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# Conjugated Polymers for Organic Solar Cells

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## 1. Introduction

Energy shortage has become a worldwide issue in the 21<sup>st</sup> century (Lior, 2008). The urge to look for renewable energy to replace fossil fuel has driven substantial research effort into the energy sector (Hottel, 1989). The solar energy has enormous potential to take the place due to its vast energy stock and availability worldwide (Balzani et al., 2008). Conventional solar energy conversion device is based on silicon technology. However, wide use of silicon based solar cell technology is limited by its high power conversion cost (Wöhrle & Meissner, 1991). To address this issue, solution-processing based organic solar cell has been developed to replace Si-solar cell (Tang, 1986). Compared with conventional Si-based solar cell, conjugated polymer based solar cell (PSC) has several important advantages: 1) solution processability by spin-coating, ink-jet printing and roll-to-roll processing to reduce manufacturing cost; 2) tunable physical properties; and 3) mechanical flexibility for PSC application on curved surfaces (Sariciftci, 2004).

During the last decade, the power conversion efficiency (PCE) of organic based solar cell has increased from *ca.* 1% (Tang, 1986) to more than 7% (H. -Y. Chen et al., 2009) with the bulk heterojunction (BHJ) concept being developed and applied. During the pursuit of high efficiency, the importance of the structure-property relationship of the conjugated polymer used in the solar cell has been disclosed (J. Chen & Cao, 2009). It might be helpful to systematically summarize this structure-property relationship to guide polymer design and further improvement of the power conversion efficiency of PSCs in the future.

This chapter will be organized as follows. Firstly, we will discuss about the general criteria for a conjugated polymer to behave as an efficient sunlight absorbing agent. Secondly, we will summarize the properties of common monomer building blocks involved for construction of solar cell polymers. Only representative polymers based on the common building blocks will be discussed due to the space limit. More quality reviews and texts are directed to interested readers (C. Li, 2010; Günes et al., 2007; Sun & Sariciftci, 2005; Cheng et al., 2009).

## 2. Criteria for an efficient BHJ solar cell polymer

For a conjugated polymer to suit in organic photovoltaic bulk heterojunction solar cell, it should possess favorable physical and chemical properties in order to achieve reasonable device efficiency. Key words are: large absorption coefficient; low band gap; high charge mobility; favorable blend morphology; environmental stability; suitable HOMO/LUMO level and solubility.

### 2.1 Large absorption coefficient

For polymers used in solar cells, a large absorption coefficient in the film state is a prerequisite for a successful application since the preliminary physics regarding photovoltaic phenomenon is photon absorption. The acceptor component of the BHJ blend, usually PC<sub>60</sub>BM or PC<sub>70</sub>BM, absorbs inefficiently longer than 400 nm (Kim et al., 2007). It is thus the responsibility for the polymer to capture the photons above 400 nm. Means to increase the solar absorption of the photoactive layer include: 1) increasing the thickness of the photoactive layer; 2) increasing the absorption coefficient; and 3) matching the polymer absorption with the solar spectrum. The first strategy is rather limited due to the fact that the charge-carrier mobilities for polymeric semiconductors can be as low as 10<sup>-4</sup>cm<sup>2</sup>/Vs (Sariciftci, 2004). Series resistance of the device increases significantly upon increasing the photoactive layer thickness and this makes devices with thick active layer hardly operational. The short-circuit current ( $J_{sc}$ ) may drop as well because of the low mobility of charge carriers. With the limitation to further increase the thickness, large absorption coefficient (10<sup>5</sup> to 10<sup>6</sup>) in the film state is preferred in order to achieve photocurrent >10 mA/cm<sup>2</sup> (Sariciftci, 2004). By lowering the band gap, absorption of the polymer can be broadened to longer wavelength and photons of  $\lambda > 800$ nm can be captured as well.

### 2.2 Low band gap to absorb at long wavelength

The solar irradiation spectrum at sea level is shown in Fig 1 (Wenham & Watt, 1994). The photon energy spreads from 300 nm to > 1000 nm. However, for a typical conjugated polymer with energy gap  $E_g \sim 2.0$  eV, it can only absorb photon with wavelength up to *ca.* 600 nm (blue line in Fig 1) and maximum 25% of the total solar energy. By increasing the absorption onset to 1000 nm ( $E_g \sim 1.2$  eV) (red line in Fig 1), approximately 70 to 80% of the solar energy will be covered and theoretically speaking an increase of efficiency by a factor of two or three can be achieved. A controversy regarding low band gap polymer is that once a polymer absorbs at longer wavelength, there will be one absorption hollow at the shorter wavelength range, leading to a decreased incident photon to electron conversion efficiency at that range. One approach to address this issue is to fabricate a tandem solar cell with both large band gap polymer and narrow band gap polymer utilized simultaneously for solar photon capture (Kim et al., 2007).

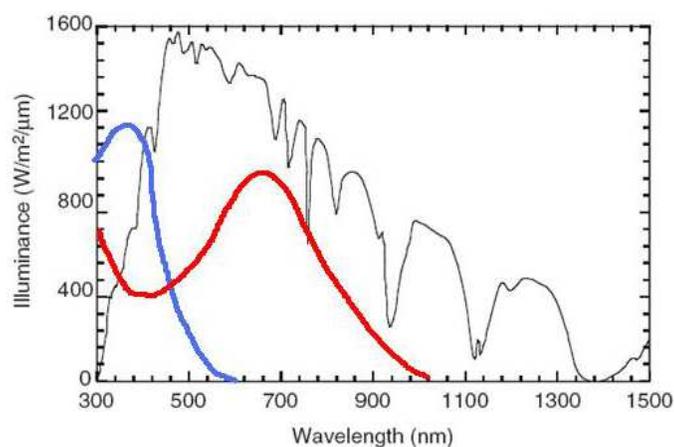


Fig. 1. Reference solar irradiation spectrum of AM1.5 illumination (black line). Blue line: typical absorption spectrum of a large band gap polymer; Red line: typical absorption spectrum of a narrow band gap polymer.

### 2.3 High charge carrier mobility

Charge transport properties are critical parameters for efficient photovoltaic cells. Higher charge carrier mobility of the polymer increases the diffusion length of electrons and holes generated during photovoltaic process and at the same time reduces the photocurrent loss by recombination in the active layer, hence improving the charge transfer efficiency from the polymer donor to the PCBM acceptor (G. Li et al., 2005). This charge transport property of the photoactive layer is reflected by charge transporting behavior of both the donor polymer and the PCBM acceptor. The electron transport property of pure PCBM thin film has been reported in details and is known to be satisfactory for high photovoltaic performance ( $\sim 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) (Mihailetchi et al., 2003). However, the mobility of the free charge carriers in thin polymer films is normally in the order of  $10^{-3}$  to  $10^{-11} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which limits the PCE of many reported devices (Mihailetchi et al., 2006). Therefore, it is promising to increase the efficiency by improving the charge carrier property of the polymer part, since there is huge space to improve if we compare this average value with the mobility value of some novel polymer organic field effect transistor materials (Ong et al., 2004; Fong et al., 2008).

### 2.4 Favorable blend morphology with fullerene derivatives

The idea that morphology of the photoactive layer can greatly influence the device performance has been widely accepted and verified by literature reports (Arias, 2002; Peet et al., 2007). However, it is still a 'state-of-art' to control the morphology of specific polymer/PCBM blend. Even though several techniques (Shaheen et al., 2001) have been reported to effectively optimize the morphology of the active layer, precise prediction on the morphology can hardly be done. It is more based on trial-and-error philosophy and theory to explain the structure-morphology relationship is still in infancy. Nevertheless, several reliable and efficient methods have been developed in laboratories to improve the morphology as well as the performance of the solar cell devices.

The first strategy is to control the solvent evaporation process by altering the choice of solvent, concentration of the solution and the spinning rate (Zhang et al., 2006). The slow evaporation process assists in self-organization of the polymer chains into a more ordered structure, which results in an enhanced conjugation length and a bathochromic shift of the absorption spectrum to longer wavelength region. It is reported (Peet. et al., 2007) that chlorobenzene is superior to toluene or xylene as the solvent to dissolve polymer/PCBM blend during the film casting process. The PCBM molecule has a better solubility in chlorobenzene and therefore the tendency of PCBM molecule to form clusters is suppressed in chlorobenzene. The undesired clustering of PCBM molecules will decrease the charge carrier mobility of electrons because of the large hopping boundary between segregated grains.

The second strategy is to apply thermal annealing after film casting process. This processing technique is also widely used for organic field effect transistor materials. The choice of annealing temperature and duration is essential to control the morphology. At controlled annealing condition, the polymer and PCBM in the blend network tend to diffuse and form better mixed network favorable for charge separation and diffusion in the photoactive layer (Hoppe & Sariciftci, 2006).

### 2.5 Stability

The air stability of the solar cell device, as it is important for the commercialization, has attracted more and more attention from many research groups worldwide. Even though

industry pays more attention to the cost rather than the durability of the solar cell device, a shelf lifetime of several years as well as a reasonably long operation lifetime are requested to compete with Si-based solar cells. The air instability of solar cell devices is mainly caused by polymer degradation in air, oxidation on low work function electrode, and the degradation of the morphology of the photoactive layer.

For a conjugated polymer to achieve such a long lasting lifetime, it should have intrinsic stability towards oxygen oxidation which requires the HOMO energy level below the air oxidation threshold (*ca.* -5.27 eV) (de Leeuw et al., 1997). Device engineering can also provide the extrinsic stability by sophisticated protection of the conjugated polymer from air and humidity.

## 2.6 Desired HOMO/LUMO energy level

The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of the polymer should be carefully tuned for several considerations. First of all, the HOMO energy level of a material, which describes the accessibility of the material molecule to be oxidized, reflects the air stability of the material. The oxidation threshold of air is -5.2 eV ~-5.3 eV against vacuum level. Therefore, the HOMO level cannot be more positive than this value to provide the air stability to the polymer. Secondly, the maximum open circuit voltage ( $V_{oc}$ ) is correlated to the difference between the LUMO energy level of PCBM and the polymer's HOMO energy level based on experimental evidence (Brabec et al., 2001; Scharber et al., 2006). Therefore, in order to achieve high  $V_{oc}$  in the device, HOMO level should be reasonably low.

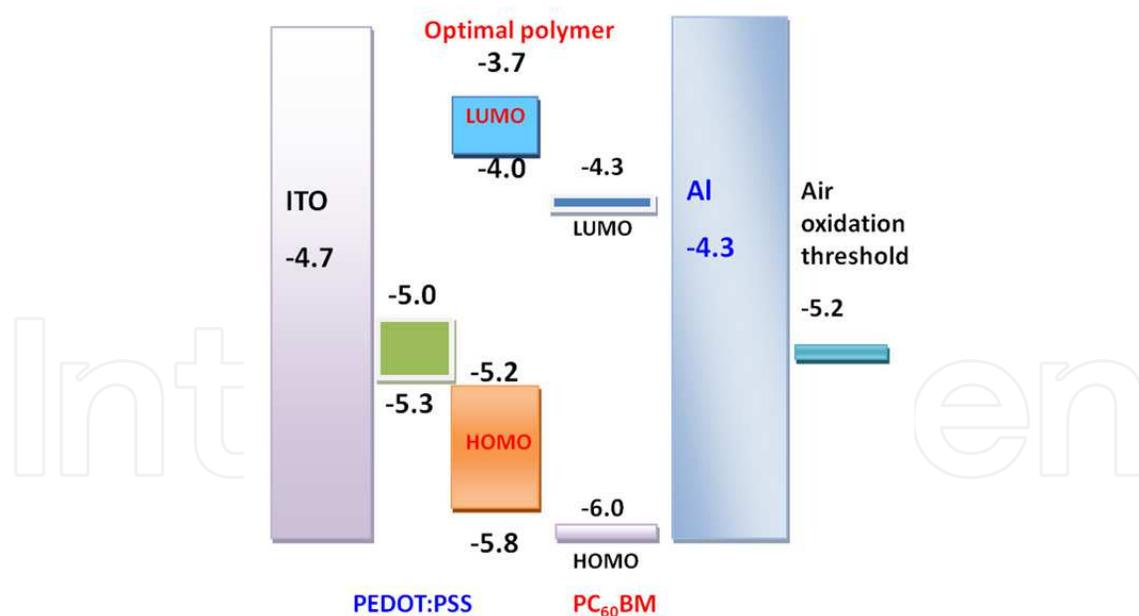


Fig. 2. Optimal HOMO/LUMO energy level of optical polymer used in BHJ solar cell with PC<sub>60</sub>BM as acceptor (Blouin et al., 2008)

To ensure efficient electron transfer from the polymer donor to the PCBM acceptor in the BHJ blend, the LUMO energy level of the polymer material must be positioned above the LUMO energy level of the acceptor by at least 0.2-0.3 eV. Based on these factors, as shown in Fig 2, the ideal polymer HOMO level should range from -5.2 eV to -5.8 eV against vacuum

level due to the compromise of stability, band gap and open circuit voltage. The ideal polymer LUMO level should range from -3.7 eV to -4.0 eV against vacuum level to assist electron injection from polymer to acceptor.

### 2.7 Solubility

Polymer prepared for solar cell application should possess reasonable solubility so that it can be analyzed by solution based characterization methods such as NMR spectroscopy. Meanwhile, polymer with poor solubility will be found inappropriate for solution processing and device performance is normally low due to unfavorable microscopic morphology of the thin film formed by spin coating. Aliphatic chains attached to the polymer backbone are essential to ensure solubility of the polymer. However, it should be noted that aliphatic chains, being electronically inactive, will dilute the conjugated part of the polymer and hence, reduce the effective mass of the polymer.

Some rules of thumb regarding the use of alkyl chains include that: 1) longer chain is better than shorter chain to solubilize polymer; 2) branched chain is better than linear chain to solubilize polymer; and 3) the more rigid or planar the polymer backbone is, the more or longer alkyl chains are needed.

## 3. Common building blocks for BHJ solar cell polymers

Common monomer building blocks to construct conjugated polymer for solar cells have been summarized in Chart 1. They are categorized by number of rings and way of linkage. Due to the space limit, we will only discuss monomers that are commonly encountered in the literature and the property of their representative polymers. Some important building blocks, even though not commonly used for PSC polymer, are also included for comparison.

### 3.1 Ethylene (double bond)

Ethylene (double bond) is a commonly adopted spacer or bridge in conjugated polymers. Common chemical methods to introduce double bond to the polymer include: Wittig-Horner reaction; Wessling sulfonium precursor method (Wessling, 1985); Gilch route (Gilch & Wheelwright, 1966) and palladium catalyzed coupling reactions.

By utilizing Wittig reaction, fully regioregular and regiorandom poly[(2-methoxy-5-((3',7'-dimethyloctyl)oxy)-1,4-phenylenevinylene)] (MDMO-PPV, P1 and P2) were synthesized following the route shown in Scheme 1 (Tajima et al., 2008). The device study on these two polymers showed that the regioregular MDMO-PPV-based device had a PCE of 3.1%, which was much higher than 1.7% out of regiorandom MDMO-PPV. The higher crystallinity of the regioregular MDMO-PPV polymer and better mixing morphology with PCBM were ascribed to the improved PCE for regioregular MDMO-PPV. This study highlighted the importance of regioregularity of PPV-based polymer to achieve good solar cell performance.

### 3.2 Acetylene (triple bond)

Polyacetylene was the first discovered conducting conjugated polymer and inspired a lot of scientific interest in the research of conjugated polymers (Shirakawa et al., 1977). The synthetic chemistry of acetylene-containing polymers has been intensively reviewed by Liu *et al.* (Liu et al., 2009). In polymers designed for solar cell, acetylene is normally introduced to the polymer backbone via Sonogashira cross coupling reaction.

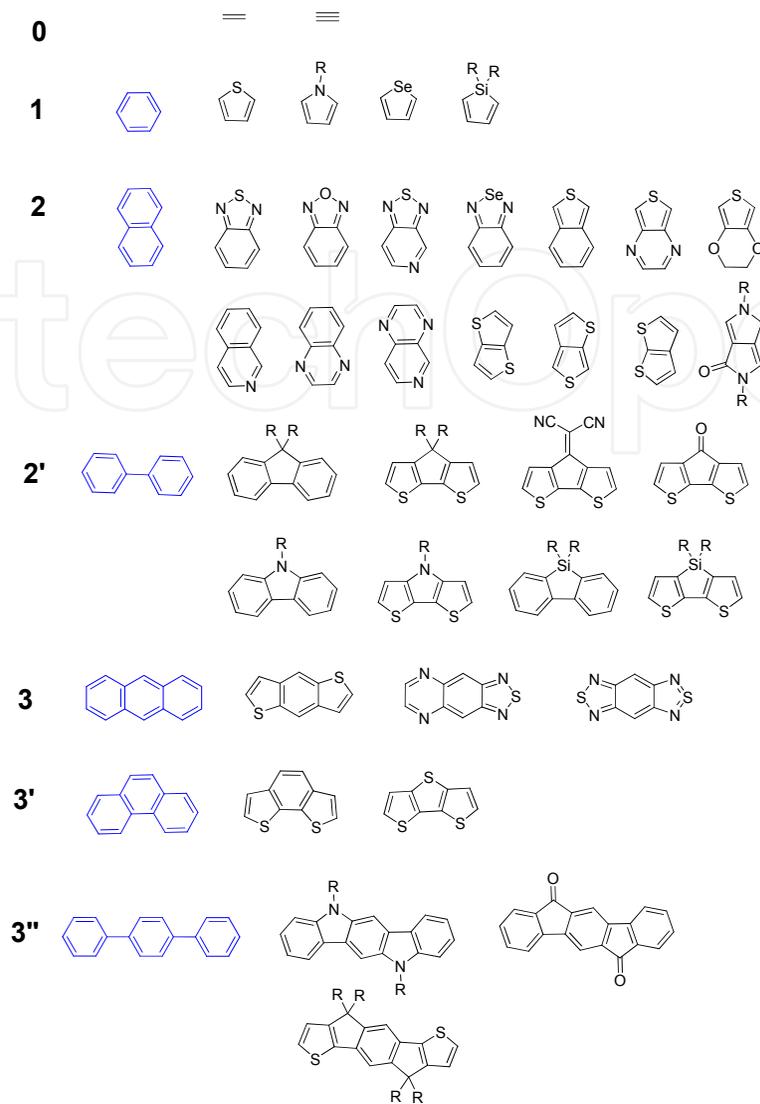
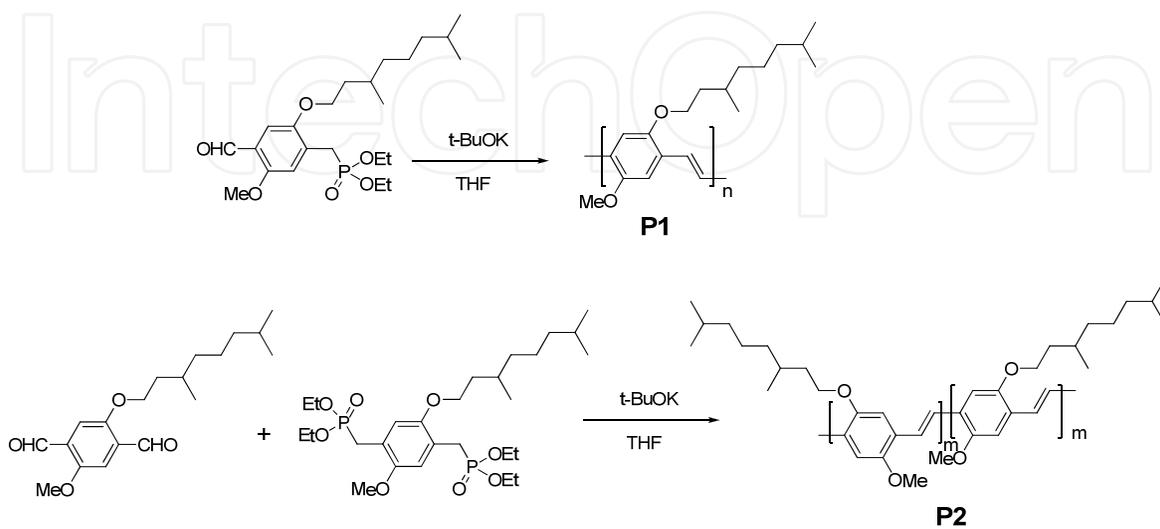
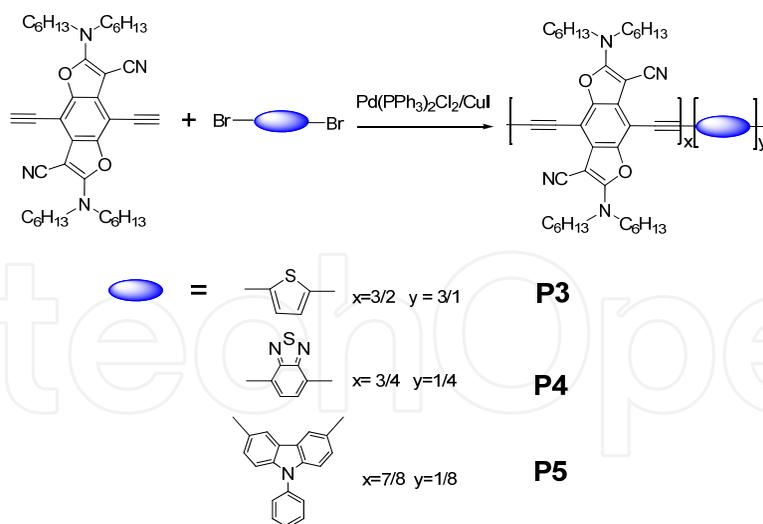


Chart 1. Common monomer building blocks used for construction of solar cell polymers



Scheme 1. synthesis of regioregular and regiorandom MDMO-PPV



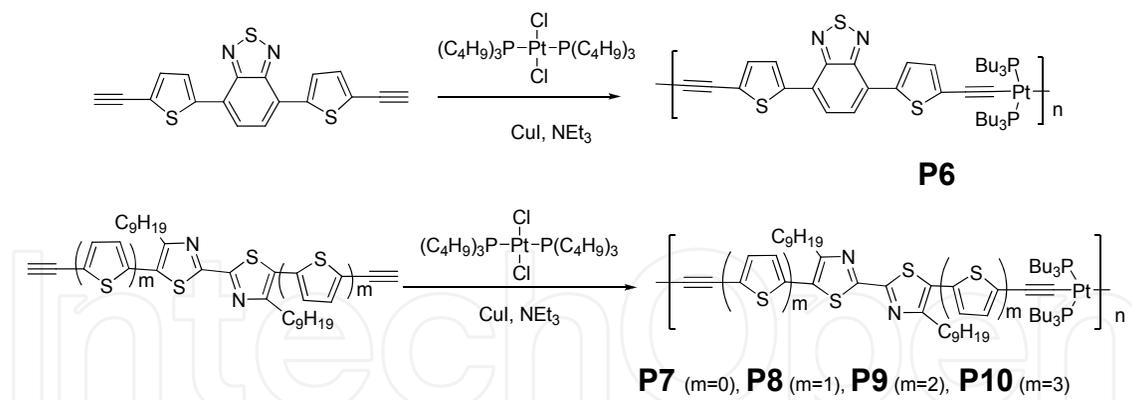
Scheme 2. Synthetic route of acetylene-containing polymers P3, P4 and P5

Benzodifuran moiety was copolymerized with thiophene, electron withdrawing benzothiadiazole and electron donating 9-phenylcarbazole, respectively, to form P3, P4 and P5 as shown in Scheme 2 (H. Li et al., 2010). The ratio of  $x/y$  is estimated from the integration of relevant peaks in their NMR spectra. The fraction of benzodifuran is more than 50% due to the self-coupling of diacetylene monomer. All three polymers absorbed beyond 600 nm in the film state and had a LUMO level above -4.0 eV. The high structural order of these three polymers was evidenced by power XRD study, as two reflection peaks, one at  $2\theta = 4.95^\circ$ - $5.5^\circ$  and the other at  $2\theta = 19.95^\circ$  -  $21.75^\circ$ , were well observed. The highest PCE  $\eta = 0.59\%$  was obtained based on P3/PCBM (1:4,  $w/w$ ) blend.

Another category of acetylene containing polymer designed for PSC is  $\pi$ -conjugated organoplatinum polyynne polymers (Baek et al., 2008). The platinum- $C_{sp}$  bond extends the conjugation of the polymer as a result of the fact that the  $d$ -orbital of the Pt can overlap with the  $p$ -orbital of the alkyne. This kind of Pt-C bond can be chemically accessible by a Sonogashira-type dehydrohalogenation between alkyne and platinum chloride precursor. Examples of this type of polymer and their synthetic routes are shown in Scheme 3 (Wong et al., 2007).

In order to tune the energy gap  $<2.0$  eV, internal D-A function was introduced between electron rich Pt-ethyne groups. This effective band gap control strategy rendered P6 UV-vis absorption maximum at 548 nm and an optical band gap of 1.85 eV. This absorption behavior was proved to occur via the charge transfer excited state but not the triplet state of the polymer by photoluminescence lifetime study and PL temperature dependence study. The electrochemical HOMO and LUMO energy level were measured to be -5.37 eV and -3.14 eV, respectively. The best P6/PCBM (1:4,  $w/w$ ) BHJ solar cell gave the open circuit voltage  $V_{oc} = 0.82$  V, the short-circuit current density  $J_{sc} = 15.43$  mA, fill factor  $FF = 0.39$  and power conversion efficiency  $\eta = 4.93\%$ .

For polymers P7-P10 (Wong et al., 2007), the electron withdrawing moiety was replaced by bithiazole heterocycles. Nonyl chains were attached to the bithiazole to assist solvation of the polymer. By extending the conjugation ( $m: 0 \rightarrow 3$ ) along the polymer backbone, the band gaps of P7-P10 decreased from 2.40 eV to 2.06 eV. The power conversion efficiency (polymer/PCBM=1:4,  $w/w$ ) was found significantly improved from  $\sim 0.2\%$  to  $\sim 2.5\%$  as the number of thiophene bridge increased from 0 to 3, most likely due to the improved charge carrier mobility of the active layer.



Scheme 3. Synthesis of organoplatinum polyynyl polymers: P6, P7-P10

### 3.3 Phenylene (benzene)

Benzene ring is the most fundamental building block for polymer solar cell materials. A lot of chemistry and reaction carried out in this research area are rooted back to the reactivity of benzene ring. Benzene can be polymerized by direct linkage at the 1,4-position to form poly(*para*-phenylene) (Chart 2). Poly(*para*-phenylene) without any substituents has a linear rod-like structure and poor solubility in common organic solvents which limits its application as organic electronics. One strategy to increase the solubility is to introduce alkyl or alkoxy chain on the backbone. However, the planarity of the poly(*para*-phenylene) will be disturbed due to the steric effect of the R group attached (Chart 2, P12) and therefore the effective conjugation between adjacent benzene rings will be sacrificed. To address this issue, bridges can be introduced between benzene rings, e.g., double bond in poly(phenylvinylene) (PPV)(Chart 2, P13).

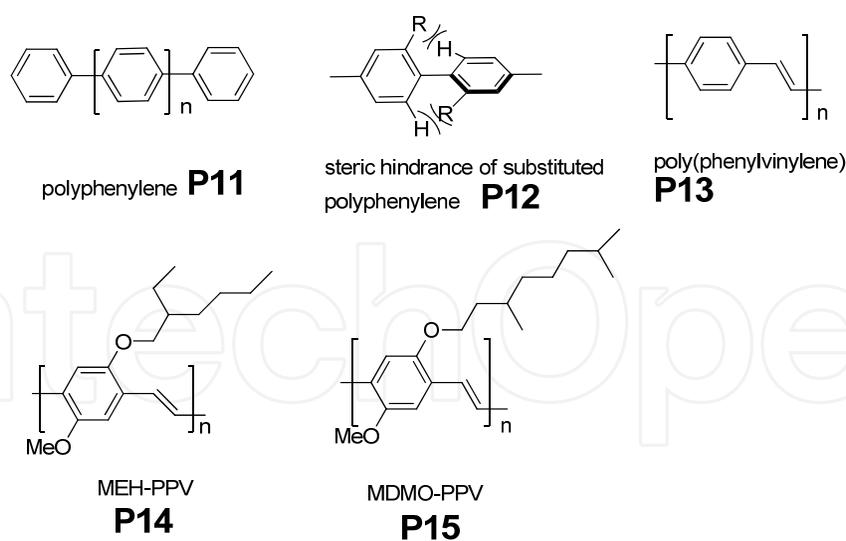


Chart 2. Structures of polyphenylene and its derivatives

PPV and its derivatives have been intensively studied in organic electronics research for OLED and PSC materials due to their excellent conducting and photoluminescent properties (Burroughes et al., 1990). Poly[2-methoxy-5-((2'-ethylhexyl)oxy)-1,4-phenylenevinylene] (MEH-PPV, P14) was utilized to fabricate bilayer solar cell with  $C_{60}$  in the early days and it was reported that photoinduced electron transferred from electron donating MEH-PPV onto

Buckminsterfullerene,  $C_{60}$ , on a picosecond time scale (Sariciftci et al., 1992). This experiment explained one fundamental physical phenomenon present in organic photovoltaic cells and the concept developed by this study significantly inspired later research on organic solar cells.

Another derivative of PPV, poly[(2-methoxy-5-(3',7'-dimethyloctyl)oxy)-1,4-phenylene vinylene] (MDMO-PPV, Chart 2) is also widely studied for solar cells and still being used nowadays. The combination of MDMO-PPV and PCBM is used in BHJ solar cell and efficiency up to 3.1% has been reported (Tajima et al., 2008). However, the relatively low hole mobility of MDMO-PPV ( $5 \times 10^{-11} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) (Blom et al., 1997) is reported to limit the charge transport inside the photoactive layer. Most PPV polymers have band gap greater than 2.0 eV and have maximum absorption around 500 nm. Furthermore, PPV materials are not stable in air and vulnerable to oxygen attack. Structural defects generated either during synthesis or by oxidation will substantially degrade the performance of the device. All these factors limit the application of PPV polymers in solar cells.

### 3.4 Thiophene

Thiophene has become one of the most commonly used building blocks in organic electronics due to its excellent optical and electrical properties as well as exceptional thermal and chemical stability (Fichou, 1999). Its homopolymer, polythiophene (PT), was first reported in 1980s as a 1D-linear conjugated system (Yamamoto et al., 1980; Lin & Dudek, 1980). Substitution by solubilizing moieties is adopted to increase the solubility of polythiophenes. The band gap of the polythiophene can also be tuned at the same time by inductive and/or mesomeric effect from the heteroatom containing substitution.

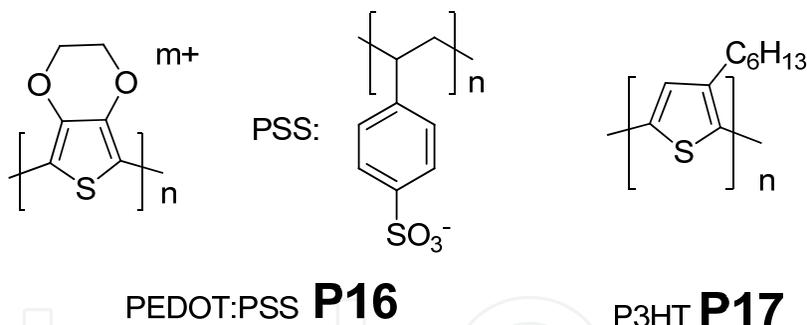


Chart 3. Chemical structures of PEDOT:PSS and P3HT

Two frequently encountered thiophene-based conjugated polymers in literature are poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS, Chart 3) in conducting and hole transport layers for organic light emitting diodes (OLEDs) and PSCs and regioregular poly(3-hexylthiophene) (P3HT, Chart 3) as a hole transporting material in organic field effect transistors (OFETs) and PSCs.

As in PPV polymer, regioregularity is essential for the thiophene unit to conjugate effectively on the same plane since in regioregular form, steric consequence of the substitution is minimized, resulting in longer effective conjugation length and a lower band gap. As shown in Chart 4, three different regioisomers, head-to-head (HH), head-to-tail (HT) and tail-to-tail (TT) can be formed when two 3-alkyl thiophene units are linked via 2,5-position. Presence of HH and TT linkage in polythiophene will cause plane bending and generate structural disorder, which consequently weaken the intermolecular interaction.

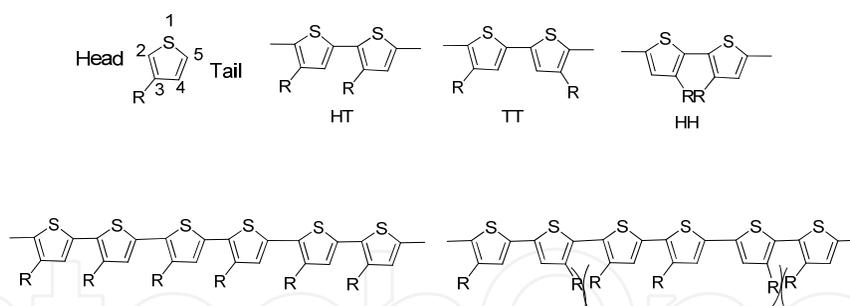


Chart 4. 3-substituted thiophene dimer isomers, regioregular P3HT and regiorregular P3HT. Regioregular P3HT was first synthesized by McCullough's group via a Grignard metathesis method (McCullough & Lowe, 1992, 1993). Polymerization with a Ni(0) catalyst yielded a highly regioregular (>99% HT) PT polymer ( $M_n=20000-35000$ ,  $PDI=1.2-1.4$ ). The mechanism of this Ni coupling reaction was proposed and justified to be a 'living' chain growth mechanism (Miyakoshi et al., 2005). Regioregular P3HT has been treated as a standard polymer for solar cell devices and commonly used for device testing and comparison. It represents the 'state of art' in the field of PSCs and efficiency up to ~5% has been reported based on P3HT/PCBM device (Ma et al., 2005).

### 3.5 Silole

Siloles or silacyclopentadienes, are a group of five-membered silacyclics with 4 accessible substitution positions on the butadiene and another 2 positions on the silicon atom. Compared with many other 5-membered heterocyclopentadiene, such as thiophene, furan or pyrrole, the silole (silacyclopentadiene) ring has the smallest HOMO-LUMO band gap and the lowest lying LUMO level due to the  $\sigma^*$  to  $\pi^*$  conjugation arising from interaction between the  $\sigma^*$  orbital of two exocyclic bonds on silicon and the  $\pi^*$  orbital of the butadiene moiety. The small band gap and lowest LUMO energy level render silole outstanding optoelectronic properties such as high PL efficiency and excellent electron mobility (Chen & Cao, 2007).

Random and alternating silole-containing copolymers P18 (Chart 5) (F. Wang et al., 2005) were synthesized via Suzuki coupling reaction from fluorene and 2,5-dithienyl-silole. The band gap of this series of polymer could be tuned from 2.95 eV to 2.08 eV by varying the silole content from 1% to 50% in the polyfluorene chain. The decrease of the band gap was found mainly due to the decrease of LUMO energy level while the HOMO of this series of polymer remained unchanged at ~ -5.7 eV. For the alternating copolymer, field effect charge mobility was measured to be  $4.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and the best PCE value was reported to be 2.01% using a P18( $m=1$ )/PCBM (1:4,  $w/w$ ) blend as active layer.

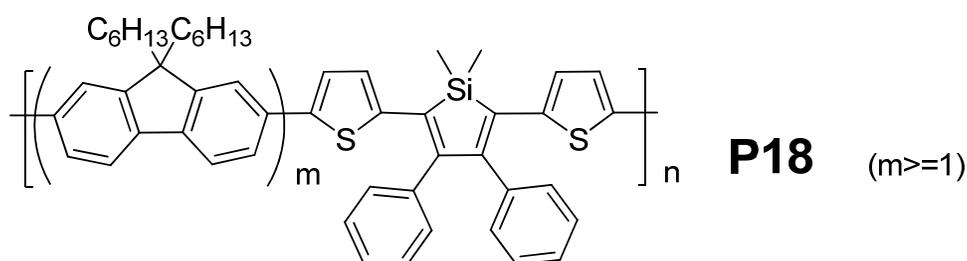


Chart 5. Chemical structure of silole containing polymer P18

### 3.6 Benzothiadiazole/ Aza-benzothiadiazole/ Se-benzothiadiazole

2,1,3-benzothiadiazole (BT, Chart 6) is an electron deficient heterocycle that has been incorporated with electron donating species to construct low band gap polymer donor for BHJ polymer solar cell. The electron withdrawing ability of BT can be further increased by replacing one carbon atom with  $sp^2$ -hybridized N atom (Chart 6). The sulfur atom in the BT unit can also be replaced to selenium, by doing so the band gap is further decreased.

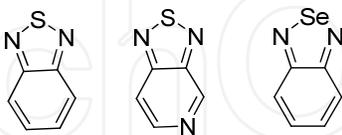


Chart 6. Structure of BT, aza-BT and Se-BT

A variety of low band gap polymers containing BT have been synthesized and tested for PSC performance (P19-P23) (Zhang et al., 2006; E. Zhou et al., 2008; Svensson et al., 2003; Slooff et al., 2007; Q. Zhou et al., 2004; Blouin et al., 2007). The electron donating moiety in the low band gap polymer varies from carbazole, fluorene, dibenzosilole, bridged thiophene-phenylene-thiophene, and dithienopyrrole. This type of polymer has a band gap <2.0 eV and gives moderate to good PCE value ranging from ~1% to ~5%, rendering a promising direction for the research of PSC donor material.

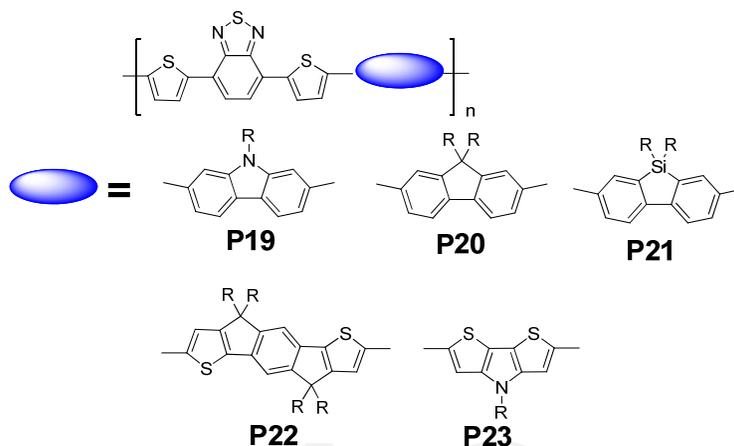
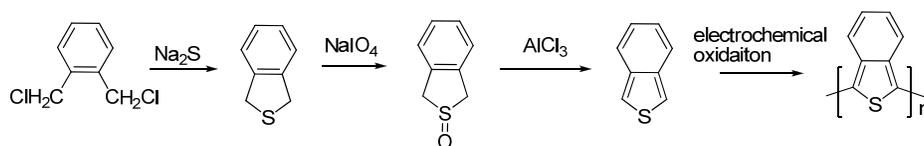


Chart 7. Benzothiadiazole containing low band gap polymers P19-P23

### 3.7 Isothianaphthene/ Thienopyrazine

The first example of poly(isothianaphthene) is reported by Wudl *et al.* in 1984 (Wudl et al., 1984) as shown in Scheme 4. Poly(isothianaphthene) has a greater tendency to adopt the quinoid structure due to the stabilization of the benzenoid ring formation (Chart 8). The quinoid structure adoption reduces the band gap of poly(isothianaphthene) to *ca.* 1.0 eV, which is about half that of polythiophene (~2.0 eV) (Kobayashi et al., 1984).



Scheme 4. Synthesis of poly (isothianaphthene)

Poly(thianaphthene) adopts a non-planar conjugation due to the steric hinderance present between benzo-H and thiophene-S atoms as shown in Chart 8. To increase the effective  $\pi$ -conjugation, one C-H can be replaced by  $sp^2$ -hybridized nitrogen to release the steric strain. As evidenced by X-ray structure analysis of 2,5-di(2-thienyl) pyridino[c]thiophene (Chart 8) (Ferraris et al., 1994), the torsional angle between the pyridinothiophene moiety and the thiophene unit on the N side is only  $3.5^\circ$ , while it is  $39^\circ$  on the other side. To further release the steric strain, the CH groups on both sides of the isothianaphthene can be replaced by N atom. Due to its effective conjugation and electron withdrawing nature, thieno[3,4-b]pyrazine is proposed as another type of electron withdrawing building block for the construction of low band gap polymers. In necessity of solubility, substituted thieno[3,4-b]pyrazines can be synthesized by condensation of 3,4-diaminothiophene with substituted 1,2-diones.

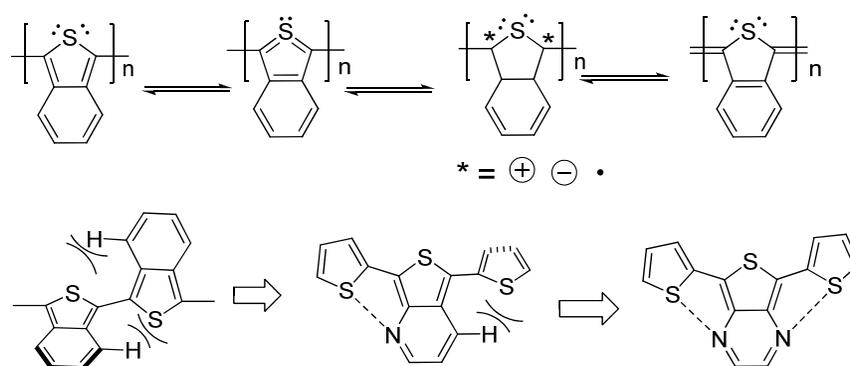


Chart 8. Resonance structure of poly(isothianaphthene) and demonstration of steric strains

The thienopyrazine unit is commonly linked to two thiophene rings at each side and coupled with electron donating moiety, such as fluorene to construct low band gap polymer (P24, P25, and P26) (Zhang et al., 2005, 2006; Mammo et al., 2007). P24 was reported to suffer from low solubility and low molecular weight. The polymerization yield was only 5% owing to the poor solubility in chloroform. The best PCE based on P24/PCBM(1:6, *w/w*) was obtained as  $\eta = 0.96\%$ . To address the solubility issue, alkyl and alkoxy chains were attached to the thienopyrazine moiety and another two low band gap polymers P25 and P26 were synthesized by copolymerization between thienopyrazine and fluorene. The addition of side chains did not change the band gap and HOMO/LUMO energy level as evidenced from absorption spectra and cyclic voltammetry measurement. These two polymers had almost identical absorption and HOMO/LUMO values. The best PCE value obtained for P25 was 1.4% while for P26 the optimal PCE value was 2.2%.

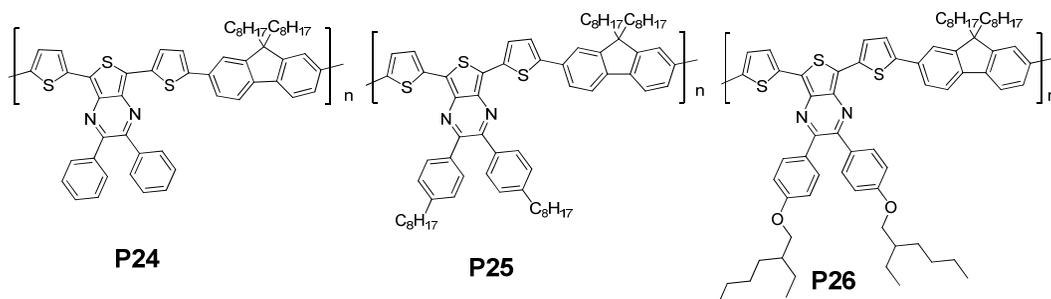


Chart 9. Chemical structures of thienopyrazine containing polymers P24, P25 and P26

### 3.8 Thieno[3,4-b]thiophene / Thieno[3,2-b]thiophene/ Thieno[2,3-b]thiophene

Annulations of two thiophene rings generates 4 isomers (Chart 10), namely, thieno[3,4-b]thiophene, thieno[3,2-b]thiophene, thieno[2,3-b]thiophene and thieno[3,4-c]thiophene. The first three isomers have been synthesized and isolated. Thieno[3,4-c]thiophene is predicted to be kinetically unstable and not isolated yet (Rutherford et al., 1992).

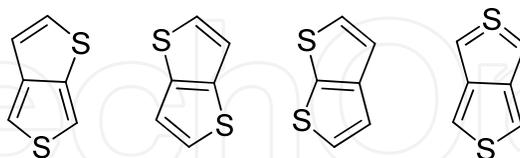


Chart 10. Isomer structure of thienothiophenes; from left to right: thieno[3,4-b]thiophene, thieno[3,2-b]thiophene, thieno[2,3-b]thiophene and thieno[3,4-c]thiophene

Thieno[2,3-b]thiophene, thieno[3,2-b]thiophene and thieno[3,4-b]thiophene are useful building blocks in preparing conjugated polymer for organic electronics applications due to their planarity and electron richness. Compared with thiophene, thienothiophene has a larger  $\pi$ -conjugated system. Therefore, it is introduced to the polymer backbone in the hope that it can facilitate interchain  $\pi$ -stacking to increase the structural order and improve the charge carrier mobility.

An efficient polymer donor P27 copolymerized by thieno[3,4-b]thiophene and benzodithiophene has been reported (Liang et al., 2009). Three dodecyl chains were used in each repeating unit to assist solvation of the polymer. BHJ solar cell fabricated using P27/PCBM(1:1 *w/w*) gave an excellent PCE of 4.76%, with  $V_{oc} = 0.58V$ ,  $J_{sc} = 12.5 \text{ mA/cm}^2$  and  $FF = 0.654$ . A further improvement of the PCE to 5.3% was obtained by utilizing PC<sub>70</sub>BM as the electron acceptor in the active layer. This high PCE value was ascribed to several factors including well tuned band gap (1.6 eV), proper HOMO/LUMO energy levels, balanced carrier mobility (P27  $\mu_h = 4.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), favorable morphology of the active layer and thieno-thiophene's ability of stabilizing the quinoid structure along the polymer backbone to enhance the planarity of the polymer.

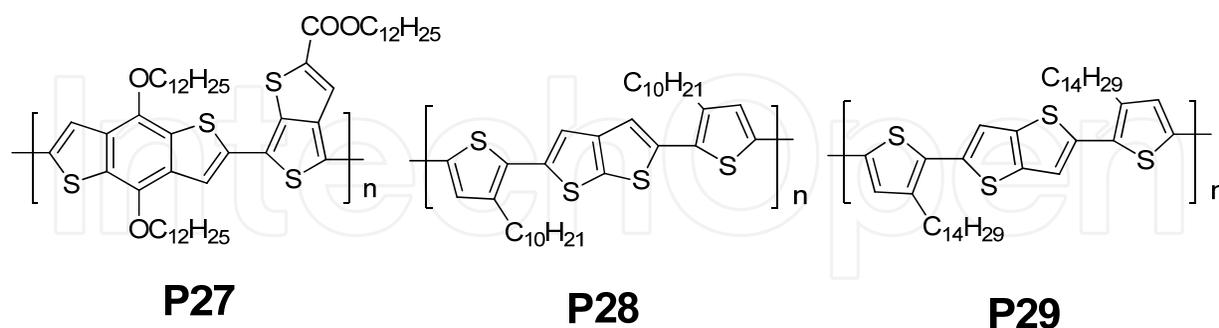


Chart 11. Chemical structures of thienothiophene containing polymer P27, P28 and P29

Liquid-crystalline semiconductor polymers P28 and P29 were prepared by copolymerization of thienothiophene and thieno[2,3-b]thiophene, respectively, with 4,4'-dialkylbithiophene unit (McCulloch et al., 2006; Heeney et al., 2005). P28 had good field effect charge mobility of  $\mu_h = 0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . However, its relatively large band gap (absorption maximum  $\lambda_{max} = 470 \text{ nm}$ ) limited its application as efficient solar cell material. For P29, the absorption maximum was red shifted to 547 nm and the field effect charge mobility was increased to

$\mu_h = \sim 0.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ . The improved mobility was suggested due to the improved control of crystallization. The PSC device fabricated from P29/PC<sub>70</sub>BM(1:4 *w/w*) blend achieved an optimized PCE  $\eta = 2.3\%$  in nitrogen atmosphere. The high lying HOMO energy level (-5.1eV) of P29, which is above the air oxidation threshold (-5.2 eV), makes the polymer relatively unstable in air.

### 3.9 Diketopyrrolopyrrole (DPP)

The DPP moiety has been utilized for construction of low band gap polymer for BHJ solar cells due to its electron deficient nature, planarity of the core and ability to accept H-bonding. D-A type low band gap polymers based on DPP have been synthesized by varying the electron donating part of the polymer (P30, P31, P32) (Wienk et al., 2008; Bronstein et al., 2011).

By combining electron rich quarterthiophene with electron deficient DPP unit, a low band gap polymer (1.4 eV in film state) P30 was obtained. P30 showed a good solubility in chloroform and tended to aggregate in dichlorobenzene (DCB). Device based on P30/PC<sub>60</sub>BM (1:2, *w/w*) BHJ thin film prepared from solution in CHCl<sub>3</sub>/DCB (4:1 *v/v*) gave a PCE of 3.2%. By utilizing PC<sub>70</sub>BM as the acceptor in the active layer, an improved PCE of 4.0% was achieved under the same condition.

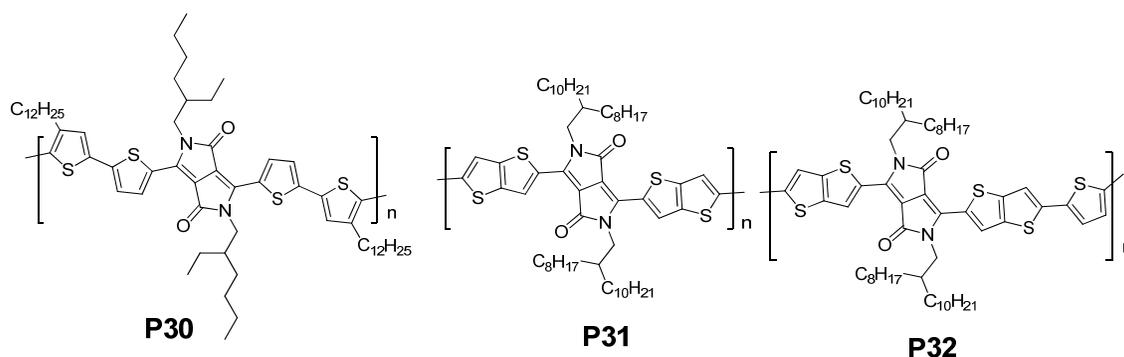


Chart 12. Chemical structures of DPP-containing polymers P30, P31 and P32

By replacing the thiophene unit with larger thieno[2,3-b] thiophene, P31 and P32 were prepared. Long branched chains have been incorporated at the DPP unit to assist solvation. Both polymers had band gap of  $\sim 1.4 \text{ eV}$  and absorbed beyond 800 nm in the film state. Ambipolar charge transport behavior was found for both of the polymers. P31 had a high hole mobility of  $0.04 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and good PCE of 3.0% based on P31/PC<sub>70</sub>BM (1:2 *w/w*) thin film prepared from CHCl<sub>3</sub>/DCB (4:1 *v/v*) solution. By modifying the backbone with one more thiophene unit introduced to the repeating unit, P32 showed an even higher hole mobility of *ca.*  $2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and the BHJ solar cell device fabricated under the same condition as that of P31 showed an improved efficiency up to 5.4%.

### 3.10 Fluorene/ cyclopenta[2,1-b:3,4-b'] dithiophene/ silafluorene/ dithieno[3,2-b:2',3'-d] silole

Fluorene based polymers have been widely explored as organic electronic material in the field of OLED, OFET and PSC due to their high photoluminescence quantum yield, high thermal and chemical stability, good film-forming properties and good charge transport properties. Polyfluorene, however, has a band gap of  $\sim 3.0 \text{ eV}$ , which limits its application in

solar cell. Therefore, fluorene is normally copolymerized with electron withdrawing moieties to construct polymers with band gap  $<2.0$  eV so as to extend sunlight harvesting to longer wavelength. Although some solar cell polymers have been prepared by copolymerization of fluorene and electron-rich moieties, such as thienothiophene and pentacene, their absorption behaviors and wide band gaps are found to account for the moderate to poor performance (Schulz et al., 2009; Okamoto et al., 2008). Palladium catalyzed cross coupling reaction is normally adopted for the polymerization due to the ease of halogenation at the 2,7-position of fluorene unit. Alkylation at the 9-position of the fluorene assists solvation for the D-A type polymer, whereas necessary, alkylation on the electron deficient counterpart is also required. Fluorene copolymers prepared from electron deficient benzothiadiazole and thienopyrazine have been discussed previously.

By replacing two benzene rings of fluorene with thiophene, cyclopenta[2,1-b:3,4-b']dithiophene can be obtained as another novel building block to construct D-A type low band gap polymer. Alkylation at the bridge  $sp^3$ -carbon renders solubility for the polymer. Cyclopenta[2,1-b:3,4-b']dithiophene based polymer P33 has been synthesized with a low band gap of *ca.* 1.4 eV (Mühlbacher et al., 2006). It was utilized by Kim *et al.* (Kim et al., 2007) to fabricate an efficient tandem solar cell. This brilliant and excellent work addressed the issue that while most low band gap polymers absorb at wavelength longer than 700 nm, there is a hollow at shorter wavelength and the lack of sufficient absorption at the hollow will drag the power conversion efficiency. In this case, P33 had an absorption maximum at *ca.* 800nm and a hollow at *ca.* 450nm. Kim et al. fabricated a tandem BHJ solar cell by utilizing P3HT ( $\lambda_{\max} \approx 550$ nm) to absorb at the hollow of P33 and low band gap polymer P33 to absorb light at the NIR region. Tandem solar cell device (Al/TiO<sub>x</sub>/P3HT:PC<sub>70</sub>BM/PEDOT:PSS/TiO<sub>x</sub>/P33:PCBM/PEDOT:PSS/ITO/glass) based on P3HT and P33 gave a typical performance parameter of  $J_{sc} = 7.8$  mA/cm<sup>2</sup>,  $V_{oc} = 1.24$  V,  $FF = 0.67$  and  $PCE = 6.5\%$ , which was among the highest values reported.

Silafluorene and dithieno[3,2-b:2',3'-d]silole are two interesting electron rich moieties that are structurally analogous to fluorene. Low band gap polymer P34 was synthesized by copolymerization of 2,7-silafluorene and dithienyl-benzothiadiazole (E. Wang et al., 2008). Field effect charge mobility of P34 was found to be  $\sim 1 \times 10^{-3}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. High efficiency up to 5.4% with  $V_{oc} = 0.9$  V,  $J_{sc} = 9.5$  mA/cm<sup>2</sup>,  $FF = 0.51$  was obtained by using P34/PCBM(1:2 *w/w*) as active layer. Polymer P35 was synthesized by Stille coupling between dithieno[3,2-b:2',3'-d]silole and benzothiadiazole (Hou et al., 2008). The optical band gap of P35 was found to be 1.45 eV, which was similar to that of P33. Hole transport mobility of the polymer was determined to be  $3 \times 10^{-3}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, about 3 times higher than that of P33. The best device based on P35 gave a PCE of 5.1% with  $J_{sc} = 12.7$  mA/cm<sup>2</sup>,  $V_{oc} = 0.68$  V and  $FF = 0.55$ .

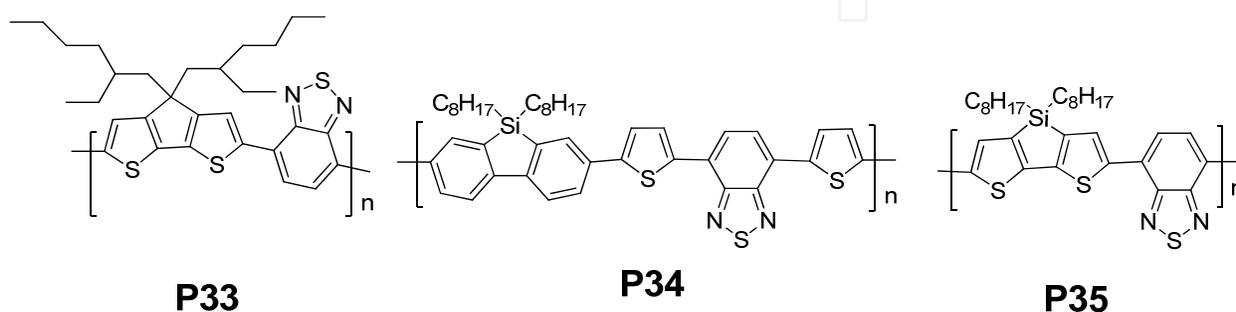


Chart 13. Structures of low band gap polymers P33, P34 and P35

#### 4. Conclusion

In this chapter, main effort has been directed to disclose the structure-property relationship for solar cell polymers. The requirements and criteria for an efficient polymer donor in BHJ solar cell have been discussed with representative examples. Key factors are: absorption efficiency, solubility, stability (thermal-, photo-), low band gap, HOMO/LUMO energy level, charge carrier mobility and morphology. In order to achieve high power conversion efficiency, a good balance among these factors should be met. On the other hand, choice of acceptor counterpart and device engineering for the BHJ device also play important roles for power conversion efficiency improvement. Nowadays choice of donor/acceptor combination and device fabrication is still 'a state of art' but more and more rules of thumb have been pointed out. Provided that if BHJ concept still prevails for the next 10 years or longer, newer device design is also urgently required. Tandem solar cell device reported is one example to address the efficiency issue from this point of view. But no matter what kind of new changes will be brought out, the photon flux capture material, which is conjugated polymer in PSC, will still be the core of the device.

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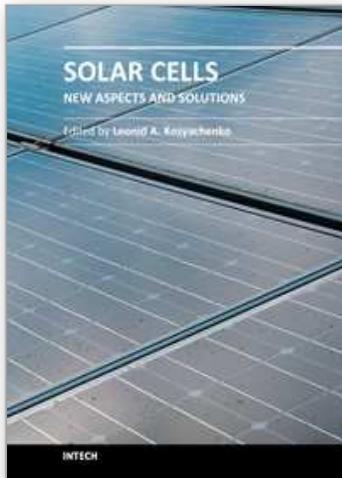
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## **Solar Cells - New Aspects and Solutions**

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The fourth book of the four-volume edition of 'Solar cells' consists chapters that are general in nature and not related specifically to the so-called photovoltaic generations, novel scientific ideas and technical solutions, which has not properly approved. General issues of the efficiency of solar cell and through hydrogen production in photoelectrochemical solar cell are discussed. Considerable attention is paid to the quantum-size effects in solar cells both in general and on specific examples of super-lattices, quantum dots, etc. New materials, such as cuprous oxide as an active material for solar cells, AlSb for use as an absorber layer in p-i-n junction solar cells, InGaAsN as a promising material for multi-junction tandem solar cells, InP in solar cells with MIS structures are discussed. Several chapters are devoted to the analysis of both status and perspective of organic photovoltaics such as polymer/fullerene solar cells, poly(p-phenylene-vinylene) derivatives, photovoltaic textiles, photovoltaic fibers, etc.

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