonylbutyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.166 g (1 mmol) 1,4-phenylenediboronic acid and 35 mg (3 mol%) $Pd(PPh_3)_4$ were dissolved in 10 mL DMSO and stirred under room temperature for 30 minutes. After that, 0.414 g K_2CO_3 (3 mmol) were dissolved in 3 mL water and added to the reaction mixture. Then the reaction mixture was allowed to raise the temperature and refluxed under nitrogen for 24 h. After the reaction, the mixture was precipitated in ethanol when it was hot. The precipitates were washed with $CHCl_3$ and acetone successively. The solid was collected and dried under vacuum at 100 ^{o}C for 24 h, yield: 91 %.

^{1}H NMR (D_2O): δ (ppm) 1.4-1.9 (C-CH$_2$), 2.8 (S-CH$_2$), 3.55 (N-CH$_2$), 7.3-7.9 (aromatic H).

$\lambda_{max}(H_2O)$:	534 nm
$\lambda_{max}(DMSO)$:	506 nm
$\lambda_{em}(DMSO)$:	565 nm
$\Phi_f(DMSO)$:	6.2 %

174
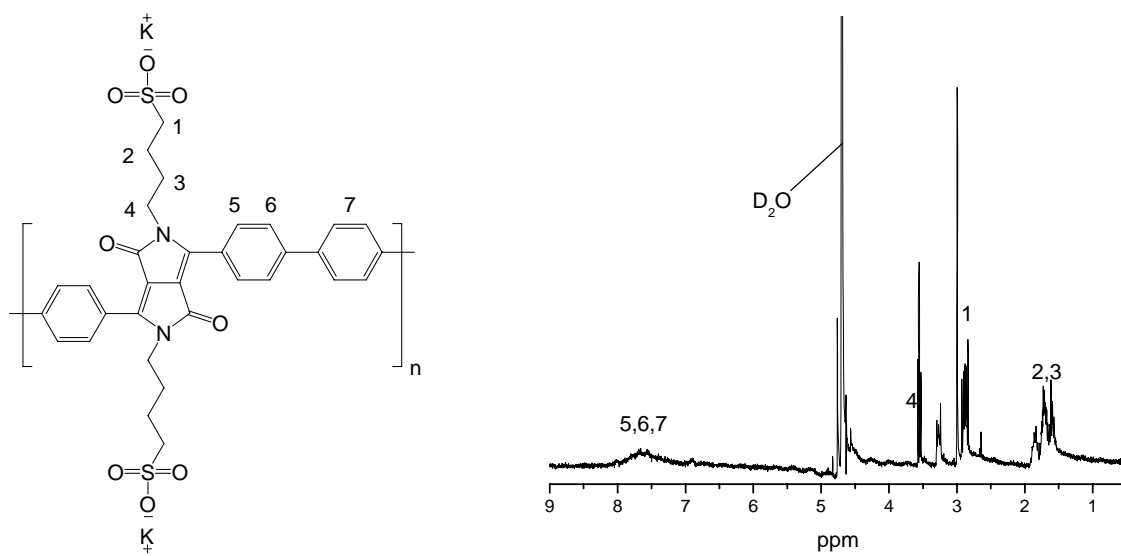
300 MHz-^{1}H-NMR spectrum in D_2O

P-SDPP-AB
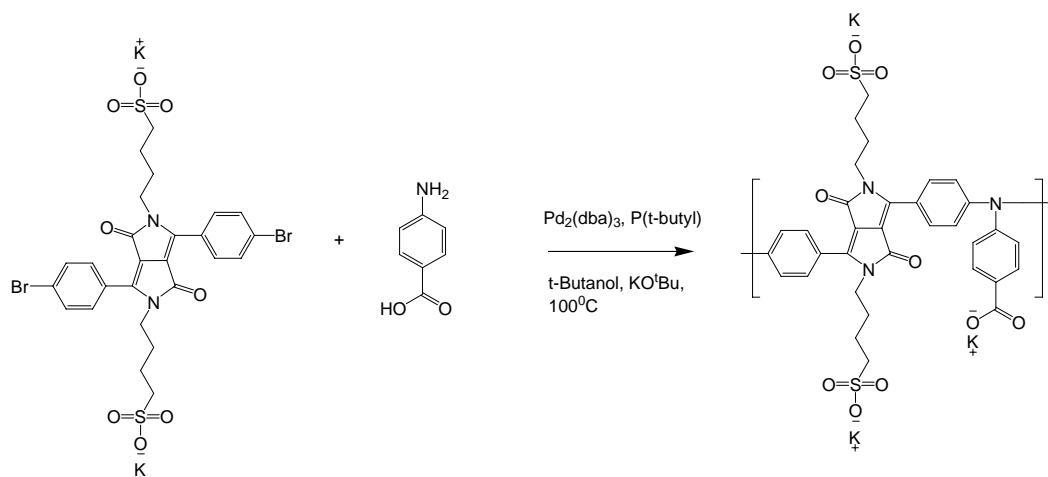
Under nitrogen atmosphere, 7 mg (3% mol) tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) and 7 mg tris-t-butylphosphine were dissolved in 2 mL t-butanol and stirred under room temperature for 30 minutes. A Schlenk tube was charged with 0.1 g (0.126 mmol) 1,4-diketo-2,5-bis(sulfonylbutyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.0173 g (0.200 mmol) 4-aminobenzoic acid, 0.034 g (0.5 mmol) sodium ethoxide and 8 ml of t-butanol. The mixture was degassed. Then the solution of the palladium complex was added and the reaction mixture was stirred at 100 °C under nitrogen for 24 h. After the reaction, the mixture was precipitated in ethanol when it was hot. The precipitates were washed with CHCl$_3$ and acetone successively. The solid was collected and dried under vacuum at 100 °C for 24 h, yield: 70 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 1.5-2.0 (C-CH$_2$), 2.8 (S-CH$_2$), 3.3 (N-CH$_2$), 6.6-7.9 (aromatic H).

λ$_{max}$(H$_2$O):	528 nm
λ$_{max}$(DMSO):	560 nm
λ$_{em}$(DMSO):	594 nm
Φ$_f$(DMSO):	45 %
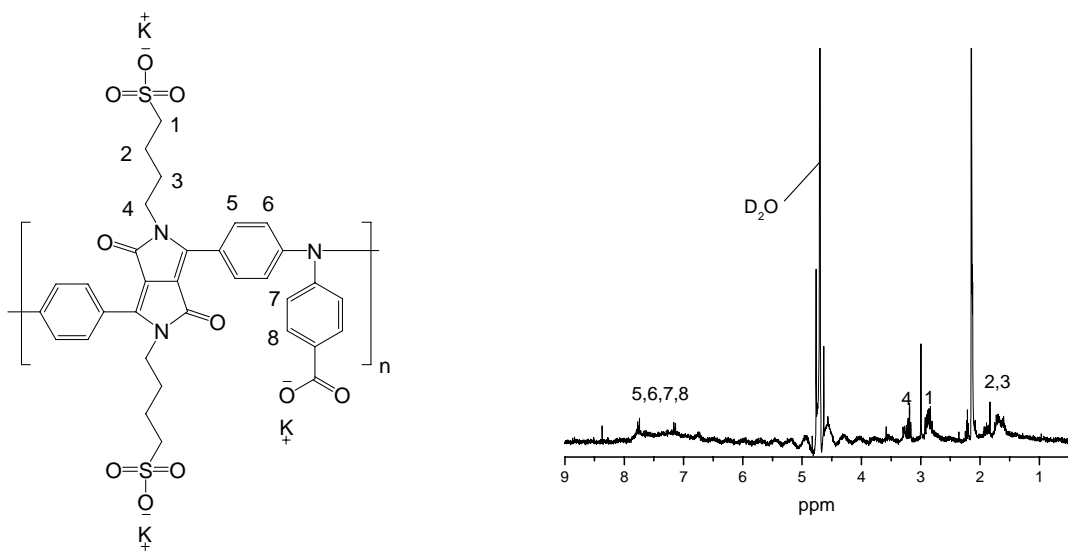
300 MHz-^{1}H-NMR spectrum in D$_2$O

P-SDPP-ABS
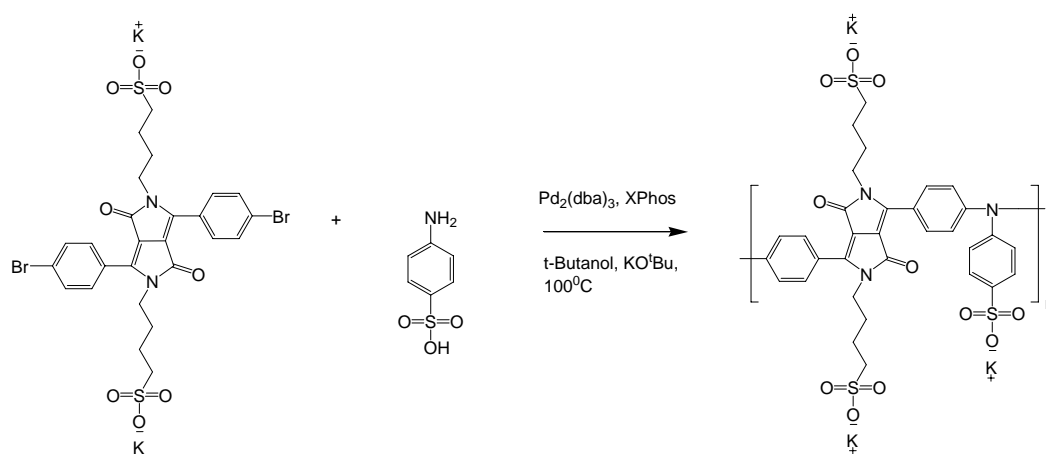
Under nitrogen atmosphere, 55 mg (3 mol%) tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) and 57 mg XPhos were dissolved in 2 mL t-butanol and stirred under room temperature for 30 minutes. A Schlenk tube was charged with 0.794 g (1 mmol) 1,4-diketo-2,5-bis(sulfonylbutyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole, 0.174 g (1 mmol) 4-aminobenzenesulfonic acid, 0.784 g (7 mmol) potassium t-butoxide and 8 ml of t-butanol. The mixture was degassed. Then the solution of the palladium complex was added and the reaction mixture was stirred at 100 °C under nitrogen for 24 h. After the reaction, the mixture was precipitated in ethanol when it was hot. The precipitates were washed with chloroform and acetone successively. The solid was collected and dried under vacuum at 100 °C for 24 h, yield: 90 %.

^{1}H NMR (CDCl$_3$): δ (ppm) 1.5-1.8 (C-CH$_2$), 2.8 (S-CH$_2$), 3.5 (N-CH$_2$), 6.8 (aromatic H), 7.1-7.9 (aromatic H).

$\lambda_{max}(H_2O)$:	524 nm
$\lambda_{max}(DMSO)$:	554 nm
$\lambda_{em}(DMSO)$:	591 nm
$\Phi_f(DMSO)$:	49 %
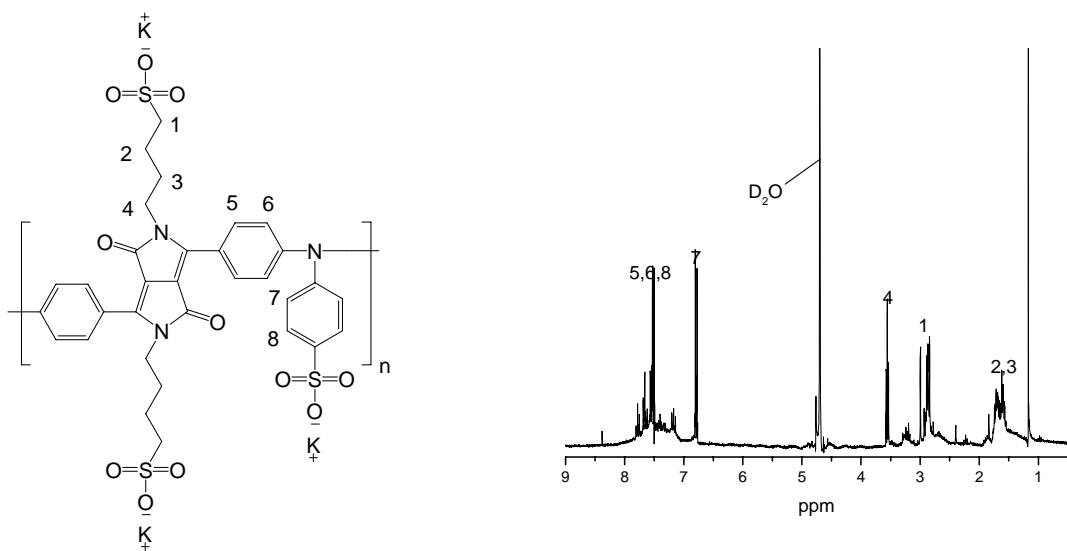
300 MHz-^{1}H-NMR spectrum in D_2O

6. Summary

- New DPP containing conjugated polymers were synthesized by introducing new building-blocks suitable for electroluminescent and electrochromic applications.
- New methods for the synthesis of DPP containing conjugated polymers were explored such as Buchwald-Hartwig coupling and electrochemical polymerization.
- New DPP containing conjugated polyelectrolytes were synthesized.

Prior to this work, Suzuki, Heck and Stille polycondensation were the only reported methods for the synthesis of DPP containing conjugated polymers. As comonomer units, only fluorene and phenylene units were reported. In this work, other important and popular building blocks such as carbazole, triphenylamine, benzothiodiazole, thiophene, and pyrrole have been used to prepare new DPP containing conjugated polymers. In addition, Buchwald-Hartwig coupling and electropolymerization have been applied for the first time to synthesize DPP containing conjugated polymers. The DPP containing polymers prepared by palladium catalyzed polycondensation reactions are summarized in Scheme 6.1.

Eight new DPP containing conjugated polymers were successfully synthesized exhibiting molecular weights between 5 and 16.5 kDa. The polymers are readily soluble in common organic solvents, the solutions exhibit bright red colours and strong red to purple photoluminescence. The **P-DPP-TPA** polymer is especially interesting because of its high photoluminescence quantum yield of 85 %. The **P-DPP-CBZ** polymer is also very promising because of its high molecular weight, excellent solubility, relatively high photoluminescence quantum yield of 46 % and quasi-reversible oxidation behavior. The polymer might be useful as active materials in PLED applications.
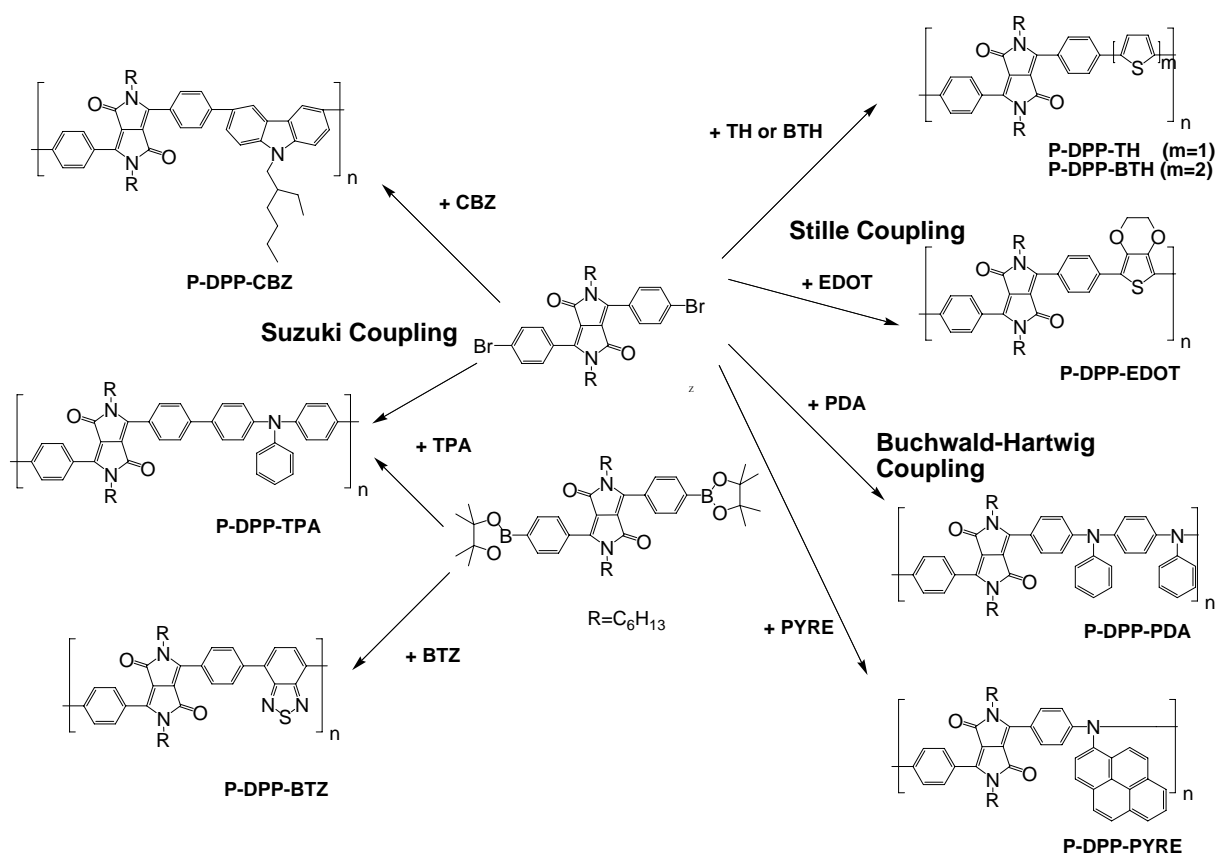
Scheme 6.1 DPP containing conjugated polymers prepared upon palladium catalyzed polycondensation reactions.

The DPP-thienylene-copolymers (**P-DPP-TH**, **P-DPP-BTH** and **P-DPP-EDOT**) are interesting because of their reversible oxidation behaviour. For some of the polymers, the bandgap is as low as 1.47 eV. The cyclovoltammetric and spectroelectrochemical studies show that **P-DPP-BTH** is able to change colours upon oxidation and the switching can be repeated many times. For the poly-DPP-iminoarylenes, the solid state luminescence of the polymers is quenched. However, they are interesting because of their low oxidation potential. The spectroelectrochemical studies show that the polymers exhibit abrupt colour changes from purple to black-green upon oxidation and reduction.
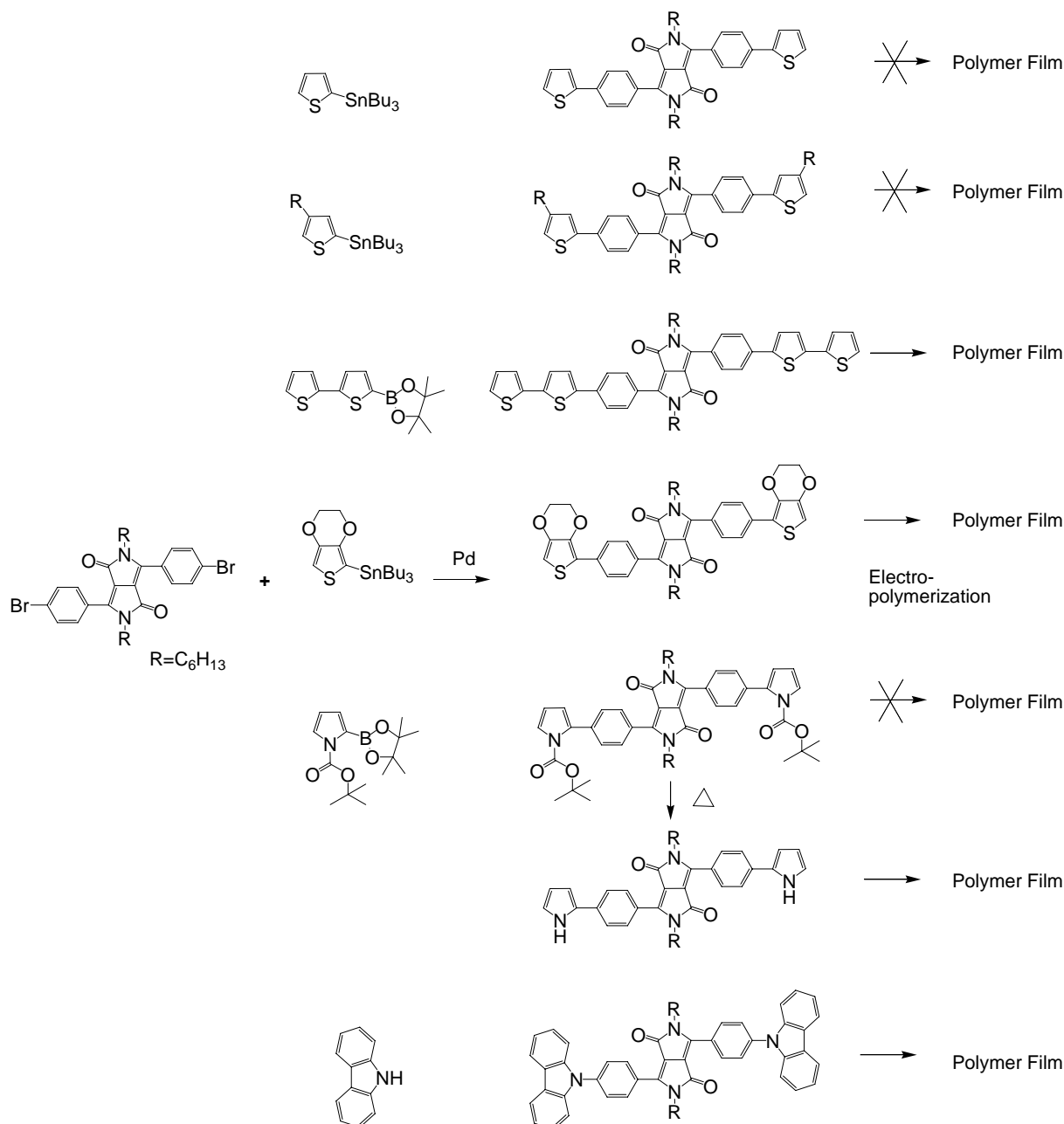
Scheme 6.2 Sandwich-type electropolymerizable DPP monomers prepared upon palladium catalyzed coupling reactions.

DPP monomers which are potentially useful for electropolymerization were prepared upon palladium catalyzed coupling reactions outlined in Scheme 6.2. Four of the monomers could be successfully electropolymerized. The polymer films are insoluble in common organic solvents and non-luminescent. The colour change from brown-red to olive green (**Poly(Bis-Bithiophene-DPP)**), deep blue to colourless (**Poly(Bis-EDOT-DPP)**), purple-red to brown-red (**Poly(Bis-Pyrrole-DPP)**) and colourless to green (**Poly(Bis-Carbazole-DPP)**) upon oxidation process are observed. It was found that a low oxidation potential of the monomer favours the film formation, because the chance for side reactions is lowered. Compared with

the polymers prepared upon chemical polycondensation, the polymers from electropolymerization have the disadvantage to be generally insoluble in common organic solvents, which prevents a detailed structure characterization. However, the monomers can be easily purified and the amount of monomer needed for electropolymerization into thin films is very small, which is advantageous. Furthermore, the stability of the electropolymerized films is generally better than that of the films prepared by solution casting. Therefore, electropolymerization is probably more suitable for the electrochromic and organic solar cells.
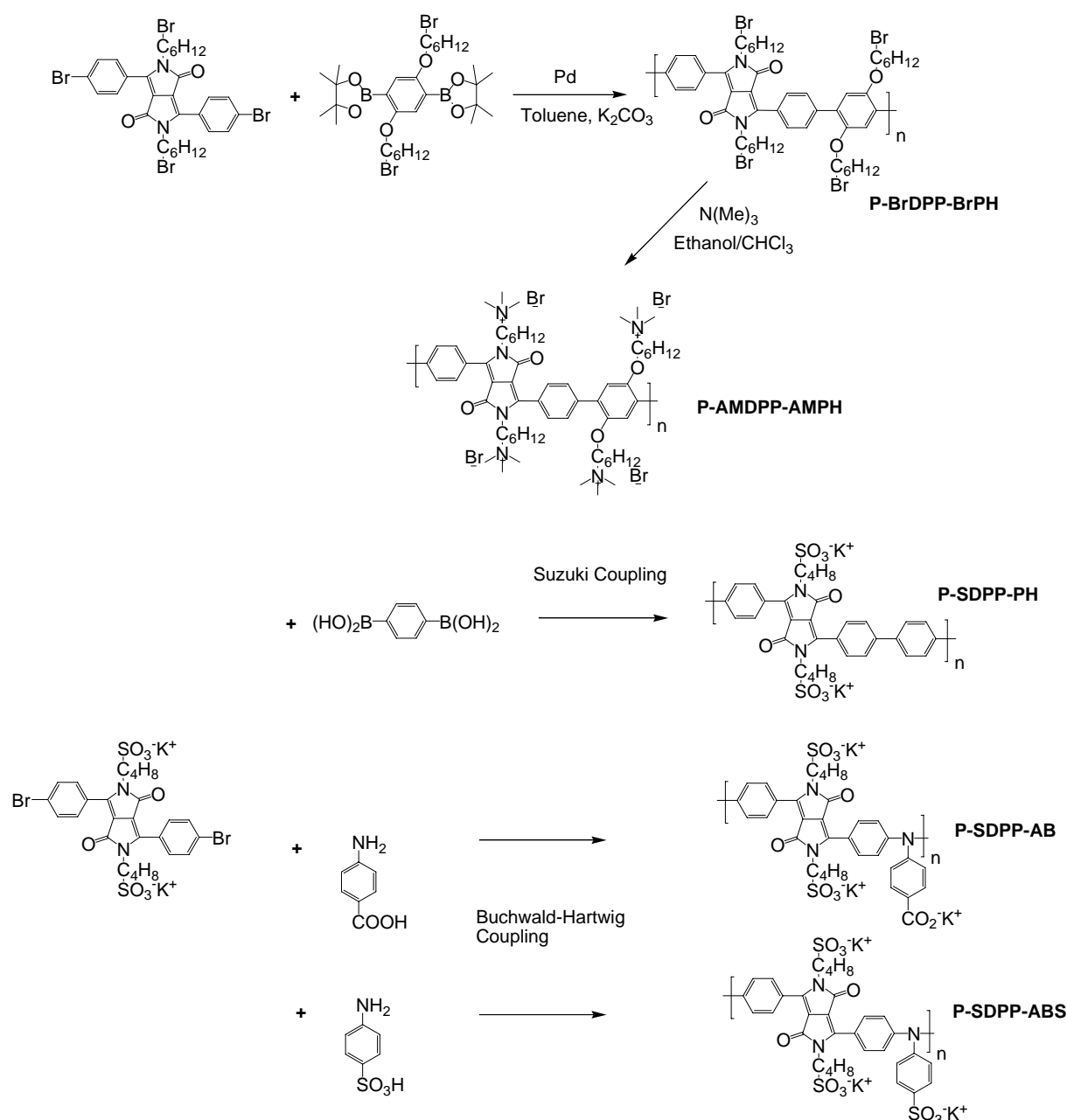
Scheme 6.3 Preparation of DPP containing conjugated polyelectrolytes.

Finally, water soluble cationic and anionic DPP containing polyelectrolytes could be successfully prepared upon Suzuki and Buchwald-Hartwig coupling. The preparation is described in Scheme 6.3. The DPP conjugated polyelectrolytes are soluble in water, methanol and DMSO. However, they are only luminescent in organic solvents or in a mixture of water and organic solvents. This may be due to aggregate formation of the polymers in aqueous solution. The polymers from Buchwald-Hartwig polycondensation exhibit a stronger photoluminescence quantum yield and solubility because the water soluble amine could be used in the reaction.

At last, a short outlook is shown in Scheme 6.4. One of the future work may be the preparation of the t-butoxycarbonyl alkylated DPP. The soluble conjugated polymer can be prepared with this monomer. Upon heating, the soluble polymer may be immobilized on the surface of electrode, which may offer better stability for the corresponding electronic devices.
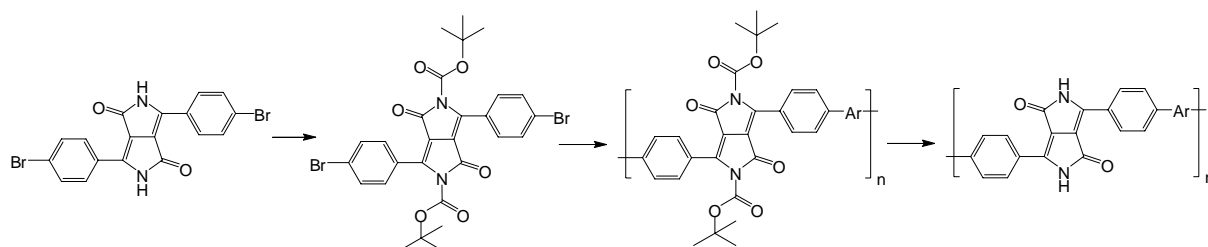
Scheme 6.4 Outlook

7. References

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8. ACKNOWLEDGEMENT

9. PUBLICATIONS AND CONFERENCES

Y. Zhu T. Beyerlein, A. R. Rabindranath and B. Tieke — Highly luminescent 1,4-diketo-3,6-diphenyl-pyrrolo [3,4-c]pyrrole- (DPP-) based conjugated polymers prepared upon Suzuki coupling, *Macromolecules*, accepted, **2007**.

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10. CURRICULUM VITAE

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University Education

09/1993 - 07/1997	Nanjing University of Technology, Nanjing, P. R. China Degree: Bachelor's Degree in Chemical engineering
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Ich versichere, daß ich die von mir vorgelegte Dissertation selbständig angefertigt, die benutzten Quellen und Hilfsmittel vollständig angegeben und die Stellen der Arbeit – einschließlich Tabellen, Karten und Abbildungen -, die anderen Werken im Wortlaut order dem Sinn nach entnommen sind, in jedem Einzelfall als Entlehnung kenntlich gemacht habe, adß diese Dissertation noch keiner anderen Fakultät order Universität zur Prüfung vorgelegen hat; daß sie – abgesehen von unten angegebenen Teilpublikationen – noch nicht veröffentlicht worden ist sowie, daß ich eine solche Veröffentlichung vor Abschluß des Promotionsverfahrens nicht vornehmen werde.

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Ich versichere, daß ich alle Angaben wahrheitsgemäß nach bestern Wissen und Gewissen gemacht habe und verpflichte mich, jedmögliche, die obigen Angaben betreffenden Veränderungen, dem Dekanat unverzüglich mizuteilen.

Unterschrift:

Köln, den 14.12.2006