Synthesis and applications of DPP-based II-conjugated polymers via direct arylation polymerization

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**SYNTHESIS AND APPLICATIONS OF DPP-
BASED Π -CONJUGATED POLYMERS VIA
DIRECT ARYLATION POLYMERIZATION**

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Abstract

Diketopyrrolopyrrole (DPP) derivatives are known in industry as efficient and stable pigments for a long time. Nowadays, arising attention is drawn to DPP-based conjugated small molecules and polymers on both bioapplications and electronic devices, owing to their superior photophysical and electrical properties. The synthesis of these materials is typically realized by conventional cross-coupling reactions, which require extra steps to synthesize organometallic reagents and involves toxic tin byproducts (Stille coupling). To overcome the drawbacks of these traditional coupling reactions, direct arylation by activation of C-H bonds has emerged as a new type of cross-coupling reaction as an economically attractive and ecologically benign way.

In this thesis, DPP unit is used as the core to construct polymers structures by either direct arylation polymerization or controlled polymerization. A series of DPP-based low-band gap conjugated polymers are synthesized by direct arylation polymerization with detailed optimization. The photophysical, electrochemical and thermal properties of these polymers are studied and the charge-transport properties are investigated in organic field effect transistors (OFETs). DPP-labelled biocompatible polymers are synthesized by ring opening polymerization and their photophysical properties are investigated in detail to understand the relationship between the polymer chain length and photophysical properties (especially fluorescent properties). DPP-labelled polymer with long polycaprolactone (PCL) chain is found to retain strong fluorescence in both nanoparticles and solid states, which inspires us to explore

its applications for cell imaging (nanoparticles) and cell interfacing and long-term tracking (polymer scaffolds). By combining direct arylation polymerization and control polymerization methods, a grafting through approach is applied to synthesize DPP-based low-band gap conjugated polymer brushes in a single step, which could be used for photothermal therapy.

The detailed contents of the thesis in each chapter are described below:

In Chapter 1, a general introduction about the synthesis of conjugated polymers is given first, followed by a review of DPP-based conjugated polymers. The applications of conjugated polymers are then described from electronic devices to biomedical area. After that, a greener synthetic method for conjugated polymers, direct arylation polymerization is discussed. This chapter is ended with the research motivation and objectives of this thesis.

From Chapter 2 to 5, DPP-based conjugated polymers are synthesized by direct arylation polymerization with comprehensive characterization and charge-transport study in OFETs.

In Chapter 2, detailed optimization of direct arylation polymerization between thiophene-flanked DPP (TDPP) and tetrafluorobenzene (TB) is first carried out to afford target polymer (PTDPP-TB) with molecular weight of over 30 kDa, which exhibits balanced hole- and electron- mobilities in OFETs of over $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ under ambient conditions.

In Chapter 3, the homo-coupling and branching defects in the synthesis of conjugated polymers via direct arylation polymerization are discussed. Dibrominated TDPP (DBrTDPP), which is used to synthesize TDPP-based

conjugated polymers, is found to form hyperbranched conjugated polymers (DBrTDPP as the only monomer) under some certain reaction conditions for direct arylation polymerization. Several different reaction parameters, including catalyst, solvent, reaction temperature, ligand and additive are exclusively examined, which could provide some insights to minimize the defects in the conjugated polymers synthesized by direct arylation polymerization in the future.

In Chapter 4, the incorporation of other different building blocks, thienoisindigo (TIIG) and benzodithiazole (BDTz) with TDPP unit into the conjugated backbones by direct arylation polymerization approach gives a series of conjugated polymers with high molecules weight, well-defined structures and tunable bandgap in high yields. The photophysical, electrochemical and thermal properties of these polymers are studied systematically. The charge transfer properties of these polymers are investigated in OFETs as well and the film morphologies of these polymer films are examined by atomic force microscopy to find out the relationship between film morphologies and charge transfer mobilities.

In Chapter 5, a series of phenyl-flanked DPP (PhDPP)-based conjugated polymers were synthesized by DAP and their photophysical, electrochemical and thermal properties were studied as well. Three PhDPP-based conjugated polymers are synthesized with TDPP, tetrafluorobenzene (TB), benzodithiophene (BDT) and 3,4-ethylenedioxythiophene (EDOT) as the other building block. These four polymers show absorption in the visible range and

are fluorescent in solutions with Stokes shift from 55 to 74 nm (non-fluorescent for PTDPP-PhDPP).

After discussing the application of DPP-based conjugated polymers for organic electronic devices, TDPP-labelled biocompatible polymers and TDPP-based conjugated polymer brushes are synthesized and studied for biomedical applications in the next two chapters.

In Chapter 6, a series of TDPP-labelled biocompatible polymers (PCL-DPP-PCL, PCL: polycaprolactone) are synthesized by ring opening polymerization with different chain lengths. It is found that the fluorescence quenching of DPP in the solid states can be efficiently compressed with extended PCL chain length. PCL-DPP-PCL with long PCL side chain is highly fluorescent and photostable in nanoparticles and solid states, which are used in cell interfacing and long-term tracking (nanofibers scaffolds).

In Chapter 7, with previous efforts in the DPP-labelled biocompatible polymers and direct arylation polymerization method to the synthesis of conjugated polymers, a grafting through approach was applied to synthesize low-band gap conjugated polymer brushes, with DPP-based conjugated backbone and biocompatible polymers as the side chain in a single step. And these polymers brushes could be served as photothermal therapy agents with strong absorption in the near-infrared range that benefits deep tissue penetration.

Finally, in Chapter 8, a summary is given for this thesis, with some outlook for the future efforts in direct arylation polymerization and facile synthetic method for conjugated polymer brushes.

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Chapter 1
Introduction

1.1. π -Conjugated polymers (CPs): general introduction and synthetic methods

1.1.1. General introduction of π -conjugated polymers

Since the seminal work on the conductivity of polyacetylene by Heeger, MacDiarmid, and Shirakawa in the 1970s, which was awarded for the Noble Prize in chemistry in 2000,^[1] a great attention has been drawn to the discovery and synthesis of semiconducting polymers and their application in organic electronics, such as organic light-emitting diodes (OLEDs),^[2, 3] organic field effect transistors (OFETs),^[4-20] and organic photovoltaics (OPVs).^[19, 21-43] In comparison with inorganic materials and small molecule organic semiconductors, semiconducting π -conjugated polymers provide several advantages including low cost, light weight, and good flexibility. More importantly, soluble polymer semiconducting materials can be readily processed and easily printed, which is a critical issue for the realization of large-scale roll-to-roll processing of printed electronics.

Due to the unique structure of conjugated polymers, they can exhibit high conductivity (even higher upon doping), excellent light absorption ability and strong fluorescence. More importantly, these properties can be fine-tuned by modifying the structure of these conjugated polymers to meet the demands for specific applications.

Scheme 1.1 Representative simple semiconducting conjugated polymers.

Polythiophene (PT), polypyrrole (PPy), poly (*p*-phenylene) (PPP), polyaniline (PANI), poly (phenylene vinylene) (PPV), polyfluorene (PFO) (**Scheme 1.1**) were among some initial research on the discovery of semiconducting polymers, while donor-acceptor (D-A) π -conjugated polymers have attracted more attention with their facile design and excellent device performance (especially OFETs^[6, 7, 10, 44] (**Scheme 1.2**) and OPVs^[22, 23] (**Scheme 1.3**)) in the past two decades. For OFETs materials, Yang et al. reported a low band gap poly(thienoisindigo-alt-naphthalene) (PTIIG-Np), which exhibited unprecedented hole mobility of $14.4 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ in top-gate/bottom-contact OFETs with poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) as a high- κ gate dielectric layer.^[44] Heeger and co-workers achieved even higher hole mobility of $23.7 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ by controlling the alignment of poly[4-(4,4-dihexadecyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)-alt-[1,2,5]thiadiazolo[3,4-c]pyridine] (PCDTPT) to make sure that charge-transport was predominantly along the conjugated backbones.^[10] High performance electron transporting^[6] and ambipolar^[7] materials were also

designed to reach charge transporting mobilities of over $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. As for conjugated polymers served as the donor in OPVs, PBDTT-DPP consisting of alkylthienylbenzodithiophene (BDTT) and DPP units in the conjugated backbones showed power conversion efficiency (PCE) of 6.6 and 8.8% in single and tandem solar cells with PC₇₁BM as the acceptor, respectively. PTB7, a star polymer for OPVs, achieved PCE of 9.2% with poly [(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) as a surface modifier. More recently, n-type conjugated polymers were developed to serve as the electron-acceptor materials to replace the fullerene derivatives in OPVs, to enhance the light absorption in the visible range, broaden the spectral width and control the bandgap as well.^[43]

Scheme 1.2 Representative D-A π -conjugated polymers with high performance for OFETs.

Scheme 1.3 Representative D-A π -conjugated polymers with high performance for OPVs.

1.1.2. Synthetic approaches for π -conjugated polymers

The construction of conjugated polymers lies essentially in the efficient carbon-carbon single bond formation between two unsaturated carbons in the aromatic units. In addition to electrochemical or chemical oxidative polymerizations, transition metal catalyzed cross-coupling reactions are demonstrated to be a powerful tool to construct π -conjugated structure with Csp^2 - Csp^2 and Csp - Csp^2 bond formation in the polymer chain.^[45] They involved a three steps catalytic cycle (**Scheme 1.4**), (1) starting from the transition metal catalyzed oxidative addition reaction across the C-X bond of an

electrophile; (2) followed by transmetalation with a main group organometallic nucleophile; (3) cyclized with a reductive elimination reaction leading to C-C bond formation and recovery of the organometallic catalyst. Thus, conjugation lengths can be extended through consecutive transformations in the catalytic cycle to form π -conjugated polymers.^[46] The organometallic nucleophiles involved can be Grignard reagents (Kumada-Corriu), stannyl (Stille), boron reagents (Suzuki-Miyaura) or copper (Sonogashira).

Scheme 1.4 Catalytic cycle for transition metal catalyzed cross-coupling reaction.^[46] Reproduced with permission from ref. 46. Copyright 2011 Macmillan Publishers Limited.

1.1.2.1. Kumada-Corriu reaction

Kumada cross-coupling reaction is a type of cross coupling reaction of Grignard reagents with alkyl, vinyl or aryl halides, reported by the groups of Robert Corriu and Makoto Kumada independently in 1972.^[47, 48] (**Scheme 1.5a**) The reaction uses transition metal catalysts, typically nickel or palladium. The mechanism of Kumada cross-coupling with palladium catalyst is described in **Scheme 1.5b** with catalytic cycle of four steps, (1) oxidative addition; (2) transmetalation; (3) *trans-cis* isomerization; and (4) reductive elimination. While the current understanding about the mechanism of nickel catalyst is still very limited, but it is believed that the reaction goes under different mechanisms with different ligands in nickel catalyst.

Scheme 1.5 a) General scheme and b) mechanism of Kumada cross-coupling reaction.

McCullough used this reaction to synthesize head-tail regioregular poly (3-hexylthiophene)^[1, 49] as shown in **Scheme 1.6**. The regioregular polymerization of 3-alkylthiophene can be achieved by selective lithiation of 2-bromo-3-

alkylthiophene with lithium diisopropylamide followed by transmetalation using magnesium bromide to yield the organomagnesium intermediate. The use of a Ni(dppp)Cl₂ catalyst for the polymerization of this intermediate gives the corresponding poly(3-alkylthiophene) with over 90% head-tail regioselectivity.

Scheme 1.6 Synthesis of poly (3-hexylthiophene) by Kumada reaction.

McCullough further reported another method for the synthesis of regioregular poly (3-alkylthiophene)s by Grignard metathesis (GRIM)^[50]. Treatment of 2, 5-dibromo-3-hexylthiophene with a variety of alkyl Grignard reagents resulted in two metalated regioisomers. Introduction of a catalytic amount of Ni(dppp)Cl₂ to this isomeric mixture afforded poly(3-hexylthiophene), with over 95% regioregularity (**Scheme 1.7**).

Scheme 1.7 Synthesis of regioregular poly (3-hexylthiophene) by GRIM method.

1.1.2.2. Migita-Kosugi-Stille cross-coupling reaction

Stille (short for “Migita-Kosugi-Stille”) coupling involves the coupling of an organostannanes compound with a variety of organic electrophiles via palladium-catalyzed coupling reaction^[51] (**Scheme 1.8**). The reaction is more suitable for thiophene-containing coupling reaction, using monomers with stannyl groups on the thiophene ring which is widely used to design thiophene containing small molecules and polymers with better conductivity and better performance in electronic devices. The mechanism of the Stille coupling is very close to the general mechanism as shown in the transition metal catalyzed cross-coupling containing oxidative addition, transmetalation and reductive elimination process.

Scheme 1.8 General scheme of Stille coupling reaction.

L. Yu et al.^[52] synthesized a thieno[3,4-b]thiophene/benzodithiophene copolymer poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][2-[[[(2-ethylhexyl)oxy]carbonyl]-3-fluorothieno[3,4-b]thiophenediyl]] (PTB7) by utilizing Stille cross-coupling reaction with Pd(PPh₃)₄ as the catalyst in toluene (**Scheme 1.9**). A record high 9.2% efficiency for polymer solar cells was obtained with PTB7 as the active layer.^[23]

Scheme 1.9 PTB7 synthesized via stille cross-coupling.

1.1.2.3. Suzuki-Miyaura coupling reaction

Suzuki (short for “Suzuki-Miyaura”) coupling^[53] is a coupling reaction occurred between a boronic acid or ester with an aryl halide catalyzed by a palladium (0) complex, which is more widely used for preparing benzene-containing polymers with boronic groups on the benzene ring of the monomer (**Scheme 1.10**). The mechanism of the Suzuki coupling also follows the general mechanism of transition metal catalyzed cross-coupling. Compared to Stille coupling, Suzuki coupling shows advantages over availability of common boronic acids, mild reaction conditions, and the less toxic byproduct. High molecular weight poly (dioctylfluorene) (PFO) can be synthesized via Suzuki coupling reaction to serve as a blue emitting material for OLED^[54] (**Scheme 1.11**).

Scheme 1.10 General scheme of Suzuki coupling reaction.

Scheme 1.11 Highly luminescent polyfluorene prepared via Suzuki coupling.

1.1.2.4. Heck reaction

Heck reaction undergoes between an unsaturated halide (or triflate) with an alkene in the presence of a base and a palladium catalyst to form a substituted alkene^[55] (**Scheme 1.12**).

Scheme 1.12 General scheme of heck reaction.

Huo et al. synthesized alternating copolymers of electron-rich arylamine/dialkoxyphenylene and electron-deficient 2,1,3-benzothiadiazole using palladium acetate as catalyst by Heck reaction^[56] (**Scheme 1.13**), with which they further studied the photovoltaic properties of the copolymers in OPVs.

Scheme 1.13 Synthesis of conjugated polymers by Heck reaction.

1.1.2.5. Sonogashira reaction

Sonogashira reaction^[57] employs a palladium catalyst to form a carbon-carbon bond between a terminal alkyne and an aryl or vinyl halide (**Scheme 1.14**). The reaction can be carried out at mild conditions, such as room temperature and mild base.

Scheme 1.14 General Scheme of Sonogashira reaction.

Bunz et al. synthesized a series of poly (aryleneethynylene)s with tunable solid state fluorescence via Sonogashira reaction^[58] as shown in **Scheme 1.15**.

Scheme 1.15 Poly(aryleneethynylene)s synthesized via Sonogashira reaction.^[58]

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1.1.2.6. Yamamoto reaction

Aryl halides catalyzed by nickel catalyst, undergo coupling reactions to give R-R which has been used by Yamamoto et al. for coupling reactions, providing a pathway for carrying out self-polymerization of single monomers (**Scheme 1.16**).

Scheme 1.16 General scheme of Yamamoto reaction.

Li et al. in 2006 synthesized soluble polycarbazole by Yamamoto reaction using Ni(COD)₂^[59] (**scheme 1.17**), with which they further studied the photovoltaic properties.

Scheme 1.17 Synthesis of polycarbazole by Yamamoto reaction.

Despite these transition metal catalyzed cross-coupling reactions for synthesizing π -conjugated polymers, some other methods have also been applied to the synthesis of specific conjugated polymers with certain structure in the polymer backbone.

1.1.2.7. Knoevenagel condensation

Knoevenagel condensation^[60] is a useful tool in the synthesis of vinylene containing conjugated polymers via the carbon-carbon double bond formation between two respective monomers. Reynolds et al. reported the synthesis of PProDOT-Hx₂:CN-PPV by Knoevenagel condensation^[61] (**Scheme 1.18**). These donor-acceptor conjugated polymers possess narrow band gaps of about 1.5-1.8 eV and good solubility in common organic solvents.

Scheme 1.18 Synthesis of PProDOT-Hx₂:CN-PPV by Knoevenagel condensation.

1.1.2.8. Gilch polymerization

In addition to Knoevenagel condensation, Gilch polymerization route provides another way to synthesize vinylene containing polymers. This involves the reaction of α, α' -dihalo-*p*-xylene with excess of base to obtain conjugated PPV through a one-pot straight forward elimination-polymerization-elimination three step procedure^[62] (**scheme 1.19**).

Scheme 1.19 Synthesis of MEH-PPV by Gilch polymerization.

1.2. Diketopyrrolopyrrole (DPP)-based π -conjugated polymers

In recent years, the electron-accepting DPP moiety has been receiving considerable attention to construct organic semiconducting polymers for a variety of applications, particularly for OFETs^[7, 17, 63-79] and OPVs^[22, 80-94] due to the well conjugated planar structure and strong π - π stacking of DPP units.

Scheme 1.20 Chemical structure of DPP-based conjugated polymers.^[94]

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DPP-based conjugated polymers are usually made up of four components: DPP core, the alkyl chain connected to the nitrogen in the DPP unit, the adjacent aromatic substituent and the π -conjugated segment (**Scheme 1.20**).

The alkyl side chains can not only effectively increase the solubility for conjugated polymers, but also modify and adjust the molecular packing (aggregation and crystallization) behaviour for the polymers in thin films. Kim et al. have studied the relationship between the number of carbons spacer in the branched side chains with the hole mobilities for conjugated polymers (PDPP-SVS) consisting DPP and selenophene vinylene selenophene (SVS) units, and

they found that the electrical properties of these polymers is related to length of space as well as the odd-even characteristics^[95] (**Figure 1.1**).

Figure 1.1 Relationship between hole mobility of PDPP-SVS with number of carbons in alkyl spacer in the polymer side chain.^[95] Reprinted (adapted) with permission from ref. 94. Copyright 2015 American Chemical Society.

The energy levels and optical properties of DPP-based conjugated polymers can be easily tuned by varying the adjacent substituent as well as the conjugated segment to meet different requirements in electronic devices. Through association of the DPP unit with appropriate electron donating building blocks, the resulting D–A molecules interact strongly in the solid state through intermolecular D–A and π – π interactions, leading to highly ordered structures at the molecular and microscopic levels. The closely packed molecules and crystalline domains are beneficial for intermolecular and interdomain or

intergranular charge transport. Proper tuning of energy levels accompanied by morphology control of DPP-based conjugated polymers give p-type, n-type, or ambipolar organic semiconductors with highly efficient charge transport properties in OFETs and high efficiency in OPVs.

Scheme 1.21 Representative examples of high performance DPP-based conjugated polymers for OFETs and OPVs.

In the past years, a number of DPP-based small molecular and semiconducting polymers have been reported to show mobility close to or greater than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (**Scheme 1.21**). DPP-based conjugated polymers have achieved record high mobility values for p-type (hole mobility: $17.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[95], n-type (electron mobility: $6.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[9], and ambipolar (hole/ electron mobilities: $3.97/2.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[7] OFETs among the known polymer semiconductors. Many DPP-based semiconducting polymers have favorable

energy levels and band gaps along with high hole mobility, which enable them as promising donor materials for OPVs. Power conversion efficiencies (PCE) of up to 8% were achieved for OPVs using DPP-based polymers^[35, 82, 96], demonstrating their potential applications for the organic solar cell technology.

Apart from the applications in electronic devices, the low bandgap nature of DPP-based conjugated polymers which can absorb the near-infrared light also offer the opportunity to be used for photothermal therapy in biomedical applications as well.

1.3. Direct arylation polymerization (DAP) as a new synthetic approach for π -conjugated polymers

1.3.1. Development of direct arylation for π -conjugated small molecules and polymers

It has been 40 years since the first report of direct aryl-benzofuran coupling using stoichiometric palladium. Some time had passed with the maturation of other conventional cross-coupling techniques until the first catalytic studies on the direct arylation of furan, thiophene, benzothiophene, and benzofuran were reported by Ohta and co-workers in the early 1990s^[97]. Since a number of possible side reactions (e.g., homocoupling, isomerization, and functional group interference) must be avoided to develop a generally practical method for the synthesis of π -conjugated small molecules and polymers, direct arylation was

not actively applied for the synthesis of organic electronic materials until recently.

The advances made in organic electronics have been driven by the synthesis of π -conjugated molecules with increasingly complex structures. For example, one polymer in the BDTT series, PBDTTT-CF, provides a PCE of 6.8% (National Renewable Energy Laboratory (NREL) certified value) and has an estimated cost of over \$400/g, requiring 10 steps to synthesize starting from basic commercial materials. The cost is approximately 25 times greater than that of poly (3-hexylthiophene-2,5-diyl) (P3HT) synthesis^[98]. Considering increasing demand for π -conjugated polymers, it is very urgent to develop new, cheaper and greener synthetic methods owing to that traditional transition metal catalyzed cross-coupling reactions suffer from several drawbacks, 1) tedious synthesis of metal-activated monomers; 2) low stability of the involved organometallic reagents; 3) formation of toxic byproducts. In particular, the preparation of stannyl reagents for Stille coupling often involves the use of low temperature ($-78\text{ }^{\circ}\text{C}$) and unstable organometallic reagents such as *n*-butyllithium, which is flammable in air and difficult to scale up. Another organometallic compound often involved in the preparation of stannyl reagents is trimethyltin chloride, which is volatile and highly toxic. Although this issue is less serious when tri(*n*-butyl)tin chloride is used as a replacement, the latter often shows less reactivity than the former in the coupling reactions with some monomers. Moreover, these stannyl-derived monomers are difficult to purify, which compromises the quality of final polymer products^[99].

Direct arylation by activation of C-H bonds has emerged as a new type of cross-coupling reaction. A generally accepted mechanism of C-H bond activation is via the first step of oxidative addition of the transition metal into the aryl halide, followed by a key C-C bond-formation step in which the exact mechanism depends on the substrate, transition metal, solvent, base, and ligand used (**Scheme 1.22**). This synthetic method, in contrast to Suzuki coupling and Stille coupling, does not involve organometallic reagents such as stannyl and boron derivatives. As a consequence, direct arylation represents an economically attractive and ecologically benign alternative to the traditional cross-coupling strategies described above (**Scheme 1.22**). Direct arylation usually requires the presence of transition-metal catalysts and an inorganic base (e.g. K_2CO_3 , Cs_2CO_3 , KOAc, *t*-BuOK and CsOPiv). $\text{Pd}(\text{OAc})_2$ has been one of the most common catalysts for direct arylation. Ligands are used in some reactions of direct arylation, particularly when the C-X bond shows low reactivity. While polar, aprotic solvents such as DMF, DMA, CH_3CN , NMP and DMSO are commonly used, nonpolar solvents such as toluene, xylene and THF have also been employed successfully. In addition, a number of papers described that the mechanisms are not unified; differing pathways may occur depending on substituent identity and reaction conditions and could be another reason for the limited applications of direct arylation in materials science. Nevertheless, direct arylation studies have made impressive progress over the past decade in organic synthesis, enabling us to design π -conjugated small molecules and polymers from unfunctionalized starting materials. Although

direct arylation has been mostly used in synthesis of small molecules^[100-106], it has been rarely applied to the synthesis of polymers until very recently^[4, 90, 107-176].

Scheme 1.22 Comparison between conventional cross-coupling with direct arylation.^[99] Reproduced with permission from ref. 98. Copyright 2013 Bentham Science Publishers.

1.3.2. Mechanism of direct arylation (polymerization)

The mechanism by which C-H activation occurs has been studied experimentally and computationally, and possible pathways include electrophilic aromatic substitution, Heck-type coupling and concerted metalation-deprotonation (CMD)^[105, 177, 178]. Most heterocycles, such as thiophenes and indoles, are believed to follow a base-assisted CMD pathway.

Two catalytic cycles for a CMD coupling of bromobenzene and thiophene using a palladium/phosphine catalytic system and cesium carbonate are shown in **Scheme 1.23** and **Scheme 1.24** ^[90]. **Scheme 1.23** depicts a carboxylate-mediated process, while **Scheme 1.24** represents the reaction process in the absence of a carboxylate additive.

Scheme 1.23 Catalytic cycle of DAP using a carboxylate additive.^[176]

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Scheme 1.24 Catalytic cycle of DAP without a carboxylate additive.^[176]

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Under carboxylate-mediated conditions (**Scheme 1.23**), oxidative addition of the carbon-halogen bond is followed by exchange of the halogen ligand for the carboxylate anion to form complex **1**. With the assistance from the carboxylate

ligand, this complex then deprotonates the thiophene substrate while simultaneously forming a metal-carbon bond and goes through transition state **1-TS**. The phosphine ligands, or the solvent, can recoordinate to the metal center following Pathway 1, or the carboxylate group can remain coordinated throughout the entire process (Pathway 2). Finally, reductive elimination renders the aryl coupled product. In the absence of a carboxylate additive, after oxidative addition of the aryl bromide, the reaction follows one of the two pathways shown in **Scheme 1.24**. If a bidentate phosphine is employed, C-H activation of thiophene can follow Pathway 1, where deprotonation is assisted intermolecularly (**2-TS**). When a monodentate phosphine is used, the reaction may follow Pathway 1 or Pathway 2. The latter mechanism most closely resembles Pathway 2 in **Scheme 1.24** where the carbonate coordinates to the metal center to give the Zwitterionic species **1'**. From here, deprotonation occurs intramolecularly through transition state **1'-TS**. Reductive elimination then renders 2-phenylthiophene.

Density functional theory (DFT) calculations (B3LYP//DZVP/TZVP) of the CMD process reveal that the energy required to form transition state **1-TS** can be broken into two components: the energy needed to distort the aryl C-H bond and the energy to be overcome when the distorted aryl fragment interacts with the metal center. The authors have computed the activation energy of a number of C-H bonds for various (hetero)arenes and compared the regioselectivity for those containing more than one reactive site. These arenes were then divided into three classes based on the factors that control the regioselectivity in the

CMD reaction: (1) Class I (hetero)arenes depend on the energy required to distort each C-H bond (i.e., benzenes and perfluorinated benzenes). (2) Class II (hetero)arenes rely on the interaction energy between the metal center and the distorted aryl fragment (i.e., furans and thiazoles). (3) Class III (hetero)arenes, where the site of reactivity depends on both the distortion and interaction energy (i.e., thiophenes and pyrroles). Interestingly, a small activation energy difference of 4.3 kcal/mol between the 2- and 3-positions in thiophene was calculated according to these criteria. This study also investigated C5-functionalization of thiophenes with electron donating and withdrawing groups in the 2-position. Thiophenes substituted with electron donating groups are good π -nucleophiles and therefore have a strong interaction with the palladium center, which gives a more negative interaction energy, but requires more energy to distort the C-H bond. In contrast, substitution with electron withdrawing groups on thiophenes decreases the π -nucleophilicity of the system, which imparts a less negative interaction energy. These thiophenes also requires less energy to distort the C-H bond. Both of these components affect reactivity, making it difficult to find trends based on electronic effects of the substituents (i.e., acidity of the proton or π -nucleophilicity of the system). These calculations displayed good correlation with experimental results.

The mechanism was examined experimentally by Ozawa and co-workers, who isolated a single crystal of complex **3** suitable for X-ray analysis and studied the catalytic activity toward C-H activation. In solution, this dimeric species disproportionates into two molecules of **4**, which is the active catalytic

species. Complex **4** was then utilized as a catalyst in a competition experiment between bromobenzene and 2-bromo-1,3-dimethylbenzene (0.5 equiv each) using 2-methylthiophene as the C-H activation substrate. They concluded that C-H activation was not the rate limiting step and that oxidative addition of the C-Br bond was most likely slower, since coupling with bromobenzene took place preferentially. However, this was not confirmed by deuterium labelling experiments.

These results, combined with the extensive library of work on small molecule coupling chemistry, compelled us to apply this synthetic tool to the polymerization for conjugated polymers. The broad scope of this reaction has been demonstrated over the past few years as there have been a growing number of publications utilizing C-H activation.

1.3.3. Applications of direct arylation polymerization

Considering the rapid development of direct arylation polymerization for π -conjugated polymer, here we only selected some representative works in this area.

1.3.3.1. 3-Alkylthiophene (P3ATs) -based homopolymers

Poly(3-alkylthiophene)s (P3ATs) represent one of the most widely used π -conjugated polymers for flexible electronic devices for their environmental and thermal stability, excellent conductivity and solubility in organic solvents. Regioregularity of P3ATs strongly affects their optoelectronic properties.

Specifically, head-to-tail (HT) P3ATs usually show higher performance than head-to-head (HH) P3ATs in optoelectronic devices. McCullough and coworkers developed a method of Kumada-Corriu coupling to achieve 98% HT-P3ATs with Ni(II) catalyst. Later on, Rieke method, Grignard metathesis (GRIM) method, Stille and Suzuki coupling were also applied to the synthesis of high-regioregularity HT-P3HTs.

Scheme 1.25 Preparation routes of P3ATs via direct arylation polymerization.

In 1999, Lemaire and coworkers first applied the concept of direct arylation to the synthesis of P3ATs^[107, 179]. The polymerization involved 2-halo-3-alkylthiophenes as the monomers and $Pd(OAc)_2$ as the catalyst, tetrabutylammonium bromide ($n-Bu_4NBr$) as the phase-transfer agent, K_2CO_3 as the base and DMF as the solvent (**Scheme 1.25**). Although only oligomers (**P1a-c** with number-average molecular weights (M_n) of 2.9 to 3.1 kDa) were obtained in their work, relatively high yields (89-93%) and ~90% of regioregularity (determined by 1H -NMR) were obtained. A proposed

mechanism for this type of polymerization was similar to Heck-type polymerization.

Ozawa et al. reported the conversion of 2-bromo-3-hexylthiophene into head-to-tail poly(3-hexylthiophene) (HT-P3HT) (**P1d**) with both high M_n and high regioregularity^[109] (**Scheme 1.26**). They observed that $\text{Pd}(\text{OAc})_2$, associated with deposition of palladium black, was not stable enough to catalyze the polymerization. Such low stability of $\text{Pd}(\text{OAc})_2$ led to low molecular weight products and poor reproducibility. In contrast to the low stability of $\text{Pd}(\text{OAc})_2$, Herrmann-Beller catalyst ($\text{Pd}(\text{OAc})(o\text{-Tol})$) formed by complexation of $\text{Pd}(\text{OAc})_2$ and $\text{P}(o\text{-tolyl})_3$, was proved to be a good catalyst precursor with high thermal stability for the polymerization of 2-bromo-3-hexylthiophene. In addition, several phosphine ligands were tested in the reaction, and $\text{P}(o\text{-Me}_2\text{NPh})_3$ was proved to be the most effective. The optimized catalytic system was established with Herrmann-Beller catalyst, $(o\text{-Me}_2\text{NPh})_3\text{P}$, Cs_2CO_3 in THF at 125 °C for 24 h, which gave 98% regioregularity of HT-P3HT with M_n of 30.6 kDa in 99% yield. This reaction condition was also applicable for the polymerization of other 2-bromo-3-alkylthiophenes ($\text{R}=7\text{-oxaoctyl}$ or 2,5-dioxahexyl).

Ozawa and coworkers further explored the direct arylation polymerization for synthesis of P3HTs end-capped with functional groups^[125]. Six derivatives of *p*-substituted-bromobenzene as end-capping reagents form complexes with $\text{Pd}[\text{P}(o\text{-tolyl})_3]_2$ as the catalyst to initiate the polymerization. This end-capping protocol is different from the one used in GRIM, where an end-capping reagent

is usually added at the end of reaction. In addition, KOAc and the phosphine ligand $P(o\text{-Me}_2\text{NPh})_3$ were introduced to the catalytic system to assure high efficiency of the reaction by avoiding the formation of oligomers and deposition of palladium black. Polymers with M_n ranging from 4.7 to 11.8 kDa, over 90% efficiency of end-capping and 98% HT regioregularity were obtained. To reveal the reaction mechanism of end-capped P3HT, the authors studied the relationship between M_n and PDI with conversion of 2-bromo-3-hexylthiophene.

Considering a rather sophisticated catalytic system and relatively high temperature (120-125 °C) in Ozawa's work as described above for the synthesis of P3HT (**P1d**), Thompson and coworkers^[123, 132] developed a modified procedure of direct arylation polymerization, without using any phosphine ligand, in the synthesis of P3HT. Instead, they used $\text{Pd}(\text{OAc})_2$, pivalic acid and K_2CO_3 in DMA at a relatively low temperature (70 or 95 °C) (**Scheme 1.25**). P3HT products with M_n of 14.3 and 15.5 kDa were obtained under 70 °C and 95 °C, respectively. However, relatively low yields (below 50%) and low regioregularity (88%) were observed in both cases.

1.3.3.2. Thieno[3,4-c]pyrrole-4,6-dione (TPD) -based conjugated copolymers

As Fagnou et al. have pointed out in the featured article,^[105, 106] if there are multiple reactive sites on the aromatic unit(s), it is very important to be able to predict the reactivity prior to synthesis. For example, when considering the case

of P3HT, α -position coupling is more likely than β -position coupling. However, the relative percentage of β -position hydrogen will increase as the polymerization proceeds, while the percentage of α -position hydrogen will decrease. Thus, even if the reactivity of the α -position proton is higher than that of the β -position, the side reaction on the β -position cannot be ignored. Therefore, for the sake of controlling polymer dimensionality, 3,4-disubstituted thiophenes are the preferable monomer for linear polymer synthesis.

Leclerc et al.^[90] reported thieno[3,4-*c*]pyrrole-4,6-dione (TPD)-based alternating copolymers synthesized via direct arylation polymerization^[115] (**Scheme 1.26**). Since the monomer is a 3,4-disubstituted thiophene, it is well suited for direct arylation polymerization. In their studies, both direct arylation polymerization and Stille coupling were used to prepare **P2** using 5,5'-dibromo-4,4'-dioctyl-2,2'-bithiophene (**M2**) and 5-(2-hexyldecyl)-5H-thieno[3,4-*c*]pyrrole-4,6-dione (**M3**). Direct arylation polymerization using Herrmann-Beller catalyst together with P(*o*-OMePh)₃ and Cs₂CO₃ in THF resulted in **P2** with a high molecular weight of 56.0 kDa in 96% yield. (Scheme 1.25) Nevertheless, **P2** obtained by Stille coupling showed a relatively low molecular weight ($M_n = 9.0$ kDa), presumably due to the loss of some functional groups during the reaction.

Other thieno[3,4-*c*]pyrrole-4,6-dione (TPD)-based polymers were also synthesized under the similar conditions as shown in **Scheme 1.26**. **P3** and **P4** reached the molecular weight of 15.0 and 34.0 kDa, respectively. These results

demonstrate that TPD unit is a suitable moiety for direct arylation polymerization.

Scheme 1.26 TPD-based copolymers via direct arylation polymerization.

1.3.3.3. Poly[(9,9-dioctylfluorene-2,7-diyl)-(2,3,5,6-tetrafluoro-1,4-phenylene)] (PDOF-TP)

Kanbara's group^[110] first reported direct arylation polymerization of 1,2,4,5-tetrafluorobenzene (**M9**) with 2,7-dibromo-9,9-dioctylfluorene (**M8**) using Pd(OAc)_2 , $\text{P}^t\text{Bu}_2\text{Me-HBF}_4$ and K_2CO_3 in DMA at 100 °C for 24 h, which gave **P5** with a molecular weight of 31500. In addition, without using a phosphine ligand, the reaction in the presence of pivalic acid gives **P5** with $M_n = 19.3$ kDa and 70% yield.

Ozawa et al.^[133] made further improvement to successfully synthesize PDOF-TP with an extremely high molecular weight (M_n up to 34.8 kDa) via DAP. The reaction was conducted using $\text{Pd}_2(\text{dba})_3\text{-CHCl}_3$ as the catalyst, with Cs_2CO_3 , PivOH and $\text{P}(\text{C}_6\text{H}_4\text{-}o\text{-OMe})_3$ in THF at a concentration of 0.5M. It was also found that a higher concentration of monomers benefits for a higher molecular weight of polymer.

Scheme 1.27 Synthesis of PDOF-TP via DAP.

1.3.3.4. Low-bandgap D-A alternating copolymers

Low-bandgap polymers (typically with a bandgap smaller than 1.8 eV) are important for applications such as solar cells, where absorption of light over a broad range of solar spectrum is essential to achieve high power-conversion efficiency. Two main strategies have been utilized to reduce the bandgap of conjugated polymers:

- (1) Stabilization of quinoid character in the conjugated system: Poly(isothianaphthene) with a bandgap of ~ 1 eV represents a classical example of a low-bandgap polymer.
- (2) Incorporation of electron-rich (donor) and electron-deficient (acceptor) in an alternating fashion in the same polymer backbone: The introduction of push-

pull driving forces facilitates electron delocalization and the formation of quinoid mesomeric structures ($D-A \rightarrow D^+=A^-$) over the conjugated main chain, thus leading to reduction of the bandgap.

As an example low-bandgap D-A alternating copolymer, poly(4,4-diakyl-cyclopenta[2,1-b:3,4-b']-dithiophene-alt-2,1,3,benzothiadiazole) (PCPDTBT, **P6**) with a bandgap of 1.2-1.4 eV, depending on the structures of the side chains, has shown outstanding performance in both bulk heterojunction (BHJ) solar cells and field effect transistors^[180, 181].

Scheme 1.28 Synthesis of low-bandgap CPDT and BT based copolymers via DAP.

Scherf and co-workers^[120] reported the synthesis of **P16** via direct arylation polymerization running with a catalytic system of Pd(OAc)₂/PCy₃-HBF₄/K₂CO₃ in DMA at 110°C. Polymerization of **M10** and **M11** gave **P16** with a molecular weight of 24.6 kDa in 80% yield (Scheme 1.24A). In contrast to the little effect of the phosphine ligand on the reaction, change of the solvent from DMA to toluene resulted in low-molecular-weight oligomers. In addition, in the absence of phosphine ligand, longer reaction time did not benefit this reaction due to an increased amount of cross-linked byproduct in the process, which was consistent with Hartwig's results^[182]. An optimized reaction condition over 24 h in the absence of any phosphine ligands resulted in **P16** with M_n as high as 40.3 kDa and a yield of 70%.

Horie et al.^[116] optimized the synthesis of **P6** using Pd(OAc)₂/pivalic acid/K₂CO₃ in NMP at 80 °C for 20 h, resulting in M_n of 37.7 kDa in 98% yield before Soxhlet extraction. Further purification with Soxhlet extraction led to **P6** with M_n of 71.7 kDa in 76% yield. This molecular weight is four times higher than that of the same polymer previously synthesized via Suzuki coupling and nearly two times of the molecular weight obtained by Stille coupling^[181]. It should be noted that some insoluble solid was left after the Soxhlet extraction, presumably a result of side reactions that lead to cross-linked or branched structures (**Scheme 1.28**). **P6** synthesized via direct arylation polymerization showed slight improvement of power conversion efficiency (PCE, 3.98%) in **P6**/PC₇₁BM BHJ solar cells compared to the PCE (3.89%) of the device involving **P6** synthesized via Suzuki coupling (Pd(PPh₃)₄, K₂CO₃, Toluene/H₂O,

80°C, 96h). Such improvement was possibly attributed to the higher molecular weight of the former as well as its branched structure that leads to better morphology in the blend with fullerenes.

Other D-A copolymers (**P7-P10**) were also synthesized under the optimized reaction condition as described above (Scheme 1.23B). However, only low-molecular-weight ($M_n < 6.0$ kDa) polymers (oligomers) were obtained. This result was attributed to either low reactivity of the monomers (**M12-13**) or formation of insoluble products (**P9-10**) caused by branching and cross-linking reactions.

1.3.3.5. DPP-based conjugated copolymers

As discussed in the previous section that DPP-based conjugated polymers show superior performance in electronic devices, it is necessary to develop a direct arylation polymerization method for DPP-based polymers as an economically save and ecologically friendly alternative to traditional transition metal catalyzed cross-coupling reaction.

You et al.^[127] systematically studied the direct arylation polymerization between DPP and other nine monomers to get polymers with molecular weight ranging from 5.5 to 45.0 kDa (**Scheme 1.29**). The direct arylation polymerization under $\text{Pd}(\text{OAc})_2$, $\text{PCy}_3 \cdot \text{HBF}_4$ and K_2CO_3 in DMAc/xylene with PivOH as the additive was effective with various monomers in most cases and the obtained low bandgap polymers covers the absorption spectra from UV-Vis

to near-infrared range. However, branching defects were observed from the NMR spectra of some polymers in this case.

Scheme 1.29 DPP-based conjugated polymers synthesized via DAP by You.^[127]

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Later on, Leclerc et al. further modified the reaction conditions for direct arylation polymerization of DPP-based conjugated polymers with three different monomers to afford low bandgap polymers with high molecular weight. And these three polymers showed n-type behavior in bottom-gate/bottom contact OFETs with electron mobilities of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$.

From the synthetic studies of DPP-based conjugated polymers by You and Leclerc,^[90, 127] it is obvious that the optimized reaction conditions for DPP

monomer dependent whether it is brominated or unactivated with C-H bonds. This could be also applicable to other monomers in the optimization of reaction conditions for direct arylation polymerization.

Scheme 1.30 Low bandgap DPP-based conjugated polymers synthesized via DAP by Leclerc.^[90] Reproduced with permission from ref. 89. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

1.3.4. Challenges in direct arylation polymerization

Direct arylation polymerization represents a green and streamlining synthetic approach to π -conjugated polymers. Some polymers synthesized by direct arylation polymerization have shown larger molecular weights (e.g. **P6**) than the structurally identical polymers synthesized by Suzuki or Stille coupling.

However, several challenges in direct arylation polymerization remain to be solved before its profound impact on both basic research and industrial applications:

- (1) The involved aromatic monomers usually contain multiple C-H bonds with similar dissociation energies. It remains a major challenge to develop regioselective methods for direct arylation. Four strategies have been employed to increase the regioselectivity of direct arylation in small-molecule synthesis: 1) electronic effect of substituting groups; 2) directing groups; 3) steric effect of substituting groups; 4) use of additives (co-catalysts) such as pivalic acid and *o*-nitrobenzoic acid^[183]. The application of these methods, together with other potentially new synthetic approaches, to the synthesis of π -conjugated polymers will effectively minimize the undesirable cross-linked and/or branched byproducts in the progress of polymerization.
- (2) The optimization of reaction conditions remains empirical to achieve polymers with high M_n , narrow PDI and high yields (i.e. minimized side reactions). It remains a challenge to minimize the batch-to-batch difference in polymer synthesis. Both experimental and theoretical work are needed to understand factors that control the reaction of direct arylation polymerization. For example, solvents play an important role in direct arylation polymerization. On the one hand, polar aprotic solvents such as DMF, NMP and DMA can dissolve the inorganic components in the catalytic system better than nonpolar solvents, but

cannot dissolve the polymer products very well. On the other hand, some reactions running in nonpolar solvents such as toluene did not result in polymers presumably due to the insolubility of inorganic base in these solvents. Therefore, new solvents compatible to both inorganic base (K_2CO_3 , Cs_2CO_3 , etc.) and the polymer products are needed in the future for efficient synthesis of high-quality (i.e. high-molecular weight, low PDI) π -conjugated polymers.

- (3) Structural defects in the conjugated polymers synthesized from direct arylation polymerization should be minimized. Although from the synthetic point of view, even Suzuki or Stille coupling could lead to either homocoupling or branching defects in the target polymers, structure defects problem is more serious in direct arylation polymerization with the evidence from either the absorption spectra or better evidence from the NMR spectra of the polymers. However, it is still possible to optimize the reaction conditions to reduce the possibility of potential defects in direct arylation polymerization methods.
- (4) Pd-based catalysts, particularly $Pd(OAc)_2$, $Pd_2(dba)_3$ and Herrmann's catalyst ($Pd(OAc)(o-Tol)$), have been exclusively used in the direct arylation polymerization for synthesis of π -conjugated polymers. There is a need to explore cheaper, earth-abundant catalysts such as Cu-, Ni- and Fe-based complexes for effective direct arylation polymerization.
- (5) Little study of device performance such as in OPVs^[35, 116, 134, 173] and

OFETs ^[90, 126, 136, 152, 164] has been carried out for π -conjugated polymers synthesized by direct arylation polymerization.

1.4. Applications of π -conjugated polymers

The unique structure and properties of π -conjugated polymers make them promising for various applications ranging from kinds of organic electronics to some bio-related applications in recent two decades. The detailed applications of conjugated polymers will be discussed in two aspects, organic electronics and bioapplications.

1.4.1. Applications of π -conjugated polymers in organic electronics

OLEDs, OFETs and OPVs based on π -conjugated polymers have now reached a stage where the performance of these devices are quite close to traditional inorganic materials, with their potential applications to replace inorganic materials due to several advantages of π -conjugated polymers based organic electronics, including fine tuning of polymer properties in the molecular level and realistic promise of flexible electronics in the near future as well as low cost, easy fabrication of devices. The quantum efficiencies of OLEDs based on conjugated polymers have outperformed those of inorganic LEDs. The highest hole and electron mobilities obtained for conjugated polymers in

OFETs reach $23.7^{[10]}$ and $6.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1[9]}$ respectively, and OPVs now have reached a power conversion efficiency (PCE) of over 9%^[23] (single cell) and 10.6%^[184] (tandem cells).

Such progress is a result of advances in both the understanding of the working principles of the devices and the development of new, more suitable organic materials. Each of the applications (we focus on OPVs and OFETs) requires compounds with a specific set of both physical and electrochemical features. For example, when blended with a fullerene derivative, conjugated polymers aimed as p-type materials (donor) for organic solar cells should have (a) HOMO energy level below -5.1 eV to ensure air stability and effective charge separation at the polymer donor: fullerene acceptor interface which results in high open circuit voltage (V_{oc}); (b) LUMO energy level in the range of -3.7 to -4.0 eV to create enough driving force to promote an exciton dissociation; and (c) relatively low optical band gap, between 1.2 and 1.9 eV , with a broad absorption spectrum to absorb as much sunlight as possible and to generate a high short circuit current (J_{sc}). Additionally they should be well soluble in common organic solvents to warrant easy processability. On the other hand, compounds suitable for OFETs should exhibit strong π - π interactions as well as preferable edge-on orientation in the solid state to promote high charge carrier mobilities^[185]. In the search for polymers fulfilling such complex requirements, researchers have prepared numerous new materials to enhance the device performances.

Among these newly designed materials, those that have been presented in **Scheme 1.2** and **Scheme 1.3** stand for the best conjugated polymers for OFETs and OPVs till now with the designing principles mentioned above.

1.4.2. Bioapplications of π -conjugated polymers

Besides the applications of π -conjugated polymers in electronic devices, a lot of attention has also been drawn into various bioapplications, such as bioimaging, photothermal therapy and drug delivery. Considering the bioapplication, most conjugated polymers are not soluble in water which requires further modification of polymers. Pendant groups can be added onto the polymer backbone, thus converting conjugated polymers into conjugated polyelectrolytes (CPEs); alternatively, conjugated polymers can also be made into nanoparticles (NPs) stabilized with amphiphilic surfactants or block copolymers^[186]. Indeed, a majority of the *in vivo* applications of conjugated polymers reported so far are conjugated polymer nanoparticles (CPNPs), due to the flexibility in conjugated polymers selection, simple synthetic protocols, excellent size range for tissue penetration and plasma circulation, high photostability, inert biochemical behaviors, and easiness of doping or mixing conjugated polymers.

Two bioapplications of conjugated polymers, bioimaging and photothermal therapy are selected to discuss in this part. Conjugated polymers have emerged as a promising new class of imaging probes due to their superior electronic and

optical properties, such as high extinction coefficients and efficient intra-/intermolecular exciton migration. In the past decade, photothermal therapy that employs heat generated from the absorbed optical energy by conjugated polymers as light-absorbing agents has attracted great attention due to many of their advantages such as high specificity, minimal invasiveness, low toxicity to normal tissues, and strong anti-tumor efficacy.

The very first trial of using conjugated polymers for *in vivo* imaging was reported by Kwon^[187] (**Figure 1.2**). They synthesized cyanovinylene-backed polymer dots (cvPDs) via *in situ* colloidal polymerization to image sentinel lymph node (SLN). The emission of the polymer dots can be easily tuned from visible to near infrared range by using different monomers. The NIR-cvPDs exhibit broadband absorption and red-to-NIR emission peaking at 693 nm. In contrast to majority of chromophores that exhibit serious aggregation-induced quenching, the CP dots in their study can maintain a quantum efficiency of 21%. Remarkably, the NIR-cvPDs are so bright that when injected into a mouse paw, not only the axillary lymph nodes but also the lymphatic vessels can be visualized by the naked eye.

The followed up studies were more focused on *in vivo* tumor imaging with conjugated polymers. Most researchers take advantages of FRET to tune the emission to the NIR for improved tissue penetration depth and reduced autofluorescence background by combining conjugated polymer donor and acceptor together into nanoparticles, either with a donor conjugated polymer

and an acceptor conjugated polymer^[188] (**Figure 1.3**) or with an intramolecular donor and acceptor segment structured conjugated polymer^[189] (**Figure 1.4**).

Figure 1.2 cvPDs NPs for sentinel lymph node imaging. (a) Colloidal synthesis of cvPDs of various emission wavelengths. (b) Pseudo-color NIR fluorescence images of a mouse injected intradermally with NIR-cvPDs into the right paw. (c and d) True-color fluorescence photographs of a cvPD-injected mouse taken by a UV handheld lamp. Two SLNs, axillary and lateral thoracic nodes, and lymphatic vessels are indicated by yellow, green arrows and arrowheads, respectively.^[187] Reproduced with permission from ref. 186. Copyright 2010 The Royal Society of Chemistry.

In the polymer design view, deep tissue imaging with polymers which have strong absorption and emission in the NIR range, as well as the improvement of

biocompatibility of conjugated polymers would be the trends of *in vivo* imaging.

Figure 1.3 Schematic of PBdot functionalization and CTX conjugation.^[188] Reproduced with permission from ref. 187. Copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 1.4 Chemical structures of PFBTDBT10 as well as the schematic illustration of PFBTDBT10-loaded folic acid-targeted NPs.^[189] Reproduced with permission from ref. 188. Copyright 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Until now, various inorganic phototherapeutic agents, such as gold nanomaterials and carbon nanomaterials, all with strong optical absorbance in

the NIR tissue-transparency window, have shown encouraging photothermal therapeutic efficiency in preclinical animal experiments. However, those inorganic nanomaterials that are not biodegradable could remain inside the body for long periods of time, raising serious concerns with their potential long-term toxicity, which limits their potential applications in the clinic^[190].

Recently, researches have uncovered that many NIR-absorbing organic materials, such as a number of low-band gap conjugated polymers, with excellent photostability, biodegradability or good biocompatibility, and high photothermal conversion efficiency, can serve as promising photothermal agents for cancer treatment. Moreover, those conjugated polymers could also serve as multifunctional drug carriers for potential applications in combination cancer therapy.

Scheme 1.31 Chemical structure of PCPDTBT, PCPDTBSe and PEDOT:PSS for photothermal therapy.

Till now, among numerous conjugated polymers, only polyaniline (PANI), polypyrrole (PPy)^[191, 192], PEDOT:PSS and PCPDTBT, PCPDTBSe^[193] have been applied to photothermal therapy (**Scheme 1.31**). Low band gap polymers

via facile design strategy would result in more suitable conjugated polymers for photothermal therapy.

1.5. Research motivation and objectives

1.5.1. Research motivation

As DPP moiety is a useful building block to incorporate into π -conjugated polymers for high performance OPVs and OFETs, demands for the synthesis of DPP-based materials are rising very quickly. To overcome existed problems for synthesizing DPP-based π -conjugated small molecules and polymers by conventional transition metal catalyzed cross-coupling reaction, direct arylation by activation of C-H bonds, which has emerged as a new type, greener cross-coupling reaction, is promising to take place of conventional cross-coupling reactions.

The early trials of this novel direct arylation reaction have been proved to be efficient in small molecules with wide substrate scope and relatively high yield, despite the regioselectivity problem remaining unsolved in certain cases ^[194-197]. Applying direct arylation to polymer chemistry, known as direct arylation polymerization (DAP) has been a hot topic in recent years. Although a lot of advances have been achieved over the past few years, there's still no clear conclusion of the optimized reaction conditions of DAP for different monomer combination. At the same time, branching and homocoupling defects were found in some of the conjugated polymers synthesized via DAP, which could

seriously affect the optical and electrical properties of these polymers, and furthermore for the application of these polymers in electronic devices. To date, there's still very limited report about device performance based on polymers synthesized by DAP, especially for high performance electronic devices.

The focus of this thesis is to develop efficient direct arylation polymerization approach to synthesize DPP-based π -conjugated polymers. Moreover, it is also necessary to find out the way to minimize the structural defects in the synthesis of conjugated polymers by DAP with screening of each parameters in the reaction. Furthermore, devices performances of DPP-based conjugated polymers synthesized via DAP should be examined to verify the quality of the polymers and the reliability of direct arylation polymerization compared to conventional cross-coupling reactions, which could lead to wider utilization of DAP in the near future for synthesizing various conjugated polymers as active materials for high performance OPVs and OFETs.

In addition to the applications of DPP-based conjugated polymers in electronic devices, DPP unit is also a good choice of building block for constructing low-band gap polymers with intense NIR absorption, which can be further applied to photothermal therapy applications. With the optimized reaction conditions for the synthesis of DPP-based conjugated polymers by direct arylation polymerization, DPP-based conjugated polymer brushes are expected to be synthesized in a greener way with fewer steps. The target

polymer brushes can absorb the near-infrared light efficiently and further convert the energy to heat for biomedical applications such as cancer therapy.

1.5.2. Research objectives

The overall objectives of this project are to synthesize a series of DPP-based π -conjugated polymers (brushes) via a promising greener direct arylation polymerization approach, which can be further used in either organic electronics or biomedical applications.

1.5.3. Specific aims

- ❖ To optimize direct arylation polymerization conditions for a DPP-based high performance polymers (previously synthesized by Suzuki/Stille coupling) to achieve well-defined structure and high molecular weight.
- ❖ To minimize the structural defects in the conjugated polymers synthesized by direct arylation polymerization with detailed optimization of each reaction parameters (using brominated DPP as the example) to enhance the selectivity of direct arylation polymerization.
- ❖ To synthesize a series of novel DPP-based π -conjugated polymers via DAP with tunable bandgap and study their charge-transport properties in OFETs.

- ❖ To prepare a series of low-band gap DPP-based conjugated polymers (brushes) with strong absorption in the near-infrared range by direct arylation polymerization for the potential biomedical application.

1.6. Outline of the thesis

In this thesis, DPP unit is used as the core to construct polymers structures either with DPP in the conjugated backbones or in the center of the biodegradable polymer for organic electronics and biomedical applications respectively. To synthesize DPP-based conjugated polymers, direct arylation polymerization is intensively studied as an alternative to conventional cross-coupling reactions. Except for the optimization of the reaction conditions for direct arylation polymerization to achieve high molecular weight, structural defects are identified and minimized to realize the full potential of direct arylation polymerization in the near future.

To start with, a DPP-based high performance conjugated polymer was synthesized by direct arylation polymerization with detailed optimization. Regardless of the high molecular weight and well-defined structure for the target polymer achieved from the optimized reaction conditions, homocoupling/branching defects were observed for polymers in some certain case. To have a deeper understanding of the structural defects in direct arylation polymerization, brominated DPP was used to synthesize the hyperbranched conjugated polymers under direct arylation polymerization. By screening of

each reaction parameters in direct arylation polymerization, the ways to minimize the structural defects were summarized. With better knowledge of direct arylation polymerization, a series of DPP- conjugated polymers were then synthesized with well-defined structures and the photophysical, electrochemical and thermal properties of these polymers were studied and the charge-transport properties are investigated in OFETs.

As for the biomedical applications, DPP-labelled biocompatible polymers were synthesized by ring opening polymerization and their photophysical properties were investigated in detail to understand the relationship between the polymer chain length and photophysical properties (especially fluorescent properties). DPP-labelled polymer with long polycaprolactone (PCL) chain was found to retain strong fluorescence in both nanoparticles and solid states, which inspired us to explore its applications cell interfacing and long-term tracking (polymer scaffolds). By combining direct arylation polymerization and ring opening polymerization methods, DPP-based low-band gap conjugated polymer brushes could be obtained in fewer steps and greener way, which could be potential photothermal agents for cancer therapy.

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Declaration

The review of direct arylation polymerization was already published in *Curr. Org. Chem.* **2013**, 17, 999. Section 1.3 about direct arylation polymerization was adapted from this publication.

Chapter 2

Synthesis of balanced ambipolar poly(diketopyrrolopyrrole-alt-tetrafluorobenzene) (PDPPTB) via direct arylation polymerization

After the introduction about conjugated polymers, especially DPP-based conjugated polymers, from synthetic methods to applications, the following work from Chapter 2 to 5 will discuss the synthesis of DPP-based conjugated polymers by direct arylation polymerization which is considered to be an economically saver and ecologically friendly method compared to conventional cross-coupling reaction, and the charge-transport properties of these polymers will be studied in OFETs. In Chapter 6, DPP-based biodegradable polymers will be synthesized and used for cell interfacing and long-term tracking before DPP-based low bandgap conjugated polymer brushes (Chapter 7) are further prepared by direct arylation polymerization from the biodegradable polymers obtained in Chapter 6. The target DPP-based polymer brushes are expected to be excellent photothermal agents for cancer therapy.

To start, in Chapter 2, we optimized the direct arylation polymerization conditions for the synthesis of a known high performance ambipolar DPP-based polymer (PDPPTB), which was synthesized by Stille coupling previously. OFETs performance were examined for the polymers obtained by direct arylation polymerization, which turned out to be comparable to the polymers synthesized by Stille coupling, considering the fact that the devices were fabricated and tested in ambient conditions.

2.1 Introduction

π -Conjugated molecules and polymers have emerged as key materials for next generation of printable flexible electronic devices such as OPVs,^[1-10] OLEDs^[11-14] and OFETs.^[15-17] In particular, DPP-based small molecules and conjugated polymers, due to the well conjugated planar structure and strong π - π stacking of DPP unit, have attracted much attention for high-performance organic electronic devices.^[18-29] Rational molecular design of polymer structures has given high charge-carrier mobility in conjugated polymers consisting of dithiophene-flanked DPP (DTDPP) units.^[30, 31] For example, a record high hole mobility of over $12 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ was achieved with a conjugated polymer consisting of alternating DTDPP and (*E*)-2-(2-(selenophen-2-yl)vinyl)selenophene in the backbone and alkyl side chains with extended branching position that enhances the intermolecular interactions with shortened π - π stacking distances.^[31] On the other hand, a pyridine-flanked DPP-based donor-acceptor copolymer showed a record high electron mobility of $6.3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ in top-gate, bottom-contact OFET devices.^[32]

To date, most of these conjugated polymers are synthesized by conventional transition-metal catalyzed cross coupling reactions, mainly Suzuki^[33] and Stille^[34, 35] couplings. However, both of these two methods suffer from the tedious activation of C-H bonds using organometallic reagents (e.g. BuLi) and low stability of organometallic monomers as well as the formation of toxic byproducts (e.g. alkyl tin derivatives). To overcome these synthetic issues

existing in conventional Suzuki and Stille couplings, direct arylation polycondensation (DAP) by directly activating C-H bonds with palladium catalyst has emerged as a new type of cross-coupling reaction for synthesis of a variety of π -conjugated polymers.^[36-54] DAP shows several advantages over conventional cross-couplings, such as a wider selection of monomers due to non-need of pre-activating monomers with flammable organometallic reagents, fewer reaction steps, and minimal formation of toxic byproducts.^[48]

DAP has been recently used to synthesize DPP-based small molecules and polymers. For instance, Chen's group as well as Marder's group reported synthesis of a series of small molecular DPP derivatives via direct arylation cross coupling.^[55, 56] You and coworkers synthesized a variety of DPP-based low-bandgap polymers via DAP under carefully optimized reaction conditions using $\text{Pd}(\text{OAc})_2$ as the catalyst.^[46] Very recently, Leclerc's group reported synthesis of DPP-based polymers via DAP using Herrmann's catalyst.^[57] The introduction of methyl groups at the β -position of thiophene rings minimizes the potential cross couplings that may lead to undesired branching and/or crosslinking. As a consequence, hole mobility as high as $1.17 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ was achieved in the polymer with a relatively high molecular weight ($M_n = 46 \text{ kDa}$).

Despite recent advances, synthesis of DPP-based n-type or ambipolar conjugated polymers under the scheme of DAP remains rarely studied. Here, we report the synthesis of such polymers (denoted as **PDPPTB**) consisting of alternating DPP and tetrafluorobenzene (**TB**) in the backbone via DAP. The effect of Pd catalysts, monomer structures and solvent on the DAP was

investigated. In particular, cross coupling of non-brominated DPP (**M1**) and dibromo-tetrafluorobenzene (**Br-TB**, **M4**) via DAP with Herrmann's catalyst gave **PDPPTB** with M_n as high as 33.2 kDa and minimal structural defects. The obtained polymers show characteristics of ambipolar charge carrier transport in OFETs fabricated under ambient conditions, with balanced hole and electron mobility as high as $1 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$. Very different results were observed in the cross coupling between dibrominated DPP (**M2**) and tetrafluorobenzene (**TB**, **M3**). The optimized DAP using $\text{Pd}(\text{OAc})_2$ as the catalyst gave **PDPPTB** with M_n up to 20 kDa, but some homocoupling of **M2** was observed. The extent of the homocoupling defects is related to the ligand as well as the solvent involved in the catalysis. Our results suggest that both the molecular structures of monomers and catalytic conditions are crucial in the synthesis of high-quality conjugated polymers via DAP.

2.2. Synthesis, structure analysis and characterization of **PDPPTB** by direct arylation polymerization

The synthetic scheme towards **PDPPTB** via DAP versus conventional Suzuki coupling and Stille coupling is presented in **Scheme 2.1**. We describe first the synthesis of **PDPPTB** (denoted as **P1**) using **M1** and **M4** as the monomers. The reaction was carried out via palladium-catalyzed DAP under five different catalytic conditions which have been mostly used for DAP. The polymerization results are summarized in **Table 1**. The DAP reaction using

Herrmann's catalyst (Entry 1, **Table 1**), which showed the best performance among all of the tested catalytic systems, gave **P1-1** with M_n of 33.2 kDa and a separation yield of 99%. The reaction was fast in the presence of Herrmann's catalyst. The progress of the reaction could be monitored from the color of reaction mixture which gradually changed from red at the beginning to purple (in 0.5 h), to deep blue (in 1 h) and finally deep green (in 3 h). The obtained polymer (**P1-1**) is soluble in common nonpolar organic solvents such as CHCl_3 and shows a maximal absorption peak at 745 nm, accompanied with a shoulder at 677 nm. The similarity of the absorption characteristics of **P1-1** to that of the same polymer ($M_n = 16.3$ kDa) synthesized via Stille coupling by Park et al.^[58] suggests the good C-H selectivity in our DAP under this catalytic condition.

Scheme 2.1 Synthesis of PDPPTB (P1-P4) via direct arylation coupling (a, b), Stille (c) and Suzuki (d) coupling.

In contrast to Herrmann's catalyst, the other four catalytic systems (Entry 2-5, **Table 2.1**) all resulted in products (mainly oligomers) with M_n of less than 10 kDa and relatively low yields. The relatively low molecular weight of **P1-(2-5)** is reflected by the obvious blue-shift of their maximum absorption (**Figure 2.2** and **2.3**) compared to that of **P1-1** (**Table 2.1**). It should be noted that the GPC trace of **P1-3** (**Figure 2.1**) showed a minor fraction of products in the high-molecular weight region (up to 3000 kDa), which is absent in the other three polymers (**P1-2**, **P1-4** and **P1-5**). These results imply the poor C-H selectivity under the catalytic condition in Entry 2, **Table 2.1**, which may result in branching and/or crosslinking in the final products. This issue is discussed in more detail in the following section.

Figure 2.1 GPC traces of **P1-1** to **P1-5** with (a) RI and (b) UV-VIS (600 nm) detector in THF.

Figure 2.2 Normalized absorption spectra of **P1-1** to **P1-5** in CHCl_3 .

Figure 2.3 Normalized absorption spectra of **P1-1**, **P2-2**, **P2-3** and **H-PDPP** in CHCl_3 solution.

Table 2.1. Synthetic results of PDPPTB (**P1**) via DAP with **M1** and **M4**^a

Entry	[Pd]	[P] ^b	Base	Solvent	T (°C)	Yield (%)	<i>M_n</i> ^c (kDa)	<i>M_w</i> / <i>M_n</i> ^c	λ _{abs,max} (nm)
P1-1	Herrmann's catalyst	L1	CS ₂ CO ₃	Toluene	120	99	33.2	2.3	745
P1-2	Pd(OAc) ₂	L2	K ₂ CO ₃	THF	100	75	6.7	2.0	640
P1-3	Pd(OAc) ₂	L3	K ₂ CO ₃	DMAc/xylene	110	30	2.9	129	623
P1-4	Pd(MeCN) ₂ Cl ₂	L1	CS ₂ CO ₃	THF	100	49	3.8	2.0	609
P1-5	Pd ₂ (dba) ₃	L1	K ₂ CO ₃	<i>o</i> -Xylene	100	70	4.3	1.7	614

^a Reaction was carried out at 0.1 M for 24 h.

^b **L1**: P(*o*-MeOPh)₃; **L2**: P^{*t*}Bu₂Me-HBF₄; **L3**: PCy₃-HBF₄.

^c *M_n* and *M_w*/*M_n* were calculated from the GPC traces.

To characterize the chemical structure of **P1** synthesized via DAP, we carried out high-temperature NMR measurements of the five products using C₂D₂Cl₄ as the solvent. The ¹H-NMR spectrum (**Figure 2.6d**) of **P1-1**, compared to those from other batches of **P1** products (**P1-2** to **P1-5**), shows significantly broadened peak at 9.0-9.3 ppm as well as weaker signals (8.76, 7.61 and 7.25 ppm) from chain end groups, consistent with the relatively high *M_n* of **P1-1**. In contrast to **P1-1**, **P1-2** to **P1-5** (**Figure 2.6** and **2.7**) all show well-resolved narrow and sharp peaks the aromatic ranges of their ¹H-NMR spectra, consistent with their low molecular weights. In particular, the two peaks at 8.95 (H_A) and 7.83 (H_B) ppm could be assigned to protons in the thiophene rings from **DPP** unit in the conjugated polymer backbone with alternating structures constructed by cross-coupling, and the protons in the end groups from **DPP** unit

could be found at 8.86 ($H_{a'}$), 8.76 ($H_{a''}$), 7.74 ($H_{b'}$) and 7.25 ppm ($H_{b''}$), respectively, together with a doublet peak at 7.61 ppm originated from α -H ($H_{c'}$) in the **DPP** unit at the chain end of the polymers. The relatively high intensity of end group signals in the ^1H -NMR spectra of **P1-2** to **P1-5** indicates that the major components in these samples are oligomers. In addition, an extra peak at 7.41 ppm, which may possibly originate from **M1-M1** homo-coupling, was observed in the ^1H -NMR spectra of both **P1-3** and **P1-5** (Figure 2.7). Similar structural defects of homo-coupling was also reported by other research groups in direct arylation polymerization of thiophene-based monomers.^[59-61]

Scheme 2.2 Synthesis of **TB-DPP-TB** via direct arylation.

To understand the effect of monomer chemical structure on the DAP, we further examined whether **PDPPTB** could be synthesized via DAP using dibromo-DPP (**M2**) and tetrafluorobenzene (**M3**) as the monomers (Scheme 2.1b). Before the synthesis of the polymers by DAP, a model reaction shown in Scheme 2.2 was first carried out between **M2** and **M3** ($n_{M2}: n_{M3}=1:20$) to synthesize a small molecule **TB-DPP-TB** to examine the reactivity of these two

monomers. **TB-DPP-TB** as a model compound with well-defined chemical structure is also helpful for analyzing the chemical structure of **PDPPTB** from the NMR spectra as shown in Figure 2. Under the same reaction condition for the synthesis of **P1-2**, the direct arylation coupling between **M2** and excess **M3** gave **TB-DPP-TB** with an isolated yield of 62%. Besides the major fraction of the target product, a minor fraction of blue and green byproducts which may correspond to oligomers and polymers, respectively, also formed in the reaction. **TB-DPP-TB** showed two absorption peaks at 557 and 591 nm, respectively, and maximum emission at 617 nm (**Figure 2.4**). The ^1H -NMR spectrum (**Figure 2.6c**) of **TB-DTDPP-TB** show two peaks at 8.93 and 7.72 ppm, respectively, which are attributed to the protons in the thiophene units, as well as a multiple peak at 7.06 ppm that can be attributed to the proton from **TB**. These results imply that both **M2** and **M3** are reactive under the catalytic condition in Entry 2, **Table 2.2** to result in the major cross-coupling product (i.e. **TB-DTDPP-TB**).

Figure 2.4 Normalized absorption and emission spectra of **TB-DPP-TB** in CHCl_3 .

Table 2.2 Synthetic results of PDPPTB (**P2**) via DAP with **M2** and **M3**^a

Entry	[Pd]	[P] ^b	Base	Solvent	T (°C)	Yield (%)	<i>M_n</i> ^d (kDa)	<i>M_w</i> / <i>M_n</i> ^d	λ _{abs,max} (nm)
P2-1	Herrmann's catalyst	L1	Cs ₂ CO ₃	Toluene	120	- ^c	- ^c	- ^c	- ^c
P2-2	Pd(OAc) ₂	L2	K ₂ CO ₃	THF	100	83	31.0	48	731
P2-3	Pd(OAc) ₂	L3	K ₂ CO ₃	DMAc/ xylene	110	45	80.0	280	741
P2-4	Pd(MeCN) ₂ Cl ₂	L1	Cs ₂ CO ₃	THF	100	- ^b	- ^b	- ^c	- ^c
P2-5	Pd ₂ (dba) ₃	L1	K ₂ CO ₃	<i>o</i> -Xylene	100	- ^c	- ^c	- ^c	- ^c

^a Reaction was carried out at 0.1 M concentration for 24 h.

^b **L1**: P(*o*-MeOPh)₃, **L2**: P^tBu₂Me-HBF₄, **L3**: PCy₃-HBF₄.

^c No polymers was obtained for further characterization.

^d *M_n* and *M_w*/*M_n* were calculated from the GPC traces.

The results of polymerization between **M2** and **M3** (*n*_{M2}: *n*_{M3} = 1:1) under a series of commonly used catalytic conditions for DAP are summarized in **Table 2**. Polymeric products were obtained only when Pd(OAc)₂ (Entry 2 and 3, **Table 2.2**) was used as the catalyst. However, multiple broad peaks in the very high *M_n* region, which presumably correspond to branching and/or crosslinking in the products, appeared in the GPC traces of both **P2-2** and **P2-3** (**Figure 2.5**). The extent of branching/crosslinking is more significant in **P2-3** than in **P2-2**. The estimated *M_n* of **P2-2** and **P2-3** from the GPC traces was 28 and 80 kDa, respectively, with a high polydispersity (*M_w*/*M_n*) for each of these two polymers.

Very different from the DAP between **M1** and **M4**, the DAP between **M2** and **M3** using Herrman's catalyst (Entry 1, **Table 2.2**), $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (Entry 4, **Table 2.2**), or $\text{Pd}_2(\text{dba})_3$ (Entry 5, **Table 2.2**) did not result in any polymer products at all. The reaction mixture remained dark red/purple over 24 h of the reaction, despite the fact that $\text{Pd}_2(\text{dba})_3$ was efficient to catalyze the polycondensation of 2,7-dibromo-9,9-dioctylfluorene (**Br-OF**) and **TB** via direct arylation coupling.

Figure 2.5 GPC traces of **P2-2** and **P2-3** with (a) RI and (b) UV-VIS (600 nm) detector in THF.

UV-VIS-NIR absorption spectra of **P2-2** and **P2-3** in CHCl_3 solution (**Figure 2.1**) offer further evidence about the nature of the branching/crosslinking structures as observed in GPC (**Figure 2.5**). While the overall absorption feature of **P2-2** is resembling to that of **P1-1**, a slight (14 nm) blue shift of the maximum absorption peak (at 731 nm) and an extra tail in the band-edge absorption extending up to 920 nm were observed. Such red-shift of the band-edge is more significant in **P2-3**, in which the absorption peak at 741 nm is

significantly broadened and the onset absorption is shifted to 980 nm. The additional absorption above 800 nm in both **P2-2** and **P2-3** is most probably attributed to the **M2-M2** homocoupling defects,^[62] which is further investigated below using ¹H-NMR spectroscopy.

To understand the nature of the potential structural defects as observed in GPC traces and UV-VIS-NIR absorption spectra of **P2-2** and **P2-3**, ¹H-NMR spectra of these two polymers were acquired in C₂D₂Cl₄ at 100 °C (**Figure 2.6-f-g**). The signals of **P2-2** in the aromatic region (6.0-9.5 ppm), except for an extra small peak at 7.41 ppm (H_{B'}) that is attributed to **M2-M2** homocoupling defects, are similar to those of **P1-1**. In contrast to **P2-2**, **P2-3** shows a much more intense peak at 7.41 ppm (H_{B'}) in the ¹H-NMR spectrum (**Figure 2.6g**). These results, consistent with the GPC (**Figure 2.5**) results and UV-VIS-NIR absorption spectra (**Figure 2.1**), further confirm that the structural defects are largely caused by **M2-M2** homocoupling. Such homocoupling defects are more significant in **P2-3** than in **P2-2**, resulting in red-shift of the band-edge absorption.

Scheme 2.3 Synthesis of **H-PDPP** by direct arylation polymerization.

Figure 2.6 Aromatic range of ^1H -NMR spectra of (a) M1, (b) M2, (c) TB-DPP-TB, (d) P1-1, (e) P1-2, (f) P2-2, (g) P2-3 and (h) H-PDPP in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 $^\circ\text{C}$.

Figure 2.7 The aromatic range of ¹H-NMR (300 MHz) spectra of (a) **P1-3**, (b) **P1-4** and (c) **P1-5** in C₂D₂Cl₄ at 100 °C.

To further prove that peaks at 7.41 and 8.84 ppm in **Figure 2.6-(f-g)** are attributed to the homocoupling defects, a DPP-homopolymer (**H-PDPP**) with a M_n of 21.6 kDa was synthesized by direct arylation polymerization (**Scheme 2.3**). From the ¹H-NMR spectrum of this polymer (**Figure 2.6h**), two major peaks ($H_{A'}$ and $H_{B'}$ located at 8.84 and 7.41 ppm, respectively) are assigned to the protons in the thiophene units in the conjugated backbones, while other

small peaks can be assigned to the end groups. The structural analysis of **H-PDPP** again proved that **M2-M2** homocoupling defects do exist in **P2-2** and **P2-3**. In addition, the absorption spectrum of **H-PDPP** showed significant red-shift up to 150 nm compared to **P2** (**Figure 2.1**), further suggesting that the red shift of the absorption in both **P2-2** and **P2-3** compared to that of **P1-1** could be majorly attributed to the **M2-M2** homocoupling.

Scheme 2.4 Possible structural defects (branching/homo-coupling) in **PDPPTB** obtained by DAP.

The results (UV-VIS-NIR absorption, GPC, and NMR spectra) described above for **P1**, **P2** and **H-PDPP** indicate that **M2** is more susceptible than **M1** to cause either homocoupling or branching side reactions, which underlies the important role of monomer structure in synthesis of high-quality conjugated polymers via DAP. It should be noted that the potential branching and/or

crosslinking from the β - and/or γ -proton of the thiophene groups in **M2** (Scheme 2.4), as observed in the GPC traces (Figure 2.5) but not distinguishable from the **M2-M2** homocoupling defects in the NMR spectra (Figure 2.6 and 2.7), may also contribute to the red-shift of the band-edge absorption shown in Figure 1. Nevertheless, further investigating the structural characteristics of these branching/crosslinking defects, for example, by measuring the viscosity of the polymers, is needed before a clear conclusion is reached.

To further identify the chemical structure of **PDPPTB** synthesized above via DAP, we tried to synthesize the same polymer via both Stille coupling and Suzuki coupling as shown in Scheme 2.1c and 2.1d. Nevertheless, the reaction between **M4** and **M5** via Suzuki coupling in presence of $\text{Pd}_2(\text{dba})_3$ and PPh_3 did not result in any polymeric products at all, which was probably due to the deborylation of the electron-rich thiophenes adjacent to the **DPP** monomer.^[63] When a strong ligand, $t\text{Bu}_3\text{P}$, was used together with $\text{Pd}_2(\text{dba})_3$ in the Suzuki coupling, **P4** was obtained with a yield of 58%. However, significant homocoupling between **M5** monomers was observed from both the peak at 7.41 ppm in the NMR spectrum (Figure 2.9) as well as the significant red-shift in the UV-VIS-NIR absorption spectrum (Figure 2.10).

Figure 2.8 GPC traces of **P3** with RI and UV (600 nm) detector.

Figure 2.9 ^1H -NMR spectra of **PDPPTB (P4)** synthesized by Suzuki coupling.

Figure 2.10 Normalized absorption spectra of **P4** in CHCl_3 .

On the other hand, Park et al.^[58] reported the synthesis of **PDPPTB** via Stille coupling in a microwave reactor, which gave polymers with M_n as high as 16.3 kg mol⁻¹ and M_w/M_n of 1.79. However, our efforts to synthesize **PDPPTB** via Stille coupling through a similar synthetic route (**Scheme 1c**) using thermostatic oil bath as the heating source only resulted in oligomers with M_n of 3400 ($M_w/M_n=1.8$).

The results described above demonstrate that our optimized DAP involving **M1** and **M4** as the monomers and Herrmann's catalyst, compared to conventional Stille coupling and Suzuki coupling, leads to polymer products (i.e. **P1-1**) with better quality (i.e. higher M_n , and less structural defects) in fewer synthetic steps without use of organometallic reagents.

2.3. OFETs performance of PDPPTB

P1-1 with the highest molecular weight and well-defined structure was used to fabricate OFETs to examine the quality of this polymer for electronic devices. The electron and hole mobilities of this polymer were investigated using bottom-gate/top-contact device architecture with gold as the source/drain electrode, heavily n-doped silicon as the gate electrode, and SiO₂ as the dielectric layer. The device annealed at 250 °C showed balanced electron and hole mobility of $1 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ (**Figure 2.11**), whereas the device annealed at 280 °C exhibited n-type dominated ambipolar behavior with a

higher electron mobility of $3 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ and a slightly lower hole mobility of $8 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ (Figure 2.12).

Figure 2.11 Performance of a transistor based on **P1-1** annealed at 250 °C. (L = 200 μm, W = 4.0 mm) OFET transfer plots of current versus V_G at (a) negative source-drain bias ($V_{DS} = -80$ V) and (b) at positive source-drain bias ($V_{DS} = 80$ V). Current-voltage output plot as a function of V_G (c) at negative source-drain bias and (d) at positive source-drain bias.

The tendency of increasing n-type dominated properties of **PDPPTB** with increasing annealing temperature was consistent with the previous reported results,^[58] although the mobility of our devices fabricated and tested under

ambient conditions was slightly lower. Further improvement of the charge carrier mobility is possible by careful optimization of the devices, for example, better surface passivation of Si/SiO₂ surfaces and/or adoption of “top-gate, bottom-contact” device configuration^[32] that is more durable against surface traps and other environmental factors such as oxygen and humidity.

Figure 2.12 Performance of a transistor based on **P1-1** annealed at 280 °C. ($L = 200$ μ m, $W = 4.0$ mm) OFET transfer plots of current versus V_G at (a) negative source-drain bias ($V_{DS} = -80$ V) and (b) at positive source-drain bias ($V_{DS} = 80$ V). Current-voltage output plot as a function of V_G (c) at negative source-drain bias and (d) at positive source-drain bias.

Table 2.3 Summary of the device performance of **P1-1** based OFETs at different annealing temperature.

Polymer	Annealing temperature (°C)	$\mu_{h,avg}$ (cm ² V ⁻¹ s ⁻¹)	$M_{e,avg}$ (cm ² V ⁻¹ s ⁻¹)	On/off ratio
P1-1	250	0.01	0.01	10 ² - 10 ³
	280	0.008	0.03	10 ² - 10 ³

2.4. Conclusions

In conclusion, we have presented the synthesis of **PDPPTB** via DAP using two different combinations of **DPP** and **TB** derivatives as the monomers. Our optimized DAP condition gave **PDPPTB** with relatively higher molecular weight (M_n up to 33.2 kDa), minimal structural defects, and ambipolar charge transport behaviour with mobility as high as $1 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ in OFET devices fabricated and tested under ambient conditions. Our results show that the rational selection of monomers as well as catalytic systems are crucial in the synthesis of conjugated polymers via DAP to obtain high-quality polymers with minimal structural defects such as homocoupling and branching/crosslinking.

2.5. Experimental Section

2.5.1. Materials and characterization

All reagents were obtained from commercial suppliers and used without further purification, including solvents as well. 2,5-bis(2-octyldodecyl)-3,6-bis(thien-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (**DPP**),^[28] 2,5-bis(2-octyldodecyl)-3,6-bis(5-bromothien-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (**Br-DPP**),^[28] 2,5-Bis(2-octyldodecyl)-3,6-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-yl]-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**B-DPP**)^[64] and 2,3,5,6-tetrafluoro-1,4-phenylene(bis(triethyltin)) (**Sn-TB**)^[58] was prepared according to the established method. Gel permeation chromatography (GPC) measurement were carried out on Agilent 1260 Infinity system using THF as eluent (1 mL/min) and polystyrene as standards at 30 °C with RI and UV (600 nm) detector. UV-Vis absorption spectra were recorded on Shimadzu UV-1800 spectrophotometer. ¹H-NMR spectra were measured on a Bruker Avance II 300 MHz spectrometer in C₂D₂Cl₄ at 100 °C.

2.5.2. General synthesis procedure for PDPPTB (P1 and P2) via DAP

Under nitrogen atmosphere, a mixture of [**M1** (0.1 mmol) and **M4** (0.1 mmol) (for synthesis of **P1**)] or [**M2** (0.1 mmol) and **M3** (0.1 mmol) (for synthesis of **P2**)], palladium source, ligand, base, PivOH and solvent (1 mL) was added in a

reaction vial with a magnetic stirring bar. The vial was sealed with an aluminium cap with PTFE/Silicone septum and then heated in a preheated oil bath for 24 hours. After being cooled to room temperature, the reaction mixture was dissolved with CHCl_3 , concentrated with rotary evaporator, added dropwise to 150 mL of ice methanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with methanol, hexane and chloroform sequentially. The chloroform fraction was concentrated and precipitated into 150 mL of ice methanol. The precipitates were collected by filtration and dried under vacuum before further characterization.

Entry 1 in **P1** and **P2**: Herrmann's catalyst (2% mol), $\text{P}(o\text{-MeOPh})_3$ (8% mol), Cs_2CO_3 (2.3 equiv), PivOH (30% mol) and toluene (1 mL) at 120 °C. Entry 2 in **P1** and **P2**: $\text{Pd}(\text{OAc})_2$ (10% mol), $\text{P}^t\text{Bu}_2\text{Me-HBF}_4$ (20% mol), K_2CO_3 (3.0 equiv), PivOH (1.0 equiv) and THF (1 mL) at 100 °C.

Entry 3 in **P1** and **P2**: $\text{Pd}(\text{OAc})_2$ (10% mol), $\text{PCy}_3\text{-HBF}_4$ (20% mol), K_2CO_3 (3.0 equiv), PivOH (1.0 equiv) and DMAc/xylene (1:1 (v/v), 1 mL) at 110 °C.

Entry 4 in **P1** and **P2**: $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (1% mol), $\text{P}(o\text{-MeOPh})_3$ (1% mol), Cs_2CO_3 (3.0 equiv), PivOH (1.0 equiv) and THF (1 mL) at 100 °C.

Entry 5 in **P1** and **P2**: $\text{Pd}_2(\text{dba})_3$ (5% mol), $\text{P}(o\text{-MeOPh})_3$ (10% mol), K_2CO_3 (5 equiv), PivOH (50% mol) and *o*-xylene (1 mL) at 100 °C.

2.5.3. Synthesis procedure for PDPPTB (P3) via Stille coupling

Br-DPP (0.1 mmol), **Sn-TB** (0.1 mmol), and PPh_3 (0.01 mmol) in a mixed solvent of toluene (2.5 mL) and DMF (0.5 mL) were added in a Schlenk tube with a magnetic stirring bar and purged with nitrogen for 30 min. $\text{Pd}_2(\text{dba})_3$ (0.005 mmol) was then added, and the mixture was stirred for 72 h at 160°C in the oil bath. Afterwards the same purification procedure were applied as for **P1** and **P2**.

2.5.4. Synthetic procedure for PDPPTB (P4) via Suzuki coupling

B-DPP (0.1 mmol), **Br-TB** (0.1 mmol), K_2CO_3 (0.25 mmol, 2M in H_2O), $t\text{Bu}_3\text{P}$ (0.01 mmol, 10% in hexane) were dissolved in 2.5 mL THF in a schelnk tube with a magnetic stirring bar and purged with nitrogen for 30 min. $\text{Pd}_2(\text{dba})_3$ (0.005 mmol) was then added, and the mixture was stirred for 24 h at 100°C in the oil bath. Afterwards the same purification procedure were applied as for **P1** and **P2**.

2.5.5. Synthetic procedure for DPP-homopolymer (H-PDPP) via DAP

Under nitrogen atmosphere, a mixture of **M1** (0.1 mmol), **M2** (0.1 mmol), Herrmann's catalyst (0.002 mmol), $\text{P}(o\text{-MeOPh})_3$ (0.008 mmol), Cs_2CO_3 (0.23 mmol), and PivOH (0.03 mmol) was dissolved in toluene (1 mL) in a reaction vial with a magnetic stirring bar. The vial was sealed with an aluminium cap

with PTFE/silicone septum and then heated in a preheated oil bath at 120 °C for 24 hours. After being cooled to room temperature, the reaction mixture was dissolved in CHCl_3 , concentrated with rotary evaporator, added dropwise to 150 mL of ice methanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with methanol, hexane and chloroform sequentially. The chloroform fraction was concentrated and precipitated into 150 mL of ice methanol. The precipitates were collected by filtration and dried under vacuum before further characterization.

2.5.6. Device fabrication

Bottom-gate/top-contact OFETs were fabricated using heavily doped Si wafer as the bottom gate electrode with 300 nm of SiO_2 layer as the gate dielectric. Gold source and drain electrodes (60 nm) were patterned by the vacuum thermal evaporation. The substrate was cleaned in acetone and isopropanol, and dried on the hot plate at 80 °C, followed by treating with plasma for 15 min. After that, the substrate was immersed in the ODTS solution (Toluene as the solvent) overnight, rinsed with toluene to remove extra ODTS and dried on the hot plate at 110 °C. The polymers were dissolved in chlorobenzene at a concentration of 10 mg/mL by stirring for four days. The polymer films were spin-cast at 2000 rpm and annealed at a designated temperature for 15 min. Finally, gold electrode with 60 nm was thermally evaporated in vacuum through a shadow mask with the following dimension

(length (L) = 200 μm and channel width (W) = 4.0 mm). The field effect mobilities were extracted from the saturation regime using the relationship $\mu_{\text{sat}} = (2I_{\text{DS}}L)/(WC(V_G - V_{\text{th}})^2)$, where I_{DS} denotes the saturation drain current, C is the capacitance ($C_i = 10.8 \times 10^{-9} \text{ F} \cdot \text{cm}^{-2}$) of SiO_2 dielectric, V_G is the gate bias, and V_{th} is the threshold voltage.

2.6. References

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Declaration

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Chapter 3

Synthesis of hyperbranched low-bandgap DPP homopolymers via direct arylation

In Chapter 2, the reaction condition for direct arylation polymerization between DPP and TB were discussed in detail. It was found that when brominated DPP (Br-DPP) was involved as one monomer in direct arylation polymerization, there's a big chance to obtain polymers with structural defects, including homocoupling and branching. To have a deep understanding on the origin of these structural defects, in Chapter 3, Br-DPP alone was used as a model monomer in various reaction conditions to obtain hyperbranched DPP polymers by direct arylation polymerization. And the relationship between each reaction parameter and the degree of structural defects was investigated by NMR and UV-Vis analysis.

3.1. Introduction

Hyperbranched polymers have been utilized in industry as additives and coating, and also applied to scientific areas such as sensors, catalysts and therapeutics.^[1-3] The synthetic methodology of hyperbranched polymers includes polycondensation, ring-opening polymerization, proton-transfer polymerization and some other combined polymerization methods.^[1, 2]

Conjugated hyperbranched polymers, an emerging kind of hyperbranched polymer, have been attracting more and more attention as novel optical, electronic and magnetic materials.^[3-5] Compared to linear conducting polymers, which are usually all para-linked, hyperbranched conjugated polymers are almost always meta-connected and have a relatively poor conjugation. As a

result, very different properties are found for the hyperbranched conjugated polymers than their linear counterparts.

Direct arylation polycondensation (DAP) by activating C-H bonds with palladium catalyst has emerged as a new type of cross-coupling reaction for synthesis of a variety of π -conjugated polymers.^[6-14] Compared to traditional cross-coupling reactions, DAP shows several advantages such as few reaction steps and less toxic byproducts. However, it is also worth to note that some structural defects such as branching or homocoupling were found in some cases of DAP.^[11, 15]

Although these structural defects in DAP could lead to ill-defined structure in the conjugated polymer backbones and would further affect the properties of these polymers as well as their performance in electronic devices, they also offer an opportunity to synthesize hyperbranched conjugated polymers using this newly established method. For example, K. Luscombe et al.^[16] reported one-pot synthesis of branched poly (3-alkylthiophene)s (b-P3AT)s via DAP and the degree of branching (DB) could be tuned by varying reaction conditions. B. C. Thompson et al.^[9] also pointed out the possibility of hyperbranched P3HT formed in the synthesis of regioregular P3HT with parameters such as reaction temperature, reaction time as well as catalyst loading.

As mentioned before the introduction of Chapter 3, structural defects in direct arylation polymerization was observed when Br-DPP was involved as a monomer, and the degree of structural defects varied with the change of

reaction conditions. And if Br-DPP was the only monomer for direct arylation polymerization, it could be possible to obtain hyperbranched DPP based conjugated polymers with different branching density.

Herein, we present a facile synthesis of hyperbranched thiophene-flanked dieketopyrrolopyrrole (TDPP)-based polymer (h-PTDPP) by direct arylation polycondensation method. Based on our previous work on the synthesis of PDPPTB, serious branching or/and homocoupling defects were observed when brominated TDPP (Br-TDPP) monomer was used as one building block. We expect that when this monomer is treated under DAP condition, h-PTDPP will be obtained and DB could be finely tuned by different combinations of palladium catalyst, ligand, solvent, temperature, base and additive. And we further explore the relationship between DB of h-PTDPP and polymers properties, including absorption spectra, bandgap, film morphology as well as performance in electronic devices.

3.2. Synthesis of hyperbranched DPP homopolymer (h-PTDPP) by direct arylation polymerization

To date, despite the fast development of direct arylation polymerization in the past few years, deeper understanding over the choice of catalytic system for direct arylation polymerization is still a mystery. There's still no obvious guideline for the selection of catalytic system for different monomers that are

involved in the direct arylation polymerization. More importantly, structure defects (both homocoupling and branching) are recognized as one of the most serious weakness compared to conventional cross-coupling reactions, which could affect the properties and furthermore the performance of the polymers in organic electronics. However, this side effect of direct arylation polymerization could be also possibly utilized to construct hyperbranched polymer networks, in which both homocoupling and branching are involved. To demonstrate the possibility of this concept, hyperbranched DPP (h-PTDPP) polymers were synthesized by direct arylation polymerization from Br-TDPP monomer alone (**Scheme 3.1**). Different reaction parameters, such as catalytic system (**Table 3.1**), temperature (**Table 3.2**), solvent (**Table 3.3**), phosphine ligand (**Table 3.4**) as well as additive (**Table 3.5**) were extensively explored to study the relationship between the selection of reaction conditions and the properties of resulting h-PTDPP with various molecular weight and branching density. The following sections will discuss each factor in direct arylation polymerization separately.

Scheme 3.1 Synthetic route of **h-PTDPP** via direct arylation polymerization.

3.2.1. Effect of catalytic system

Table 3.1 h-PTDPP synthesized by DAP with different catalytic system. ^a

Entry	[Pd]	[P] ^b	Base	Solvent	T (°C)	Yield (%)	<i>M_n</i> (KDa)
1	Pd(OAc) ₂	P1	K ₂ CO ₃	THF	100	84	15.6
2	Pd(OAc) ₂	P2	K ₂ CO ₃	DMAc/ Xylene	110	77	26.0
3	Herrmann's catalyst	P3	Cs ₂ CO ₃	Toluene	120	- ^c	- ^d
4	Pd(MeCN) ₂ Cl ₂	P3	Cs ₂ CO ₃	THF	100	- ^c	- ^d
5	Pd ₂ (dba) ₃	P3	K ₂ CO ₃	<i>o</i> -Xylene	100	- ^c	- ^d

^a DAP condition: Catalyst, ligand, base, PivOH (1 eq) at 0.1 mmol concentration in a certain solvent at different temperature for 24 h.

^b P1: P^tBu₂Me·HBF₄; P2: PCy₃·HBF₄; P3: P(*o*-MeOPh)₃.

^c No polymers were obtained.

^d Not measured.

The study of catalytic system is to find out a typical reaction condition, upon which further modification of different reaction parameters could be made. In the five typical catalytic systems in our study which were chosen from the previous research of direct arylation polymerization, success polymerization only occurred within first two entries in **Table 3.1**, using $\text{Pd}(\text{OAc})_2$ as the catalyst with either $\text{P}^t\text{Bu}_2\text{Me-HBF}_4$ or $\text{PCy}_3\text{-HBF}_4$ ligand. The process of polymerization could be easily monitored by the colour change of the reaction mixture, and no obvious colour change was observed for Entry 3-5 in **Table 3.1**. And it is interesting that the polymers obtained from Entry 1 and 2 could reach very high molecular weight of 15.6 and 26.0 KDa respectively. We then followed to examine other effects in direct arylation polymerization based on the reaction condition for Entry 1 in **Table 3.1**.

3.2.2. Temperature effect

Considering the different reactivity for the activation of C-H bonds in direct arylation polymerization, it is easy to understand that the polymerization of Br-TDPP by DAP is obviously temperature-dependent. Based on the reaction conditions for Entry 1, when the reaction temperature was decreased from 100 to 90 °C (**Table 3.2**, Entry 6), the molecular weight of resulting polymer was decreased to 11.9 KDa with a significant lower yield of 55 %. And almost no polymer was formed at ever lower temperature (80 °C) (**Table 3.2**, Entry 7).

This trend is reasonable as the reactivity of Br-TDPP should be decreased at lower reaction temperature.

Table 3.2 h-PTDPP synthesized by DAP at different temperature. ^a

Entry	T (°C)	Yield (%)	<i>M_n</i> (KDa)	<i>λ_{abs, max}</i> (nm)
1	100	84	15.6	784
6	90	55	11.9	783
7	80	Trace	- ^b	- ^b

^a DAP condition: Pd(OAc)₂ (5 %), P^tBu₂Me-HBF₄ (10 %), K₂CO₃ (3 eq), PivOH (1 eq) in THF at 0.1 mmol concentration at different temperature for 24 h.

^b Not measured.

3.2.3. Solvent effect

Solvent, especially polarity of the solvent was found to be crucial in the optimization for direct arylation polymerization conditions. For example, Kanbara et al. studied the effect of solvent in direct arylation polymerization for thiophene derivatives. For electron-deficient thiophenes, toluene was found to be more effective; while dimethylacetamide (DMAc) was a better choice for electron-rich thiophenes.^[19] This solvent effect over the monomers with different electronic nature in direct arylation polymerization could be explained that the rate-determining step is depended on the monomer and the electronic

properties of the monomer could contribute to the change of reaction rate, and further affect the final conjugated polymers obtained by direct arylation polymerization.

Table 3.3 h-PTDPP synthesized by DAP with different solvent. ^a

Entry	Solvent	Polarity index	Yield (%)	<i>M_n</i> (KDa)	$\lambda_{\text{abs, max}}$ (nm)
1	THF	4.0	84	15.6	784
8	Toluene	2.4	5	2.7	654
9	<i>o</i> -Xylene	2.5	21	4.3	679
10	Mesitylene	-	4	2.9	639
11	1,4-Dioxane	4.8	57	5.9	705
12	Anisole	-	77	5.6	712
13	DMAc	6.5	16 ^b	4.6	629
14	DMF	6.4	30 ^c	6.6	727

^a DAP condition: Pd(OAc)₂ (5 %), P^tBu₂Me-HBF₄ (10 %), K₂CO₃ (3 eq), PivOH (1 eq) in solvent at 0.1 mmol concentration at 100 °C for 24 h.

^b Insoluble part after Soxhlet extraction: 81 %;

^c Insoluble part after Soxhlet extraction: 56 %.

In our study, Br-TDPP, which is a more complicated monomer compared to substituted thiophenes, was then also explored in direct arylation polymerization with several solvents of different polarity (**Table 3.3**). The overall trend is that higher molecular weight of h-PTDPP was obtained with increased polarity from toluene, *o*-xylene, mesitylene, 1,4-dioxane, anisole to THF. When highly polar solvents, DMAc and DMF were used in the reaction, most products were found to be insoluble in hot CHCl₃, probably due to the formation of cross-linked structures. Only 16 % and 30 % soluble polymeric product was obtained for DMAc and DMF as the solvent, respectively. It could be concluded that the reactivity of direct arylation polymerization for Br-TDPP is generally higher with increased polarity of the solvent, but cross-linked polymer networks could be formed in highly polar solvent as well.

3.2.4. Ligand effect

Phosphine ligand also played an important role in direct arylation polymerization. Ozawa et al.^[20] found that for the synthesis of conjugated polymers with dithienosilole and thienopyrroledione units by direct arylation polymerization, P(*o*-MeOPh)₃ ligand could result in insoluble polymeric product, while P(*o*-Me₂NPh)₃ ligand provided no polymer at all. It is very interesting that by combining these two phosphine ligands, well-defined alternating conjugated polymers with molecular weight up to 25.8 KDa were

achieved. Although the secret behind this phenomenon is still unknown yet, it is worthy to further study the ligand effect on direct arylation.

Table 3.4 h-PTDPP synthesized by DAP with different ligands.^a

Entry	Ligand	Yield (%)	M_n (KDa)	$\lambda_{\text{abs, max}}$ (nm)
1	P ^t Bu ₂ Me-HBF ₄	84	15.6	784
15	PPh ₃	9 ^b	4.6	703
16	PCy ₃ -HBF ₄	14	5.4	723
17	P(o-tolyl) ₃	- ^c	- ^d	- ^d
18	P(o-MeOPh) ₃	Trace	- ^d	- ^d
19	dppe	97	32.0	808, 897
20	dppb	93	11.0	780
21	dppf	- ^c	- ^d	- ^d
22	-	- ^c	- ^d	- ^d

^a DAP condition: Pd(OAc)₂ (5 %), ligand (10 %), K₂CO₃ (3 eq), PivOH (1 eq) in THF at 0.1 mmol concentration at 100 °C for 24 h.

^b Insoluble part after Soxhlet extraction: 90 %;

^c No polymers were obtained.

^d Not measured.

Various phosphine ligands were screened for DAP of Br-TDPP as shown in **Table 3.4**. The very simple phosphine ligand PPh_3 showed similar results to direct arylation polymerization carried out in highly polar solvents, giving insoluble materials up to 90 % yield. Other monodentate phosphine ligands (Entry 16-18, **Table 3.4**) showed low reactivity in DAP of Br-TDPP giving h-PTDPP of molecular weight below 5.4 KDa, while bidentate phosphine ligand, 1,2-bis(diphenylphosphino) ethane (dppe) surprisingly converted Br-TDPP to h-PDTPP at 97% yield with very high molecular weight of 32.0 KDa. The bulkier bidentate phosphine ligand such as 1,2-bis(diphenylphosphino) butane (dppb) led to slightly lower yield with moderate molecular weight of 11.0 KDa. And the even bulkier ligand 1,2-bis(diphenylphosphino) ferrocene (dppf) didn't give any polymers at all. These findings suggested that less bulky phosphine ligands tend to have higher reactivity in DAP of Br-TDPP, which is consistent with the previous study by Ozawa about the ligands effect on direct arylation of heteroarenes.^[21]

3.2.5. Additive effect

Finally, additive was selected as another factor in direct arylation polymerization for a complete screening of reaction conditions. Thompson et al. suggested that a bulkier carboxylate additive (neodecanoic acid in their study) could help to suppress the β -defects (branching) in the synthesis of poly(3-hexylthiophene) (P3HT) by direct arylation polymerization.^[9]

Several different carboxylate additive with different acidity and bulkiness were compared with most widely used PivOH in DAP (**Table 3.5**). Both acetic acid (AcOH) and 1-adamantanecarboxylic acid showed lower reactivity (monitored by the colour change of the monomers) as well as lower molecular weight below 6 KDa at moderate yields. CF₃COOH, which is a very strong acid, however gave no polymer at all. Direct arylation polymerization carried out without additive or even without ligand both ended with no formation of polymers.

Table 3.5 h-PTDPP synthesized by DAP with different ligands.^a

Entry	Additive	Yield (%)	<i>M_n</i> (KDa)	$\lambda_{\text{abs, max}}$ (nm)
1	PivOH	84	15.6	784
23	AcOH	56	4.3	694
24	CF ₃ COOH	- ^b	- ^c	- ^c
25	1-Adamantanecarboxylic acid	69	5.8	724
26	-	- ^b	- ^c	- ^c
27	- (no ligand)	- ^b	- ^c	- ^c

^a DAP condition: Pd(OAc)₂ (5 %), P^tBu₂Me-HBF₄ (10 %), K₂CO₃ (3 eq), Additive (1 eq) in solvent at 0.1 mmol concentration at 100 °C for 24 h.

^b No polymers were obtained.

^c Not measured.

The detailed discussion on DAP to synthesize h-PTDPP showed that Br-TDPP monomer is reactive under most reaction conditions for DAP. h-PTDPP with higher molecular weight could be obtained in high temperature, polar solvent, less bulkier phosphine ligand as well as carboxylate additive. This study on the other hand also provided some insights on the strategies to minimize either homocoupling or branching defects when Br-TDPP was involved in the synthesis of alternating conjugated polymers as a monomer by direct arylation polymerization.

3.3. Characterization of h-PTDPP synthesized by direct arylation polymerization

To further study h-PTDPP synthesized above, three **h-PTDPP** polymers with molecular weight of over 10 KDa were selected from Entry 1, 2 and 19, denoted as **h-PTDPP-1**, **h-PTDPP-2** and **h-PTDPP-3**. **h-PTDPP-1** was obtained with a M_n of 15.6 KDa and a small bump at lower elution time could be observed in the GPC traces (**Figure 3.1**). The intensity of the bump was greatly increased for **h-PTDPP-2** and **h-PTDPP-3** with PCy₃-HBF₄ and dppe as the ligand respectively, which suggested a possible high degree of branching in these two polymers. And the absorption spectra of **h-PTDPP-3** showed significant red-shift compared to **h-PTDPP-1** and **h-PTDPP-2** (**Figure 3.2**), with maximal absorption peak at 897 nm, suggesting the longest conjugated length for **h-PTDPP-3** among these three hyperbranched DPP polymers.

Table 3.6 Synthetic results of h-PTDPP via direct arylation polymerization

h-PTDPP	[Pd]	[P]	Base	Solvent	T (°C)	<i>M_n</i> (kDa) ^a	<i>λ</i> _{abs, max} (nm)
1	Pd(OAc) ₂	P'Bu ₂ Me-HBF ₄	K ₂ CO ₃	THF	100	15.6	781
2	Pd(OAc) ₂	PCy ₃ -HBF ₄	K ₂ CO ₃	DMAc/ Xylene	110	26.0	793
3	Pd(OAc) ₂	dppe	K ₂ CO ₃	THF	100	32.0	897

^a *M_n* was calculated based on the CHCl₃ fraction of GPC results (whole range from 3 to 10 min).

Figure 3.1 GPC traces of h-PTDPP-1, h-PTDPP-2 and h-PTDPP-3 with (a) RI and (b) UV (600 nm) detector.

Two DPP-based homopolymers **P1** and **P2** were then synthesized via direct arylation polymerization by Herrmann’s catalyst with molecular weight of 45.5 KDa and 21.6 KDa, respectively as model polymers for comparison with h-

PTDPP (**Scheme 3.2**). The small bump observed in the GPC traces of **P1** could be mainly due to the branching at β -position in the thiophene rings of DPP units, as no homocoupling between Br-hTDPP was observed at the same reaction conditions. In contrast, **P2** showed a broad bump in the GPC traces even no homocoupling between Br-TDPP occurred (Entry 3, **Table 3.1**). This could be explained by the introduction of hexyl- group in Br-hTDPP unit that helps to suppress the branching defects when coupled with H-TDPP unit. Interestingly, **P2** showed very similar absorption spectra and close onset absorption to that of **h-PTDPP-3**, suggesting very good conjugation for **h-PTDPP-3**. And electron donating hexyl- group in the 3- position in the thiophene rings helps to raise the HOMO level of **P1**, which resulted in red shift in the absorption spectra as well as a narrow bandgap for **P1** compared to **P2**.

Scheme 3.2 Synthetic route of two model polymers **P1** and **P2** via direct arylation polycondensation.

Figure 3.2 Absorption spectra of **h-PTDPP-1**, **h-PTDPP-2** and **h-PTDPP-3** in CHCl_3 .

We then utilized high temperature NMR to examine the structure of three **h-PTDPP**, **P1** and **P2**. All three **h-PTDPP** showed similar peaks for protons (H_a , H_b) in the conjugated polymer backbones, and also the protons in the end groups from polymers could be observed for peaks at 8.78 ($\text{H}_{a'}$), 8.71 ($\text{H}_{a''}$), 7.60 ($\text{H}_{b'}$) and 7.24 ($\text{H}_{b''}$) ppm. However, protons from branching defects could hardly be observed, although a broad peak only appeared at around 7.0 ppm for **h-PTDPP-2**. Model polymer **P2** showed almost the same NMR spectra in the aromatic range to those for **h-PTDPP-1** and **h-PTDPP-3** (**Figure 3.3**). These results imply that **h-PTDPP-1** and **h-PTDPP-3** may have lower degree of branching, while **h-PTDPP-2** which showed an extra peak at 7.0 ppm could have higher degree of branching. Another model polymer **P1**, however

exhibited different peaks in the aromatic range for protons in the thiophene rings. With the introduction of hexyl- group, H_c from hTDPP unit up-shifted to 8.67 ppm while H_a from TDPP unit down-shifted to 8.93 ppm, and H_b remained at the same position to those in **h-PTDPP** and **P2**.

Figure 3.3 Aromatic range of ^1H -NMR spectra of **Br-TDPP**, **h-PTDPP-1**, **h-PTDPP-2**, **h-PTDPP-3**, **P1** and **P2** synthesized by DAP in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C.

3.4. OFETs performance of h-PTDPP, P1 and P2

The hole mobilities of **h-PTDPP-3**, **P1** and **P2** were investigated using bottom-gate/top-contact device architecture with gold as the source/drain electrode, heavily n-doped silicon as the gate electrode, and SiO₂ as the dielectric layer.

For **h-PTDPP-3**, the transfer curves were quite noisy due to the low current signal and a relatively low hole mobility of $1.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained when annealed at 150 °C. For **P1**, the device annealed at 150 °C showed highest hole mobility of $3.8 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ (**Figure 3.4b**), which is one magnitude higher than that of **h-PTDPP-3**, whereas the device annealed higher temperature exhibited lower hole mobility of 1.6×10^{-4} (200 °C) and 1.6×10^{-5} (250 °C) $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$. This was probably due to the poor films quality annealed at higher temperature, especially when annealed at 250 °C. As for **P2**, which has similar structure to **h-PTDPP-3**, one magnitude higher hole mobilities ($1.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was also observed when **P2** film was annealed at 150 °C.

To understand the effect of film morphology and phase separation upon thermal annealing on the hole mobilities in OFETs studied above, atomic force microscopy (AFM) and X-ray diffraction (XRD) spectroscopy were employed to characterize the thin films of these polymers annealed at different temperatures. The XRD spectra (**Figure 3.5**) of three polymers annealed at 150 °C showed they are all amorphous even after annealing process. The AFM images of **h-PTDPP-3** (**Figure 3.6a**) indicated its smooth nature without

obvious phase separation, whereas both **P1** and **P2** films annealed at 150 °C showed bicontinuous networks (**Figure 3.6b** and **3.6c**) which could contribute to one magnitude higher hole mobilities of **P1** and **P2** when compared to **h-PTDPP-3**.

Figure 3.4 Performance of a transistor based on (a) **h-PTDPP-3**, (b) **P1** and (c) **P2** annealed at 150°C. ($L = 200 \mu\text{m}$, $W = 4.0 \text{ mm}$) OFET transfer plots of current versus V_G at negative source-drain bias ($V_{DS} = -80 \text{ V}$). Current-voltage output plot as a function of V_G at negative source-drain bias.

Table 3.7 Summary of the device performance of **h-PTDPP**, **P1** and **P2** based OFETs annealed at 150 °C.

Polymer	$\mu_{h,avg}$ (cm ² V ⁻¹ s ⁻¹)	V_{th} (V)	On/off ratio
h-PTDPP-3	1.3×10^{-5}	-20	10^1 - 10^2
P1	3.8×10^{-4}	3	10^3 - 10^4
P2	1.1×10^{-4}	8	10^3 - 10^4

Table 3.8 OFETs performance of h-PTDPP-3.

Annealing temperature (°C)	$\mu_{h,avg}$ (cm ² V ⁻¹ s ⁻¹)	V_{th} (V)	On/off ratio
100	2.7×10^{-6}	-8	10^1 - 10^2
150	1.3×10^{-5}	-20	10^1 - 10^2
200	-	-	-
250	2.7×10^{-5}	-23	10^1 - 10^2

Table 3.9 OFETs performance of P1.

Annealing temperature (°C)	$\mu_{h,avg}$ (cm ² V ⁻¹ s ⁻¹)	V_{th} (V)	On/off ratio
100	7.9×10^{-5}	-3	10^2 - 10^3
150	3.8×10^{-4}	3	10^3 - 10^4
200	1.6×10^{-4}	10	10^3
250	1.6×10^{-5}	-1	10^2

Table 3.10 OFETs performance of P2.

Annealing temperature (°C)	$\mu_{h,avg}$ (cm ² V ⁻¹ s ⁻¹)	V _{th} (V)	On/off ratio
100	6.2×10 ⁻⁵	4	10 ²
150	6.7×10 ⁻⁵	10	10 ³
200	1.1×10 ⁻⁴	8	10 ³ -10 ⁴
250	3.6×10 ⁻⁵	4	10 ²

Figure 3.5 XRD spectra of (a) h-PTDPP-3, (b) P1, (c) P2 thin films annealed at R.T. and 150 °C and (d) glass substrate (background of XRD spectra).

Figure 3.6 Tapping mode AFM images of (a) h-PTDPP-3, (b) P1 and (c) P2 thin film annealed at 150 °C on silicon wafers in ambient conditions. (Height images in the left and amplitude images in the right.)

3.5. Conclusion

Hyperbranched TDPP-based polymers (**h-PTDPP**) were synthesized by DAP, and their photophysics properties as well as structures were studied. Different

parameters were examined to minimize the structural defects that could occur in DAP. Two DPP homopolymers were synthesized for comparison with **h-PTDPP**. OFETs performance of a model polymer as well as **h-PTDPP-3** with highest molecular weight among **h-PTDPP** were tested and lower hole mobilities were observed for **h-PTDPP-3** compared to two model polymers, which could be explained by both branching in the polymer backbones as well as poor film qualities of **h-PTDPP-3**.

3.6. Experimental Section

3.6.1. Materials and characterization

All reagents were obtained from commercial suppliers and used without further purification, including solvents as well. 2,5-bis(2-octyldodecyl)-3,6-bis(thien-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione (**H-TDPP**),^[17] 2,5-bis(2-octyldodecyl)-3,6-bis(5-bromothien-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione (**Br-TDPP**)^[17] and 3,6-Bis(5-bromo-4-methylthiophen-2-yl)-2,5-bis(2-hexyldecyl)pyrrolo[3,4-c]pyrrole-1,4-(2*H*,5*H*)-dione (**Br-hTDPP**)^[18] was prepared according to the established method. Gel permeation chromatography (GPC) measurement were carried out on Agilent 1260 Infinity system using THF as eluent (1 ml/min) and polystyrene as standards at 30 °C with RI and UV (600 nm) detector. UV-Vis absorption spectra were recorded on Shimadzu UV-1800 spectrophotometer. ¹H-NMR spectra were measured on a Bruker Avance II 300 MHz spectrometer in C₂D₂Cl₄ at 100 °C.

3.6.2. General synthesis procedure for h-PTDPP via DAP

Under nitrogen atmosphere, a mixture of **Br-TDPP** (0.025 mmol), palladium source, ligand, base, PivOH and solvent (0.25 ml) was added in a reaction vial with a magnetic stirring bar. The vial was sealed with an aluminium cap with PTFE/Silicone septum and then heated in a preheated oil bath for 24 hours. After being cooled to room temperature, the reaction mixture was dissolved with CHCl_3 , concentrated with rotary evaporator, added dropwise to 150 mL of ice methanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with methanol, hexane and chloroform sequentially. The chloroform fraction was concentrated and precipitated into 150 mL of ice methanol. The precipitates were collected by filtration and dried under vacuum before further characterization.

3.6.3. Synthesis procedure for P1 and P2 via DAP

H-TDPP (0.1 mmol), **Br-hTDPP** (0.1 mmol), Herrmann's catalyst (2% mol), $\text{P}(o\text{-MeOPh})_3$ (8% mol), Cs_2CO_3 (2.3 equiv), PivOH (30% mol) and toluene (1 ml) were added in a Schlenk tube with a magnetic stirring bar and purged with nitrogen for 30 min and the mixture was then stirred for 24 h at 120°C in the oil bath. Afterwards the same purification procedure was applied as for **h-PTDPP**.

3.6.4. Device fabrication

Bottom-gate/top-contact OFETs were fabricated using heavily doped Si wafer as the bottom gate electrode with 300 nm of SiO₂ layer as the gate dielectric. Gold source and drain electrodes (60 nm) were patterned by the vacuum thermal evaporation. The substrate was cleaned in acetone and isopropanol, and dried on the hot plate at 80 °C, followed by treating with plasma for 15 min. After that, the substrate was immersed in the ODTS solution (Toluene as the solvent) overnight, rinsed with toluene to remove extra ODTS and dried on the hot plate at 110 °C. The polymers (**h-PTDPP-1**, **h-PTDPP-2**, **h-PTDPP-3**, **P1** and **P2**) were dissolved in chlorobenzene at a concentration of 10 mg/mL by stirring for two days. The polymer films were spin-cast at 2000 rpm and annealed at a designated temperature for 15 min. Finally, gold electrode with 60 nm was thermally evaporated in vacuum through a shadow mask with the following dimension (length (L) = 200 μm and channel width (W) = 4.0 mm). The field effect mobilities were extracted from the saturation regime using the relationship $\mu_{\text{sat}} = (2I_{\text{DS}}L)/(WC(V_G - V_{\text{th}})^2)$, where I_{DS} denotes the saturation drain current, C is the capacitance ($C_i = 10.8 \times 10^{-9} \text{ F} \cdot \text{cm}^{-2}$) of SiO₂ dielectric, V_G is the gate bias, and V_{th} is the threshold voltage.

3.7. References

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Chapter 4

Synthesis, characterization and OFETs performance of TDPP-based π -conjugated polymers via direct arylation polymerization

In Chapter 2 and 3, the reaction condition for direct arylation polymerization of TDPP-based monomers was optimized and structural defects were found to be minimized with proper selection of each reaction parameters. In Chapter 4, followed by previous results in Chapter 2 and 3, another two building blocks, thienoisindigo (TIIG) and benzodithiazole (BDTz), were incorporated into polymer backbones with TDPP unit to afford two different low bandgap conjugated polymers by direct arylation polymerization. In addition, β -protection group was introduction to TDPP unit to further minimize the structural defects in direct arylation polymerization. The optical, thermal and electrochemical properties of these polymers were investigated systematically, and the charge-transport properties were examined in OFETs.

4.1. Introduction

Thiophene-flanked diketopyrrolopyrrole (TDPP) building block has been widely used in the construction of high performance π -conjugated polymers for OPV^[1-3] and OFETs^[4-8] applications, due to its high coplanarity and strong intermolecular interactions. Superior performance of TDPP-based conjugated polymers especially in OFETs has been intensively investigated during the past decade, which pushed their highest mobility to over $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[8]

To date, most TDPP-based polymers were synthesized conventional cross-coupling reactions, mainly Suzuki or Stille couplings. However, these coupling reactions suffer from tedious synthesis of organotin or organoboron precursors

and production of toxic byproduct as well. To overcome these two major problems in the conventional cross-coupling reactions, a new approach, direct arylation polymerization, by the reaction between (hetero)arene and aryl halide with palladium catalys, phosphine ligand, and additive has been emerging as an alternative in the recent years.^[9-12]

Specially for TDPP-based conjugated polymers, there has been some attempts to access these polymers via direct arylation polymerization with relatively high molecular weight.^[13-18] However, most of these TDPP-based polymers were already reported before they were synthesized by direct arylation polymerization, and the performance of TDPP-based conjugated polymers obtained from direct arylation polymerization in organic electronics was rarely studied.

In this chapter, by incorporating either thienoisindigo (TIIG) or benzodithizole (BDTz) as the building block, two TDPP-based conjugated polymers PTIIG-TDPP and PTDPP-BDTz were synthesized by direct arylation polymerization. The structure, optical and thermal properties of these polymers, as well as the charge-transport characteristics in OFETs were systematically studied in this chapter in the following sections.

4.2. Synthesis, characterization and OFETs performance of PTIIG-TDPP by direct arylation polymerization

Among a variety of building blocks, both thienoisindigo (TIIG) and diketopyrrolepyrrole (DPP) have been widely used to construct low bandgap polymer. Both TIIG and DPP have a planar structure with excellent π - π stacking in the solid states, which is beneficial for creating conjugated polymers with high mobilities. To date, several TIIG [19-21] or DPP [4-7, 22] based conjugated polymers exhibited high charge-carrier mobilities over $1 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. For example, PTIIG-Np composed of TIIG and naphthalene alternating units in the conjugated backbones exhibited a hole mobility as high as $14.4 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, [20] which is comparable to amorphous silicon.

In this section, two ultra-low bandgap polymers consisting TIIG and DPP units were synthesized by direct arylation polymerization. The introduction of hexyl-group in the β -position of thiophene rings in the DPP units (hDPP) was expected to further lower the bandgap of conjugated polymer compared to a similar polymer containing bare-thiophene flanked DPP, and also reduce the possibility of β -branching defects in the DAP reaction. Under the optimized conditions explored by our group previously, [23-26] the target conjugated polymers were expected to be obtained with high molecular weight and well-defined structure, which were further used as charge-transport materials in the OFETs.

4.2.1. Synthesis of PTIIG-TDPP by direct arylation polymerization

For a monomer with more than one active C-H bond involved in the direct arylation polymerization, regioselectivity could be a serious issue which could lead to branching defects in the target polymer. To address this problem, the common strategy is to optimize the reaction conditions to increase the selectivity of C-H bond activation. However, the systematic optimization of direct arylation polymerization could be tedious and may vary from different combination of monomers. On the contrary, blocking other reactive sites with alkyl chains and leaving only one active C-H bond for the monomer could avoid the branching defects more effectively. Leclerc et al.^[17] synthesized several DPP-based polymers by direct arylation polymerization from β -protected DPP monomers, and they found that blocking the β -position in the DPP monomer could increase the selectivity in the reaction and further lead to high molecular weight. However, the inductive effect of alkyl group in the β -position might lower the reactivity of C-H bond in the α -position as well. To balance the selectivity and reactivity for direct arylation polymerization, introducing β -protecting group in the brominated monomer was finally found to give the conjugated polymers with well-defined structures and high molecular weight as well.

To synthesize the conjugated polymer consisting of TIIG and DPP units, hexyl groups were introduced to the β -position in the thiophene rings of DPP

units (hDPP) for better regioselectivity. The synthetic scheme of DAP between TIIG and DPP under our optimized reaction conditions^[23] is shown in **Scheme 4.1**. The coupling reaction between TIIG and dibromo-hDPP catalyzed by $\text{Pd}_2(\text{dba})_3/(\text{o-MeOPh})_3\text{P}$ in the presence of K_2CO_3 and pivalic acid in *o*-xylene gave **P1** with a molecular weight of 24.0 kDa in 75% yield as a deep black solid. Under the same reaction condition, **P2** was obtained by the reaction of TIIG and dibromo-DPP as a black solid with a molecular weight of 21.6 kDa in 68% yield. The higher molecular weight obtained from brominated-hDPP compared to brominated-DPP monomer was consistent with Leclerc's results,^[17] and β -protecting group for the brominated monomer will not lower the reactivity in the direct arylation polymerization. And the regioselectivity issue will be discussed in the following section by structural analysis from NMR spectra of **P1** and **P2**.

Scheme 4.1 Synthesis of **P1** and **P2** by direct arylation polymerization.

4.2.2. Characterization of PTIIG-TDPP

To verify the structure of **P1** and **P2**, high temperature NMR spectra were recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C. The ^1H -NMR spectrum of **P1** (**Figure 4.2a**)

showed two sharp peaks in the aromatic range at 8.69 and 6.93 ppm, respectively, which could be attributed to the protons in the thiophene rings of hDPP and TIIG units respectively. **P2**, without hexyl-group in the DPP unit showed lower solubility and stronger intermolecular interactions, which resulted in the broader peaks in the aromatic range located at 8.81, 7.47 and 6.92 ppm, respectively. The chemical shift for proton **a'** in **P2** is slightly down shifted compared to proton **a** in **P1**, owing to the absence of hexyl group in **P2**. Other small peaks in the aromatic range for both **P1** and **P2** could be assigned to the protons from end groups from either (h)DPP or TIIG units as shown in **Figure 4.2**. The protons from homocoupling defects were found to be located at around 7.6 ppm in the previous study^[18], but no additional signals attributed to the homocoupling were observed in the NMR spectra for both **P1** and **P2**, which demonstrated well-defined structure in the conjugated polymer backbone for these two polymers.

Figure 4.1 GPC traces of (a) **P1** and (b) **P2** with RI detector in CHCl_3 at 80 °C.

Figure 4.2 ^1H -NMR (300 MHz) spectra of (a) **P1** and (b) **P2** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C.

UV-Vis-NIR absorption spectra of **P1** and **P2** in CHCl_3 solution and thin films were presented in **Figure 4.3**. In solutions, the main absorption band for both **P1** and **P2** covered from 600 to 1300 nm, and **P1** showed a sharp peak at

1062 nm accompanied by a shoulder peak located at 957 nm, while **P2** only exhibited a broad peak at 965 nm. As for thin films, the absorption onsets of **P1** and **P2** were both extended to 1800 nm. Again, **P1** showed two peaks (967 and 1140 nm) in thin films which were slightly red-shifted compared to those in the solution. In contrast, a mono-peak at 1060 nm was observed for **P2** in thin films. The optical bandgaps calculated from the onset of absorption spectra of **P1** and **P2** in films were determined to be 0.82 and 0.91 eV, respectively. Regardless of the slight difference in the molecular weight between **P1** and **P2**, the lower bandgap of **P1** could be mainly attributed to the introduction of hexyl group in the DPP units in **P1** which could enhance the donor-acceptor effect in the polymeric backbones. This phenomenon was consistent with the inductive effect of alkyl chains that could reduce the bandgap by stronger donor-acceptor behaviour, as reported by Leclerc and coworkers.^[17]

Figure 4.3 Normalized absorption spectra of (a) **P1** and (b) **P2** in CHCl_3 solution and thin films.

Figure 4.4. Cyclic voltammograms in dry acetonitrile with 0.1 M Bu₄NPF₆ as the supporting electrolyte, a Pt electrode with a diameter of 2 mm, a Pt wire, and an Ag wire electrode were used as the working electrode, the counter electrode, and the reference electrode, respectively, with a scan rate at 50 mV s⁻¹.

The electrochemical properties of **P1** and **P2** in acetonitrile were examined by cyclic voltammetry (CV) (**Figure 4.4**). **P1** showed an oxidation peak at 0.73 V accompanied by a shoulder peak at 0.90 V, which were both quasi-reversible. Similar to **P1**, **P2** also showed two quasi-reversible peaks located at 0.51 and 0.82 V, respectively. The onset oxidation potentials ($E_{ox, onset}$) of **P1** and **P2** were determined to 0.38 and 0.33 V, respectively. Given the optical bandgap obtained from the UV-Vis-NIR spectra, the LUMO and HOMO energy levels of **P1** and **P2** could be calculated by the following equations: $HOMO = -(E_{ox, onset} + 4.8)$ eV, $LUMO = HOMO + E_{g, opt}$. The HOMO/LUMO energy levels of

P1 and **P2** were then determined to -5.19/-4.36 eV and -5.13/-4.22 eV, respectively.

The thermal stabilities of **P1** and **P2** were then investigated by thermogravimetric analysis (TGA) under N₂ flow with a heating rate of 10 °C min⁻¹ (**Figure 4.5**). The decomposition temperature (*T_d*) of **P1** and **P2** were found to be 367 and 303 °C, respectively, which confirmed their excellent thermal stability for organic electronic devices with thermal annealing process.

Figure 4.5. Thermogravimetric analysis (TGA) curves of **P1** and **P2**

Table 4.1. Summary of synthesis and characterization results of **P1** and **P2**.

Polymer	<i>M_n</i> (kDa)	Yield (%)	<i>T_d</i> (°C)	<i>λ_{abs, max}</i> (nm)		<i>λ_{abs, onset}</i> in film (nm)	<i>E_{g, opt}</i> (eV)	<i>E_{ox, onset}</i> (V)	<i>HOMO</i> (eV)	<i>LUMO</i> (eV)
				Solution	Film					
P1	32.5	75	367	1062	1140	1510	0.82	0.38	-5.18	-4.36
P2	25.6	68	303	965	1060	1360	0.91	0.33	-5.13	-4.22

The charge transport properties of **P1** and **P2** were studied in the OFETs with bottom-gate/top-contact (BGTC) architecture under ambient conditions. Only hole transport characteristics were observed for both **P1** (**Figure 4.6**) and **P2** (**Figure 4.7**) thin films at different annealing temperatures. After thermal annealing at 100 °C, a hole mobility of $1.18 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved for **P1**. Further increasing the annealing temperature could only slightly affect the hole mobility with highest hole mobility of $2.61 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ obtained at 150 °C. Similar to **P1**, the highest hole mobility of **P2** up to $1.41 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved at 150 °C, which was slightly lower compared to that of **P1**. The hole mobility of **P2** was comparable to the similar polymer with THIIG and TDPP units in the backbones synthesized by Stille coupling polymerization^[27].

Figure 4.6 OFETs transfer curves of **P1** thin films annealed at (a) 100 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C at negative source-drain bias ($V_{DS} = -80 \text{ V}$).

Figure 4.7 OFETs transfer curves of **P2** thin films annealed at (a) 100 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C at negative source-drain bias ($V_{DS} = -80$ V).

In order to understand the thermal annealing effect on the device performance, especially the effect of the film morphology and phase separation, atomic force microscopy (AFM) was employed to characterize the thin films formed by **P1** and **P2**, respectively. The AFM images of **P1** annealed at 100 °C (**Figure 4.8a**) showed obvious phase separation with relatively large domain size, and the domain size decreased when **P1** thin films were annealed at 150 °C (**Figure 4.8b**). However, when the annealing temperature was further increased to 200 and 250 °C (**Figure 4.8c** and **4.8d**), the phase separation became blurred. Different from **P1**, **P2** showed smooth films with some small-size aggregates after being annealed at different temperature. Some short-range phase separation could be observed from the phase image of **P2** thin films after being annealed at 150 °C (**Figure 4.9b**). Further annealing at higher temperatures up to 250 °C (**Figure S9c** and **4.9d**) had no obvious effect on the

morphology and phase separation of **P2** in thin films. The most well-defined phase separation and morphologies observed at annealing temperature of 150 °C for both **P1** and **P2** are consistent with their respective highest charge carrier mobility observed in OFETs devices (**Table 4.2**).

Table 4.2 Summary of the device performance of **P1** and **P2** based OFETs at different annealing temperatures.

Polymer	Annealing temperature (°C)	V _{th} (V)	μ _{h,ave} (cm ² V ⁻¹ S ⁻¹)	On/off ratio
P1	100	12	1.18 × 10 ⁻⁴	10 ²
	150	5	2.61 × 10 ⁻⁴	10 ²
	200	11	1.05 × 10 ⁻⁴	10 ¹ - 10 ²
	250	14	6.64 × 10 ⁻⁵	10 ¹
P2	100	14	5.67 × 10 ⁻⁵	10 ² - 10 ³
	150	12	1.41 × 10 ⁻⁴	10 ³
	200	6	5.27 × 10 ⁻⁵	10 ¹ - 10 ²
	250	-3	3.72 × 10 ⁻⁵	10 ²

Figure 4.8 Tapping mode AFM images ($5 \times 5 \mu\text{m}^2$) of **P2** thin films test on silicon wafers in ambient conditions. Height (left) and phase (right) images are shown for thin films annealed at (a) 100 °C, (b) 150 °C, (c) 150 °C and (d) 250 °C.

Figure 4.9 Tapping mode AFM images ($5 \times 5 \mu\text{m}^2$) of **P2** thin films test on silicon wafers in ambient conditions. Height (left) and phase (right) images are shown for thin films annealed at (a) 150 °C, (b) 200 °C and (c) 250 °C.

4.2.4. Conclusion

In summary, two ultra-low bandgap π -conjugated polymers consisting of (h)DPP and TIIG units were synthesized by direct arylation polymerization with molecular weight up to 24.0 kDa. The slightly higher molecular weight

obtained for **P1** synthesized from hDPP suggested that hexyl protecting groups in brominated-hDPP will not affect the reactivity compared to brominated DPP. The structural analysis from $^1\text{H-NMR}$ spectra confirmed the well-defined alternating structure of **P1**, which demonstrated that β -protecting group in the monomer could ensure the regioselectivity in the direct arylation polymerization. The UV-Vis-NIR spectra indicated the ultra-low bandgap nature of these two polymers, and the optical bandgap of **P1** and **P2** were calculated to be 0.82 and 0.91 eV, respectively. Both two polymers were highly thermally stable with decomposition temperature over 300 °C. In bottom-gate/top-contact OFETs devices, **P1** and **P2** showed p-type characteristics with the highest mobility of $2.61 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **P1** and $1.19 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **P2** at annealing temperature of 150 °C under ambient atmosphere.

In contrary to previous work in direct arylation polymerization focused on the detailed optimization of various reaction parameters to minimize the structure defects, the introduction of protecting group is a more efficient and universal strategy for monomers with more than one reactive C-H bonds to reduce the branching defects, but maintain the reactivity at the same time. In addition, the bandgap of conjugated polymers could be also tuned by changing the protecting groups with different electronic nature.

4.3. Synthesis, characterization and OFETs performance of PTDPP-BDTz by direct arylation polymerization

Benzobisthiazole (BDTz) is a weak electron-donating building block for D-A copolymers with a coplanar structure. Most BDTz-based monomers were thiophene/furan flanked building blocks, which in one hand could extend the conjugation length and were suitable for the synthesis of conjugated polymers via conventional cross-coupling reactions^[31-34].

BDTz monomer, with hydrogens in the thiazole rings are very acidic, making it a very good option to be used in the study of DAP. Previous study on direct arylation of small molecules with either thiazole^[35] or benzobisthiazole^[36] required the use of Pd/Cu co-catalyst system and also no DAP of BDTz-based conjugated polymers have been studied yet. In this perspective, we study the synthesis of **PTDPP-BDTz** polymers with brominated TDPP and BDTz units via DAP. And the photophysical, electrochemical and charge transport properties were further investigated exclusively. **PTDPP-BDTz** with a molecular weight of 14.3 KDa showed the hole mobilities of $2.17 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in bottom-gate, top-contact OFETs and good phase separation of thin films suggests that the performance of this polymer could be further improved with detailed optimization.

4.3.1. Synthesis of PTDPP-BDTz by direct arylation polymerization

The monomer **BDTz** is synthesized according to the literature with 48% yield after recrystallization^[37] (**Scheme 1**). The ¹H-NMR spectra of **BDTz** is shown in **Fig. 4.10**. The protons in the thiazole rings can be assigned to the peaks at 9.3 ppm, whereas the protons in the benzene rings are located at 8.9 ppm.

Scheme 4.2 Synthetic route of **BDTz**.

Figure 4.10 ¹H-NMR (300 MHz) spectra of **BDTz** in $\text{DMSO}-d_6$.

Novel donor-acceptor conjugated polymer **PTDPP-BDTz** were then synthesized by direct arylation polymerization with dibromo thiophene-flanked DPP (**Br-TDPP**) and BDTz as two building blocks (**Scheme 4.3**). C-H bonds in the thiazole rings of the BDTz units are expected to be very active with the electron withdrawing nature of thiazole unit. Two typical reaction conditions for DAP were explored for the synthesis of **PTDPP-BDTz**. Either Pd(OAc)₂/P^tBu₂Me·HBF₄ (for **PTDPP-BDTz-1**) or Pd₂(dba)₃/P(*o*-MeOPh)₃ (for **PTDPP-BDTz-2**) catalytic combination were applied for DAP with K₂CO₃ as the base in *o*-xylene. Initially, the reaction temperature is set to 100 °C and no obvious colour change is observed after 24 hour. After increasing the temperature to 120 °C, the red reaction mixture turns to light blue which suggests the coupling between two monomers with intended conjugated length. When the reaction temperature is further increased to 135 °C, the final reaction mixture after 24 hours turned to bluish green for **PTDPP-BDTz-1** and deep blue for **PTDPP-BDTz-2**. It was already studied by S. Marder et al. that high boiling point solvent and higher reaction temperature would increase the yield of the direct arylation between **BDTz** and aryl-bromide^[36], which is consistent with our findings that the C-H bonds in the thiazole unit of **BDTz** are more reactive at higher temperature.

After Soxhlet extraction, **PTDPP-BDTz-1** is obtained with 93% yield as a black solid, while **PTDPP-BDTz-2** has a slight lower yield of 80% (for CHCl₃ fraction) which is a black solid as well. The molecular weight of **PTDPP-BDTz-1** and **PTDPP-BDTz-2** is determined to be 14.3 and 12.2 kDa from the

GPC recorded at 80 °C with CHCl₃ as eluent (**Figure 4.11**). The synthetic results are summarized in **Table 4.3**.

Scheme 4.3 Synthesis of **PTDPP-BDTz** via DAP.

Figure 4.11 GPC traces of (a) **PTDPP-BDTz-1** and (b) **PTDPP-BDTz-2** with RI and UV (at 600 nm) detector in CHCl₃ at 80 °C.

Table 4.3 Synthetic results of **PTDPP-BDTz** via direct arylation polymerization

Polymer	[Pd]	Ligand	<i>M_n</i> (kDa)	<i>M_w</i> / <i>M_n</i>	Yield (%)
PTDPP-BDTz-1	Pd(OAc) ₂	P ^t Bu ₂ Me·HBF ₄	14.3	1.8	93
PTDPP-BDTz-2	Pd ₂ (dba) ₃	P(o-MeOPh) ₃	12.2	2.9	80

4.3.2. Characterization of PTDPP-BDTz

To confirm the structure of PTDPP-BDTz, ^1H -NMR spectra were performed at 100 °C in $\text{C}_2\text{D}_2\text{Cl}_4$ as shown in (Figure 4.12 and 4.13). The protons in the thiophene rings from TDPP units could be assigned to be the broad peaks located at around 8.8 ppm and the other peak at around 7.4 ppm, while the protons in the thiazole rings from BDTz units could be found at 8.5 ppm. No additional peaks from the branching or homocoupling defects could be observed for two polymers, which confirmed the well-defined alternating conjugated polymer backbones for PTDPP-BDTz.

Figure 4.12 ^1H -NMR (300 MHz) spectra of PTDPP-BDTz-1 in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C.

Figure 4.13 ^1H -NMR (300 MHz) spectra of **PTDPP-BDTz-2** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 $^\circ\text{C}$.

The UV-Vis spectra of **PTDPP-BDTz-1** and **PTDPP-BDTz-2** in CHCl_3 and thin films were shown in **Fig. 4.14**. **PTDPP-BDTz-1** showed a maximal absorption peak at 659 nm, accompanied by a shoulder peak located at 712 nm in CHCl_3 solution, with slightly red-shift of the absorption spectra in the thin film. And it is notable that the intensity of shoulder peak which can be assigned to the vibration peak in the absorption spectra also increased a little bit, which suggests that the strong intermolecular interactions of **PTDPP-BDTz-1** in thin films. On the contrary, although **PTDPP-BDTz-2** shows a 31 nm red-shift in the maximal absorption peak in the thin films compared to that in the solution, no vibration peaks could be observed probably due to the lower molecular

weight of the polymer as well as the weaker intermolecular interactions especially in the thin films.

Figure 4.14 Normalized absorption spectra of (a) **PTDPP-BDTz-1** and (b) **PTDPP-BDTz-2** in CHCl_3 solution and thin films.

The electrochemical properties of **PTDPP-BDTz-1** and **PTDPP-BDTz-2** were studied by cyclic voltammetry (CV) in acetonitrile solutions with polymer films dip coated onto the working electrode (**Figure 4.15**). Quasi-reversible oxidation/reduction peaks are found for these two polymers, and the HOMO energy levels were determined by to be $-(E_{\text{onset}}^{\text{ox}} + 4.8)$ eV, where $E_{\text{onset}}^{\text{ox}}$ is the onset of the oxidation peaks. This gives the HOMO energy levels of **PTDPP-BDTz-1** and **PTDPP-BDTz-2** -5.37 and -5.34 eV, respectively. And the LUMO energy levels were calculated by subtracting optical band gap ($E_{\text{g}}^{\text{opt}}$) from HOMO energy levels, which is -3.98, and -3.94 for **PTDPP-BDTz-1** and **PTDPP-BDTz-2**, respectively.

The thermal stability of two **PTDPP-BDTz** polymers were then investigated by thermogravimetric analysis (TGA) under N₂ flow with a heating rate of 10 °C min⁻¹ (**Figure 4.16**). The decomposition temperature (T_d) of **PTDPP-BDTz-1** and **PTDPP-BDTz-2** were found to be 398 °C for both, which showed excellent thermal stability for thermal annealing in organic electronic devices fabrication process.

All the characteristic properties of **PTDPP-BDTz** are summarised in **Table 4.4** below.

Figure 4.15 Cyclic voltammograms of **PTDPP-BDTz-1** and **PTDPP-BDTz-2** thin films in acetonitrile with 0.1 M Bu₄NPF₆ as the supporting electrolyte, a Pt electrode with a diameter of 2 mm, a Pt wire, and an Ag wire were used as the working electrode, counter electrode and reference electrode respectively at a scan rate of 50 mV S⁻¹.

Table 4.4. Summary of optical, electrochemical and thermal properties of PTDPP-BDTz synthesized by DAP.

Polymer	M_n (KDa)	$\lambda_{abs, max}$ (nm)		$\lambda_{abs, onset}$ film (nm)	$E_{g, opt}$ (eV)	$E_{ox, onset}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	T_d (°C)
		Solution	Film						
PTDPP-BDTz-1	14.3	659, 712	673, 729	892	1.39	0.57	-5.37	-3.98	398
PTDPP-BDTz-2	12.2	640	671	885	1.40	0.54	-5.34	-3.94	398

Figure 4.16 TGA curves of PTDPP-BDTz-1 and PTDPP-BDTz-2.

4.3.3. OFETs performance of PTDPP-BDTz

Figure 4.17 OFET transfer plots of current versus V_G at negative source-drain bias ($V_{DS} = -80$ V) for (a-c) **PTDPP-BDTz-1** and (d-f) **PTDPP-BDTz-2** at (a,d) room temperature, annealed at (b,e) 100 and (c,f) 200 °C.

The charge transfer properties of **PTDPP-BDTz-1** and **PTDPP-BDT-2** were then examined by OFETs with bottom-gate top-contact architecture. Only p-

type hole transport signals are collected for both polymers. For **PTDPP-BDTz-1**, the highest hole mobilities $2.17 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are achieved when the thin films are annealing at 200 °C and a slightly increase of hole mobilities is observed from room temperature, to 100 and 200 °C (**Figure 4.17a-c**). Very similar to **PTDPP-BDTz-1**, hole mobilities of **PTDPP-BDTz-2** (**Figure 4.17d-f**) also show no significant change regardless of the annealing temperature, but generally its hole mobilities are one magnitude lower compared to those of **PTDPP-BDTz-1**. The detailed OFETs performance of **PTDPP-BDTz** is summarized in **Table 4.5** for comparison.

Table 5. Summary of charge transport properties of PPhDPP-TDPP at different annealing temperature.

Annealing Temperature (°C)		V _{th} (V)	μ _{h,ave} (cm ² V ⁻¹ S ⁻¹)	On/off ratio
PDPP-BDTz-1	R.T.	6	1.67×10 ⁻⁴	10 ³
	100	7	1.97×10 ⁻⁴	10 ³
	200	8	2.17×10 ⁻⁴	10 ³ -10 ⁴
PDPP-BDTz-2	R.T.	-3	2.53×10 ⁻⁵	10 ²
	100	-1	2.47×10 ⁻⁵	10 ² -10 ³
	200	3	4.27×10 ⁻⁵	10 ³

Figure 4.18 Tapping mode AFM images ($2 \times 2 \mu\text{m}^2$) of **PTDPP-BDTz-1** thin films test on silicon wafers in ambient conditions. Height (left) and phase (right) images are shown for thin films annealed at (a) R.T., (b) 100 °C and (c) 200 °C.

Figure 4.19 Tapping mode AFM images ($2 \times 2 \mu\text{m}^2$) of PTDPP-BDTz-2 thin films test on silicon wafers in ambient conditions. Height (left) and phase (right) images are shown for thin films annealed at (a) R.T., (b) 100 °C and (c) 200 °C.

The film morphologies of **PTDPP-BDTz** are studied by atomic force microscopy (AFM) as shown in **Figure 4.18** and **4.19** for **PTDPP-BDTz-1** and **PTDPP-BDTz-2**, respectively. From the phase images of these two polymers, bicontinuous interpenetrating networks could be easily observed at different annealing temperatures. This type of uniform phase separation might be favourable for the charge transport performance in OFETs devices. The film morphologies of these polymers films almost keep the same with thermal annealing, which is consistent with the charge transport behaviours of these polymers.

4.3.4. Conclusion

PTDPP-BDTz were synthesized via direct arylation polymerization with molecular weight over 10 KDa. **PTDPP-BDTz** showed wide absorption spectra from visible to near-infrared range and quasi-reversible ox/red electrochemical properties. **PTDPP-BDTz-1** with higher molecular weight exhibits hole mobilities of $2.17 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which was one magnitude higher compared to those of **PTDPP-BDTz-2** with slightly lower molecular weight. The bicontinuous networks for these thin films could be beneficial for charge transport and the OFETs performance might be further improved with detailed optimization.

4.4. Experimental section

4.4.1. Materials and characterization

All reagents were obtained from commercial suppliers and used without further purification, including solvents as well. Br-DPP^[28], Br-hDPP^[29] and TIIG^[30] were prepared according to the established method. Gel permeation chromatography (GPC) measurement were carried out on Agilent 1260 Infinity system using CHCl₃ as eluent (1 ml/min) and polystyrene as standards at 80 °C with RI and UV (600 nm) detector. UV-Vis-NIR absorption spectra were recorded on Shimadzu UV-1800 spectrophotometer. ¹H-NMR spectra were measured on a Bruker Avance II 300 MHz spectrometer in C₂D₂Cl₄ at 100 °C. Thermogravimetric (TGA) analysis was run on TA Q500 TGA from room temperature to 800 °C with a heating rate of 10 °C/min, and the decomposition temperature (T_d) was determined by the temperature at which 5% weight loss was occurred. AFM images were obtained by using a Dimension 3100 (Veeco, CA) in tapping mode with a Si tip (Veeco, resonant frequency, 320 kHz; spring constant, 42 N m⁻¹) under ambient conditions with a scanning rate of 1 Hz and a scanning line of 512. The thin films of AFM samples were prepared by spin casting polymer solutions (10 mg/ml in chlorobenzene) onto silicon substrates and annealed at different temperatures separately for 15 min under N₂ atmosphere.

Figure 4.20 ¹H-NMR (300 MHz) spectra of hDPP in CDCl₃.

Figure 4.22. ¹H-NMR (300 MHz) spectra of Br-hDPP in CDCl₃.

4.4.2. Synthesis of P1 and P2 via direct arylation polymerization

A 5 mL microwave tube with a magnetic stir bar was charged with mixture of $\text{Pd}_2(\text{dba})_3$ (0.005 mmol), K_2CO_3 (0.30 mmol), $\text{P}(o\text{-MeOPh})_3$ (0.010 mmol), PivOH (0.050 mmol), Br-DPP or Br-hDPP (0.10 mmol) and TIIG (0.10 mmol) and then placed in the glove box. *o*-Xylene (1 mL) was added into the mixture and the tube was capped with a septum before taking out of the glove box. The mixture was stirred at room temperature for 5 min and then placed in a pre-heated oil bath at 100 °C for 24 hours. After cooling to room temperature, the reaction mixture was poured into ice methanol. The resulting solid was filtered and subjected to Soxhlet extraction in methanol and hexane for the removal of low molecular weight materials and impurities. The remaining polymer was extracted with chloroform, precipitated again from ice methanol and dried under vacuum.

4.4.3. Synthesis of PTDPP-BDTz-1 and PTDPP-BDTz-2 via direct arylation polymerization

For **PTDPP-BDTz-1**, a 5 mL microwave tube with a magnetic stir bar was charged with mixture of $\text{Pd}(\text{OAc})_2$ (0.010 mmol), K_2CO_3 (0.30 mmol), $\text{P}^t\text{Bu}_2\text{Me}\cdot\text{HBF}_4$ (0.020 mmol), PivOH (0.10 mmol), Br-DPP or Br-hDPP (0.10 mmol) and TIIG (0.10 mmol) and then placed in the glove box. *o*-Xylene (1 mL) was added into the mixture and the tube was capped with a septum before taking out of the glove box. The mixture was stirred at room temperature for 5

min and then placed in a pre-heated oil bath at 100, 120 and 135 °C for 24 hours (for each temperature). After cooling to room temperature, the reaction mixture was poured into ice methanol. The resulting solid was filtered and subjected to Soxhlet extraction in methanol and hexane for the removal of low molecular weight materials and impurities. The remaining polymer was extracted with chloroform, precipitated again from ice methanol and dried under vacuum.

For **PTDPP-BDTz-2**, a 5 mL microwave tube with a magnetic stir bar was charged with mixture of Pd₂(dba)₃ (0.005 mmol), K₂CO₃ (0.30 mmol), P(*o*-MeOPh)₃ (0.010 mmol), PivOH (0.050 mmol), Br-DPP (0.10 mmol) and BDTz (0.10 mmol) and then placed in the glove box. *o*-Xylene (1 mL) was added into the mixture and the tube was capped with a septum before taking out of the glove box. The mixture was stirred at room temperature for 5 min and then placed in a pre-heated oil bath at 100, 120 and 135 °C for 24 hours (for each temperature). After cooling to room temperature, the reaction mixture was poured into ice methanol. The resulting solid was filtered and subjected to Soxhlet extraction in methanol and hexane for the removal of low molecular weight materials and impurities. The remaining polymer was extracted with chloroform, precipitated again from ice methanol and dried under vacuum.

4.4.4. Device fabrication

Bottom-gate/top-contact OFETs were fabricated using heavily doped Si wafer as the bottom gate electrode with 300 nm of SiO₂ layer as the gate dielectric. Gold source and drain electrodes (60 nm) were patterned by the vacuum thermal evaporation. The substrate was cleaned in acetone and isopropanol, and dried on the hot plate at 80 °C, followed by treating with plasma for 15 min. After that, the substrate was immersed in the ODTS solution (Toluene as the solvent) overnight, rinsed with toluene to remove extra ODTS and dried on the hot plate at 110 °C. The polymers were dissolved in chlorobenzene at a concentration of 10 mg/mL by stirring for four days. The polymer films were spin-cast at 2000 rpm and annealed at a designated temperature for 15 min. Finally, gold electrode with 60 nm was thermally evaporated in vacuum through a shadow mask with the following dimension (length (L) = 200 μm and channel width (W) = 4.0 mm). The field effect mobilities were extracted from the saturation regime using the relationship $\mu_{\text{sat}} = (2I_{\text{DS}}L)/(WC(V_G - V_{th})^2)$, where I_{DS} denotes the saturation drain current, C is the capacitance ($C_i = 10.8 \times 10^{-9} \text{ F} \cdot \text{cm}^{-2}$) of SiO₂ dielectric, V_G is the gate bias, and V_{th} is the threshold voltage.

4.5. Conclusion

In summary, direct arylation polymerization between DPP and THIIG or BDTz were processed successfully with the optimized reaction conditions to give high molecular weight conjugated polymers with low bandgaps. These polymers

covered the absorption spectra from visible to near-infrared range and exhibited hole mobilities of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ in bottom-gate/top-contact OFETs.

For conjugated polymers consisting DPP and TIIG units, the slightly higher molecular weight obtained for **P1** synthesized from hDPP suggested that hexyl protecting groups in brominated-hDPP did not affect the reactivity compared to brominated DPP. The structural analysis from $^1\text{H-NMR}$ spectra confirmed the well-defined alternating structure of **P1**, which demonstrated that β -protecting group in the monomer could ensure the regioselectivity in the direct arylation polymerization.

PTDPP-BDTz-1 with higher molecular weight exhibited one magnitude higher hole mobility compared to that of **PTDPP-BDTz-2**, which could be contributed to the bicontinuous networks in thin films for **PTDPP-BDTz-1**, that could be beneficial for charge transport in OFETs.

4.6. References

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Chapter 5

Synthesis of phenyl-DPP based conjugated polymers via direct arylation polymerization

After the systematic study on the synthesis of TDPP-based conjugated polymers by direct arylation polymerization from Chapter 2-4, four phenyl-DPP (PhDPP)-based conjugated polymers were then synthesized and characterization in Chapter 5.

5.1. Introduction

DPP moiety, which could date back to very ancient times as a key unit in some pigments, has been receiving considerable attention for constructing donor–acceptor (D–A) type organic semiconductors as an electron acceptor in recent years. DPP-based conjugated small molecules and polymers have shown exceptional performance in organic electronics, including organic electrochromic devices^[1, 2], OFETs^[3-7] and OPVs^[8-11]. Through association of the DPP unit with appropriate electron donating building blocks, the resulting D–A molecules interact strongly in the solid state through intermolecular D–A and π – π interactions, leading to highly ordered structures at the molecular and microscopic levels. The closely packed molecules and crystalline domains are beneficial for intermolecular and interdomain or intergranular charge transport. Furthermore, the energy levels can be readily adjusted, affording p-type, n-type, or ambipolar organic semiconductors with highly efficient charge transport properties in OFETs. In the past decade, a number of DPP-based small molecules and semiconducting polymers with charge-carrier mobility greater than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been reported.^[4-6, 10, 12, 13] Thiophene- or pyridine-flanked DPP based polymers have achieved record high mobility values for p-

type (hole mobility: $12.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[4], n-type (electron mobility: $6.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[6], and ambipolar (hole/ electron mobilities: $3.97/2.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[3] OFETs among the known polymer semiconductors. Many DPP-based semiconducting polymers have favourable energy levels and band gaps along with high hole mobility, which enable them as promising donor materials for OPVs. Power conversion efficiencies (PCE) up to 6.05 %^[11] were achieved for OPVs using DPP-based polymers, demonstrating their potential applications for the organic solar cells technology. Apart from utilizing electronic properties of DPP-based materials, proper modification of DPP unit could lead to highly fluorescent materials, which can serve as bioimaging agent^[14, 15] or chemical sensors^[16, 17].

The aforementioned DPP-based conjugated polymers were often synthesized by conventional cross-coupling reactions, i.e., Suzuki or Stille couplings. However, unstable organometallic reagents, tedious synthesis of metal-activated monomers along with formation of toxic byproducts were involved in conventional transition metal catalyzed cross-coupling reaction. As a consequence, a more environment friendly approach named direct arylation polymerization (DAP), in which an aryl halide can be directly arylated with another aromatic monomer without pre-synthesis of organometallic monomer, is emerging as an alternative method for polymer chemists to synthesize conjugated polymers in a greener way^[18-26]. The pioneer works in DAP have shown that this method can give conjugated polymers with comparable qualities (regarding molecular weight and structural defects) and performances in devices. Specifically for DPP-based polymers, several groups^[27-30] have studied

the synthesis of thiophene-flanked DPP (TDPP)-based conjugated polymers as well as the performance of these polymers in either OFETs or OPVs. As for phenyl-flanked DPP (PhDPP), on the contrary, very limited attention has been paid to direct arylation method to synthesize conjugated small molecules or polymers. Chen and coworkers synthesized three PhDPP-based small molecules by direct arylation coupling with moderated to high yields^[31]. Kanbara and coworkers reported the direct arylation polymerization between bithiophene and PhDPP to give the copolymer with M_n of 18.1 KDa at 96% yield^[32].

To extend the scope of DAP synthetic approach, especially for DPP-based monomers, herein we report the synthesis of four phenyl-DPP (PhDPP)-based conjugated polymers by direct arylation polymerization method and studied their photophysical, electrochemical and thermal properties, as well as their potential applications in electronic devices.

5.2. Synthesis of PhDPP-based conjugated polymers by direct arylation polymerization

Although TDPP-based conjugated polymers could be brightest stars in DPP-based materials considering their wide applications in electronic devices, PhDPP-based conjugated polymers also have some unique features, like strong fluorescence or medium bandgap, which could be a good addition to TDPP-based polymers series for DPP polymer family.

Four PhDPP-based conjugated polymers were synthesized by direct arylation polymerization with the reaction conditions developed by our group previously^[19] between dibromo-phenyl DPP (**DBrPhDPP**) and four non-functionalized aromatic monomers, thiophene-flanked DPP (**TDPP**), 1,2,4,5-tetrafluorobenzene (**TB**), benzodithiophene (**BDT**) and 3,4-ethylenedioxythiophene (**EDOT**), ranging from electron acceptors to electron donors (**Scheme 5.1**). Basically, **DBrPhDPP** and another monomer were treated with a catalytic combination $\text{Pd}_2(\text{dba})_3$ and $\text{P}(o\text{-MeOPh})_3$, which is in corporation with pivalic acid as the additive and potassium carbonate as the base in *o*-xylene for 24 hours. DAP between **DBrPhDPP** and **TDPP** was going very fast and a deep blue solution was formed in less than 15 min, which proved the successful coupling reaction with extension of conjugation length, and finally gave product **PPhDPP-TDPP (P1)** in 98% yield as a dark purple solid. The following trials with either **TB** or **BDT** somehow exhibited slower reaction rates by monitoring the colour change of the reaction mixture, and the resulting polymer products **PPhDPP-TB (P2)** and **PPhDPP-BDT (P3)** were obtained as oligomers from hexane fraction in the Soxhlet extraction at 80 and 55% yields, respectively. The lower reactivity of monomer **TB** could be explained by the higher activation energy of C-H bonds in the benzene rings compared to those in the thiophene rings (**TDPP** for example). It should be noted that the final product of **P3** was very sticky probably due to long branched alky chains in both building blocks. Finally, when **EDOT** was coupled with **DBrPhDPP**, a higher reaction rate was observed by colour change

of reaction mixture which was even faster compared to that of synthesizing **PPhDPP-TDPP**, associated with very high yield of 97% for **PPhDPP-EDOT** (**P4**). This was mainly contributed to the electron-donating nature of ethylenedioxy- substitution in thiophene rings for **EDOT**, which could further facilitate C-H activation during DAP process. Compared with recent work for the synthesis of **P4** via direct arylation polymerization by Kanbara and coworkers,^[33] in which they ran the reaction with Pd(OAc)₂, KOPiv in DMAc by microwave heating, higher molecular weight and yield was obtained in this study with our previously optimized conditions.^[19] The above discussion about the synthesis of four PhDPP-based conjugated polymers by DAP demonstrated that the reactivity of DAP highly depends on the activation energy of C-H bonds in the aromatic monomers.

Scheme 5.1 Synthesis of PhDPP-based conjugated polymers by DAP.

5.3. Characterization of PhDPP-based conjugated polymers

To confirm the structures of **P1-P4**, high temperature ^1H -NMR spectra of four PhDPP-based conjugated polymers were recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C (**Figure 5.1**). The protons from the phenyl rings in the PhDPP units could be easily found from 7.3 to 7.7 ppm, with slightly variation when different monomers were coupled with PhDPP. For **P1**, apart from the peaks that could be assigned to PhDPP unit, another two peaks in the aromatic region at 8.85 ppm and 7.84 ppm can be attributed to the protons in the thiophene rings of TDPP unit. However, the integration ratio of protons in TDPP was lower than the theoretic value, which could be possibly attributed to the stronger aggregation between TDPP units even at a relatively high temperature. This phenomenon was not found for other three polymers (**P2-P4**) with weaker intermolecular interactions. Other major peaks in the NMR spectra of **P1-P4** could be easily assigned to the side chains attached to the building blocks, while some small residual peaks in the aromatic region could be recognized as the end groups in each polymer. The higher ratio of residual peaks was significant evidence on the lower molecular weight for the polymers. From this perspective, **P1** and **P4** showed much higher molecular weight compared to that of **P2** and **P3**, which was further confirmed by gel permeation chromatography results.

Figure 5.1 ^1H -NMR (300 MHz) spectra of (a) P1, (b) P2, (c) P3, and (d) P4 in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100°C .

The molecular weight (M_n) and polydispersity (M_w/M_n) of PhDPP-based polymers were estimated by GPC using CHCl_3 as the eluent at 80 °C to minimize the aggregation of these polymers and give a more accurate relative molecular weight (**Figure 5.2**). As expected in the NMR analysis, the M_n of **P1** and **P4** were 22 and 27 KDa respectively, which was significantly higher than **P2** and **P3** of 5.4 and 4.5 KDa respectively. And slightly larger polydispersity of **P1** and **P4** of over 3.0 were also observed but still at a reasonable value considering the relatively high molecular weight.

Figure 5.2 GPC traces of PhDPP-based conjugated polymers with (a) RI and (b) UV detector (500 nm).

Table 5.1 Summary of PhDPP-based conjugated polymers synthesized by DAP.

Polymer	M_n (KDa)	M_w/M_n	Yield (%)
P1	22.0	3.5	98
P2	5.4	1.9	80
P3	4.5	1.9	55
P4	27.0	3.0	97

The UV-Vis-NIR absorption spectra of **P1-P4** were recorded in both CHCl_3 solution (**Figure 2a**) and thin films (**Figure 5.3**). Clear structure-properties relationship could be found when different monomers were incorporated into PhDPP-based polymers. Among four polymers, **P2** showed a shortest maximum absorption peak at 501 nm because of its poor coplanarity. When **BDT** or **EDOT**, two electron donating monomers were brought into the conjugated polymer chain, the absorption spectra of **P3** and **P4** exhibited obvious red-shift compared to that of **P2**. The maximum absorption peaks of **P3** and **P4** in CHCl_3 were located at 527 and 565 nm respectively. The 38 nm red-shift for **P4** was mainly owing to the stronger electron donating ability of **EDOT** as well as the higher molecular weight of **P4** itself. **P1** with even better coplanarity and conjugation with the incorporation of **TDPP** unit showed nearly 100 nm red-shift compared to **P4**, and the maximum absorption peaks of **P1** appeared at 644 nm with absorbance extended to almost 800 nm in the near-infrared region. The absorption spectra of **P1-P4** in thin films (**Figure 2b**) did not show much red-shift (less than 10 nm) of the maximum absorption peaks compared to those in solutions. But it is noteworthy to mention that obvious enhancement of the vibration peak at around 690 nm was found for **P1** in thin films, suggesting relatively strong intermolecular interactions. The optical bandgaps of four polymers were determined to be 1.55, 2.14, 2.00 and 1.89 eV for **P1-P4** respectively by the onset of absorption spectra in thin films.

Figure 5.3 Normalized absorption spectra of PhDPP-based conjugated polymers in (a) CHCl₃ solution and (b) thin films.

Figure 5.4 Normalized fluorescence spectra of **P2-P4** in CHCl₃ solution (λ_{ex} = 480 nm).

Since PhDPP itself is a fluorescent building block, we also investigated the fluorescent properties of these conjugated polymers. Except that **P1** was non-fluorescent in either solid or diluted solutions, **P2-P4** all showed strong fluorescence in CHCl_3 solutions. The maximum emission peaks for **P2-P4** fell on 546, 593 and 639 nm respectively, with moderate Stokes shift of 55, 66 and 74 nm (**Figure 5.4**). Among these three fluorescent polymers, only **P2** could exhibit very weak fluorescence in solid states, while **P3** and **P4** were non-fluorescent in solids due to strong intermolecular interaction caused fluorescence quenching.

Figure 5.5. Cyclic voltammograms of P1-P4 thin films in acetonitrile with 0.1 M Bu_4NPF_6 as the supporting electrolyte, a Pt electrode with a diameter of 2 mm, a Pt wire, and an Ag wire were used as the working electrode, counter electrode and reference electrode respectively at a scan rate of 50 mV S^{-1} .

The electrochemical properties of **P1-P4** were studied by cyclic voltammetry (CV) in dichloromethane solutions (**Figure 5.5**). Non-reversible oxidative peaks were found for these polymers, and the HOMO energy levels were determined by to be $-(E_{\text{onset}}^{\text{ox}} + 4.8)$ eV, where $E_{\text{onset}}^{\text{ox}}$ is the onset of the oxidation peaks. This gives the HOMO energy levels of **P1-P4** of -5.36, -5.24, -4.87 and -5.04 eV respectively. And the LUMO energy levels were calculated by subtracting optical band gap (E_g^{opt}) from HOMO energy levels, which is -3.81, -3.10, -2.87 and -3.15 for **P1-P4**.

Figure 5.6. TGA curves of PhDPP-based conjugated polymers under N₂ flow.

Thermogravimetric analysis (TGA) was then performed to examine the thermal stability of PhDPP-based polymers, as it is an important parameter for fabricating organic electronics with conjugated polymers. The decomposition

temperature (T_d , defined as 5% weight loss) was determined to be 413, 407, 340 and 405 °C for **P1-P4** respectively (Figure 5.6).

The detailed optical, electrochemical and thermal properties of **P1-P4** are summarized in Table 5.2 for comparison.

Table 5.2 Summary of optical, electrochemical and thermal properties of PhDPP-based conjugated polymers synthesized by DAP.

Polymer	Solution		Film		E_g^{opt}	E_{onset}^{ox}	E_{HOMO}	E_{LUMO}	T_d
	λ_{max}^{abs} (nm)	λ_{onset}^{abs} (nm)	λ_{max}^{abs} (nm)	λ_{onset}^{abs} (nm)	(eV) ^a	(V)	(eV) ^b	(eV) ^c	(°C)
P1	644	-	639	796	1.56	0.51	-5.31	-3.75	413
P2	501	556	506	579	2.14	0.29	-5.09	-2.95	407
P3	527	593	530	618	2.00	0.07	-4.87	-2.87	340
P4	565	639	559	655	1.89	0.47	-5.27	-3.38	360

^a $E_g^{opt} = 1240/\lambda_{onset}^{abs}$, where E_g^{opt} is the optical bandgap and λ_{onset}^{abs} is the onset of the absorption spectra of polymers in thin films.

^b $E_{HOMO} = -(E_{onset}^{ox} + 4.8)$ eV, where E_{onset}^{ox} is the oxidation onset verse $E_{Fc/Fc+}$.

^c $E_{LUMO} = (E_{HOMO} + E_g^{opt})$ eV

5.4. OFETs performance of PhDPP-based conjugated polymers

Considering the high molecular weight and better conjugation of **P1**, bottom-gate top-contact OFETs were fabricated to investigate its charge-transport properties. Only p-type hole transport signals were collected for **P1** thin films

annealed at 100, 150, 200 and 250 °C. The highest hole mobility $1.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved at the annealing temperature of 100 °C and no improvement regarding charge transport were observed with increasing annealing temperature (under $1.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for annealing temperature at 150, 200 and 250 °C) (**Figure 5.7**).

Figure 5.7 OFET transfer plots of current versus V_G at negative source-drain bias ($V_{DS} = -80 \text{ V}$) for P1 annealed at (a) 100 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C .

Table 5.3 Summary of charge transport properties of PPhDPP-TDPP at different annealing temperature.

Annealing temperature (°C)	μ_h (cm ² V ⁻¹ s ⁻¹)	on/off ratio	V _{th} (V)
100	1.5×10^{-4}	10 ³	-5
150	9.3×10^{-5}	10 ²	-18
200	7.1×10^{-5}	10 ¹ -10 ²	-28
250	5.3×10^{-5}	10 ²	-7

The film morphologies were studied by atomic force microscopy (AFM) as shown in **Figure 5.8**. No obvious phase separation was observed at four different annealing temperatures, while some aggregates were found instead which could be attributed to the strong intermolecular interactions. It should be noted that when **P1** films were annealed at 100 °C, less aggregates were observed which could contribute to the highest hole-mobilities for **P1** among four different annealing temperatures. The lower mobilities of **P1** annealed at higher temperature might be explained by the formation of large aggregates upon further annealing process.

Figure 5.8 Tapping mode AFM images ($2 \times 2 \mu\text{m}^2$) of P1 thin films test on silicon wafers in ambient conditions. Height (left) and phase (right) images are shown for thin films annealed at (a) 100 °C (b) 150 °C (c) 200 °C and (d) 250 °C.

5.5. Conclusion

In summary, four PhDPP-based conjugated polymers were synthesized by direct arylation polymerization with molecular weight up to 27 KDa. Due to the high reactivity of C-H bonds in the thiophene rings, **TDPP** and **EDOT** can give high molecular weight polymers when coupled with **DBrPhDPP**. These four polymers cover the absorption from visible to near-infrared region with variation of monomers, and three of them, i.e., **PPhDPP-TB**, **PPhDPP-BDT** and **PPhDPP-EDOT** were fluorescent in CHCl_3 solutions with Stokes shift of 55, 66 and 74 nm. **PPhDPP-TDPP** with high molecular weight and good conjugation in the polymer backbones was selected to examine the charge transport behaviour. Hole mobilities of $1.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ achieved when annealing at 100 °C were obtained as the best performance for this polymer.

5.6. Experimental section

5.6.1. Materials and characterization

Monomer **DBrDPP**, **TDPP**, **BDT** were synthesized according to the literature procedures. 1,2,4,5-Tetrafluorobenzene (**TB**) and 3,4-ethylenedioxythiophene (**EDOT**) was purchased from Sigma-Aldrich. All the solvents and other chemicals were purchased from Sigma-Aldrich without further purification.

^1H -NMR spectra were measured on a Bruker Avance II 300 MHz spectrometer in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C. Absorption spectra were obtained from Shimadzu UV 2450 ultraviolet-visible spectrometer. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of polymers were characterized by Agilent Infinity-1260 GPC at 80 °C, using polystyrene as standard and CHCl_3 as eluent with RI and UV (500 nm) detector. Cyclic voltammetry (CV) was test in acetonitrile with 0.1 M Bu_4NPF_6 as the supporting electrolyte, a Pt electrode with a diameter of 2 mm, a Pt wire, and an Ag wire were used as the working electrode, counter electrode and reference electrode respectively at a scan rate of 50 mV S^{-1} . The polymer films were dip coated from CHCl_3 solution to form a thin film on the surface of the working electrode for CV test. Thermogravimetric (TGA) analysis was run on TA Q500 TGA from room temperature to 600 °C with a heating rate of 10 °C/min under N_2 flow, and the decomposition temperature (T_d) was determined by the temperature at which 5% weight loss was occurred. AFM images were obtained by using a Dimension 3100 (Veeco, CA) in tapping mode with a Si tip (Veeco, resonant frequency, 320 kHz; spring constant, 42 N m^{-1}) under ambient conditions with a scanning rate of 1 Hz and a scanning line of 512. The thin films of AFM samples were prepared by spin casting polymer solutions (10 mg/ml in chlorobenzene) onto silicon substrates and annealed at different temperatures separately for 15 min under N_2 atmosphere.

5.6.2. General synthesis procedure of DPDPP-based conjugated polymers via DAP

A 5 mL microwave tube with a magnetic stir bar was charged with mixture of $\text{Pd}_2(\text{dba})_3$ (6.9 mg, 0.0075 mmol), K_2CO_3 (62.1 mg, 0.45 mmol), $\text{P}(o\text{-MeOPh})_3$ (5.3 mg, 0.015 mmol), PivOH (7.7 mg, 0.075 mmol), 3,6-bis(4-bromophenyl)-2,5-bis(2-hexyloctyl)-pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (**DBrPhDPP**) (134.3 mg, 0.15 mmol) and the other building block (**TDPP**, **TB**, **BDT** or **EDOT**) (0.15 mmol) and then placed in the glove box. *o*-Xylene (1 mL) was added into the mixture and the tube was capped with a septum before taking out of the glove box. The mixture was stirred at room temperature for 5 min and then placed in a pre-heated oil bath at 100 °C for 24 hours. After cooling to room temperature, the reaction mixture was poured into ice methanol. The resulting solid was filtered and subjected to Soxhlet extraction in methanol and hexane for the removal of low molecular weight materials and impurities. The remaining polymer was extracted with chloroform, precipitated again from ice methanol and dried under vacuum.

P1: 98% yield, dark purple solid; **P2**: 80% yield, red solid; **P3**: 55% yield, deep red sticky gel; **P4**: 97% yield, purple solid.

5.6.3. Device fabrication

Bottom-gate/top-contact OFETs were fabricated using heavily doped Si wafer as the bottom gate electrode with 300 nm of SiO_2 layer as the gate

dielectric. Gold source and drain electrodes (60 nm) were patterned by the vacuum thermal evaporation. The substrate was cleaned in acetone and isopropanol, and dried on the hot plate at 80 °C, followed by treating with piranha solution at 90 °C for 2 hours, washing with water, drying on the hot plate at 110 °C. After that, the substrate was immersed in the ODTS solution (Toluene as the solvent) overnight, rinsed with toluene to remove extra ODTS and dried on the hot plate at 110 °C. The polymers were dissolved in chlorobenzene at a concentration of 10 mg/mL by stirring for two days. The polymer films were spin coating onto the substrate at 2000 rpm and annealed at a designated temperature for 10 min. Finally, gold electrode with 60 nm was thermally evaporated in vacuum through a shadow mask with the following dimension (length (L) = 200 μ m and channel width (W) = 4.0 mm). The field effect mobilities were extracted from the saturation regime using the relationship $\mu_{\text{sat}} = (2I_{\text{DS}}L)/(WC(V_G - V_{th})^2)$, where I_{DS} denotes the saturation drain current, C is the capacitance ($C_i = 10.8 \times 10^{-9}$ F·cm⁻²) of SiO₂ dielectric, V_G is the gate bias, and V_{th} is the threshold voltage.

5.7. References

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Chapter 6

Synthesis and applications of highly fluorescent

DPP-based biodegradable polymer

From Chapter 2-5, the focus is to synthesize DPP-based conjugated polymers by novel direct arylation polymerization method, and these polymers served as charge-transport materials in OFETs. As mentioned in Section 1.4., π -conjugated polymers can be useful in both electronic devices and biomedical application. After the study on electronics applications for DPP-based polymers synthesized by direct arylation polymerization in previous four chapters, we further explored the potential of DPP-based polymers (brushes) in biomedical area.

In the following two chapters, the major target is to synthesize DPP-based low bandgap conjugated polymer brushes with biodegradable side chains (**Scheme 6.1**), which could absorb near-infrared light for photothermal therapy with good biocompatibility as well.

With our experience on direct arylation polymerization for DPP-based conjugated polymers from Chapter 2-4, the target polymer brushes could be obtained by direct arylation polymerization between a building block and DPP-based monomer with a functional group in the side chain, followed by grafting biodegradable polymer to the conjugated backbones (route 1); in an alternative way, a grafting through method (route 2) by direct arylation polymerization between a biodegradable DPP-based polymer and another building block could afford DPP-based conjugated polymer brushes as well. The polymer brushes are expected to show low bandgap nature and strongly absorb near-infrared light. The biodegradable polymer side chains could also minimize the

cytotoxicity issue considering the application of these polymer brushes for photothermal therapy.

Scheme 6.1 Two synthetic routes towards DPP-based conjugated polymer brushes.

Before obtaining target polymer brushes, in this chapter, we first synthesized and characterized simple model polymers (PCL-DPP-PCL) which contain DPP core linked with biodegradable polymers (polycaprolactone (PCL) in this study) of different chain lengths. The relationship between optical properties, especially fluorescent properties of PCL-DPP-PCL and PCL chain length was

investigated from solution to solid states. The strong fluorescence of PCL-DPP-PCL with long PCL chains enabled the application of this polymer as polymeric scaffolds for cell interfacing and long-term tracking.

Further applications of PCL-DPP-PCL as a macromonomer for synthesis of low bandgap π -conjugated polymer brushes will be described in Chapter 7.

6.1. Introduction

Fluorescent organic and polymeric materials with high fluorescence quantum yield, particularly in solid states, are important for applications such as light emitting diodes,^[1, 2] fluorescent sensors^[3, 4] and bioimaging.^[5, 6] Despite advances in synthesis of a great number of fluorescent molecules and polymers to match these increasing demands,^[4, 7-14] most of these materials could be highly fluorescent only in dilute solution where the intermolecular aggregation is minimal. In films or bulk solid states, however, these molecules/polymers that normally consist of π -conjugated aromatic groups tend to aggregate and lead to partial or complete quenching of fluorescence.

To overcome this effect of aggregation-caused quenching (ACQ), Tang and coworkers^[7, 15-17] have developed a series of organic dyes that show aggregation-induced emission (AIE), i.e. non-fluorescence or relatively weak fluorescence in dilute solution of a good solvent in which the intermolecular aggregation of dyes is negligible, but strong fluorescence when the dyes form aggregates in the form of nanoparticle dispersions or bulk solid states. AIE

effect, nevertheless, has been observed only in limited groups of organic dyes and polymers. Other strategies to reduce ACQ effect of π -conjugated systems have also been developed. For example, dispersing these fluorophores in a solid matrix of polymers helps to suppress the intermolecular aggregation. Mainly two approaches have been utilized to incorporate fluorescent dyes into polymeric materials: physical blending^[18-21] and chemical linkage.^[15, 22, 23] Physically mixing organic dyes into polymers has advantage of attaining new properties without synthesizing new polymer structures. Fluorescence quenching induced by phase separation, however, can occur when the dye is not compatible in the polymer matrix. Distinct from physical blending, chemical linkage offers the opportunity to tune the phase separation by introducing dyes in polymers by (1) growth of polymer chains from a dye as the initiator^[24] (“grafting from”); (2) post-modification of a polymer at a reactive position at side chains, the chain end,^[25] or the junction^[26] between blocks with a functionalized dye (“grafting to”); and (3) polymerization of a dye-labeled monomer^[27] (“grafting through”).

Dye-labeled polymers at specific sites have been synthesized using a variety of living/controlled polymerization methods.^[24-30] There are mainly two approaches of introducing a single organic dye in the middle of a polymer chain. The first is to introduce an organic dye at one end of a polymer chain, followed by growth of the second polymer chain from the dye as the joint.^[26] The second is to synthesize an organic dye with dually functionalized initiating groups, followed by the growth of polymer chains outwards. For example, water-

soluble linear^[9] and dendritic^[31, 32] polymer chains have been grafted from perylene derivatives to retain strong fluorescence in aqueous solution for bioimaging applications. Zhu and coworkers synthesized an amphiphilic PEG-*b*-PMMA polymer containing green fluorescent protein (GFP)-like chromophore in the polymer chain, which was also utilized for cell imaging.^[33] O'Bryan et al. synthesized a poly(ϵ -caprolactone) (PCL) labelled photochromic indolinospiropyran which had a significant mechanochromic response to an induced stress.^[34] Fraser and coworkers studied a series of BF₂dbm-capped PLA polymers with different chain lengths. They found that the increase of molecular weight of the polymers resulted in blue-shift of the emission spectra in both powder and film states.^[35]

Despite these recent advances, the effect of polymer chain length on fluorescence properties of polymer-dye adducts has been rarely studied. Herein we focus on the “grafting from” approach in order to introduce a single organic dye in the middle of a polymer chain. We expected that when the polymer chain is long enough, the steric effect brought by polymer chains could suppress the intermolecular π - π stacking between the organic dyes, thus maintaining high fluorescence quantum yield in solid states. Meanwhile, the low weight fraction of the organic dye in the polymer matrix is favorable to maintain the inherent properties of the polymer itself.

As a proof of concept, we chose polycaprolactone (PCL) which is an aliphatic polyester with good mechanical properties due to its high crystallinity.

It possesses excellent thermoplastic properties with a melting temperature around 60 °C, and it is soluble in a number of solvents and even polymers.^[36] As a result, PCL can be manufactured relatively inexpensively. Recent study has shown that the raw material can be obtained from vegetable oil as well as from traditional petroleum-based sources, which is expected to be more biologically safe and economically viable. The most noteworthy property of PCL is its biodegradability into nontoxic small molecules which can be excreted by a human body, accomplished either by autocatalysis or under the help of enzyme. These properties have led to a number of biomedical applications such as tissue engineering^[37] and drug delivery.^[38]

DPP derivatives are known in industry as efficient and stable pigments for a long time. In the past decade, DPP-based small molecules and polymers have been widely studied in OPVs ^[39-47] and OFETs ^[48-53]. Besides their excellent performance in electronic devices, strong fluorescence of DPP-based materials also attracted attention to biomedical applications such as in bioimaging^[54, 55] and DNA elongation.^[8] However, small molecular DPP derivatives, particularly thiophene-flanked DPP (1,4-diketo-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole (DTDPP)) derivatives, tend to aggregate in solid states via strong intermolecular π - π interaction.^[56] Such aggregation leads to nearly complete quenching of fluorescence.

To retain DTDPP's strong fluorescence in solid states, herein we report the synthesis and characterization of four DTDPP-labelled PCL polymers (denoted

as **PCL-DPP-PCL (P1-P4)**, **Scheme 1**) with different PCL chain lengths via ring-opening polymerization (ROP). In particular, we studied how the chain length of PCL affects the fluorescent properties of DTDPP in solid states. A combination of UV-Vis absorption spectroscopy, steady-state and dynamic fluorescence study confirmed that when the number-average degree of polymerization (n) of PCL side chain extended to $n > 100$, the intermolecular aggregation of DTDPP can be reduced significantly due to segregation effect of PCL, resulting in bright fluorescence in different forms of condensed states including nanoparticle dispersions, films and solid powders.

6.2. Synthesis and characterization of PCL-DPP-PCL polymers

6.2.1. Synthesis of PCL-DPP-PCL

The synthetic route to **PCL-DPP-PCL** is shown in **Scheme 6.2**. Four **PCL-DPP-PCL** polymers with extended chain lengths from **P1** to **P4** were obtained through ring opening polymerization with different initiator/monomer ratios in toluene, using a DPP derivative (**DPP-OH**) as the initiator and tin octoate as the catalyst.

Scheme 6.2 Synthetic route to **PCL-DPP-PCL** and molecular structure of **PCL-EG-PCL**.

6.2.2. Structure characterization and thermal properties of **PCL-DPP-PCL**

The $^1\text{H-NMR}$ spectra of **P4** (Figure 6.1b) showed characteristic peaks of the protons in the thiophene rings which are similar to those in **DPP-OH** (Figure 6.1a) at 8.9, 7.6 and 7.3 ppm, respectively. The peaks at 4.0, 2.3, 1.6 and 1.4 ppm, respectively, are attributed to the protons in PCL chain of **P4**. The number-average molecular weight (M_n) and M_w/M_n of the obtained polymers determined from GPC results are presented in Figure 6.2 and Table 6.1. The M_n of **P1-P4** was 6720, 11800, 25000 and 38300, respectively. M_n estimated

from the integration ratio of the thiophene protons over those of the PCL chain was consistent with the results measured by GPC. TGA analysis of **P1-P4** showed that the decomposition temperature (T_d) in the range from 273 to 306 °C increased with the increase of M_n (**Figure 6.3a**). To investigate the effect of DPP unit on the properties of PCL itself, we compared the thermal properties of **PCL-DPP-PCL** with those of a commercial **PCL** ($M_n = 8.0 \times 10^4$, denoted as **PCL (80K)**) and a model polymer **PCL-EG-PCL** ($M_n = 2.17 \times 10^4$, **Scheme 1**) bearing an ethylene glycol in the middle of the polymer. TGA curves of **PCL-EG-PCL** and **PCL (80K)** showed that they decomposed at 285 and 379 °C, respectively, and the decomposition both ended over 400 °C.

Melting temperatures (T_m) of **P1-P4** based on the DSC curves (**Figure 6.3b**) were determined to be 51, 52, 56 and 57 °C, respectively. This result indicates that the increase of M_n led to higher T_m for **PCL-DPP-PCL**. The values of T_m of **PCL-EG-PCL** (58 °C) and **PCL (80K)** (57 °C) were closer to **P1-P4**, while the T_d rose significantly with increasing molecular weight from **P1**, **P2**, **PCL-EG-PCL**, **P3**, and **P4** to **PCL (80K)**. Among the polymers of **P1-P4**, **P1** with the highest percentage of DPP unit in the PCL chain showed the lowest T_m in the DSC curve, whereas **P4** with the lowest percentage of DPP showed a T_m identical to that of the commercial **PCL (80K)**. These results suggested that **PCL-DPP-PCL** polymers (e.g. **P4**) with a relatively low amount of the dye tend to exhibit the intrinsic properties of pristine PCL, which may benefit the applications of these functionalized polymers, for example, for biomedical engineering.^[57]

Figure 6.1 ¹H-NMR (300 MHz) spectra of (a) DPP-OH and (b) P4 in CDCl₃.

Figure 6.2 GPC traces of **P1-P4** with (a) RI and (b) UV-Vis (550 nm) detector.

Table 6.1 Characterization data of **PCL-DPP-PCL (P1-P4)** and **PCL-EG-PCL**.

Polymer	$n_{\text{initiator}} : n_{\text{CL}}$ (mol/mol)	M_n^a	M_w/M_n	n^a	n^b	Yield ^c	T_m (°C)	T_d (°C)
P1	1:50	6720	1.42	27	32	48%	51	273
P2	1:100	11800	1.41	50	56	82%	52	281
P3	1:200	25000	1.70	107	115	89%	56	304
P4	1:1000	38300	1.98	185	198	94%	57	306
PCL-EG-PCL	1:215	21700	1.32	94	103	95%	58	285
PCL (commercial)	-	80000	< 2	-	-	-	57	379

^a Values determined by GPC; n represents the number-average degree of polymerization of one PCL chain in the polymer.

^b Values determined by ¹H-NMR; n represents the number-average degree of polymerization of one PCL chain in the polymer.

^c Values determined based on the amount of ϵ -CL in the polymer chain.

Figure 6.3 (a) TGA and (b) DSC curve of **P1-P4**, **PCL-EG-PCL** and **PCL 80K**.

6.2.3. Optical properties of PCL-DPP-PCL

6.2.3.1. Optical properties of PCL-DPP-PCL in THF solutions

After structural characterization of **P1-P4**, we further characterized their optical properties. We started by examining the solutions of **P1-P4** in THF (1.0×10^{-7} M). The UV-Vis absorption spectra of **P1-P4** (**Figure 6.4**) show two characteristic peaks of DTDPP unit around 510 and 550 nm, respectively, owing to the intramolecular charge transfer from the electron-donating thiophene to the electron-accepting DPP unit.^[58]

The steady-state fluorescence (FL) emission spectra (**Figure 6.4b**) of **DPP-OH** show a sharp peak at 558 nm, accompanied by a shoulder peak at 602 nm. The emission spectra of **P1-P4** appear similar to that of **DPP-OH**. In addition, dynamic FL spectra shown in **Figure 6.4c** indicate that the FL lifetime (8.9 to 9.3 ns) of **P1-P4** remained similar to each other, which was higher than that of

DPP-OH (8.2 ns). All of these curves showed mono-exponential decay dynamics. These results conclude that the attached PCL side chains do not affect the optical properties of DTDPP unit in a good solvent (e.g. THF) for both DTDPP and PCL, and that there is no obvious π - π aggregation between DTDPP units in diluted THF solution.

Figure 6.4 Normalized (a) absorption, (b) fluorescence spectra and (c) fluorescence decay curves of **P1-P4** and **DPP-OH** in THF solution.

6.2.3.2. Optical properties of PCL-DPP-PCL nanoparticles in aqueous dispersions

To understand how the chain-length variation of PCL affects the optical properties of DPP in solid states, we characterized the optical properties of **DPP-OH** and **P1-P4** in the form of nanoparticles (NPs) prepared through a nanoprecipitation process using Pluronic-127 as the stabilizer (The detailed procedure is described in Experimental Section). The sizes of the resulting NPs were determined from the SEM results (**Figure 6.5**). The NPs formed by **DPP-OH** showed an average diameter of 30 ± 3 nm. The NPs formed by **P1** had a similar size to that of **DPP-OH**, while the size of NPs formed by **P2** was slightly larger (42 ± 5 nm). **P3** and **P4** NPs in water suspension showed even larger particle size of 174 ± 8 nm and 221 ± 12 nm, respectively. The prolonged PCL side chains attached to **DPP** core for **P3** and **P4** significantly increased the intermolecular distance which resulted in the larger **NPs** size for **P3** and **P4** in some extent. In addition, **P3** and **P4** NPs tended to form some aggregates, which might also contribute to the larger NPs size as well. The formation of aggregates could be also observed from less spherical NPs in the SEM images of **P3** and **P4**.

Figure 6.5 SEM images of (a) **DPP-OH**, (b) **P1**, (c) **P2**, (d) **P3** and (e) **P4** NPs from water dispersions.

Figure 6.6 Digital photos of **DPP-OH** and **P1-P4** NPs in water dispersions under room light (left) and under UV (365 nm) light (right).

Figure 6.6 shows the digital photographs of the NP dispersions of **DPP-OH** and **P1-P4** in water under ambient light and UV light (365 nm), respectively. **P3** and **P4** NPs showed strong yellow fluorescence under irradiation of UV light, while **P1** and **P2** exhibited weak pink fluorescence and **DPP-OH** appeared non-fluorescent at all. **Figure 6.7** shows the absorption spectra of the NP dispersions formed by initiator and four polymers. The maximal absorption

peak of **DPP-OH** in the form of NPs dispersion red-shifted to 590 nm (**Figure 6.7b**), suggesting the presence of *J*-aggregates^[58, 59] formed by DPP units inside the NPs. In contrast to **DPP-OH**, the absorption spectra of **P1** and **P2** remained similar to those in THF solution. Due to the relatively large particle size formed by **P3** and **P4**, the light scattering effect led to the up-shifted baseline and blurring of the absorption peaks around 510 and 550 nm, respectively. **P4** NPs with various loading concentrations ranging from 1×10^{-6} M to 4×10^{-5} M all showed significant light scattering effect even with a relatively smaller size (e.g. 80 nm, obtained from DLS) at a lower loading concentration (e.g. 1×10^{-6} M). Nevertheless, there was no shift of the characteristic absorption peaks of DPP units in **P4** (**Figure 6.7a-b**) at all of the tested concentrations.

In order to further understand the aggregation state of DPP units in the NPs, we characterized these samples by both steady-state (**Figure 6.7c-d**) and dynamic FL spectroscopy (**Figure 6.8a**). The steady-state emission spectra (**Figure 6.7c**) of the NPs show that the FL of the NPs formed by **DPP-OH** was dramatically quenched compared to other NPs formed by the polymers (i.e. **P1-P4**), consistent with the digital photograph shown in **Fig. 3**. There was a slight increase of the emission intensity from **P1** NPs to **P2** ones, followed by a more significant increase of the FL intensity from **P2** to **P3**. **P3** and **P4** showed comparable FL intensity when their absorption spectra were matched well.

Figure 6.7 Non-normalized (a) absorption, (c) emission (excited at 480 nm) spectra and normalized (b) absorption, (d) emission spectra of **DPP-OH** and **P1-P4** NPs in water dispersions.

The normalized FL spectra (**Figure 6.7d**) show that there was a slight blue shift of the maximal emission peak with the increase of the M_n . More detailed analysis of the relative FL intensity of the two emission peaks (around 560 and 602 nm, respectively) are shown in **Table 6.2**. The ratio (I_{602}/I_{560}) of the emission intensity at 602 nm over that at 560 nm remained 0.25 for **P3** and **P4** both in THF solution and in NP dispersions, implying little aggregation of DPP units in **P4** NPs.^[60, 61] Moreover, different loading concentrations of **P4** NPs all showed similar normalized emission spectra with the same ratio of I_{602}/I_{560}

(around 0.25). For NPs formed by **P1** and **P2** with lower M_n and moderate FL intensity, the ratio of I_{602}/I_{560} is slightly larger (0.30 for **P2** and 0.33 for **P1**). Among all of the NP samples, the one formed by **DPP-OH** with the weakest FL intensity showed the largest ratio (0.56) of I_{602}/I_{560} , implying the significant *J*-aggregation inside the NPs when no PCL chains were grafted from the DPP unit.

Table 6.2 Summary of UV-Vis absorption and steady-state FL results of **DPP-OH**, **P1-P4** in NPs.

Compound	$\lambda_{\text{abs, max}}$ (nm)	$\lambda_{\text{em, max}}$ (nm)	I_{602}/I_{560}^a
DPP-OH	589	568	0.56
P1	552	564	0.33
P2	552	563	0.30
P3	- ^b	560	0.25
P4	- ^b	560	0.25

^a I_{602} and I_{560} represent the FL intensity at two peaks around 602 and 560 nm, respectively; I_{602}/I_{560} represents the ratio of FL intensity at 602 nm over that at 560 nm.

^b The maximum absorption wavelength of **P3** and **P4** in NPs is not listed due to the poorly-defined absorption spectra caused by light-scattering effect of the aggregates.

Figure 6.8 Normalized fluorescence decay curves of (a) **P1-P4** NPs in water dispersions and (b) **P3**, **P4** in films.

We further employed dynamic FL spectroscopy to study the aggregation behavior of these NP dispersions. The FL signal of NPs samples formed by **DPP-OH** was too weak and the FL decay was too fast to be detectable using a nanosecond fluorometer. In contrast to **DPP-OH**, NPs formed by **P1-P4** in an aqueous dispersion all showed a mono-exponential decay curve (**Figure 6.8a**). The FL lifetime of **P1** and **P2** NPs decreased to 6.2 and 6.5 ns, respectively, compared to 9.3 ns of these two polymers in THF solution. The FL lifetime of the NP dispersion formed by **P3** and **P4** was 8.8 and 9.1 ns, respectively, which was comparable to the FL lifetime of these two polymers in THF solution. These results indicate some aggregation of DPP units in **P1** and **P2** NPs in aqueous dispersions, whereas such aggregation was more effectively suppressed in the NPs formed by higher-molecular-weight polymers such as **P3** and **P4**. Such difference could be attributed to the fact that the longer PCL side

chains tend to form a much tighter coil to minimize unfavorable interactions with the solvent (i.e. water). In addition, the intermolecular π - π stacking between DPP fluorophores is suppressed and strong fluorescence in the aqueous dispersion is retained.

The results above imply that PCL as the side chain with an average chain length of $n = 50$ (i.e. **P2**) is not long enough to suppress the π - π aggregation of DPP units in the form of NPs. Nevertheless, a further increase of the PCL chain length up to $n > 100$ (i.e. **P3** and **P4**) reduces the intermolecular aggregation among DPP units effectively. The ability to retain strong fluorescence of fluorophore (**DPP** in this case) in NPs dispersions by covalently attaching biodegradable side chains with certain chain length showed that our approach could be promising to bioimaging applications for those fluorophores with strong intermolecular interactions. And the segregation effect of PCL side chains was further observed in thin films and bulk solid states as discussed in the following section.

6.2.3.3. Optical properties of PCL-DPP-PCL in films and bulk solid states

Figure 6.9 shows the digital photographs of **DPP-OH** and **P1-P4** in films (**Figure 6.9a**) and bulk solid states (i.e. powders) (**Figure 6.9b**) under room light and UV (365 nm) light, respectively. It is clear that only **P3** and **P4** retain bright yellow fluorescence in these solid states, whereas **P1** and **P2** show dim red fluorescence and **DPP-OH** is non-fluorescent at all.

Figure 6.9 Digital photos of **DPP-OH** and **P1-P4** (a) films and (b) solid powders under room light (left), under UV (365 nm) light (right).

Figure 6.10 (a) Non-normalized and (b) normalized absorption spectra of **DPP-OH** and **P1-P4** in films; (c) non-normalized and (d) normalized emission (excited at 480 nm) spectra of **P1-P4** in films.

Such different optical properties can be seen more quantitatively in the UV-Vis absorption and FL emission spectra of these samples in films. As shown in **Figure 6.10**, the maximal absorption peak of **DPP-OH** again showed a significant red-shift of 40 nm compared to those of the PCL-DPP-PCL polymers (**P1-P4**), whereas **P1-P4** showed two characteristic peaks around 510 and 550 nm, respectively (**Figure 6.10a-b**). The steady-state FL emission spectra (**Figure 6.10c**) of **P3** and **P4** appeared similar in the films. Both of them maintained high FL intensities with emission characteristics similar to theirs in THF solutions, whereas the FL intensities of **P1** and **P2** were rather weak. The normalized FL emission spectra (**Figure 6.10d**) show a 40 nm red shift of the maximal emission peak in solid films formed by **P1** and **P2** in comparison to those of **P3** and **P4**. In addition, the emission spectra of **P1** and **P2** in films were obviously broader than those of **P3** and **P4**. It should be noted that the steady-state FL emission from the film of **DPP-OH** was too weak to be detected, consistent with the digital photo presented in **Figure 6.9a**.

Again, dynamic FL spectroscopy was employed to further characterize the FL properties of **DPP-OH** and **P1-P4** in films. **P3** and **P4** in films (**Figure 6.8b**) both exhibited mono-exponential FL decay curves that gave FL lifetime of 8.6 and 8.7 ns, respectively. The FL lifetimes in films of these two polymers were only slightly shorter than those (8.9 and 9.2 ns for **P3** and **P4**, respectively) observed in THF solutions. The FL decay curves of **DPP-OH**, **P1** and **P2** in films, however, could not be obtained from the nanosecond fluorometer due to their extremely weak FL signals.

Figure 6.11 presents the relationship between the relative FL intensity of **P1-P4** and the PCL chain length (n) in films. The FL intensity of PCL-DPP-PCL in films remained almost same with n increasing from 27 (**P1**) to 50 (**P2**) (both relatively weak), followed by a dramatic FL enhancement when n was further increased from 50 (**P2**) to 107 (**P3**). The FL intensity reached a plateau in solid films when n was increased from 107 (**P3**) to 185 (**P4**). These results imply that the critical chain length (n^*) of PCL to suppress the intermolecular aggregation of the DPP units lies in the range of $50 < n^* \leq 110$.

Figure 6.11 The fluorescence intensity (normalized) of **P1-P4** in films vs. the number-average degree of polymerization (n) of one PCL chain in **PCL-DPP-PCL** polymers.

6.2.3.4. Comparison of optical properties of **P4** in different states

Figure 6.12 and **Table 6.3** summarize the difference of the steady-state (**Figure 6.12a**) and dynamic (**Figure 6.12b**) FL properties of **P4** in different

states, i.e. dilute solution in THF, NP dispersion in water, and drop-cast films. The red shift of the maximal FL peak of **P4** from THF solution to films implies that even for **P4**, aggregation behavior among DPP units is slightly more serious in films than that in NP dispersions. But overall, there was no significant change of the FL lifetime of **P4** from THF solution, NP suspensions to films (**Fig. 7b**).

Figure 6.12 Normalized (a) steady-state fluorescence emission spectra ($\lambda_{\text{ex}} = 480$ nm) and (b) fluorescence decay curves of **P4** in THF, NPs and films.

Table 6.3 Summary of optical properties of **P4** in different states.

State of P4	$\lambda_{\text{abs, max}}$ (nm)	$\lambda_{\text{em, max}}$ (nm)	I_{602}/I_{560}^a	FL lifetime (ns)
THF solution	548	557	0.25	9.2
NPs dispersion	- ^b	560	0.25	9.1
Film	549	562	0.37	8.7

^a I_{602} and I_{560} represent the FL intensity at two peaks around 602 and 560 nm, respectively;

I_{602}/I_{560} represents the ratio of FL intensity at 602 nm over that at 560 nm.

^b The maximum absorption wavelength of **P4** in NPs is not listed due to the poorly-defined absorption spectra caused by light-scattering effect of the aggregates.

Scheme 6.3 A schematic illustration of the covalent strategy of tuning fluorescent properties of DPP-based fluorophores using polymers such as PCL in condensed states: (a) DPP small molecules (**DPP-OH**), (b) low M_n PCL-DPP-PCL (**P1**, **P2**) and (c) high M_n PCL-DPP-PCL (**P3**, **P4**).

Scheme 6.3 shows a proposed mechanism of this covalent strategy of tuning FL properties of DPP-based fluorophores using polymers such as PCL. For DPP small molecules (e.g. **DPP-OH**) with relatively short alkyl chains, the strong π - π interaction leads to significant intermolecular aggregation and tendency of crystallization in condensed states. When the DPP unit is covalently linked in the middle of PCL chain with a relatively low molecular weight (e.g. $n < 50$, **P1** and **P2**), PCL chains tends to segregate DPP units to some extent, but there is still certain extent of intermolecular interaction (largely π - π stacking) among DPP units in solid states. When the PCL chain is extended to a certain length (e.g. $n > 100$, **P3** and **P4**), the steric effect of the

PCL chains dominates and effectively segregates DPP units, resulting in strong fluorescence in condensed states (i.e. NP suspensions, films, and solid powders).

6.3. PCL-DPP-PCL polymeric nanofibers as scaffolds for cell interfacing and long-term tracking

In tissue engineering, artificial substrates are developed to mimic the natural *in vivo* micro-environment in which cells reside.^[62, 63] How cells respond to and interact with these substrates provides essential information in stem cell therapies and regenerative medicine.^[64, 65] In order to accurately evaluate the mechanisms behind cell-substrate interactions, fluorescence labeling has been used extensively for visualization and tracking. To date, much effort has focused on cells – e.g. tracking cellular uptake of biomolecules with labeled DNA/RNA^[66, 67] or labeled nanoparticles^[68], or tagging intracellular components^[69, 70]. However, the study of cell-substrate interactions also includes visualization of the substrate on which cells grow. Unfortunately, the development in this aspect remains rarely explored.

Thus far, commercialized fluorescent compounds, such as FITC and Rhodamine, are the most commonly used approaches for labeling and visualizing extracellular materials such as proteins or polysaccharides^[71-73]. However, the leaching and poor photo-stability of these dyes remain the major obstacles to their wide-spread applications, especially for long-term tracking

and imaging purposes. Recently, a semiconducting luminescent polymer was developed for long-term optical non-invasive tracking, but the detailed interaction between cells (especially stem/progenitor cell) and its underlying substrate remains undetectable^[74]. More delicate tracking such as cell-substrate temporal interaction requires new functional polymeric scaffolds with good biocompatibility and fluorescent properties.

Very recently, we have designed and synthesized a series of highly fluorescent and photostable polycaprolactones (PCLs) covalently linked with fluorescent DPP in the middle of each polymer chain.^[75] The fluorescence properties of these polymers (denoted as **PCL-DPP-PCL**) in solid states are determined by the average polymer chain length of PCL. Particularly, these polymers with a number-average degree of polymerization (n) of PCL over 100 show strong yellow fluorescence that is intrinsic to aggregation-free DPP in different states such as solid films and aqueous dispersion of nanoparticles.^[75] Moreover, the highly fluorescent and photostable nanoparticles composed of PCL-DPP-PCL ($n = 185$) can be internalized by tumor cells and multipotent stromal cells for cell imaging.^[75] Nevertheless, the potential of these functional PCL polymers as cell extracellular matrix for tissue engineering has not been explored so far.

Here, we present highly fluorescent and photostable electro-spun polymeric nanofibers that serve as scaffolds for cell interfacing. These fluorescent nanofibers composed of **PCL-DPP-PCL (P4, $n = 185$)**^[75] provide striking

contrast for studying cell-substrate interactions and are useful for long-term tracking. As compared to various cellular tracking compounds, the methods of labeling scaffold are still limited to using FITC or Rhodamine, which are always tagged to the end groups of biomolecules that make up the extracellular matrix or scaffold. Unfortunately, in these methods, dyes that are tagged to the matrices often suffer from fast photobleaching because of their intrinsic nature of poor photostability, as they are easily exposed to the environment by being tagged to the ends of biomolecules. This leads to the limitation of their applications in long-term tracking of cell-substrate interactions. As compared to the common sulforhodamine-labeled electrospun fibers in which the dye was physically dispersed in the polymer matrix^[73], our **PCL-DPP-PCL** fibers show superior photostability and significantly less leaching. Importantly, by using human dermal fibroblasts and primary rat oligodendroglial precursor cells (OPCs) as the model adult somatic cell and progenitor cell respectively, we demonstrate that the cytocompatibility and cell attachment were not compromised as compared to unmodified commercial PCL. In addition, these **PCL-DPP-PCL** fibers enabled clear visualization of intricate cell-substrate interactions such as oligodendrocyte (OL) myelination.

Figure 6.13 summarizes the overall experimental approach taken in this study. **PCL-DPP-PCL** fibers were fabricated from **PCL-DPP-PCL** and commercial PCL mixture by electrospinning method. The superior photostability of **PCL-DPP-PCL** fibers offers the opportunity to monitor cell-substrate interaction for long-term tracking. More specifically, as a proof of

concept, OPCs were treated with **PCL-DPP-PCL** fibers to visualize and provide better understanding of OPC myelination, which is related to cell-extracellular environmental interactions.

Figure 6.13 Schematic illustration of **PCL-DPP-PCL** fibers fabrication and interaction with Oligodendrocyte precursor cell (OPC).

Figure 6.14 SEM images of electrospun nanofiber scaffolds: (A) PCL, (B) PCL-DPP-PCL fiber scaffolds. Fluorescence images of: (C) PCL-DPP-PCL fibers (20% mol in PCL), (D) DPP-EH fiber (20% mol in PCL), and (E) R6G fiber (20% mol in PCL) in 1 min under 514 nm light irradiation (2W). The scale bars shown in images recorded at 60 s are applicable to images recorded at 0 s, 20 s and 40 s for (C), (D) and (E). Leaching profile (F) of R6G, DPP-EH and PCL-DPP-PCL nanofibers in PBS buffer at 37°C in 7 days.

As shown in **Figure 6.14**, when processed under the same electrospinning parameters, PCL (**Figure 2A**, $2.044 \pm 0.367 \mu\text{m}$) and **PCL-DPP-PCL** fiber scaffolds (**Figure 6.14B**, $1.985 \pm 0.62 \mu\text{m}$) possessed similar substrate morphology and average fiber diameters. These images indicated that DPP conjugation did not affect the diameter of electrospun fibers.

We then investigated the photostability of **PCL-DPP-PCL** in solid states, specifically in fibrillar scaffolds that are ultralong but very thin (sub-micron to nanometers) in diameter. Another commonly used fluorophore R6G as well as a DPP-based small molecule (DPP-EH) were chosen as controls. As shown in **Figure 6.14-(C-E)**, only **PCL-DPP-PCL** nanofibers (**Figure 6.14C**) retained relatively strong fluorescence intensity after 60 s of 2W-laser irradiation, while the two small molecular fluorophores, DPP-EH (**Figure 6.14D**) and R6G (**Figure 6.14E**), showed significant photobleaching phenomenon under the same conditions. These results are consistent with the photostability of PCL-DPP-PCL in colloidal spherical nanoparticles,^[75] which further demonstrates that our molecular design of **PCL-DPP-PCL** is efficient in suppressing fluorescence quenching and improving the photostability of organic fluorophores in both nanoparticles and other forms of solid states (e.g. nanofibers and thin films).^[75]

Due to the hydrophilic nature of R6G, obvious leaching (up to nearly 8% after 7 days) of the organic dye was observed, whereas almost no leaching (less than 0.01 %) could be detected from the nanofibers that were composed of

either DPP-EH or **PCL-DPP-PCL** as they are both hydrophobic (**Figure 6.14F**). To summarize, both photostability and leaching tests suggested that PCL-DPP-PCL nanofibers were stable and could potentially be used for long-term imaging and monitoring of cell-substrate interactions.

Figure 6.15 Actin cytoskeleton structures of HDFs (A and B, 40X, day 14) and OPCs (C and D, day 3) on PCL (A, C) or **PCL-DPP-PCL** (B, D) fiber scaffolds, as revealed by Phalloidin staining. And (F) quantification of OPC cell

viability (mean $\pm$ SD, N = 3). * $p < 0.05$ (ANOVA), ** $p < 0.01$ (ANOVA) and *** $p < 0.001$ (ANOVA) compared with absorbance (570nm) of same group on day 4, ## $p < 0.01$ (ANOVA) compared with absorbance (570nm) of same group on day 7.

To evaluate the potential of **PCL-DPP-PCL** fiber scaffolds as constructs for understanding cell-substrate interactions, we cultured human dermal fibroblasts (HDF) as the model human adult somatic cell onto **PCL-DPP-PCL** scaffolds. After 14 days of culture, cell attachment appeared unaffected by the presence of DPP conjugation. Specifically, HDF attached firmly on both PCL and **PCL-DPP-PCL** fiber scaffolds (**Figure 6.15A** and **6.15B**), as evident by their typical well-spread morphology and the presence of actin stress fibers throughout the cell bodies.

Besides looking at cell attachment, fluorescent fibers may also serve as useful platforms for evaluating more specific cell functionalities that are related to cell-extracellular environmental interactions, such as myelination. As shown in **Figure 6.15C** and **6.15D**, OPCs on both PCL and PCL-DPP-PCL fiber scaffolds revealed typical structures with a polygonal soma and a multipolar tree of fine processes.^[76] Furthermore, as shown in **Figure 6.15E**, MTT assay indicated similar viability of OPCs on both PCL and **PCL-DPP-PCL** fibers at each time point. As compared to day 4, OPC viability on day 7 was much higher on every scaffold. On day 15, a slight decrease in cell viability was

observed on both PCL and **PCL-DPP-PCL** fiber scaffolds, which may result from cellular contact inhibition. Altogether, DPP conjugation into PCL fiber scaffolds did not affect the cell viability and attachment of primary OPCs. Importantly, given the fact that OPCs are very sensitive to their microenvironment, the normal attachment and viability of primary OPCs as observed on our **PCL-DPP-PCL** scaffolds underscores the cytocompatibility and relevance of our constructs as study platforms for analyzing delicate cell-substrate interactions.

Figure 6.16 OPC-fiber interaction between MBP⁺ (green) OL and PCL-DPP-PCL fiber scaffolds (red) on day 7: (A) (40X) and (B) (100X); day 15 (C) (40X) and (D) (100X). Blue color represents DAPI.

Within the central nervous system (CNS), OPC interacts closely with its microenvironment^[77] and plays critical roles in myelinating nerves. Demyelination leads to devastating outcomes as seen in diseases such as multiple sclerosis (MS). Unfortunately, effective treatments are lacking due in part due to the limited knowledge on OPC myelination^[78]. Therefore, any improvements in experimental strategies and platforms that can facilitate studies and visualization of the myelination process, such as that provided by our **PCL-DPP-PCL** fiber platform has great potential in advancing the field.

OL-substrate interaction is divided into three stages: contacting, extending and wrapping^[79], according to different modes of interaction^[80]. As shown in **Figure 6.16A** and **Figure 6.16B**, after 7 days of differentiation, OL contacted and extended along the fiber, but no wrapping was seen. On day 15, obvious wrapping of OL around our fibers was detected (**Figure 6.16C** and **6.16D**), although most of the cellular extensions remained at an earlier stage such as extending. The extension of OL clearly wrapped around **PCL-DPP-PCL** fiber (as shown by the box and arrow in **Figure 6.16D**), followed by the formation of myelin membrane which ensheathed the bright red PCL-DPP-PCL fiber. Oligodendroglial-neuronal co-culture has been the traditional strategy for understanding OL myelination process. However, decoupling of indirect (neuronal) effects from direct (oligodendroglial) effects is difficult when using such co-cultures^[73]. Although electrospun fibers have been used to investigate OL-substrate interactions^[81], these fibers were labeled with rhodamine, rendering them unstable and unsuitable for long-term fluorescent imaging and

tracking. In contrast, as shown in this study, **PCL-DPP-PCL** nanofibers retained strong fluorescent signals even after 15 days of prolonged cell culture.

6.4. Conclusion

In summary, four **PCL-DPP-PCL** polymers (**P1-P4**) with different chain lengths of PCL were synthesized via ring opening polymerization from an initiator of **DPP-OH**. The structures and properties of these polymers were characterized with $^1\text{H-NMR}$, GPC, TGA, DSC, UV-Vis absorption spectroscopy and fluorescence spectroscopy. The optical properties of these polymers in comparison with a small molecule of DPP derivative (**DPP-OH**) were studied. It was found that **P3-P4** with relatively long PCL side chain ($n > 100$) effectively suppressed the π - π interaction between DPP units, resulting in bright fluorescence of DPP in solid states. We expect that this approach will be applicable to other organic chromophores to address the common problem of aggregation-induced quenching effect.

P4 with longest PCL chain, which is highly fluorescent in films and solid, were used to fabricate **PCL-DPP-PCL** fibers to provide a cytocompatible substrate for primary somatic and precursor cell proliferation and differentiation. Given that fibroblasts attached firmly as seen by stress fiber formation, OPCs proliferated as seen by increased viability, and OPCs differentiated into MBP positive cells that myelinated the fibers, our results demonstrate that **PCL-DPP-PCL** is cytocompatible and not cytotoxic. More importantly, the

enhanced photo-stability of **PCL-DPP-PCL** fiber scaffolds renders these constructs as useful platforms for understanding cell-substrate interactions.

6.5. Experimental Section

6.5.1. Materials and characterization

3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**1**) was prepared according to the published method.^[40] DPP-EH was synthesized according to the literature.^[75] Potassium *tert*-butylate, 2-thiophenecarbonitrile, dimethyl succinate, potassium carbonate, 6-bromo-1-hexanol, magnesium sulfate, Pluronic 127, Rhodamine 6G (R6G), polycaprolactone (PCL, Mw: 80 kDa), 3,4-dihydroxy-L-phenylalanine (DOPA), 2,2,2-trifluoroethnal (TFE, $\geq$ 99.0%), Tris-EDTA (TE) buffer solution (pH 8.0), triiodothyronine (T3), thiazolyl blue tetrazolium bromide (MTT, 98%), dimethyl sulfoxide (DMSO), 10% formalin, triton X-100 and fluoromount medium, 4',6-diamidino-2-phenylindole (DAPI) were purchased from Sigma-Aldrich. Laminin (1mg/ml), Alexa-Fluro 488 goat anti-mouse antibody was purchased from Life Technologies. Mouse anti-myelin basic protein (MBP) (MAB387) antibody was purchased from Merck. Basic fibroblast growth factor (bFGF) was purchased from Peprotech. All solvents were used as received. Anhydrous solvents were obtained through a solvent purification system (Innovative Technologies).

^1H -NMR spectra were measured on a Bruker Avance II 300 MHz spectrometer. Absorption spectra were obtained from Shimadzu UV 2450 ultraviolet-visible spectrometer. Fluorescence spectra were recorded on Perkin-Elmer LS-55 fluorometer. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of polymers were characterized by Agilent Infinity-1260 GPC at room temperature, using polystyrene as standard and THF as eluent. Thermogravimetric (TGA) analysis was run on TA Q500 TGA from room temperature to 500 °C with a heating rate of 10 °C/min, and the decomposition temperature (T_d) was determined by the temperature at which 5% weight loss was occurred. Differential scanning calorimetry (DSC) analysis was performed on TA Q1000 DSC, starting at -80°C and ramping up to 120 °C at 10 °C/min for 3 cycles, and melting temperature (T_m) was determined at third cycle of the curve. Scanning electron microscope (SEM) images were obtained from JEOL JSM6701F FESEM on silica substrate. Dynamic light scattering (DLS) measurement was performance on NanoBrook ZetaPALS particle size analyzer. Dynamic fluorescence (FL) spectra were measured at room temperature using a commercial laser-flash photolysis spectrometer (Edinburgh Instruments LP920-KS), a photomultiplier tube (Hamamatsu R928), a gated CCD (Princeton Instruments, PI-MAX ICCD camera) and a digital oscilloscope (Tektronix TDS-3012C). The samples were excited using a 480 nm laser pulse and the fluorescence decay curves were recorded at the maximal emission wavelength. The FL lifetime is obtained by fitting the FL decay curves using mono-exponential function:

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

Where $I(t)$ is the FL intensity at the time of t with I_0 representing fluorescent intensity at time of 0 and τ in the equation is the fluorescence lifetime.

6.5.2. Synthesis and sample preparation

6.5.2.1. Synthesis of 2,5-bis(6-hydroxyhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (DPP-OH)

A 100 mL round bottom flask was charged with a stir bar, 3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (**1**) (3.60 g, 12 mmol), K_2CO_3 (4.97 g, 36.0 mmol) and DMF (50 mL). The reaction mixture was bubbled with nitrogen under stirring for 10 min at room temperature and heated at 120 °C. Then 6-bromo-1-hexanol (8.68 g, 48 mmol) in 10 mL of DMF was added dropwise (in 30 min) to the reaction mixture. The reaction was kept at 120 °C overnight and the mixture was then cooled to room temperature, poured into 250 mL of water and filtered through a Büchner funnel. The filter cake was washed with water and the obtained crude product was further purified by flash chromatography (dichloromethane: tetrahydrofuran = 20:1 to 1:1) to give dark purple solids (1.68 g, yield: 28%).

6.5.2.2. General procedure for the synthesis of PCL-DPP-PCL polymers (P1-P4)

DPP-OH was added into a sealed Schlenk tube with nitrogen protection. 5 mL of anhydrous toluene was then added to dissolve the initiator under stirring. Then a certain amount of ϵ -caprolactone (CL) (the ratio between **DPP-OH** and CL was shown in **Table 1**) was injected into the reaction mixture, followed by addition of stannous octoate (1mg, 0.002 mmol) as the catalyst. The reaction mixture was then bubbled with nitrogen for 10 min before the Schlenk tube was heated to 110 °C overnight. After being cooled down to room temperature, the resulting mixture was dissolved in 5 mL of THF and then precipitated in ice methanol for three times. All of products were dried overnight at 30 °C in a vacuum oven.

6.5.2.3. Synthesis of PCL-EG-PCL

Ethylene glycol (45.8 mg, 0.73 mmol) was added to a sealed Schlenk tube with nitrogen protection, and dissolved in anhydrous toluene (2 mL) under continuous stirring. ϵ -Caprolactone (18 g, 157 mmol)) was injected into the reaction mixture, followed by addition of stannous octoate (1mg, 0.002 mmol) through the rubber septum with a syringe. The reaction mixture was then bubbled with nitrogen for 10 min before the Schlenk tube was heated to 110 °C overnight. The following separation and purification procedure was the same as described above in synthesis of **PCL-DPP-PCL**.

6.5.2.4. Nanoparticle preparation

Each of the solid samples (**DPP-OH** and **P1-P4**) was first dissolved in THF at a concentration of 1.25×10^{-4} mM (based on the molar amount of DPP unit). A surfactant solution (6.64×10^{-5} M) was prepared by dissolving Pluronic 127 in deionized water (DI water). 5 mL of the surfactant solution was then added into 1 mL of the THF solution of **DPP-OH** or the polymer in the vials using a syringe pump (1 mL/min) under stirring. Afterwards the vials were left uncapped over 24 hours to allow evaporation of THF. The nanoparticles were then separated by centrifugation at 10000 rpm, and redispersed into DI water for further characterization.

6.5.2.5. Film preparation

Each of the compounds **DPP-OH** and **P1-P4** was first dissolved in THF at a concentration of 1×10^{-3} M (based on the amount of DPP unit). Then the solution was drop-cast onto a quartz substrate and used for further characterization after solvent evaporation at room temperature.

6.5.2.6. Fabrication of PCL-DPP-PCL fibers

To electrospin fibers for photobleaching and leaching tests, 10% (mol concentration) of R6G, DPP-EH and PCL-DPP-PCL were mixed with PCL (80K) in TFE with 12 wt% of PCL (80K) separately. Each of these three solutions was first treated with ultrasonication, wrapped with aluminium foil

and then placed on a multi-axe rotating mixer overnight for thorough mixing and complete polymer dissolution. Thereafter, each solution was dispensed at a flow rate of 1.5 ml/h through a 21G needle for electrospinning. The collector was located 12 cm away. A 16 kV (+12 kV and -4 kV) potential was applied between the syringe needle and the rotating collector (2100 rpm). Finally, the morphology of the fibers was evaluated using scanning electron microscopy (SEM) (JEOL, JSM-6390LA, Japan) after sputter-coating with platinum.

6.5.2.7. Photobleaching test

All electrospun samples were irradiated with 514 nm light (2W) under the fluorescent microscope for 100 s. A series of fluorescence images of the nanofibers were recorded every 50 ms for the comparison of photostability of the nanofibers with different fluorescence agents.

6.5.2.8. Leaching test

Each set of electrospun scaffold ($n=3$, average mass = 40.2 ± 1.4 mg for DPP-EH, 45.6 ± 1.7 mg for PCL-DPP-PCL, 43.0 ± 3.3 mg for Rhodamine 6G) was immersed into 10 ml of $1\times$ PBS buffer (pH=7.4) in a 15 ml centrifuge tube. The centrifuge tubes were then placed in the shaking bath at 37 °C and 0.5 mL of solution was collected every 12 h. The leaching percentage of R6G, DPP-EH and PCL-DPP-PCL was determined by fluorescence intensity of each fluorophore that leached into PBS buffer over the total theoretical mass of

fluorophore in the scaffolds (i.e. 0.072 ± 0.003 mg for DPP-EH, 4.15 ± 0.15 mg for PCL-DPP-PCL and 0.054 ± 0.004 mg for Rhodamine 6G).

6.5.2.9. Preparation for poly(DOPA)-laminin coated fibers

To ensure OPC attachment onto fiber scaffolds, coating of PCL and PCL-DPP-PCL fibers was carried out using our published protocol^[82-84]. Briefly, after cutting the scaffolds into 2 cm²- discs to fit 24-well plates, all scaffolds were pre-wet with deionized water overnight. Thereafter, the scaffolds were submerged into 0.5 mg/ml of DOPA that was dissolved in poly(DOPA) coating buffer (50 mM NaCl and 10 mM Bicine, pH=8.5) and agitated at 120 rpm on an orbital shaker for 4 h. Following that, all scaffolds were washed with deionized water to remove residual monomer and lyophilized overnight. Next, after UV sterilization, poly(DOPA) coated scaffolds were immersed into 300 µl of laminin solution at 10 µg/cm² for 2 h.

6.5.2.10. Primary OPC isolation and differentiation

Approved by the Institutional Animal Care and Use Committee (IACUC) at Nanyang Technological University, Singapore, primary OPC was isolated from p1-p2 neonatal rats^[85]. The cortices of neonatal pups were digested with 0.01 % trypsin and 0.01 mg/ml Dnase I for 15 min at 37 °C. After mechanical homogenization, the suspension was passed through a 70 µm cell strainer (BD Biosciences, USA) and seeded in T75 flasks at a density of 10⁶ cells. After 9-10

days of culture, the OPCs were purified by shaking on an orbital shaker for 18-20 h at 37 °C. Thereafter, the cell suspension was passed through a 20 µm sterile screening Nylon pouch (Sefar American, USA) and the OPCs were then seeded onto poly(DOPA)-laminin coated scaffolds at a density of 50, 000 cells in OPC differentiation medium with 10 ng/ml bFGF and 15 nM T3. The medium was changed every other day.

6.5.2.11. Cell viability assay

At indicated time points, three independent scaffolds were collected and washed with 1× PBS. After immersing into 1 ml of MTT solution (1 mg/ml in 1× PBS), the scaffolds were incubated at 37 °C for 4-6 h. Thereafter, MTT solution was discarded and 500 µl of DMSO was added into each well to react with the purple formazan product on the scaffolds. Finally, absorbance at 570 nm was read using a microplate reader (Tecan®, Infinite 200, Austria).

6.5.2.12. Cell skeleton staining

At indicated time points, cell-seeded nanofiber scaffolds were collected and fixed in 10 % formalin and permeabilized with 0.3 % Triton-X 100 in PBS for 20 min. Thereafter, the samples were incubated with phalloidin-488 (1 : 500) and DAPI (1 : 1000) at 37 °C for 30 min followed by imaging under a Zeiss LSM 710 confocal microscope.

6.5.2.13. Immunofluorescent staining

After 15 days of culture, scaffolds were fixed with 10 % formalin and permeabilized with 0.1 % Triton-X 100 in PBS for 20 min. After being blocked with 1.5 % goat serum for 1 h, the samples were incubated with primary anti-MBP antibody (1 : 200) overnight at 4 °C followed by incubation with secondary antibody (1 : 700) for 1 h at room temperature. DAPI was used for nuclei counterstaining. Finally, all samples were mounted and imaged under a confocal microscope (Zeiss LSM 710).

6.5.2.14. Statistical analysis

Quantitative values are presented as mean $\pm$ standard deviation. After F-test, the one-way ANOVA and Turkey post-hoc tests were used when samples had equal variances. Otherwise, the Kruskal-Wallis and Mann-Whitney *U*-tests were used.

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Chapter 7

Synthesis of DPP-based conjugated polymer brushes by direct arylation polymerization

In Chapter 6, model DPP-based biodegradable polymers were successfully synthesized before pushing forward to the conjugated polymers brushes in Chapter 7. In this Chapter, two synthetic strategies were used to obtain polymer brushes (**Scheme 6.1**): (1) synthesize the DPP-based conjugated polymer backbones by direct arylation polymerization first, and then graft polymers from the conjugated backbones; (2) direct arylation polymerization between PCL-DPP-PCL synthesized in Chapter 6 and another building block can directly lead to the formation of conjugated polymer brushes in a grafting through approach. The photothermal effect of these conjugated polymer brushes will be studied in the future.

7.1. Introduction

Molecular brushes refer to polymers possessing densely grafted side chains on a linear long polymer main chain. These polymers have attracted great interest in both experimental scientists and theoreticians over the past decade, owing to the fact that their properties and behavior are very unlike those of common linear polymer chains. Rather than being randomly coiled, molecular brushes show a characteristic cylindrical or worm-like conformation as a result of the intramolecular excluded-volume interactions among the densely grafted side chains.

Molecular brushes can be synthesized via “grafting through”, “grafting onto” and “grafting from” (**Figure 7.1**)^[1] as well as a combination of these

approaches with free radical polymerization, controlled/living radical polymerization, anionic polymerization, ring opening polymerization and “click chemistry”.

Figure 7.1 Common synthetic methods towards polymer brushes. Reproduced with permission from ref. 1. Copyright 2010 The Royal Society of Chemistry.

Many of the anticipated applications of brush-like polymers arise from their unique molecular architecture. The side chains of molecular brushes are bound to a single polymer backbone at an extremely high grafting density, which is typically four chains per 1nm of the backbone or even a higher number. This highly congested and constrained structure affords interesting properties, which cannot be easily achieved in other systems. Unlike linear polymers of the same chemical composition, molecular brushes do not overlap due to steric repulsion

of the densely grafted side chains.

Regarding their implications in technology, molecular brushes demonstrate potential applications as templates for inorganic nanoparticles or nanowires and for development of novel material properties, such as supersoft elastomers. In addition, researchers have made significant advances in the development of stimuli-responsive molecular brushes, including those that response to the change of temperature^[2], pH^[3], light^[4] and other physical or chemical properties. And a combination of more than one stimuli-responsive properties in a single molecular brushes could maximize the potential of these materials, especially in drug delivery and cancer therapy applications.^[5, 6]

Low bandgap conjugated polymers, with absorption up to near-infrared range could be possible candidates as photothermal agents for cancer therapy, which can convert the absorbed light to heat to kill the cancer cells.^[6-11] In addition, the excellent photostability, biodegradability or good biocompatibility, and high photothermal conversion efficiency of these low bandgap polymers could be more efficient compared to commonly used gold nanoparticles^[12, 13] for photothermal therapy applications. Moreover, with proper design of the polymer structures, those conjugated polymers could also serve as multifunctional drug carriers for potential applications in combination cancer therapy.

In this chapter, several thiophene-flanked diketopyrrolopyrrole (TDPP)-based polymers were synthesized with direct arylation polymerization method which has been discussed from Chapter 2 to 5 as a greener and more convenient

synthetic approach instead of using conventional cross-coupling reactions to construct conjugated backbones. Two synthetic routes were designed: (1) synthesize the conjugated polymers by DAP with functional groups in the side chain, and then graft biodegradable polymers to obtain polymer brushes; (2) the target polymer brushes can be directly achieved by “grafting through” method with direct arylation polymerization between the DPP-based biodegradable polymers and another building blocks. These low band gap conjugated polymer brushes were expected to show strong absorption in near-infrared range and could be used for efficient photothermal therapy agents.

7.2. Synthesis of conjugated polymers brushes

7.2.1. Synthesis of hTDPP derivatives

Scheme 7.1 Synthetic route of hTDPP derivatives.

Considering the fact that more than one C-H bond can be activated in thiophene-flanked diketopyrrolopyrrole (**TDPP**), which could possibly cause branching structure in the synthesis of **TDPP**-based conjugated polymers via DAP, blocking one of the reactive sites in the thiophene rings of **TDPP** unit could be a choice to minimize the branching structures in the target polymer. **Scheme S1** shows the synthetic route to **hTDPP** derivatives with β -position in the thiophene rings blocked with hexyl group. The starting material, 3-hexylthiophene (**1**) was treated with $\text{TMPMgCl} \cdot \text{LiCl}$ (Knochel-Hauser-base) which has higher regioselectivity in deprotonation and further reacted with DMF to afford 4-hexylthiophene-2-carbaldehyde (**2**) with 93% yield. 4-Hexylthiophene-2-carbonitrile was then synthesized with through a two-step reaction from 4-hexylthiophene-2-carbaldehyde with a total yield of 73%. 3,6-Bis(4-hexylthiophene-2-yl)pyrrolo[3,4-*c*]pyrrolo-1,4(2*H*,5*H*)-dione (**hTDPP**) was then synthesized via a well-established DPP synthetic method by cyclization with diisopropyl succinate in the presence of potassium *tert*-butoxide as the base. To increase the solubility of **hTDPP**, *N*-Alkylation reaction of **hTDPP** with 2-octyldodecyl bromide afforded **hTDPP-R** (**5**) with 33 % yield and the further bromination of compound **5** resulted in **Br-hTDPP-R** (**6**) at 84% yield.

7.2.2 Model reaction to synthesize DPP-based homo-polymer via DAP

Scheme 7.2. Synthesis of DPP-based homo-polymer via DAP.

Before synthesizing DPP-based polymer brushes via DAP, a model reaction was first performed to synthesize DPP-based homo-polymer by DAP. The target polymer **P1** was synthesized from unbrominated DPP-monomer (**7**) and **hTDPP** (**6**) under Herrmann's catalyst with $\text{P}(o\text{-MeOPh})_3$ as a ligand and Cs_2CO_3 as a base in Toluene at 120 °C for 24 h. The chloroform fraction of **P1** was obtained with a relatively high molecular weight of 45.5 kDa at 53% yield. Despite the high molecular weight obtained at this reaction condition, a small bump at low elution time was observed in both RI and UV traces (**Figure 7.2**). As no homo-coupling could be observed when only compound **6** was treated under the same reaction condition, the presence of the bump in the GPC traces could be attributed to the branching structure with more than one C-H bond in the thiophene rings could be activated in compound **7**. But it is also notable that compared with relatively higher intensity of extra peaks or bumps found in the synthesis of **PDPPTP** via DAP, this result showed less branching density and almost no homo-coupling was observed which was found to be serious structure defects for DAP with $\text{Pd}(\text{OAc})_2$ as the catalyst. The absorption spectra of **P1** in CHCl_3 showed two peaks at 837 nm and 923 nm, suggesting very good conjugation along the polymer backbone, which also confirmed only very

limited branching defects were existed in **P1** (**Figure 7.3**).. The ^1H -NMR spectra of **P1** recorded at 100 °C in $\text{C}_2\text{D}_2\text{Cl}_4$ (**Figure 7.4**) further confirmed the well-defined structure of polymer with each proton assigned to the major peaks in the spectra.

Figure 7.2 GPC traces of **P1** with RI and UV detector (600 nm).

Figure 7.3 Absorption spectra of P1 in CHCl_3 .

Figure 7.4 ^1H -NMR (300 MHz) spectra of P1 in $\text{C}_2\text{D}_2\text{Cl}_4$ 120°C .

To minimize the branching defects in DPP-based homo-polymer via DAP, kinetic study of this reaction under the same condition was performed. From GPC traces of **P1** collected from different reaction time via DAP as shown in **Figure 7.5** and **Figure 7.6**, it is clear that with the reaction time of less than 2 h (i.e., 1 h and 2 h), low-molecular-weight (around 10 kDa) polymers were obtained with no structure defects. However, when the reaction time extended to 3 h, a platform could be observed in the GPC traces, suggesting some certain branching structure were formed in 3 h. With even extended reaction time, the fraction at lower elution time (i.e., extremely high molecular polymer) increased, meaning higher branching density in the resulted polymer. Only when the reaction time reached 24 h, the extra peak at lower elution time disappeared probably due to the formation of some cross-linked structure that can be hardly soluble in CHCl_3 . The absorption spectra of the polymers obtained at different reaction time was presented in **Figure 7.7**. It is obvious that the relative intensity of the peaks at around 920 nm increased with extended reaction time from 1 h to 3 h and remained almost the same when further reacted for a total of 24 h. And the peaks at shorter wavelength significantly red-shifted from around 710 nm to 820 nm when the reaction time was extended to 3h and again remained unchanged after 24 h reaction time. These results suggested that branching structure in DPP-based homo-polymer synthesized via DAP could be minimized with Herrmann's catalyst at 120 °C with less than 3 h reaction time.

Figure 7.5 GPC traces (RI detector) of **P1** via DAP with different reaction time.

Figure 7.6 GPC traces (UV detector, 600 nm) of **P1** via DAP with different reaction time.

Figure 7.7 Absorption spectra of **P1** in chloroform via DAP with different reaction time.

7.2.3. Synthesis of DPP-based polymer brushes via DAP and ROP

After studying the model reaction of DPP-based homo-polymer via DAP, we further explored the synthesis of DPP-based polymer brushes via DAP and ROP. The polymer brushes were first prepared by DAP to form the conjugated polymer backbone with functional groups in the side chains (**Scheme 7.3**), followed by the ROP to obtain polymer brushes with conjugated backbone.

Scheme 7.3 Synthesis of DPP-based conjugated polymers with functional groups in the side chains.

Several unbrominated DPP-based monomers with different functional groups have been synthesized before and were applied to synthesize DPP-based polymers via DAP using Herrmann's catalyst system. Initially, **P2-P4** were synthesized using optimized DAP conditions for 24 h, **P2** ($M_n = 74.7$ kDa) and **P3** ($M_n = 19.5$ kDa, calculated from major peak in the GPC traces) were obtained as deep green solids, whereas no polymers were obtained for **P4**. From the GPC traces of **P2** and **P3** (Figure 7.8), obvious structure defects could be observed again. For **P2**, these structure defects were mainly caused by branching while for **P3**, cross-linked structure could be also a possible side reaction which undergoes the heck coupling reaction as some insoluble green polymer were found to be remained in the Soxhlet extractor after extraction with CHCl_3 . From the absorption spectra of **P2** and **P3** (Figure 7.9), a significant red-shift of the maximal absorption peak of **P3** from 908 nm to 927

nm was observed, which was consistent with the higher molecular weight of **P3** compared to **P2**. Considering all these results mentioned above, the further optimization was focused on **P2**. By shorten the reaction time to 3 h, the structure defects could be hardly found in this case although the molecular weight ($M_n = 11.9$ kDa) was lower than that obtained for reacting 24 h (**Figure 7.10**), along with a slightly blue-shifted in the absorption spectra compared to **P2** obtained after 24 h (**Figure 7.11**).

Figure 7.8 GPC traces of **P2** and **P3** with (a) RI and UV (600 nm) detector.

Figure 7.9 Absorption spectra of P2 and P3 in CHCl_3 .

Figure 7.10 GPC traces of P2 (3h) with RI detector.

Figure 7.11 Absorption spectra of **P2 (3h)** in CHCl_3 .

To further convert the conjugated polymers to polymer brushes, grafting through method was used to attach the polymer side chains from the conjugated backbones (**Scheme 7.4**). **P2** was treated with HCl in THF/MeOH mixture to remove the THP protection group to give **P2-OH** with hydroxyl group, which could be recognized as the macroinitiator for ring opening polymerization to graft PCL from the backbone to give the final polymer brushes (**P2-g-PCL**).

Scheme 7.4 Synthesis of DPP-based polymer brushes.

Figure 7.12 GPC traces of **P2**, **P2-OH** and **P2-g-PCL** with (a) RI and (b) UV detector.

After deprotection step from **P2**, **P2-OH** was obtained with molecular weight of 37900, which was significantly lower than the theoretical value. This could be explained by the stronger aggregation of **P2-OH** in THF for GPC test due to the existence of hydroxyl group in the polymer chain end. The polymer brush **P2-g-PCL** was obtained by grafting PCL polymer chain from **P2-OH** with molecular weight of 89400 from GPC results. And the average repeating unit of PCL in **P2-g-PCL** side chain was calculated to be 10 and 9.5 from GPC and NMR results, respectively.

The UV-Vis-NIR spectra of **P2**, **P2-OH** and **P2-g-PCL** in CHCl_3 (**Figure 7.13**) showed that different side chains attached to the polymer backbones didn't change the optical properties of these three polymers significantly. All

three polymers exhibited strong absorbance in the near infrared range, which could be good candidates for further photothermal therapy applications.

Figure 7.13 UV-Vis-NIR spectra of **P2**, **P2-OH** and **P2-g-PCL** in CHCl_3 .

The structure analysis of above three polymers was carried out by NMR performed in $\text{C}_2\text{D}_2\text{Cl}_4$ 120 °C (**Figure 7.14-16**). Compared to the NMR spectrum of P2 with THP protect group which showed characteristic peaks from THP unit located at around 4.5 ppm, almost no signals from THP group could be observed in the NMR spectrum of **P2-OH**. After further grafting PCL side chains from **P2-OH** to give **P2-g-PCL**, protons from PCL chains could be easily found in the NMR spectrum of **P2-g-PCL**. And the protons in the conjugated polymers showed relatively weak signals in the aromatic ranges due to the large fraction of PCL chains in the total polymer brushes.

Figure 7.14 ^1H -NMR (300 MHz) spectra of **P2** in $\text{C}_2\text{D}_2\text{Cl}_4$ 120 $^\circ\text{C}$.

Figure 7.15 ^1H -NMR (300 MHz) spectra of **P2-OH** in $\text{C}_2\text{D}_2\text{Cl}_4$ 120 $^\circ\text{C}$.

Figure 7.16 ¹H-NMR (300 MHz) spectra of **P2-g-PCL** in C₂D₂Cl₄ 120 °C.

Table 7.1 Synthetic results of **P2**, **P2-OH** and **P2-g-PCL**.

	<i>M_n</i> ^a (kDa)	<i>M_w</i> / <i>M_n</i>	λ _{abs, max} (nm)	m _{GPC} /m _{NMR}
P2	74.7	4.8	927	-
P2-OH	37.9	3.3	921	-
P2-g-PCL	89.4	2.0	926	10/9.5

The deprotection of THP in **P2 (3h)** was performed in several conditions, including 1) R.T for 30 min (HCl); 2) R.T. for 60 min (HCl); 3) 60 °C for 30 min (HCl); 4) R.T. for 1 day (*p*-TsOH). It was found that for condition 2) and

3), the color of the polymer solution changed from deep green to light yellow, suggesting that the conjugated polymer backbone was destroyed under these conditions. However, if the deprotection using HCl at R.T. for just 30 min, no color change was observed. Anyhow, it's still very hard to control the degree of deprotection at this condition. When the acid catalyst was changed to an organic acid, *p*-TsOH, the deprotection was not successful under R.T. even after one day.

Scheme 7.5 Synthetic route to polymer brushes by grafting through methods.

Considering the fact that the deprotection of **P2** was difficult to reproduce due to the stability of DPP-based conjugated backbones under acidic conditions, another synthetic route was designed to synthesize polymer brushes with grafting through methods. With PCL-DPP-PCL polymer that we have

synthesized before, by treating PCL-DPP-PCL with aryl-bromide under DAP conditions, the polymer brushes with similar structure to **P2-g-PCL** were expected to obtain by this grafting through approach (**Scheme 7.5**).

Table 7.2 Synthesis of polymer brushes by grafting through with hTDPP or fluorene.

Ar	[Pd]	[P]	Base	Solvent	Temp (°C)	M_n	Yield (%)
hTDPP	Herrmann's catalyst	P(<i>o</i> -MeoPh) ₃	CS ₂ CO ₃	THF	120	^a	^a
Fluorene	Herrmann's catalyst	P(<i>o</i> -MeoPh) ₃	CS ₂ CO ₃	THF	120	^a	^a

^a no polymeric product at 110 °C, or even increase the temperature to 140 °C.

Note: all reactions were run with PivOH at a concentration of 0.04 M; PCL-DPP-PCL (8.8 kDa).

When hTDPP or fluorene was used as the building block for constructing conjugated polymer backbones, no desired polymeric product could be obtained. Expect for the reason that the ratio of two monomers could be difficult to control due to the nature of PCL-DPP-PCL itself, which was a macromonomer with a polydispersity of 1.4, relatively large size of either hTDPP or fluorene could be also contribute to the low reactivity in this case. The long PCL side chain in the macromonomer could act as a shield which limited the entrance of other small molecules with large size and then lower the possibility of collision

between macromonomer and the other small molecule. To further confirm our hypothesis, another monomer benzothiazole was used as the monomer for trial.

When DAP between PCL-DPP-PCL and BT was conducted at 110 °C to synthesize the target polymer **P(DPP-g-PCL)-BT**, no polymerization was observed and further increasing the reaction temperature to 140 °C could result in severe swelling to form blue gel. And when the reaction temperature was set to 130 °C for 48 h, only 5% oligomer could be obtained with molecular weight of 6000 and most of the products were still blue insoluble solids. If the reaction time was shortened to 24 h, high molecular weight (15.0 kDa) as well as yield for soluble products (40 %) could be obtained. Due to the relatively low molecular weight of, the absorbance of **P(DPP-g-PCL)-BT-3** only showed a maximal absorption at 600 nm with the one set at 786 nm, which was not in the ideal range for photothermal therapy applications.

Figure 7.16 GPC traces of **PCL4K**, **P(DPP-g-PCL)-BT-2** and **P(DPP-g-PCL)-BT-3** with (a) RI and (b) UV detector.

Table 7.3 Synthesis of polymer brushes by grafting through with BT

Ar	Temp (°C)	<i>M_n</i> (kDa)	Yield (%)
BT-1	110	^a	^a
BT-2	130 (48 h)	6.0	5 ^c
BT-3	130 (24 h)	15.0	40 ^d

^a no polymeric product at 110 °C; Serious swelling (deep blue gel) at 140 °C.

^b no polymeric product at 110 °C; Serious swelling (deep blue gel) at 140 °C.

^c 90 % gel like product (swelling, deep blue and green gel).

^d 56 % gel like product (swelling, deep blue and green gel).

Note: all reactions were run with Pd(OAc)₂, PCy₃·HBF₄, K₂CO₃ and PivOH in DMAc/xylene at a concentration of 0.1 M; PCL-DPP-PCL (4.0 kDa).

Figure 7.17 UV-Vis-NIR spectra of **P(DPP-*g*-PCL)-BT-3** in CHCl₃.

Although these trials for the synthesis of DPP-based polymer brushes were not successful at this stage, they also offer us some insight to further work on this project. For example, the size of the monomer could be a factor and by controlling the reaction temperature as well as the reaction time could also provide the target polymer brushes with high molecular weight and yield.

7.3. Conclusion

hTDPP derivatives were synthesized and used for constructing DPP-based conjugated polymers with functional groups in the side chains via DAP to minimize structure defects. These functional groups can be further used to introduce the polymer chain to form the polymer brushes, which can be self-assembled into nanoparticles and find their applications in biomedical engineering such as photothermal therapy. Although our preliminary results showed some problems to get high quality conjugated polymer brushes using either grafting from or grafting through methods, they offered the insights to further improve the synthetic strategies, to obtain high molecular weight polymer brushes with extended conjugated length to absorb light in the near-infrared region for better performance in the photothermal therapy application.

7.4. Experimental Section

7.4.1. Materials and characterization

All reagents were obtained from commercial suppliers and used without further purification, including solvents as well. Gel permeation chromatography (GPC) measurement were carried out on Agilent 1260 Infinity system using THF as eluent (1 mL/min) and polystyrene as standards at 30 °C with RI and UV (600 nm) detector. UV-Vis absorption spectra were recorded on Shimadzu UV-1800 spectrophotometer. ¹H-NMR spectra were measured on a Bruker Avance II 300 MHz spectrometer in C₂D₂Cl₄ at 100 °C.

7.4.2. General synthetic procedure for polymer brushes by grafting through methods

Under nitrogen atmosphere, a mixture of **PCL-DPP-PCL** (0.04 mmol), brominated monomer (Br-hTDPP, Br-fluorene or Br-BT) (0.04 mmol), Herrmann's catalyst (0.0008 mmol), P(*o*-MeOPh)₃ (0.0032 mmol), Cs₂CO₃ (0.092 mmol), and PivOH (0.012 mmol) was dissolved in toluene (0.4 mL) in a reaction vial with a magnetic stirring bar. The vial was sealed with an aluminium cap with PTFE/silicone septum and then heated in a preheated oil bath at desired temperature for 24 or 48 hours. After being cooled to room temperature, the reaction mixture was dissolved in CHCl₃, concentrated with rotary evaporator, added dropwise to 150 mL of ice methanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with methanol, hexane and chloroform sequentially. The chloroform fraction was concentrated

and precipitated into 150 mL of ice methanol. The precipitates were collected by filtration and dried under vacuum before further characterization.

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Chapter 8

Summary and outlook

8.1 Summary

In this thesis, DPP building block was used as the core to construct polymers structures mainly by direct arylation polymerization approach.

A series of DPP-based low-band gap conjugated polymers were synthesized with well-defined structures and high molecular weight by direct arylation polymerization after the systematic optimization. The photophysical, electrochemical and thermal properties of these polymers were studied and the charge-transport properties were investigated in OFETs (Chapter 2, 4 and 5).

The homo-coupling and branching defects were found in the conjugated polymers synthesized via direct arylation polymerization, which could strongly affect the quality of the polymers. By detailed optimization with brominated-DPP for the model reaction, structure defects could be minimized by choosing less active palladium catalyst, large-size phosphine ligand and non-polar solvent under lower temperature. However, the balance between the reactivity and the side reactions should also be considered in determining a proper reaction conditions for direct arylation polymerization. This study could be useful for achieve high quality conjugated polymers by direct arylation polymerization in a more efficient way (Chapter 3).

Except for the application in organic electronics for DPP-based polymers, biodegradable polymers were introduced to DPP core or DPP-based conjugated polymer backbones to construct DPP-based biodegradable polymers or polymer brushes, which could be used as bioimaging or photothermal therapy agents.

When biodegradable PCL was attached to the DPP core to afford PCL-DPP-PCL with long side chains by ring opening polymerization, the long PCL chains could effectively suppress the strong intermolecular interaction between DPP units to retain high fluorescence in films and solid states, which inspired us to explore its applications in cell interfacing and long-term tracking (PLC-DPP-PCL as polymer scaffolds). In addition, by varying the chain length of PCL, the relationship between the polymer chain length and photophysical properties (especially fluorescent properties) was well understood, which offered the opportunity to solve the fluorescence quenching problem for most fluorescent organic dyes in the condensed states (films and solids) (Chapter 6).

Furthermore, with previous efforts in the DPP-labeled biocompatible polymers and direct arylation polymerization method to the synthesis of conjugated polymers, two approaches were applied to synthesize DPP-based low-band gap conjugated polymer brushes, with DPP-based conjugated backbone and biocompatible polymers as the side chain. And these polymers brushes could be photothermal therapy agents with strong absorption in the near-infrared range for deep penetration with good biocompatibility as well. (Chapter 7)

8.2. Outlook

8.2.1. Outlook for direct arylation polymerization

Even with a lot of experience in direct arylation polymerization for the past four years, challenges still remain to be solved before its profound impact on both basic research and industrial applications.

For example, a more universal reaction condition or at least a guideline for the choice of each parameter is required for wider application of direct arylation polymerization. Compared to conventional cross-coupling reactions, due to the different reactivity of C-H bonds as well as electronic properties of each monomer, it is still difficult to summarize a general rule for proper selection of reaction conditions for direct arylation polymerization. However, for some specific monomers, especially simple substituted thiophenes, which have been intensively studied, toluene (basically non-polar solvent) was found to be a suitable solvent for electron-deficient thiophenes, whereas dimethylacetamide (DMAc) (solvent) was suitable for electron-rich thiophenes.^[1] Although deep understanding of the relationship between this rule and the reaction mechanism is still under mystery, these findings at least could be helpful for proper choice of reaction conditions for thiophene based monomers in direct arylation. And it is worthy to mention that in Chapter 3 of this thesis, we also summarized the ways to minimize structural defects in direct arylation polymerization for thiophene-flanked DPP monomer. All these studies could push forward to finding general rules for direct arylation polymerization.

In addition, almost all direct arylation polymerizations were conducted with palladium catalysts, which are heavy metal based materials and expensive as well. However, in the small molecular synthesis by direct arylation, non-heavy

metal catalyst or even light driven reaction has been realized in good yield and selectivity. But there's still no report regarding these even greener reaction conditions for direct arylation polymerization yet.

8.2.2. Outlook for dye-labeled DPP polymer

With our previous study on dye-labeled polymers in Chapter 3, it was found that long PCL chains could effectively suppress the fluorescence quenching of DPP in solid states.

To have a deeper understanding on these results, we plan to synthesize more DPP-labeled polymers with polystyrene, polylactide and poly(methyl methacrylate). We expect that different glass transition temperature (T_g) of these attached polymers could affect the fluorescent properties of dye-labeled polymers, which can be investigated from steady-state and dynamic fluorescence spectroscopy.

Scheme 8.1 Structures of different DPP-labeled polymers.

The further study on this topic could give more insights to effectively retain the fluorescence of dyes in solid states by properly introducing polymers to the core of the dye.

8.2.3. Outlook for the synthesis of DPP-based conjugated polymer brushes

In the synthesis of DPP-based conjugated polymer brushes by direct arylation polymerization described in Chapter 7, we encountered problems for both synthetic routes.

For route 1, DPP-based conjugated backbones was not stable under deprotection of THP group in acid conditions. The conjugation was broken mainly due to the broken of the amide bond in the DPP core (**Scheme 8.2**). To solve this problem, the deprotection could be processed by thermal cleavage of THP group from DPP unit to afford DPP-based conjugated polymer with functional groups. And then the biodegradable polymers can be grafted to the conjugated backbones to afford target polymer brushes.

Scheme 8.2 Possible side reaction to DPP unit under acidic conditions.

For route 2, it was difficult to control the molar ratio of macromonomer (PCL-DPP-PCL) to another building block to be 1:1, owing to the huge difference in molecular weight between PCL-DPP-PCL and the other monomer. To solve this problem, we may synthesize PCL-DPP-PCL with relatively short PCL chains first, followed by direct arylation polymerization with another monomer, and further graft PCL with controlled length to get polymer brushes. (Scheme 8.3)

Scheme 8.3 New synthetic route to DPP-based conjugated polymer brushes.

8.3. Reference

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Chapter 9

Publication and conference

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9.2. Conferences

1. 2013: Natural Products and Health in Singapore. Poster presentation: Synthesis of PCL-DPP-PCL Polymers with Strong Solid State Fluorescence.
2. 2015: 3th International Conference of Polymers for Advanced Technology (PAT2015), Hang Zhou, China. Poster Presentation: Highly fluorescent polycaprolactones decorated with di(thiophene-2-yl)-diketopyrrolopyrrole: A covalent strategy of tuning fluorescence properties and their applications in bioimaging. (**Best Poster Award**)
3. 2015: International Conference on Materials for Advanced Technologies (ICMAT 2015), Singapore. Poster presentation: Direct Arylation Polycondensation: A Facile and Straightforward Way to Synthesize π -Conjugated Copolymers.