JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 16, No. 11-12, November – December 2014, p. 1257 - 1268

Organic photovoltaic materials: a review on synthesis, structure and properties

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The need of energy is most discussed issue these days and among various renewable energy sources, solar energy is most reliable one. Collection of solar energy and then conversion to electricity requires semiconducting materials. After inorganic junctions, Organic materials have got a pretty attention because of many advantages of them. In this review we discussed and compiled a variety of organic semiconductors, their synthesis, structure, properties and future scopes for the potential applications in photovoltaic devices. The review will serve as a compiled note for the researchers working in the field of flexible electronics.

(Received December 19, 2013; accepted November 13, 2014)

Keywords: Photovoltaic materials, Silafluorene, Carbazole, Fluorene, Solar cell, Flexible electronics

1. Introduction

Energy is one of the most important factor of concern to human life in the 21st century [1]. The greatest increase in consumption of fossil fuels resulted in causing global warming and environmental pollution. So alternate renewable energy sources are main focus of research and sustainable development throughout the scientific communities now a days. Scientists are focusing on the development of renewable energy [2] generated from natural resources such as sunlight, wind, rain, tides, and geothermal heat. Among these resources, the sun has the potential to make the largest energy contribution: only one hour of sunshine (3.8 × 1023 kW) is more than enough to satisfy the highest human demand for energy for an entire year (1.6 × 1010 kW in 2005). [3-6] Photovoltaic devices [7], also called solar cells, converts solar energy to electric energy, represent a promising technology to use renewable energies. These devices work under known photovoltaic effect and convert sunlight directly into electricity. Easily fabricated and low-cost, these devices paved the way to a new generation of economic photovoltaic modules, appearing as a promising alternative for energy resources.

Based upon the material used, solar cells can be divided into silicon-based (including monocrystalline, polycrystalline and amorphous silicon), semiconducting compound-based (including gallium arsenide and copper indium gallium selenide), organic solar cells and organic inorganic blends. The standard solar panels based on multicrystalline silicon have power conversion efficiencies around 15% [8] and for multijuction it has reached to 30%. However, the expensive investment and non-ecofriendly waste in semiconductor-processing technologies of the silicon-based solar cells have limited their popularization in our lives. The various factors which affect the efficiency of a solar cells are open circuit voltage, short circuit current density and fill factor of the device. Because of light weight, ecofriendly and flexible nature, researchers are more concerned now a day with Organic electronics. Recently Heliatek have reported the 12% certified efficiency of organic photovoltaic (OPVs) [9]

Another class known as, DSCs solar cells were first demonstrated by Gra¨tzel and co-workers. [10] Currently, a maximum efficiency of 12.3% had been achieved by designing various photosensitive dyes with a broad light adsorption range. [11] Several reports have been published to review the use of conjugated polymers in solar cell applications. [12-19]. Because of rapid growth of this active field in recent years, this review has been written to cover the selected representative conjugated polymers that have had a significant impact in the field as well as to update their latest progress. Particular attention is focused on synthetic approaches for making these polymers as well as the useful and important building blocks leading to the necessary monomers. For a conjugated polymer to suit in organic photovoltaic bulk heterojunction (BHJ) solar cell, it should possess favorable physical and chemical properties in order to achieve reasonable device efficiency. Ideal conjugated polymer should simultaneously possess good film-forming properties, strong absorption ability, high hole mobility, and suitable HOMO-LUMO energy levels.

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 [20-22] or chemical [23] oxidative polymerizations, transition-metal-catalyzed cross-coupling reactions provide an alternate route for Csp^2-Csp^2 and Csp-Csp^2 bond formation. [24]

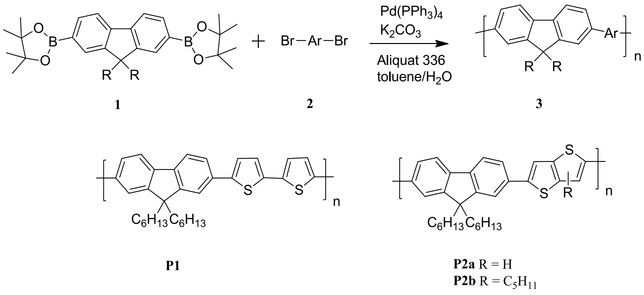
Generally, the reaction involves a transition-metal-catalyzed oxidative addition reaction across the C--X bond of an electrophile and then transmetalation with a main group organometallic nucleophile, followed by a reductive elimination step leading to the carbon--carbon bond formation. Nickel and palladium based complexes are the most commonly used transition-metal catalysts, although other metals have also been used. The organometallic nucleophiles can be Grignard reagents (Kumada-Corriu), [25] stannyl (Stille), [26] boron reagents (Suzuki-Miyaura), [27] or copper (Sonogashira). [28] Thus, conjugation lengths can be extended through consecutive transformations in the catalytic cycle. When the electrophilic and nucleophilic centers of the monomeric substrates are readily accessible, regioregularity of the polymers can be easily achieved. Another advantage is that these reaction conditions are generally mild and can tolerate many functional groups. This is particularly important for synthesizing conjugated polymers with various functional groups. Stille and Suzuki coupling reactions using two distinct monomers are the most efficient and widely used methods for preparing alternating copolymers. It is noteworthy that stannyl groups substituted on the benzene ring of the monomer substrate always give poor reactivity with aryl halides under Stille coupling conditions. [29] Therefore, Stille coupling is more suitable for thiophene-containing polymers using monomers with stannyl groups on the thiophene ring, whereas Suzuki coupling is more widely used for preparing benzene-containing polymers with boronic groups on the benzene ring of the monomer. On the other hand, nickel-mediated Yamamoto dehalogenation coupling reactions also provide an alternative pathway for carrying out self-polymerizaiton of single monomers. [30]

In the following review, we compiled information on selected p-type conjugated polymers classified according to the structures of the representative electron-rich fragments along the main chain. Synthesis, structure and properties of these materials are presented to serve as a compiled note for the researchers working in the field of flexible electronics.

2. Fluorene-based conjugated polymers

Fluorene-containing molecules have received considerable attention due to their unique photophysical properties and potential for chemical modification. Fluorene and its derivatives are rigid, planar molecules that are highly stable towards photodegradation and thermal oxidation during device operations. Because of easily structural modification possibilities, the molecular manipulations to enhance solubility and conjugation extension can be tuned accordingly. Because of their high fluorescence quantum yield, excellent hole-transporting properties, good film-forming properties, and exceptional chemical stability, Polyfluorene-based (PF) conjugated polymers have been extensively studied and utilized in the field of light-emitting diodes. [31-32] Fluorine derivatives are expected to achieve higher open circuit voltage and short-circuit currents because of low lying HOMO levels and high mobility. Hence fluorene unit can emerge as a highly promising building block for the design of new p-type materials for photovoltaic applications. However, the optical band gap of poly(9,9-dialkylfluorene) is ca. 3.0 eV, which is too high for efficient sunlight harvesting where the maximum photon flux is around 1.7 eV. This problem can be solved by incorporating an electron accepting unit into the main polyfluorene chain to form a donor-acceptor alternating arrangement and hence narrowing the band gap of the resulting copolymers for optimal sunlight collection.

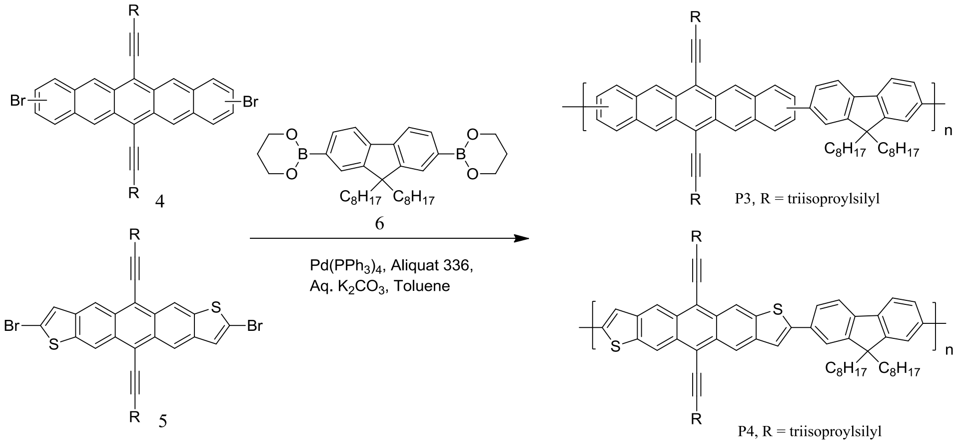
In general, PF-based polymers are synthesized by using Suzuki coupling. As far as the synthetic feasibility and reactivity are concerned, the 2,7-positions of the 9,9-dialkylfluorene unit are always functionalized with two boronic esters, whereas the dibromo functionality is placed at another coupling aromatic unit. In a typical Suzuki coupling reaction, a palladium complex such as $Pd(PPh_3)_4$ is used as the catalyst to carry out the polymerization in the presence of base K_2CO_3 and a phase-transfer catalyst, Aliquat 336, in a solvent mixture (toluene/degassed water). During the polymerization process, the fluorenylboronic ester and the aromatic dibromide react with each other to give well-defined alternating PF copolymers. The molecular weights of the PF derivatives obtained are moderate (*M*n) 10000-50000) with low PDI values.



Scheme 1

A conjugated polymer (**P1**) consisting of alternating fluorene and electron-rich bithiophene units was synthesized by Suzuki coupling and is shown in Scheme 1. [33] The HOMO and LUMO levels of **P1** were estimated to be -5.41 and -2.52 eV, respectively. Because of extended conjugation between the fluorene and thiophene units, the optical band gap of **P1** is reduced to 2.41 eV. The chemical structure of alternating copolymers containing 9,9-dihexylfluorene and unsubstituted or alkylated thieno[3,2-*b*]thiophene units synthesized via Suzuki coupling are shown in scheme 10. Compared with bithiophene-based **P1** (454 nm), **P2a** shows a blue-shifted absorption maximum at 430 nm in chloroform due to its shorter effective conjugation length. When a pentyl group is introduced into the *β*-position of thieno[3,2-*b*]thiophene in **P2b**, the absorption maximum is further blue-shifted to 388 nm as a result of steric-hindrance induced main chain distortion.

Linearly fused arene- and heteroarene-based organic semiconductors have been intensively investigated for OFET and OLED applications. [34] Due to the extended and planar π-conjugated system, pentacene and its derivatives possess relatively low band gaps of 1.7 eV and have high thin-film transistor mobility. It is of great interest that incorporation of a pentacene unit into a conjugated polymer will generate a new class of promising p-type materials for photovoltaic applications. [35] In addition to pentacene, anthradithiophene, with two thiophenes on each end of anthracene, is more stable than pentacene and can form a more coplanar structure with other conjugated units. [36] Two alternating high molecular weight polyfluorene-based polymers containing pentacene (**P3**) or anthradithiophene (**P4**) units were successfully synthesized by Suzuki coupling (Scheme 2). [37] The synthetic routes to (triisopropylsilyl)-ethynyl-substituted pentacene and anthradithiophene have been previously reported. [35, 38] **P3** and **P4** show more red shifted absorption spectra than their corresponding monomers **4** and **5** and have optical band gaps of 1.78 and 1.98 eV, respectively.



Scheme 2

Electron-deficient 2,1,3-benzothiadiazole units have been widely incorporated into PF-based copolymers to alter the energy levels and fine-tune the emitting color over the entire visible region. [39] Fig. 1 shows a series of 2,1,3-benzothiadiazole-containing PF derivatives (**P5**-**P14**) synthesized *via* Suzuki coupling reactions.

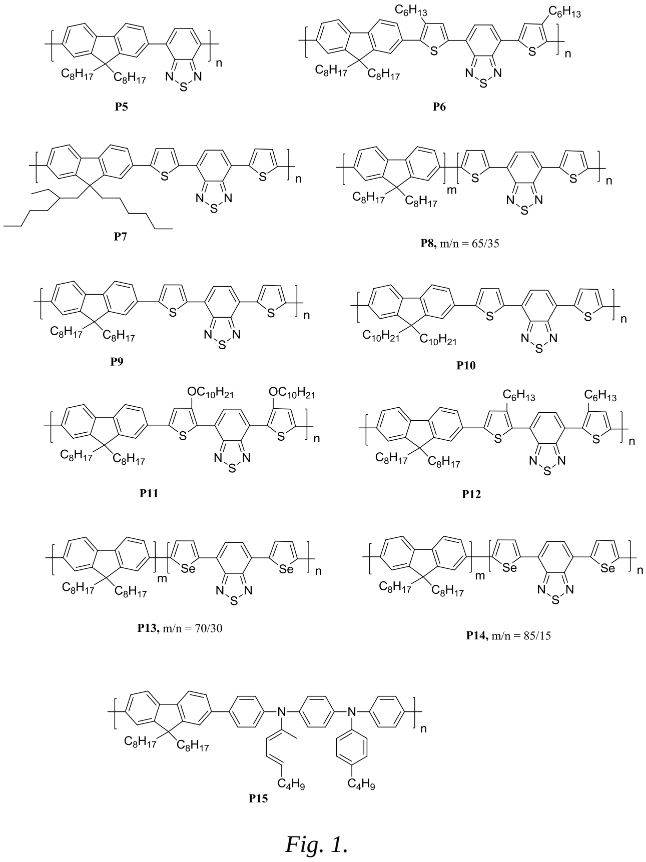


Fig. 1.

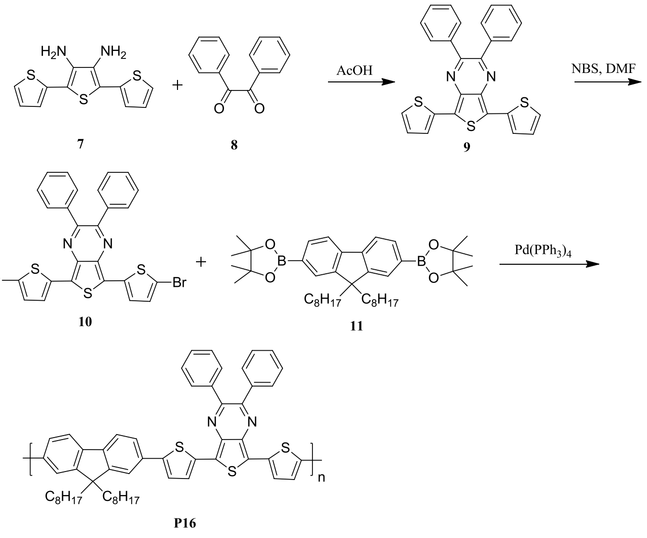
In spite of the high hole mobility and weak electron transport nature of polyfluorene, alternating poly(9,9-dioctylfluorene- *co*-benzothiadiazole) (**P5**) exhibits a reduced LUMO level and thereby enhanced electron mobility (10^{-3}cm^2/(V s)). This is a result of the high content of electron deficient benzothiadiazole units and results in it being categorized as an electron-transport material. [40] When combined with the triarylamine-based polyfluorene **P15** (Figure 1) as the electron donor with a high hole mobility of 10^{-4} cm^2/(V s), **P5** serves as an electron acceptor in polymer/polymer bulk heterojunction photovoltaic devices. [41-43] The charge-carrier-transporting properties of **P5** can be further tuned by copolymerizing fluorene with the 4,7- bis(3-hexylthiopen-5-yl)-2,1,3-benzothiadiazole unit to yield the polymer **P6**. [44] With two additional electron-rich thiophene rings attached to both sides of the benzothiadiazole unit, the hole mobility of **P6** is expected to be improved compared to that of **P5**. On the other hand, **P7**, which is structurally analogous to **P6**, serves as a promising electron donor in a photovoltaic device in combination with PCBM as the electron acceptor due to its higher hole mobility. [45]

The polymer **P8** contains 9,9-dioctylfluorene (DOF) and 4,7-di-2-thienyl-2,1,3-benzothiadiazole (DTBT) with different feeding ratios. [46] Two absorption bands with maxima at 383 and 540 nm were observed. The shorter wavelength absorbance comes from the higher energy of the fluorene unit, whereas the lower energy band is attributed to intramolecular charge transfer from the electron-rich unit to the benzothiadiazole segment so that its intensity increases with increasing DTBT content. When the ratio of DOF to DTBT was 65:35 in **P8**, the best photovoltaic performance based on **P8**:PCBM (1:2, w/w) was obtained, showing a *J*sc of 5.18 mA/cm^2, a *V*oc of 0.95 V, and a PCE value of 2.24%.

The long alkoxy group can be introduced to the *β*-position of the thiophene unit in the polymer **P11** to strengthen its electron-donating ability. [47] **P11** exhibited a significantly red shifted absorption maximum of 581 nm and smaller band gap of 1.78 eV relative to its alkyl counterpart **P12** [48] with 525 nm and 2.06 eV due to the stronger donating strength of thiophene and thus more efficient intramolecular charge transfer. The solar cell based on a **P11**/PCBM (1:4, w/w) blend reached a *J*sc of 4.31 mA/cm^2, a *V*oc of 0.76, an FF of 0.48, and a PCE of 1.6%. The efficiency can be further improved to 2.4% by using PC71BM as the acceptor to strengthen the light-harvesting ability. [49]

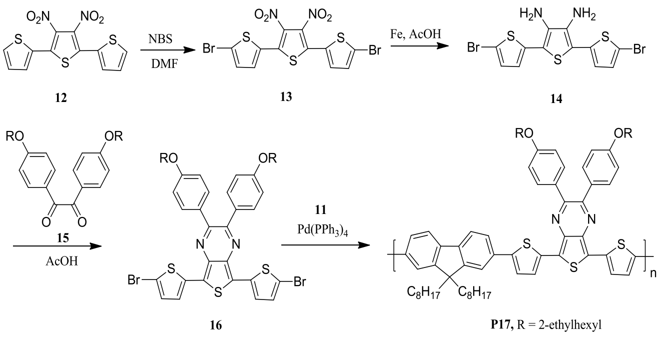
It has been shown that selenium-containing heterocycles such as selenophene and benzoselenadiazole have stronger abilities to lower the band gaps of conjugated polymers than their sulfur analogues thiophene and benzothiadiazole. [50] Diselenophene-ylbenzothiadiazole and diselenophene-ylbenzoselenadiazole units have both been incorporated into the polyfluorene main chain to furnish **P13** and **P14**, respectively. [51] The optical band gaps deduced from the onset absorption are about 1.85 eV for **P13** and 1.77 eV for **P14**. Both of them have a relatively low-lying HOMO level of -5.5 eV. The best photovoltaic performance for a device based on **P14**/PCBM (1:4, w/w) reached a *J*sc of 2.53 mA/ cm^2 and a very high *V*oc of 1.0 V and PCE of 1%. However, a device based on **P13**/PCBM (1:4, w/w) showed only 0.1% under the same conditions. This result can be attributed to the fact that **P14** has a weaker CT absorption band in the longer wavelength than **P13**. The syntheses of **P13** and **P14** are similar to that of **P8**.

Scheme 3 shows the synthesis of alternating PF derivatives containing electron-accepting thieno[3,4-*b*]pyrazine units. Diamino **7** was reacted with 1,2-diketone **8** in presence of AcOH resulted in cyclization product **9** containing the thieno [3,4- *b*]pyrazine unit. Bromination with *N*-Bromosuccimide (NBS) yielded the monomer **10**, which was allowed to polymerize with **11** to give **P16**. [52,53] The HOMO and LUMO levels of **P16** were estimated to be -5.6 and -3.6 eV, respectively, determining an electrochemical band gap of 2.0 eV.



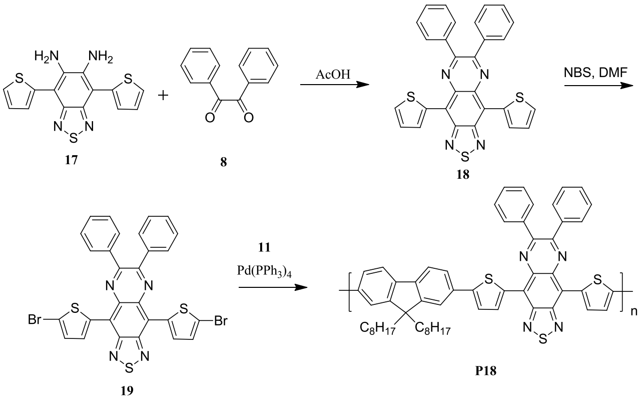
Scheme 3

The polymer **P17** has a conjugated backbone similar to that of **P16**, with two additional (2-ethylhexyl)oxy substituents on the pendent phenyl rings of the thieno[3,4-*b*]pyrazine unit. The synthesis of the monomer **16** was obtained through a series of steps: bromination of the thiophene ring in **12** and reduction of the nitro groups in **13** followed by imine formation of **14** with 1,2-diketone **15** resulting to **16** and finally leading to **P17** through a Suzuki coupling (Scheme 4) [54].

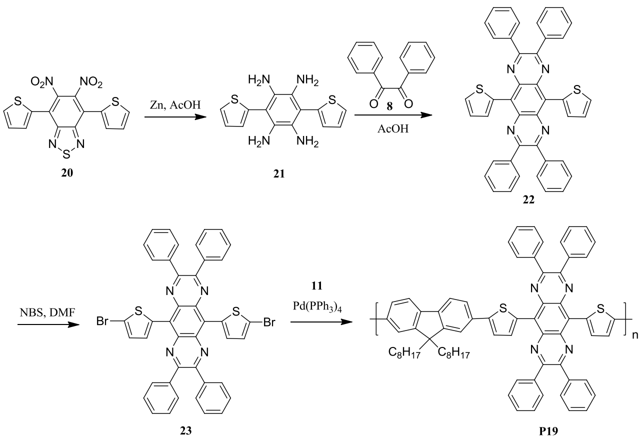


Scheme 4

The polymer **P18**, which contains [1,2,5]thiadiazolo[3,4-*g*]quinoxaline units in the main chain was synthesized by same synthetic route as that of **P17**, as shown in Scheme 5 [53].



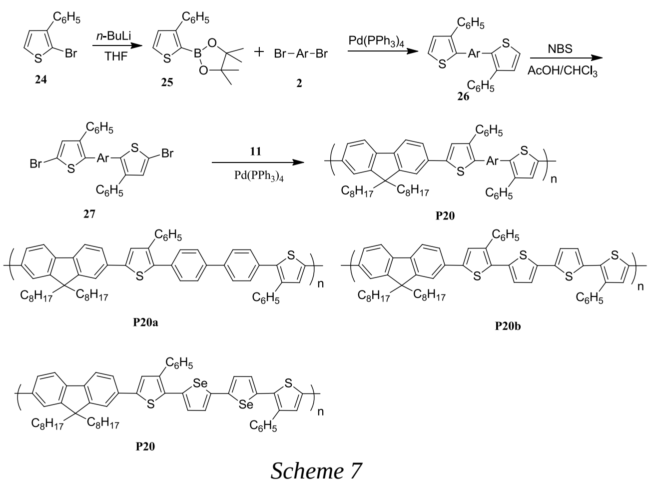
Scheme 5



Scheme 6

Polymer **P19**, was also prepared by a similar procedure, as shown in Scheme 5. [55] The HOMO and LUMO levels were estimated to be -5.7 and -3.9 eV, respectively, with an electrochemical band gap of 1.8 eV.

Polymers containing 9,9-dioctylfluorene and thiophene derivatives **P20a**, **P20b** and **P20c** are synthesized by a palladium-catalyzed Suzuki polymerization (Scheme 7). The polymers were thermally stable up to 400°C, and readily soluble in common organic solvent. The HOMO/LUMO levels for **P20a**, **P20b** and **P20c** were estimated to be -5.61/-2.91 eV, -5.28/-3.12 eV, -5.24/-3.16 eV with electrochemical band gap of 2.70 eV, 2.16 eV and 2.08 eV respectively [56].

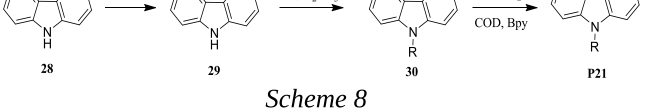


Scheme 7

3. Carbazole-based conjugated Polymers

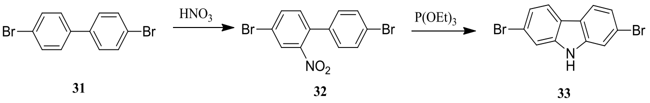
Carbazole, also known as 9-azafluorene, is one of the most attractive heterocyclic units with electronic applications in the field of conjugated polymers. The replacement of carbon by nitrogen in the fluorene skeleton makes tricyclic carbazole fully aromatic and electron rich as well as rules out the susceptibility to oxidation of the 9-position toward ketone formation leading to undesired electronic and optical properties. The availability of nitrogen atom functionalization in carbazole with an alkyl chain also ensures sufficient solubility. As a result, carbazole derivatives have been widely used as p-type semiconductors due to their ability to form stable radical cations, as well as their excellent thermal and photochemical stabilities, relatively high charge mobility, and easy availability. For example, poly(*N*-vinylcarbazole) (PVK), a nonconjugated linear polymer with pendent carbazole units, acts not only as a superb photoconductor [57] but also as a hole-transporting and electron-blocking material. [58] In addition, it serves as a large band gap host in polymer light-emitting devices [59]. Alternatively, conjugated poly(carbazole) derivatives have been successfully applied in organic field-effect transistors [60]. These properties make the carbazole unit a promising candidate for incorporation into low band gap polymers for solar cell applications [61].

In general, the carbazole unit can be connected and extended in a symmetrical manner through either the 3,6-positions or 2,7-positions to yield linear conjugated polymers. Connecting carbazole via the 3,6-positions results in a *meta*-linkage of phenylene with limited conjugation. On the other hand, the 2,7-positions lead to a *para*-linkage and a higher effective conjugation length. [62] The 2,7-linked carbazole-based conjugated polymers are much more promising for use as donor materials in photovoltaic devices in terms of better charge migration along the more conjugated main chain. Bromination of carbazole **28** by NBS takes place regioselectively and quantitatively at the 3,6-positions, which are *para* to the directing nitrogen, to obtain **29** (Scheme 8). After *N*-alkylation with an alkyl halide under basic conditions, poly(3,6-carbazole) **P21** with a high molecular weight can be synthesized using a Yamamoto coupling [63].



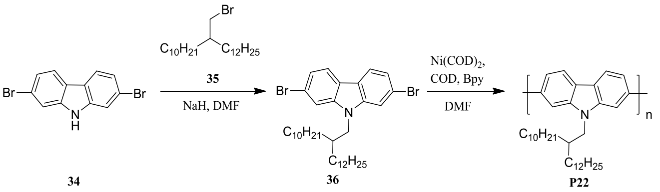
Scheme 8

In contrast, the preparation of 2,7-dibromocarbazole is not that straightforward. [64] Mullen and coworkers have developed a facile route to its synthesis in two steps (Scheme 9). [65] Nitration of 4,4′-dibromobiphenyl (**31**) by nitric acid gave **32**. A Cadogan reductive cyclization of **32** using triethyl phosphate afforded 2,7-dibromocarbazole (**33**) [66].



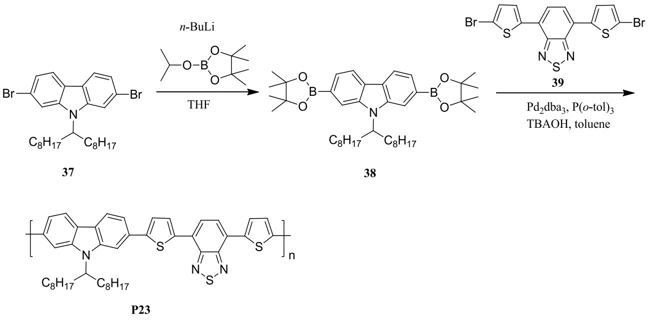
Scheme 9

Due to their poor solubilities, poly(2,7-carbazole) homopolymers generally have low molecular weights, which limits their use in thin-film devices. A soluble and processable poly(2,7-carbazole) with a branched 2-decyltetradecyl substituent on nitrogen **P22**, was designed and synthesized by a Ni(COD)$_2$-mediated Yamamoto coupling polymerization (Scheme 10) [67].



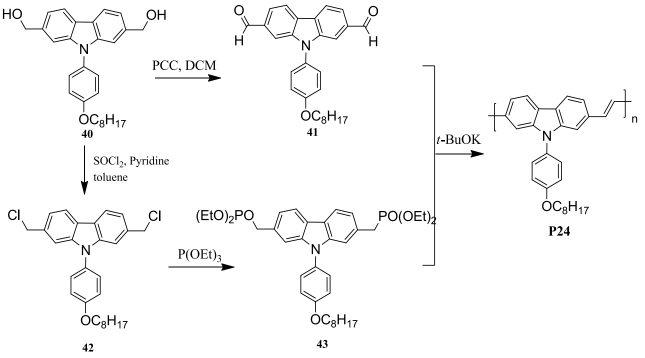
Scheme 10

The band gap of poly(2,7-carbazole) can be reduced by incorporating an electron-accepting unit to generate a new class of D-A poly(2,7-carbazole)-based polymers. Leclerc and coworkers have synthesized copolymer **P23,** comprised of alternating 2,7-carbazole units and DTBT moieties via a Suzuki coupling reaction (Scheme 11) [68].

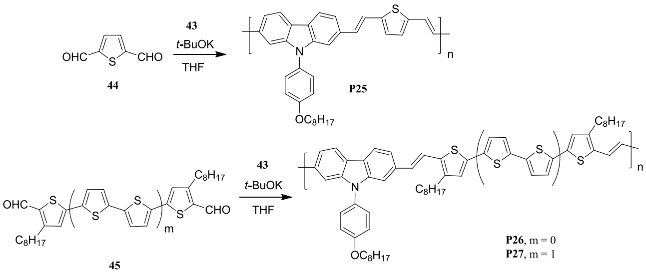


Scheme 11

Schemes 12 and 13 show the synthetic routes to a series of poly(2,7-carbazolenevinylene) (PCV) polymers using different polymerization methods. [69] **P24** is a PCV homopolymer with an (octyloxy)benzyl side group on the nitrogen of the carbazole unit. The polymers **P25-P27**, on the other hand, are PCV copolymers incorporating different lengths of oligothiophenes into the main chain. To obtain high molecular weights, an *all-trans* double bond configuration, and low contamination, the Horner-Emmons reaction was employed to synthesize the polymers **P24-P27** by reacting the dialdehyde and corresponding diphosphonate derivatives in the presence of excess amounts of *t*-BuOK in anhydrous THF.

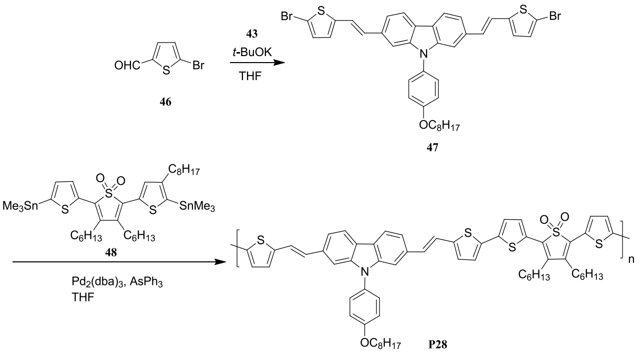


Scheme 12



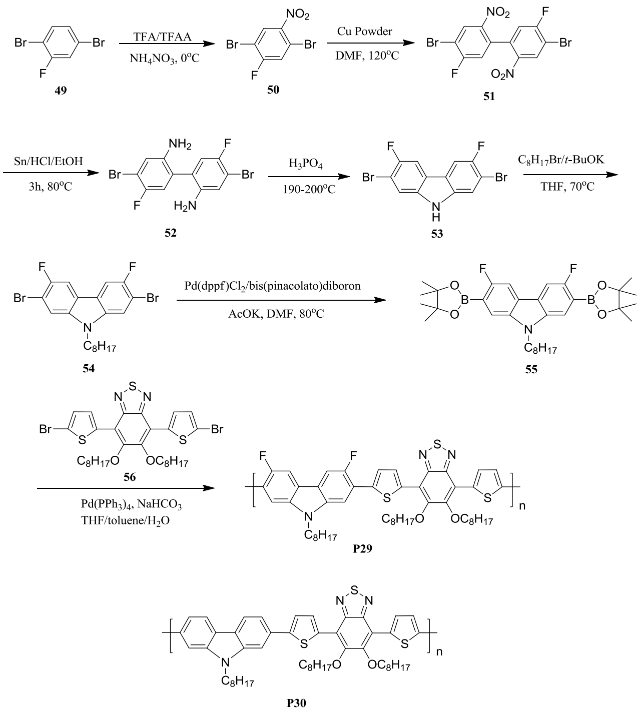
Scheme 13

Polymer **P28** was prepared by the Stille cross-coupling reaction of the dibromo monomer **47** and distannyl compound **48** in the presence of Pd$_2$(dba)$_3$ and AsPh$_3$ in THF (Scheme 14).



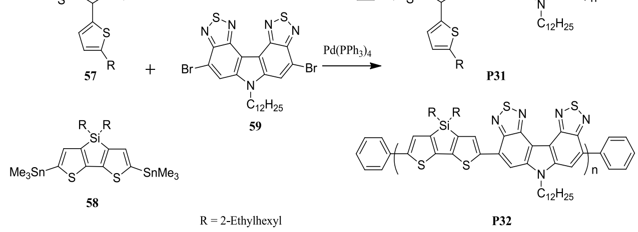
Scheme 14

A novel donor–acceptor (D–A) copolymer **P29** with 3,6-difluoro substituted carbazole as the donor unit and dialkoxy substituted benzothiadiazole as the acceptor unit has been synthesized and used as a donor material for bulk heterojunction polymer solar cells (BHJ PSCs) (Scheme 15) [70]. **P29** possesses a band gap of 1.75 eV, a low-lying HOMO energy level of -5.23 eV, and a good thermal and electrochemical stability. In comparison with the corresponding non-fluoro substituted **P30** with HOMO energy level of 5.21 eV, and an optical band gap of 1.86 eV [71], the incorporation of two fluoro atoms in the carbazole donor unit lowers the HOMO and the LUMO energy levels of the polymer resulting in better thermal and electrochemical stability. The fluoro containing **P29** showed stronger intermolecular interactions and formed closer π–π stacking and more ordered packing in the solid state. In comparison with **P30**, the better stability, higher Voc, and narrower band gap indicate that **P29** is a very promising donor material for high efficiency polymer solar cells.



Scheme 15

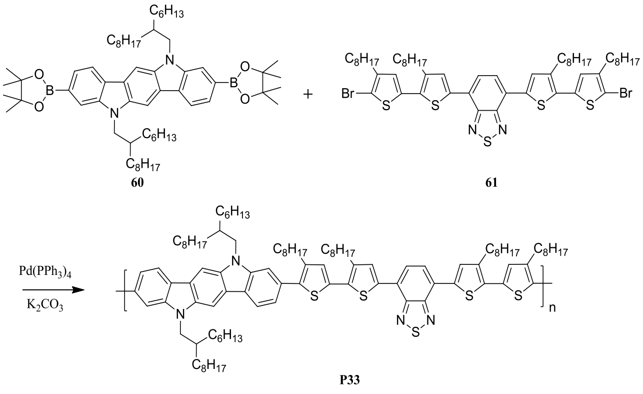
Two novel conjugated copolymers **P31** and **P32** have been synthesized by alternating copolymerzation of N-alkyl-carbazole[3,4-c:5,6-c]bis[1,2,5]thiadiazole (CBT) **59** with alkylthienyl benzodithiophene (TBDT) **57** and dithenosilole (DTS) **58**, respectively (Scheme 16). **P31** showed the lowest band gap (1.53 eV), which matches the solar flux well, but the low degree of crystallinity and absence of preferential alignment of the π□π stacking result in a relative low PCE of 1.52%. However, **P32** having larger band gap, but its 2-D structure endows with favorable molecular packing possess the PCE of 1.71% under illumination (AM 1.5G 100 mW cm^{-2}) without considerable optimization [72].



Scheme 16

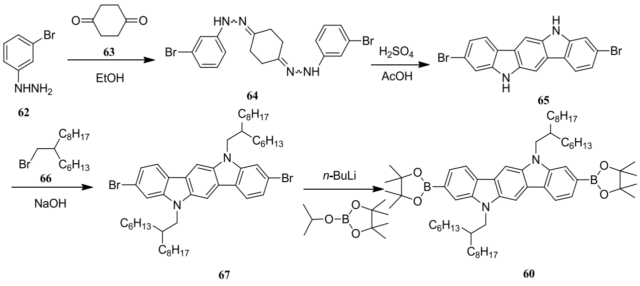
4. Indolo[3,2-b] carbazole-based Polymers

Indolo[3,2-*b*]carbazole can be regarded as two carbazoles fused together. It is envisaged that indolo[3,2-*b*]carbazole based materials will have stronger donating abilities than carbazole with advantages of carbazole such as hole-transporting properties, enhanced photostability and thermal stability. For the indolo[3,2-*b*]carbazole-based small molecule and homopolymer a very high mobility in FET has been achieved.[73-74] There are many intrinsic advantages making indolo[3,2-*b*]carbazole a promising electron-rich building block for the construction of a new class of donor-acceptor conjugated polymers. First, the pentafused heterocyclic unit of indolocarbazole provides a large coplanar *π*-conjugated system. Second, the low-lying HOMO feature of indolocarbazole is expected to be beneficial for obtaining a high *V*oc. The arylamine-type structure of indolocarbazole is known to be a good hole transporter. As a result, the copolymer **P33**, composed of an electron accepting benzothiadiazole oligothiophene and an electron donating indolocarbazole unit, has been synthesized by the Suzuki coupling of **60** and **61** (Scheme 17). [75] In order to ensure sufficient solubility of the polymer, both long and branched aliphatic chains must be introduced onto the nitrogen atom. The indolocarbazole polymerization site is at the 3,9-positions so that the fully conjugated main chain of the polymer can be obtained.



Scheme 17

The preparation of the 3,9-indolo[3,2-*b*]carbazole unit is shown in Scheme 18. Treatment of 1,4-cyclohexadione (**63**) with (3-bromophenyl)hydrazine (**62**) formed the bishydrazone **64**, which underwent a double Fischer indole cyclization and reduction under acidic conditions (H_2SO_4/AcOH), resulting in the formation of **65**. [76] After *N*-alkylation of **65** to introduce an aliphatic chain, the dibromo functionality in **67** was then converted to diboronic ester to produce the final monomer **60**.

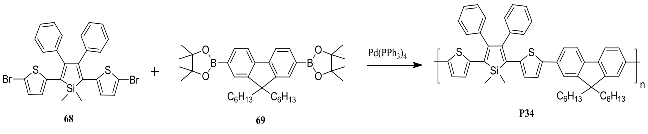


Scheme 18

5. Silafluorene - and Dithieno [3,2-*b*:2',3'-*d*] silole-based Polymers

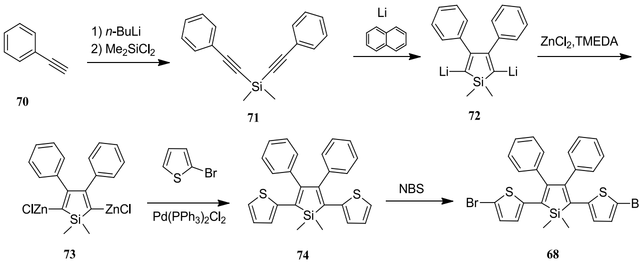
Silole (silacyclopentadiene) ring has the smallest HOMO-LUMO band gap and the lowest lying LUMO level due to the σ^*-π^* conjugation between the π-symmetrical σ^* orbital of two σ exocyclic bonds on silicon and the π^* orbital of the butadiene moiety compared with many heterocyclic arenes such as thiophene, furan, or pyrrole. [77] As a result, a variety of conjugated small molecules and polymers consisting of silole derivatives exhibit extraordinarily unique properties such as high fluorescence efficiency and electron affinity and excellent electron mobility. [78-81] Conjugated polymers containing alternating electron-rich pyrroles or thiophenes and silole units have shown considerably smaller band gaps, which is indicative of the electron-accepting ability of silole to induce intramolecular charge transfer. [82-84] It is envisioned that the silole unit can serve as a useful building block in the molecular design of new conjugated polymers for use in organic solar cell applications.

P34, derived from 9,9-dihexylfluorene **69** and the 1,1-dimethyl-3,4-diphenyl-2,5-bis(2′-thienyl)-silole unit **68**, was synthesized by a Suzuki coupling (Scheme 19). [85] The HOMO and LUMO levels and the optical band gap of **P34** were determined to be -5.71, -3.6, and 2.08 eV, respectively.



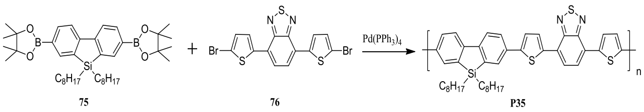
Scheme 19

Tamao *et al* have described a facile synthesis for accessing 2,5-difunctional silole derivatives (Scheme 20). [86] Upon treatment with lithium naphthalenide, bis(phenylethynyl)dimethylsilane (**71**) undergoes intramolecular reductive cyclization to form 2,5-dilithiosilole **72**, which was then transformed into 2,5-dizincated silole **73**. A Negishi Pd-catalyzed cross-coupling of this intermediate with 2-bromothiophene afforded 2,5-bis(2′-thienyl)silole **74**, which was further brominated by NBS to furnish **68**.



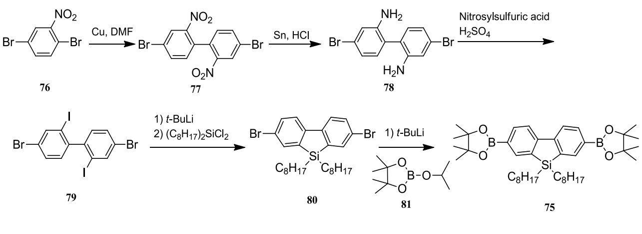
Scheme 20

The fluorene-containing D-A conjugated polymer **P8** and its derivatives have all been shown to have good photovoltaic properties as well as to deliver high PCEs over the 2-3% range. When the carbon atom on the 9-position of the fluorene unit is replaced with a silicon atom, a new type of building block, namely, silafluorene evolves. By fusing a silole ring between two phenyl rings, the silafluorene is expected to combine the advantages of both the silole and fluorene intrinsic properties. The tetravalence of the silicon atom in the silole ring opens up two additional substitution sides for the introduction of solubilizing groups. Cao and co-workers have synthesized the copolymer **P32**, by the Suzuki coupling [87] of 2,7-silafluorene **75** and dithienylbenzothiadiazole unit **76** (Scheme 21).



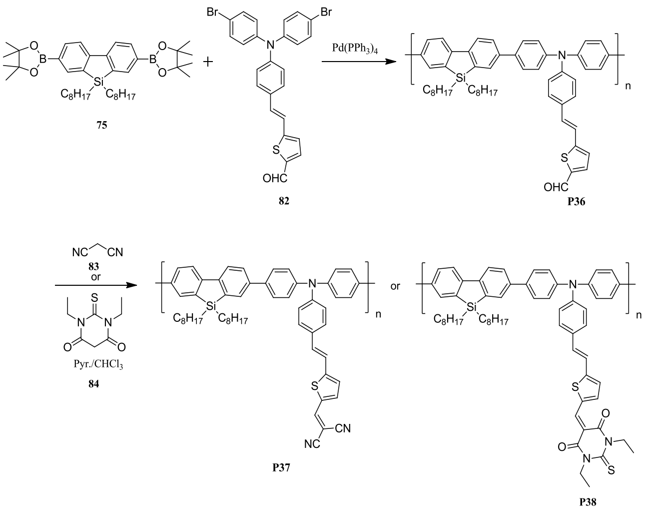
Scheme 21

The synthetic route for monomer **75** was developed by Holmes and co-workers (Scheme 22). [88] An Ullmann coupling of compound **76** gave the dimerization product **77**. Reduction of the nitro groups in **77** yielded the amino compound **78**. This was followed by iodination via a diazonium pathway to generate **79**. Selective lithiation of the iodo groups of **79** by *tert*-butyllithium to react with dioctyldichlorosilane led to the formation of the central silole ring of **80**. Finally, the bromo groups in **80** can be easily transformed to the bis(boronic ester) **75**.



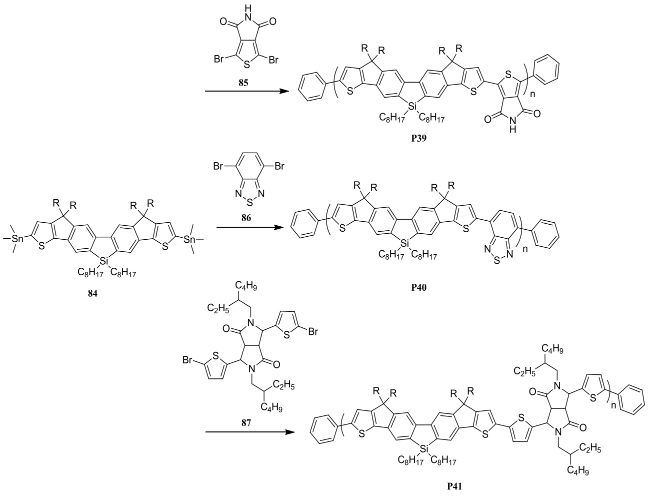
Scheme 22

Cao and coworkers have synthesized two low band gap conjugated polymers **P37** and **P38** consisting alternate silafluorene **75** and trimethylamine intermediates **82** and malonitrile **83** and 1,3-diethyl-2-thiobarbituric acid **84** as pendent acceptor groups with styrylthiphene **P33** as π-bridge (Scheme 23). Bulk heterojunction BHJ sloar cells with **P37** and **P38** possess power conversion efficiency of 2.50% and 3.15% respectively [89].



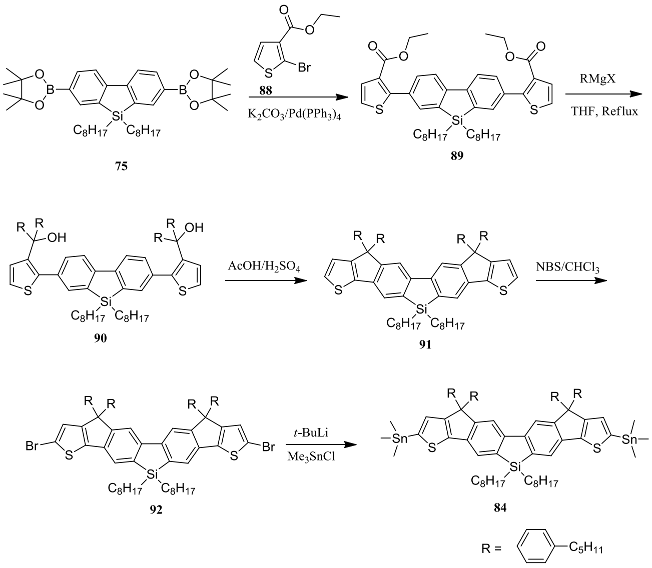
Scheme 23

Luscombe *et al* has successfully designed and synthesized a ladder-type multifused thienyl-fluorene-thienyl unit with rigid and coplanar backbone. The distannyl building block **84** was copolymerized with electron-deficient thieno[3,4-c]pyrrole-4,6-dione (PD) **85**, benzothiadiazole (BT) **86**, and dithienyldiketopyrrolopyrrole (DPP) **87** units by Stille polymerization to afford three alternating donor−acceptor copolymers, **P39**, **P40** and **P41** respectively (Scheme 24). [90]



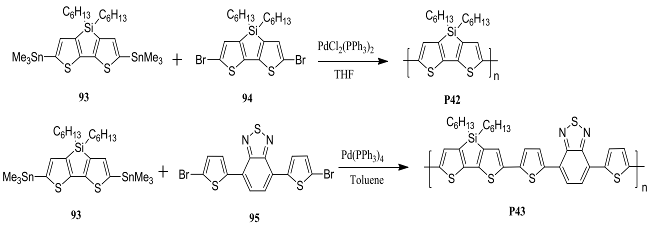
Scheme 24

The synthetic route of the monomer **84** is shown in Scheme 25. Suzuki coupling of 2,7-diboronic ester silafluorene **75** with ethyl 2-bromothiophene-3-carboxylate **88** afforded compound **89**. Double nucleophilic addition of freshly prepared 4-(n-pentyl)-phenylmagnesium bromide to the ester groups of compound **89** led to the formation of tertiary benzylic alcohol compound **90**, which was subjected to intramolecular annulation through Lewis acid-mediated Friedel−Crafts reaction to furnish **91**, which was brominated with NBS/$CHCl_3$ to yield compound **92** in good yield. Treatment of compound **92** with *t*-BuLi followed by quenching with trimethyltin chloride successfully afforded the distannyl compound **84**. [90]



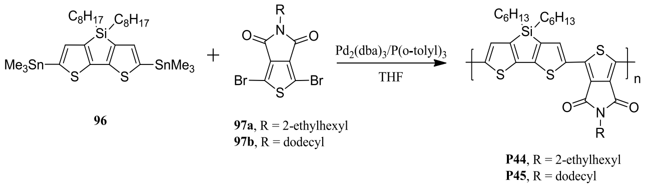
Scheme 25

In view of the beneficial molecular design on going from fluorene to silafluorene, the exceptional cyclopentadithiophene system is further modified by substituting the carbon atom with a silicon bridge to generate a dithienosilole having a silole ring embedded in the center of dithiophene. A dithienosilole homopolymer (**P42**) and an alternating dithienosilole and dithienylbenzothiadiazole copolymer (**P43**) were reported and synthesized by Stille coupling reactions (Scheme 26).[91] Due to the incorporation of electron-accepting units, the copolymer **P42** has both lower HOMO level, -5.13 eV, and a smaller band gap, 1.4 eV, than the homopolymer **P43** (-4.85 and 1.9 eV, respectively).



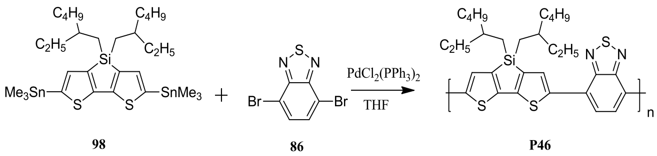
Scheme 26

Thieno[3,4-c]pyrrole-4,6-dione (TPD) copolymers **P44**, **P45** based on Dithienosilole (DTS) **96** as electron-donating units and TPD **97** as electron-accepting units (**97a** and **97b**) were designed and synthesized (Scheme 27). The best device after process optimization shows up to 4.4% PCE [92].



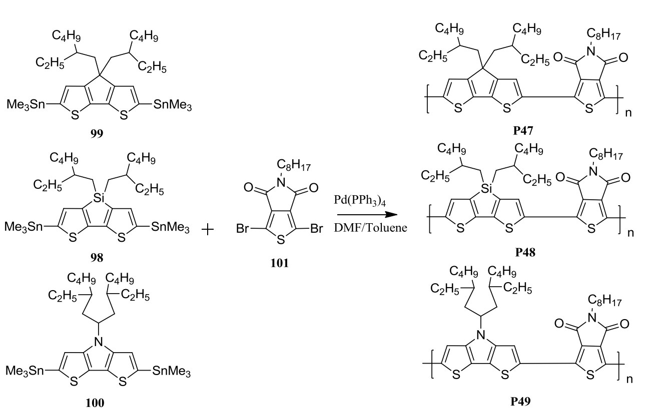
Scheme 27

Yang and co-workers has reported another dithienosilole-containing copolymer (**P46**) (Scheme 28). [93] The HOMO and LUMO of the polymer were estimated to be -5.05 and -3.27 eV, respectively. The optical band gap of **P46** is 1.45 eV, the substitution of the silicon atom significantly improved the hole-transport properties.



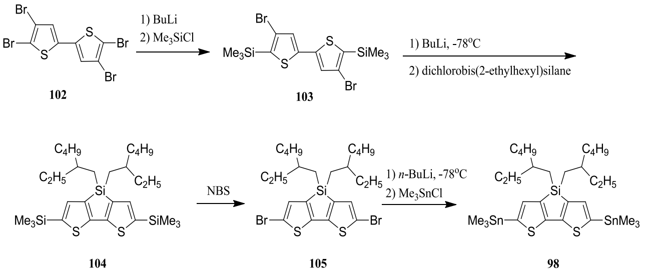
Scheme 28

Jen and coworkers have synthesized a series of low band-gap conjugated polymers (**P47**, **P48** and **P49**) containing electron-rich C-, Si-, and N-bridged bithiophene and electron-deficient thienopyrroledione units *via* Stille coupling polymerization (Scheme 29). All these polymers possess a low-lying energy level for the HOMO (as low as -5.44 eV). As a result, photovoltaic devices derived from these polymers show high open circuit voltage (V_{oc} as high as 0.91 V). These rigid polymers also possess respectable hole mobilities of 1.50×10^{-3}, 6.0×10^{-4}, and 3.9×10^{-4} cm^2 V^{-1}s^{-1} for **P47**, **P48**, and **P49**, respectively. The combined high V_{oc} and good hole mobility enable BHJ photovoltaic cells to be fabricated with relatively high power conversion efficiency about 3.74% for the **P47** based device [94].



Scheme 29

The synthesis of the distannyldithienosilole **98** is shown in Scheme 30. By a selective lithium-bromide exchange followed by nucleophilic substitution, the trimethylsilyl group was introduced into the 5,5′-positions of the bithiophene compound **102** to act as a protecting group. As a consequence, the subsequent lithiation in compound **103** only occurred at the 3,3′-positions of the bithiophene, which then underwent cyclization through double addition to dialkyldichlorosilane and gave **104**. NBS bromination *via* electrophilic aromatic substitution to replace the trimethylsilyl moiety resulted in the formation of compound **105**, which was then converted to the distannyl compound **98** by lithiation and final quenching with trimethyltin chloride [93].



Scheme 30

The requirements of specific intrinsic properties necessary for an ideal donor material include (1) sufficient solubility to guarantee solution-processability as well as miscibility with n-type materials, (2) a low optical band gap for a strong and broad absorption spectrum to capture more solar energy, and (3) high hole mobility for accelerating charge transport, which in turn allows a thicker active layer required for increased light harvesting as well as reduced charge recombination and series resistance. In combination with a fixed electron acceptor, specific characteristics between a D-A pair are required. These include (a) appropriate HOMO and LUMO energies to ensure a large *V*oc and a downhill energy offset for exciton dissociation and (b) formation of an interpenetrating network with the optimum morphology for creating two distinct bicontinuous highways for transporting free charge carriers. In addition to the choice of viable molecular designs already in the “toolbox” such as chemical planarization, quinoidiation, and D-A arrangement, a new influx of molecular designs and synthetic endeavors has led to a range of novel p-type conjugated polymers. These advances have ensured an important step toward a better understanding of structure-property relationships. Structural analysis of the current successful low band gap conjugated polymers reveals that an alternating D-A arrangement is essential and must be combined with the necessary newly designed donor segments composed of multicyclic aromatic rings with enforced planarity. In accordance with these guidelines, the further development of promising donors might be fortuitously directed toward hybridizing different electron-rich aromatic units into mutually fused structures in the anticipation of benefiting from the individual intrinsic advantages. This will require more elegant designs and challenging synthesis. Without optimal control of the morphology on the nanoscale, it becomes difficult to translate the microscopic intrinsic properties of the conjugated polymer into macroscopic device performance.

The development of amorphous-oriented conjugated polymers exhibiting high hole mobility might be an alternative way to overcome this problem and potentially eliminate the need of post-treatment to induce polymer crystallinity. By integrating new advanced device concepts and the nanostructure engineering of the morphology, [95] the future development of functional conjugated polymers will ensure their key role in bringing high-efficiency and low cost plastic solar cells one step closer to successful commercialization.

6. Conclusion

This article reviews the important and growing research covering the synthesis and development of custom-tailored polymers for use in the increasingly relevant application of high-performance solar cells. Overview of new organic molecules and their synthesis will stimulate further important research in this exciting field. This review covering synthesis, structure and properties of these organic materials will serve a compiled note for the researchers working in the field of flexible electronics.

Acknowledgements

One of the author Dinesh Pathak would like to thanks the Ministry of Education, Youth and Sports of the Czech Republic, Project CZ.1.07/2.3.00/30.0021 “Strengthening of Research and Development Teams at the University of Pardubice“, who financially supported him.

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