

Towards High-Efficiency Organic Solar Cells: Polymers and Devices Development

Enwei Zhu¹, Linyi Bian¹, Jiefeng Hai¹, Weihua Tang^{1,*} and Fujun Zhang^{2,*}

¹Nanjing University of Science and Technology,

²Beijing Jiaotong University

People's Republic of China

1. Introduction

The effective conversion of solar energy into electricity has attracted intense scientific interest in solving the rising energy crisis. Organic solar cells (OSCs), a kind of green energy source, show great potential application due to low production costs, mechanical flexibility devices by using simple techniques with low environmental impact and the versatility in organic materials design (Beal, 2010). In the past years, the key parameter, power conversion efficiencies (PCE), is up to 7% under the standard solar spectrum, AM1.5G (Liang et al., 2010). The PCE of solar cells are co-determined by the open circuit voltage (V_{oc}), the fill factor (FF) and the short circuit density (J_{sc}). Researchers have made great efforts in both developing new organic materials with narrow band gap and designing different structural cells for harvesting exciton in the visible light range.

Solution processing of π -conjugated materials (including polymers and oligomers) based OSCs onto flexible plastic substrates represents a potential platform for continuous, large-scale printing of thin-film photovoltaics (Krebs, 2009; Peet, 2009). Rapid development of this technology has led to growing interest in OSCs in academic and industrial laboratories and has been the subject of multiple recent reviews (Cheng, 2009; Dennler, 2009; Krebs, 2009; Tang, 2010). These devices are promising in terms of low-cost power generation, simplicity of fabrication and versatility in structure modification. The structure modification of π -conjugated materials has offered wide possibilities to tune their structural properties (such as rigidity, conjugation length, and molecule-to-molecule interactions) and physical properties (including solubility, molecular weight, band gap and molecular orbital energy levels). This ability to design and synthesize molecules and then integrate them into organic-organic and inorganic-organic composites provides a unique pathway in the design of materials for novel devices. The most common OSCs are fabricated as the bulk-heterojunction (BHJ) devices, where a photoactive layer is casted from a mixture solution of polymeric donors and soluble fullerene-based electron acceptor and sandwiched between two electrodes with different work functions (Yu et al., 1995). When the polymeric donor is excited, the electron promoted to the lowest unoccupied molecular orbital (LUMO) will lower its energy by moving to the LUMO of the acceptor. Under the built-in electric field caused by the contacts, opposite charges in the photoactive layer are separated, with the holes being transported in the donor phase and the electrons in the acceptor. In this way, the blend can be considered as a network of donor-acceptor heterojunctions that allows efficient

charge separation and balanced bipolar transport throughout its whole volume. Remarkably, the power conversion efficiency (PCE, defined as the maximum power produced by a photovoltaic cell divided by the power of incident light) of the OSCs has been pushed to more than 7% from 0.1% after a decade's intensive interdisciplinary research. The current workhorse materials employed for PSCs are regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). This material combination has given the highest reported PCE values of 4%~5% (G. Li, 2005). Theoretically, the PCE of polymer solar cells can be further improved (ca 10%) (Scharber et al., 2006) by implementing new materials (Cheng, 2009; Peet, 2009; Tang, 2010) and exploring new device architecture (Dennler, 2008; Ameri, 2009; Dennler, 2009) after addressing several fundamental issues such as bandgap, interfaces and charge transfer (Li, 2005; Chen, 2008; Cheng, 2009).

In this account, we will update the recent 4 years progress in pursuit of high performance BHJ OSCs with newly developed conjugated polymers, especially narrow bandgap polymers from a viewpoint of material chemists. The correlation of polymer chemical structures with their properties including absorption spectra, band gap, energy levels, mobilities, and photovoltaic performance will be elaborated. The analysis of structure-property relationship will provide insight in rational design of polymer structures and reasonable evaluation of their photovoltaic performance.

2. Fluorene-based conjugated polymers

Fluorene (FL) and its derivatives have been extensively investigated for their application in light-emitting diodes due to its rigid planar molecular structure, excellent hole-transporting properties, good solubility, and exceptional chemical stability.

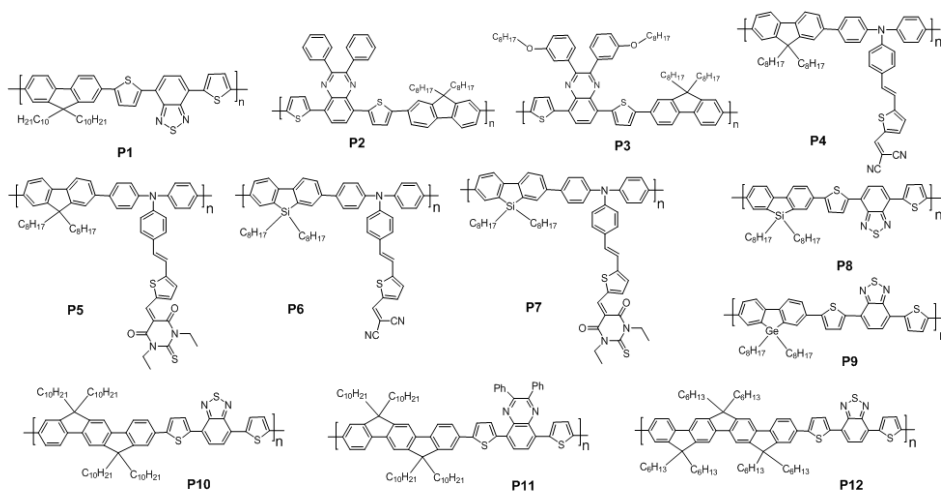


Chart 1. Fluorene based narrow band gap polymers.

Along with their low-lying HOMO levels, polyfluorenes (PFs) are expected to achieve higher V_{oc} and J_{sc} in their PSC device, which makes fluorene unit a promising electron-

donating moiety in D-A narrow band gap polymers' design. Besides, feasible dialkylation at 9-position and selective bromination at the 2,7-positions of fluorene allow versatile molecular manipulation to achieve good solubility and extended conjugation *via* typical Suzuki or Stille cross-coupling reactions. By using 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) as electron accepting unit and didecylated FL as donating unit, Slooff (Slooff et al., 2007) developed **P1** (**P1-12** structure in Chart 1) with extended absorption spectrum ranging from 300 to 800nm. Spin-coated from chloroform solution, the device ITO/PEDOT:PSS/**P1**:PCBM(1:4, w/w)/LiF/Al harvested a extremely high PCE of 4.2% (Table 1). An external quantum efficiency (EQE) of 66% was achieved in the active layer with a film thickness up to 140 nm, and further increasing the film thickness did not increase the efficiency due to limitations in charge generation or collection. For 4.2% PCE device, a maximum EQE of about 75% was calculated, indicating efficient charge collection.

By using quinoxaline as electron accepting unit, **P2** was synthesized with an E_g of 1.95eV (Kitazawa et al., 2009). The device performance is dependent upon the ratio of chloroform(CF)/chlorobenzene(CB) in co-solvent for blend film preparation and a maximal J_{sc} is achieved with CF/CB (2:3 v/v) co-solvent. The optimized device showed 5.5% PCE by inserting 0.1nm LiF layer between BHJ active layer and Al cathode with the structure ITO/PEDOT:PSS/**P2**:PC71BM/LiF/Al. Similarly structured **P3** achieved 3.7% PCE by blending with PC71BM (1:3 w/w) (Gadisa et al., 2007).

Polymer	λ_{max}^{abs} nm	E_g eV	μ_h $cm^2 V^{-1} s^{-1}$	HOMO /LUMO, eV	Polymer: PCBM ^b	J_{sc} mA/cm ²	V_{oc} V	FF	PCE
P1	-	-	-	-	1:4	7.7	1.0	0.54	4.2
P2	540	1.95	-	-5.37/-	1:4 ^a	9.72	0.99	0.57	5.5
P3	542	1.94	-	-6.30/-3.60	1:3	6.00	1.00	0.63	3.7
P4	545	1.87	5.3×10^{-4}	-5.30/-3.43	1:4	9.62	0.99	0.5	4.74
P5	580	1.76	1.2×10^{-3}	-5.26/-3.50	1:4	9.61	0.99	0.46	4.37
P6	541	1.83	1.8×10^{-4}	-5.32/-3.49	1:4 ^a	6.69	0.85	0.37	2.50
P7	579	1.74	2.1×10^{-4}	-5.35/-3.61	1:4 ^a	6.22	0.90	0.45	3.15
P8	565	1.82	1.0×10^{-3}	-	1:2	9.50	0.90	0.51	5.4
P9	580	1.79	1.1×10^{-4}	-5.58/-3.91	-	6.9	0.79	0.51	2.8
P10	543	1.97	4.2×10^{-3}	-5.47/-3.44	1:3.0	6.10	1.00	0.40	2.44
P11	541	2.00	9.5×10^{-4}	-5.45/-3.36	1:3.5 ^a	7.57	1.00	0.40	3.04
P12	531	1.96	9.7×10^{-3}	-5.45/-3.45	1:4.0 ^a	10.3	1.04	0.42	4.50

λ_{max}^{abs} : maximum absorption peak in film; E_g : optical band gap; μ_h : hole mobility; J_{sc} : short-circuit current density; V_{oc} : open-circuit voltage; FF: fill factor; PCE: power conversion efficiency; ^apolymer:PC71BM; ^bpolymer:PCBM in weight ratio.

Table 1. The optical, electrochemical, hole mobility, and PSC characteristics of **P1-12**

Different from the common linear D-A alternating polymer design, Jen and his coworkers designed a series of novel two-dimensional narrow band gap polymers, whose backbone adopts high hole transporting fluorene-triarylamine copolymer (PFM) and is grafted with malononitrile (**P4**) and diethylthiobarbituric acid (**P5**) through a styrylthiophene π -bridge (Huang et al., 2009). Both of them show two obvious absorption peaks, where the first absorption peaks at ~ 385 nm are corresponding to the π - π^* transition of their conjugated main chains and the others are corresponding to the strong ICT characters of their side chains. Two polymers show narrowed down E_g (< 2 eV) and present similar HOMO energy

level as that of PFM, while these two polymers exhibit much lowered LUMO levels (-3.43 and -3.50 eV for **P4** and **P5**, respectively) than PFM. The devices with structure of ITO/PEDOT:PSS(40nm)/**P4-5**:PC71BM(1:4 w/w, 85nm)/Ca(10nm)/Al(100nm) exhibit a PCE of 4.74% and 4.37% for **P4** and **P5**, respectively (refer to Table 1). Determined by using space-charge-limited-current (SCLC) method, the hole mobility of these two polymer/P71BM blend films was found to be $5.27 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for **P4** and $1.16 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for **P5**, respectively, which is even higher than that of P3HT with similar device configuration (G. Li, 2005). These two-dimensional polymers are thought to possess better isotropic charge transport ability than linear polymers, which is beneficial for PSC applications. By replacing FL in **P4** and **P5** with silafluorene (2,7-dibenzosilole) unit, similarly structured two-dimensional conjugated polymers **P6** and **P7** were developed (Duan et al., 2010) developed. With an E_g of 1.83 and 1.74 eV, **P6** and **P7** OSCs harvest high PCE as 2.5% and 3.51%, respectively, with device configuration ITO/PEDOT:PSS/**P6-7**:PC71BM/Ba/Al. It should be noted that the silofluorene polymers display lower hole transport ability than FL-based **P4** and **P5**.

By alternating silafluorene and DTBT units, copolymer **P8** was synthesized (Boudreault et al., 2007a). With an E_g of 1.82 eV, **P8** films presented an absorption spectrum blend covered the range from 350 to 750 nm. **P8** device displayed a PCE of 1.6% under AM 1.5 (90 mW/cm²) illumination with the structure ITO/PEDOT:PSS/**P8**:PCBM(1:4)/Al. By using similar polymer, **P8**:PCBM (1:2 w/w) blend film delivered as high as PCE of 5.4% under AM 1.5 (80 mW/cm²) (Zhou et al., 2004). By using DTBT as electron accepting unit, Leclerc (Allard et al., 2010) developed germafluorene based polymer **P9** whose device displayed a good PCE of 2.8% with the structure of ITO/PEDOT:PSS/**P9**:PC71BM/LiF(20nm)/Al.

In order to extend π -conjugation of polymer backbone, the ladder-type oligo-*p*-phenylenes (indenofluorene) consisting of several "linearly overlapping" fluorene was developed. Compared to FL unit, indenofluorene presents a broader more intense absorption band. Solubilizing alkyl chains can be easily introduced into this unique molecular backbone, which may provide a better solution processability of the polymers. Zheng (Zheng et al., 2010) reported three alternating D-A copolymers (**P10-12**) combining indenofluorene as the donor and DTBT or 5,8-dithien-2-yl-2,3-diphenyl quinoxaline (DTQX) as the acceptor unit. By spin-coating from chlorobenzene (CB):*o*-dichlorobenzene (DCB) (4:1 v/v) co-solvent, **P10** with decylated indenofluorene presents good solubility and its device achieved 2.44% PCE with the configuration ITO/PEDOT:PSS/**P10**:PCBM/Cs₂CO₃/Al (Veldman et al., 2008). In comparison with **P10**, **P12** with one more phenylene group in indenofluorene unit presents greatly improved device PCE (3.67%) with the same configuration, due to great improvement of J_{sc} . By blending with PC71BM in 1:4 weight ratio, **P18** OSC showed significantly improved PCE (4.5%). The DTQX-containing **P11** presents a good PCE of 2.32%, which was attributed to broad absorption spectra and high J_{sc} .

3. Carbazole-based conjugated polymers

Structurally analogous to FL, carbazole has been also known as 9-azafluorene. The central fused pyrrole ring makes tricyclic carbazole fully aromatic and electron-rich with its donating nitrogen. The alkyl chains introduced into nitrogen of carbazole improve the solubility. Carbazole derivatives have been widely used as electron-donor materials due to their excellent thermal and photochemical stabilities as well as relatively high charge mobility and good solubility with 9-position alkylation. When two carbazoles fused together

to form indolo[3,2-*b*]carbazole (IC) unit, it exhibits even stronger electron-donating properties, higher hole mobility and better stability than carbazole (Boudreaux, 2007b; Li, 2006). With bulky heptadecanyl modified carbazole to improve solubility, Leclerc (Blouin et al., 2007a) developed DTBT-based conjugated poly(N-alkyl-2,7-carbazole) (PC) **P13** (**P13-26** structure in Chart 2), which exhibits excellent thermal stability, relatively high molecular weight and good solubility. Spin-coated from CF solution, **P13**:PCBM(1:4 w/w) OSC delivered a high PCE of 3.6% (Table 2). Such high PCE and excellent stability show its potential application in OSC. By using longer alkyl chain, Hashimoto (Zou et al., 2010) reported a similar PC **P14**, whose device based on **P14**:PCBM (1:3w/w) showed 3.05% PCE, with all photovoltaic parameters similar to those of **P13**. By using 4,7-dithien-2-yl-2,1,3-benzothiadiazoxaline (DTBX) as accepting unit, Leclerc (Blouin et al., 2007b) synthesized **P15**. Due to its symmetrical backbone, **P15** showed good structural organization, which leads to good hole mobility and thus resultant improvement of J_{sc} and FF for its OSC. **P15** based OSC achieved a good PCE of 2.4%.

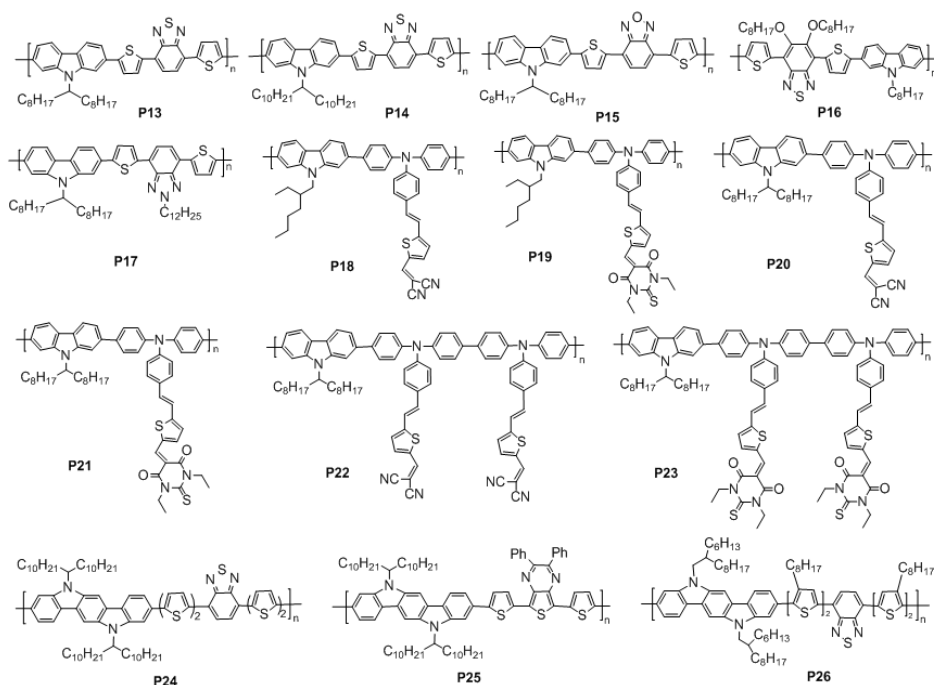


Chart 2. Carbazole based narrow band gap polymers

In order to improve the solubility and close packing of polymer backbone, Zhang (Qin et al., 2009) designed **P16** with planar polymer conformation by introducing two octyloxy chains onto benzothiazole (BT) ring and an octyl chain onto carbazole ring. **P16** showed good solubility at elevated temperature and an E_g of 1.95eV. Spin-coated from DCB mixture solutions with 2.5% 1,8-diiodooctane (DIO), **P16**:PC71BM device showed extremely high

PCE of 5.4% with the structure ITO/PEDOT:PSS/**P16**:PC71BM(1:2.5 w/w)/LiF/Al. By replacing the BT unit with benzotriazole, Cao (Zhang et al., 2010) developed PC **P17**, with an E_g of 2.18eV, which was broader than that of P3HT. The optimized device of **P17** achieved improved PCE from 1.51% to 2.75% by sandwiching a thin layer of PFN between Al cathode and active layer.

On the basis of successful design of two-dimensional PF **P4** and **P5**, Cao [Duan et al., 2010b] developed a series of carbazole-based two-dimensional polymers **P18-23**, with their E_g ranging from 1.7 to 1.9eV. **P18-23** present similar HOMO energy levels as the conjugated backbone while their LUMO levels were mainly determined by narrow band gap side-chains. Among them, **P22** and **P23** exhibited stronger absorption intensity and broader absorption spectra. The photovoltaic performance of **P22** and **P23** devices indicates the 2-ethylhexyl chains had little influence on the V_{oc} of OSC while the bulky heptadecanyl chains on carbazole led to a significant decrease in J_{sc} and FF. In comparison with that of **P4** and **P5**, **P18** devices exhibited excellent PCE of 4.16%. **P18-23** OSCs possessed high V_{oc} (>0.8eV) values, which was relevant with their relatively low HOMO levels. As known, V_{oc} is related to the offset between the HOMO levels of donor materials and the LUMO levels of acceptor materials. The alkyl chains on carbazole unit had important influence on the hole-transporting ability of the resultant polymers: **P18** and **P19** with short side-chains demonstrated hole mobility high as 2.4×10^{-4} and $1.1 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively, which are much higher than those of **P20-P23** with bulkier alkyl side-chains. The bulky alkyl chains possibly are thought to result in imbalanced electron transporting and consequently decreased FF of polymer.

Polymer	$\lambda_{\text{max}}^{\text{abs}}$ nm	E_g eV	μ_h $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	HOMO /LUMO, eV	Polymer: PCBM	J_{sc} mA/cm^2	V_{oc} V	FF	PCE
P13	576	1.87	-	-5.50/-3.60	1:4	6.92	0.89	0.63	3.6
P14	551	1.72	-	-5.48/-3.46	1:3	7.66	0.80	0.50	3.05
P15	-	1.87	1×10^{-4}	-5.47/-3.65	1:4	3.70	0.96	0.60	2.4
P16	579	1.95	1×10^{-4}	-5.21/-3.35	1:2.5 ^a	9.8	0.81	0.69	5.4
P17	523	2.18	-	-5.54/-3.36	1:2	4.68	0.9	0.65	2.75
P18	548	1.83	2.4×10^{-4}	-5.23/-3.40	1:4 ^a	8.94	0.91	0.51	4.16
P19	586	1.74	1.1×10^{-3}	-5.25/-3.51	1:4 ^a	8.18	0.92	0.47	3.52
P20	545	1.88	5.3×10^{-5}	-5.29/-3.41	1:4 ^a	7.51	0.91	0.44	2.91
P21	575	1.77	1.5×10^{-4}	-5.30/-3.53	1:4 ^a	6.23	0.89	0.38	2.09
P22	546	1.83	8.8×10^{-5}	-5.20/-3.37	1:4 ^a	7.18	0.83	0.39	2.34
P23	598	1.74	1.6×10^{-4}	-5.24/-3.50	1:4 ^a	6.53	0.84	0.40	2.19
P24	551	1.85	-	-5.43/-3.62	1:3	4.83	0.90	0.48	2.07
P25	527	1.91	-	-5.53/-3.54	1:4 ^a	7.38	0.80	0.43	2.54
P26	-	-	-	-5.17/3.15	1:2	9.17	0.69	0.57	3.6

Definitions for all parameters are the same as those in Table 1.

Table 2. The optical, electrochemical, hole mobility, and PSC characteristics of **P13-26**

It is widely accepted that the formation of strong intermolecular π - π stacking is necessary to achieve high charge mobility in OSC (Payne, 2004; McCulloch, 2006). Rigid coplanar fused aromatic rings can efficiently enhance this interaction and hence improve charge mobilities. Indolo[3,2-*b*]carbazole (IC) has large-size fused aromatic ring, making closer packing of

conjugated structure. Hashimoto (Zou et al., 2009) developed narrow band gap (1.90eV) PIC **P24** by alternating IC donating unit and DTBT accepting unit. The optimized **P24** device ITO/PEDOT:PSS/**P24**:PCBM1:3(w/w)/Al demonstrated a PCE of 2.07%. The study reveals that the formation of an interpenetrated network of donors and acceptors inside active layer is critical for obtaining high-performance OSCs. Such interpenetrated networks can be built by tuning device processing parameters such as the ratio of polymer to PCBM in the blend and post-annealing treatment at suitable temperatures. Besides, a simple and effective method to improve the photovoltaic performance of OSCs is to increase the number of unsubstituted thienyl units in D-A copolymers consisting of DTBT as acceptor. The V_{oc} of **P24** is similar with those of some DTBT based narrow band gap polymers with donating units like FL (1.0eV) (Slooff et al., 2007) dibenzosilole (0.9–0.97eV) (Boudreault et al., 2007) or carbazole (0.88 eV) (Blouin et al., 2007) but higher than those of D-A derivatives with donating units such as cyclopenta[2,1-b:3,4-b']dithiophene (0.6eV), dithienosilole (0.44eV) (Liao et al., 2007) or dithieno[3,2-b:2',3'-d] pyrrole(0.52eV) (Zhou et al., 2008). By adopting DTTP as accepting unit, the same group developed **P25**, with an E_g of 1.91 Hashimoto (Zhou et al., 2010a). Spin-coating from CF solution, **P25**:PCBM (1:4, w/w) based OSC contributed a PCE of 1.56% and was further improved to 2.54% by using DCB instead of CF.

By using hexylthiophene moiety in DTBT accepting unit and shorter alkyl chains in IC unit, Movileanu (Lu et al., 2008) developed **P24** analogous PIC **P26**. Long solubilizing side-chains generally resulted in lower charge mobility, balance of the alkyl chains in conjugated polymers was important for charge mobility. **P26** film showed pronounced peak broadening and significant red shift (100nm) in absorption spectra than its solution. **P26** device ITO/PEDOT:PSS/**P26**:PCBM(1:2w/w)/LiF/Al achieved a high PCE of 3.6%.

As discussed above, both PC and PF exhibit relatively low-lying HOMO level and thus high V_{oc} for OSCs via copolymerizing with accepting unit including DTBT, DTTP and DTQX. In contrast with other accepting units, DTBT-containing polymers may maintain deep HOMO and narrow the band gap through reducing LUMO, which results in a high V_{oc} . However, PCs devices generally display low J_{sc} and FF, which was similar to PFs.

4. Thiophene-based conjugated polymers

Polythiophenes (PTs) are considered as the most important conjugated polymers for a broad spectrum of optoelectronic applications such as light-emitting diodes, field-effect transistors, and OSCs due to their excellent optical and electrical properties as well as exceptional thermal and chemical stability (Roncali, 1992).

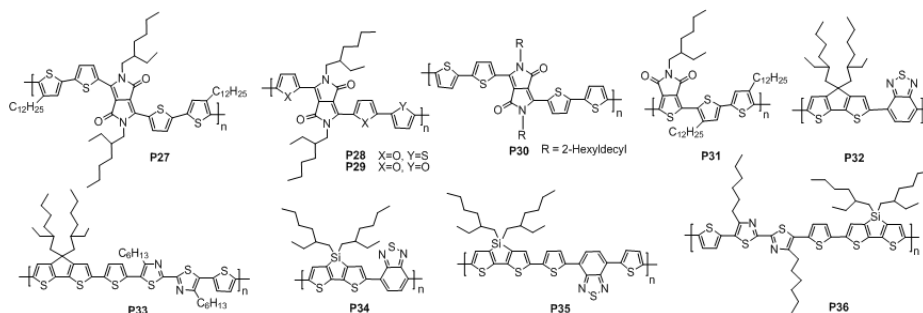


Chart 3. Thiophene-based narrow band gap polymers

By alternating quaterthiophene and diketopyrrolopyrrole (DPP) units, Janssen (Wienk et al., 2008) developed PT **P27** (**P27-36** structure in Chart 3), with an E_g of 1.4eV (Table 3). The absorption spectrum of **P27** in DCB showed stronger red-shift than its solution in CF. Fast evaporation of CF did not allow **P27** to crystallize, which results in poor morphology when spin-coating **P27**:PCBM blend film from CF solution. Certain degree of crystallization could be achieved by heating the film at 130°C. Spin-coated from CF:DCB (4:1 v/v) mixture solution, **P27**:PCBM (1:2 w/w) optimized OSC reached highest PCE of 4%, while OSC achieving only 1.1% PCE using CF as blending solvent and good PCE of 3.2% when prepared from DCB.

Furans have been used as an alternative to thiophenes in organic dyes for dye-sensitized solar cells and have shown very similar optical and electronic properties (R. Li et al., 2009). The first furan-containing DPP-based low band gap polymers **P28-29** were developed (Claire et al., 2010). By spin-coating from CB solution with 1vol% high-boiling-point 1-chloronaphthalene (CN), **P28** device achieved slightly improved PCE from 3.4% to 3.8% with the structure ITO/PEDOT:PSS/**P28**:PCBM(1:3w/w)/LiF/Al, due to optimized blend morphology. The best **P28**:PC71BM (1:3w/w) OSC contributed a PCE of 5.0% with the addition of 9% CN in CB. The device with blend **P29**:PC71BM (1:3 w/w) a PCE of 4.1% with 5% CN addition in CB. The addition of CN led to much finer phase separation between polymer and fullerene to form a fiber-like inter-penetrating morphology at the length scale of 20 nm, which is close to the ideal domain size, assuming an exciton diffusion length of 5-10 nm (Markov et al., 2005; Scully et al., 2006; Shaw et al., 2008). By alternating bithiophene donating unit and DPP accepting unit, Janssen (Johan et al., 2009) developed **P30**, with an E_g of 1.3eV. Terthiophene induced additional planarity, which enhanced packing and charge carrier mobility, as **P30**-based transistors exhibited nearly balanced hole and electron mobilities of 0.04 and 0.01cm²V⁻¹s⁻¹, respectively. The optimized device of **P30**:PCBM (1:2w/w) presented 3.8% PCE by spin-coating from CB solution with a small amount of DIO. The corresponding optimized device of **P30**:PC71BM achieved a PCE of 4.7% by adding 100mg/mL DIO in CF solution, due to low solubility of PC71BM in CF.

Polymer	$\lambda_{\text{max}}^{\text{abs}}$ nm	E_g eV	μ_h cm ² V ⁻¹ s ⁻¹	HOMO /LUMO, eV	Polymer: PCBM	J_{sc} mA/cm ²	V_{oc} V	FF	PCE
P27	650	1.4	-	-	1:2 ^a	11.5	0.61	0.58	4.0
P28	789	1.41	-	-5.40/-3.80	1:3 ^a	11.2	0.74	0.60	5.0
P29	767	1.35	-	-5.50/-3.80	1:3 ^a	9.1	0.73	0.58	4.1
P30	-	1.36	0.04	-5.17/-3.61	1:2 ^a	11.8	0.65	0.60	4.7
P31	572	1.82	1.0×10 ⁻⁴	-5.56/-3.10	1:1.5	8.02	0.95	0.62	4.7
P32	775	1.40	-	-5.30/-3.57	1:3	11.0	0.70	0.47	3.2
P33	560	1.84	-	-5.07/-3.55	1:1	7.70	0.68	0.53	2.79
P34	-	1.45	3×10 ⁻³	-5.05/-3.27	1:1 ^a	12.7	0.68	0.55	5.1
P35	652	1.53	3.0×10 ⁻⁶	-4.99/-3.17	1:1 ^a	9.76	0.60	0.50	2.95
P36	558	1.85	3.1×10 ⁻⁴	-5.18/-3.09	1:1 ^a	7.85	0.68	0.54	2.86

Definitions for all parameters are the same as those in Table 1.

Table 3. The optical, electrochemical, hole mobility, and PSC characteristics of **P27-36**

By alternating bithiophene donating unit and thieno[3,4-*c*]pyrrole-4,6-dione (TPD) accepting unit, Wei (Yuan et al., 2010) prepared **P31**, with an E_g of 1.82eV. TPD presented strong electron-withdrawing properties, which were attributed to improvement of intramolecular

interactions and reduction of E_g as well as relatively low HOMO level due to its symmetric, rigidly fused, coplanar structure (Zou et al., 2010). Controlling the active layer thickness of device ITO/PEDOT:PSS/**P31**:PCBM(1:2 w/w)/Al between 90 and 100nm, the best device presented 4.7% PCE, with relatively high V_{oc} (0.95V) attributed to its deep HOMO level.

By alternating cyclopentadithiophene (CPDT) and BT unit, Mühlbacher (Mühlbacher et al., 2006) developed **P32**, which exhibited an E_g of 1.40eV and an absorption spectrum ranged from 300 to 850nm. The device based on **P32**:PCBM obtained a PCE of 3.2%. By incorporating CPDT with bithiazole unit, Lin (K. Li et al., 2009) developed polymer **P33**, with the best device contributed a PCE of 3.04% with the configuration of ITO/PEDOT:PSS/**P33**:PCBM(1:2 w/w)/Ca/Al.

Recently, dithieno-[3,2-*b*:2',3'-*d*]silole-containing polymers have attracted considerable attention due to their potential applications in the field of optoelectronic devices. Many silole-containing polymers have been proven to achieve high V_{oc} by reducing the LUMO levels of polymers (Lu et al., 2008). It is feasible to realize a low-lying HOMO energy level and high V_{oc} simultaneously under the condition of ensuring a sufficient energy level offset (0.3-0.5V) between the LUMO level of silole-containing donor and the LUMO of PCBM. Furthermore, silole-containing polymers applied in OSC have also proved to be effective in improving hole mobility and rendering higher efficiencies compared to CPDT (Wang, 2008; Hou, 2008). By alternating dithieno-[3,2-*b*:2',3'-*d*]silole and BT unit, Yang (Hou et al., 2008) developed **P34**, with an E_g low 1.45eV. **P34** has a broader absorption spectrum ranging from 350-800nm. Its device ITO/PEDOT/PSS/**P34**:PC70BM/Ca/Al achieved an average PCE of 4.7 % for 100 devices, with the OSC showing a PCE of 5.1%. The same group reported DTBT-based silole-containing polymers **P35** (Huo et al., 2009). The device presented 3.43% PCE with the structure of ITO/PEDOT:PSS/**P35**:PCBM/Ca/Al. By alternating dithieno-[3,2-*b*:2',3'-*d*]silole and dithiazole unit, Li (Zhang et al., 2010) designed **P36**, whose device (ITO/PEDOT:PSS/**P36**:PC71BM(1:2 w/w)/Al) achieved a PCE of 2.86%.

Recently, the polymers containing benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) have been successfully applied to field-effect transistor (FET) and PSC devices (Huo, 2008; Pan, 2007; Chen, 2009) with a high mobility of 0.15-0.25cm²V⁻¹s⁻¹, owing to the large and planar conjugated structure promoting π - π stacking and thus benefiting charge transport. By incorporating alkoxy BDT with thieno[3,4-*b*]thiophene, **P37** (**P37-50** structure in Chart 4) was developed, with an E_g 1.62eV (Liang et al., 2009a). Thieno[3,4-*b*]thiophene repeating units contributed to the stability of the quinoidal structure of the backbone narrowing the energy gap of resulting polymer (Sotzing & Lee, 2002). Thieno[3,4-*b*]thiophene with ester substituents in **P37** contributed both good solubility and oxidative stability. The absorption of **P37** coincided with the corresponding maximum photon flux region in solar spectrum. **P37** OSC with the structure of ITO/PEDOT:PSS/**P37**:PCBM(1:1 w/w)/Ca/Al achieved a PCE of 4.76% (Table 4). **P37**:PC71BM presented an improved PCE of 5.30% with the same device structure. The absorption spectra of two devices almost covered the whole visible range. Furthermore, high EQEs were obtained for both **P37**:PCBM and **P37**:PC71BM OSCs. For the former, the maximum EQE was over 60% at 650 nm and was 50% in the range of 550-750 nm; the latter exhibited a higher EQE, almost all over 60% in the range from 400 to 750 nm.

By changing side-chain substituents, **P37** analogous polymers **P38-41** were developed (Liang et al., 2009b). All polymers showed very close between 2.6×10^{-4} and 4.7×10^{-4} cm²V⁻¹s⁻¹ and similar absorption spectra, covering the whole visible region.

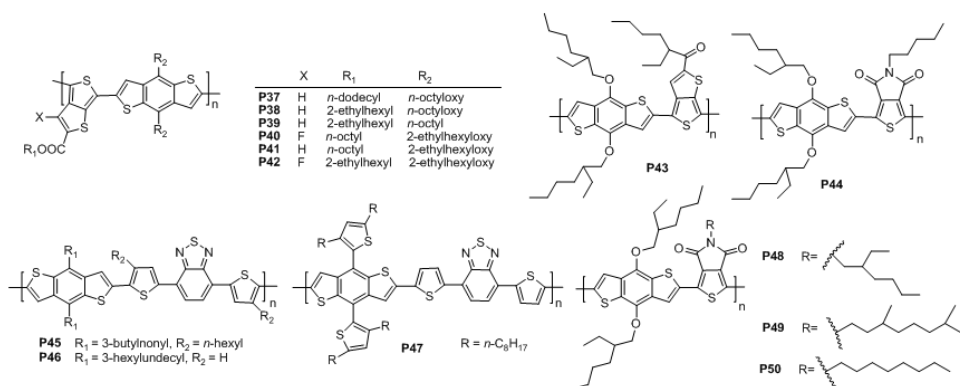


Chart 4. BDT based narrow band gap polymers.

The substitution of octyloxy to octyl group lowered the HOMO energy level of **P38** from -4.94 to -5.04 eV (**P39**). With electron-withdrawing fluorine in polymer backbone, **P40** had significantly lower HOMO level in comparison to **P41**. The devices based on ITO/PEDOT:PSS/**P38-41**:PCBM (1:1 w/w)/Ca/Al exhibited a PCE of 5.10%, 5.53%, 3.20% and 3.02%, respectively, with active layer spin-coated from DCB solution. By using DCB/DIO (97:3 v/v) mixture solvent, PCE of **P39-P41** can be dramatically improved to 5.85%, 5.90% and 4.10%, respectively. By replacing octyl group in **P40** into 2-ethylhexyl, **P52** was further developed (Liang et al., 2010). Spin-coated from DCB solution, **P51**:PC71BM harvested a PCE of 5.74%, 6.22% and 5.58%, respectively at their D/A weight ratio as 1:1, 1:1.5 and 1:2. The best device contributes PCE as high as 7.4% with the mixture solvent of CB/DIO(97:3 v/v), where uniform morphology of blend film was prepared.

Polymer	$\lambda_{\max}^{\text{abs}}$ nm	E_g eV	μ_h $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	HOMO/ LUMO, eV	Polymer: PCBM	J_{sc} mA/cm^2	V_{oc} V	FF	PCE
P37	687	1.62	4.5×10^{-4}	-4.90/-3.20	1:1.2 ^a	15.0	0.56	0.63	5.30
P38	683	1.59	4.0×10^{-4}	-4.94/-3.22	1:1	12.8	0.60	0.66	5.10
P39	682	1.60	7.1×10^{-4}	-5.04/-3.29	1:1	13.9	0.72	0.58	5.85
P40	682	1.63	7.7×10^{-4}	-5.12/-3.31	1:1	13.0	0.74	0.61	5.90
P41	677	1.62	4.0×10^{-4}	-5.01/-3.24	1:1	10.7	0.66	0.58	4.10
P42	675	1.61	5.8×10^{-4}	-5.15/-3.31	1:1.5 ^a	14.5	0.74	0.69	7.4
P43	675	1.61	2×10^{-4}	-5.12/-3.55	1:1.5 ^a	14.7	0.7	0.64	6.58
P44	610	1.80	-	-5.56/-3.75	1:2 ^a	9.81	0.85	0.66	5.50
P45	595	1.70	1.6×10^{-5}	-5.26/-2.96	1:1	9.70	0.81	0.55	4.31
P46	644	1.70	3.8×10^{-5}	-5.33/-3.17	1:1	7.79	0.83	0.60	3.85
P47	596	1.75	-	-5.31/-3.44	1:2 ^a	10.7	0.92	0.58	5.66
P48	608	1.75	-	-5.48/-	1:2	8.1	0.87	0.56	4.0
P49	616	1.70	-	-5.57/-	1:1.5	9.7	0.81	0.67	5.7
P50	627	1.73	-	-5.40/-	1:1.5	11.5	0.85	0.68	6.8

Definitions for all parameters are the same as those in Table 1.

Table 4. The optical, electrochemical, hole mobility, and PSC characteristics of **P37-50**

BDT-containing polymers can finely tune the HOMO level and efficiently narrow the band gap (Pan, 2007; Liang, 2008; Liang, 2009). Besides, alkoxy groups have been proved to be beneficial to reduce the HOMO level of polymer due to its stronger electron-donating property (Liang et al., 2009b). By removal of the oxygen atom on ester group in thieno[3,4-*b*]thiophene unit, ketone-substituted polymer **P43** (Chen et al. 2009) was developed to further reduce the HOMO level. The best OSC based on **P43**:PC71BM showed a high PCE of 6.58%.

By alternating BDT and TPD, Leclerc (Zou et al, 2010) presented polymer **P44**, with an E_g of 1.8eV and HOMO/LUMO energy levels -5.56eV/-3.75eV, respectively. The device ITO/PEDOT:PSS/**P53**:PC71BM/LiF/Al showed a high PCE of 5.5%. By incorporating BDT with DTBT, You (Price et al., 2010) synthesized **P45-46**. Compared with **P45**, **P46** exhibited higher molecular weight while lower hole mobility than other BDT-containing **P37-43**. **P45-46** device showed a PCE of 3.85% and 4.31%, respectively. By introducing thiophene moiety onto BDT, Yang (Huo et al., 2010) synthesized **P45** analogous polymer **P47**, with an E_g of 1.75eV. Spin-coated from DCB, **P47** device (ITO/PEDOT:PSS/**P47**:PC71BM(1:2 w/w)/Ca/Al) contributed the optimized PCE of 5.66% without annealing treatment.

By changing the alky substituent in TPD unit, Frechet (Piliago et al., 2010) synthesized **P44** analogue polymers **P48-50**, with E_g ranging from 1.70 to 1.75 eV and HOMO levels lowered down to -5.4~ -5.57 eV. Spin-coated from CB, **P48-50**:PCBM devices achieved a PCE of 2.8%, 3.9%, 6.4%, respectively. Clearly, the device performance increased as the branch length was decreased in **P48-50**. By spin-coating from CB solution with a small amount of DIO, **P48** and **P49** OSCs achieved improved PCE of 4.0% and 5.7%, respectively (Peet et al., 2008). However, for **P50**, the addition of DIO led to only slight improvements, which was attributed to a high level of order of **P50** in the blend without DIO. It was concluded that alkyl-substituted groups had much impact on the PCE of **P48-50**. The use of DIO is effective in promoting the packing of the polymer by preventing excessive crystallization of PCBM.

Dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) has good planarity and stronger electron-donating ability of nitrogen atoms. Geng (Yue et al. 2009) synthesized BT-based P(DTP)s **P51-52** (Chart 5), with an E_g ~1.43eV. Owing to different alkyl chain, **P52** exhibited stronger absorption in the range of 600-900nm compared to **P51**. **P51-52** devices showed a PCE of 2.06% and 2.8%, respectively with the structure ITO/PEDOT:PSS/**P51-52**:PCBM(1:3 w/w)/LiF/Al, at the optimized blend film thickness of 100 nm for **P51** and 90 nm for **P52**. The device of **P51-52** delivered a V_{oc} in the range of 0.4-0.54V, leading to relatively low PCE. By adopting DTP and DTBT units as the donor and acceptor segments, Hashimoto (Zhou et al., 2008) synthesized **P53** with an E_g of 1.46eV, which was the lowest compared with other D-A copolymers based on DTBT acceptor segment with other donor segments such as FL, silafluorene, carbazole, DTS, and CPDT (Slooff, 2007; Blouin, 2007; Moulle, 2008). **P53** device exhibited a PCE of 2.18% and a high J_{sc} of 9.47mA/cm², which was attributed to its broad absorption spectrum. However, **P53** device presented a V_{oc} of 0.52V, which is lower than that of the devices based on DTBT-containing D-A copolymers with FL (1V), silafluorene (0.9V) or carbazole (0.9V) as donating unit.

3,6-Dithien-2-yl-2,5-dialkylpyrrolo[3,4-*c*]pyrrole-1,4-dione (DTDPP) emerged as a promising electron acceptor in the design of photovoltaic polymers (Wienk et al., 2008). With DTDPP as accepting unit, Hashimoto (Zhou et al., 2010b) presented **P54**, with an E_g lowed down to 1.13eV. **P54** presented a hole mobility of 0.05cm²V⁻¹s⁻¹, 1-2 orders of magnitude higher than that of other D-A polymers. Spin-coated with mixing solution of CF and DCB (4:1 v/v), **P54** device with structure of ITO/PEDOT:PSS/**P54**:PCBM(or PC71BM)/LiF/Al showed a PCE of 2.34% with PCBM and 2.71% with PC71BM as acceptor in the blend films. The PCE of **P54**

was lower than that of P3HT, which was mainly attributed to the lower V_{oc} , resulting from its high-lying HOMO level (-4.90eV). It was expected that the device performance would be improved by further reducing the HOMO and LUMO level.

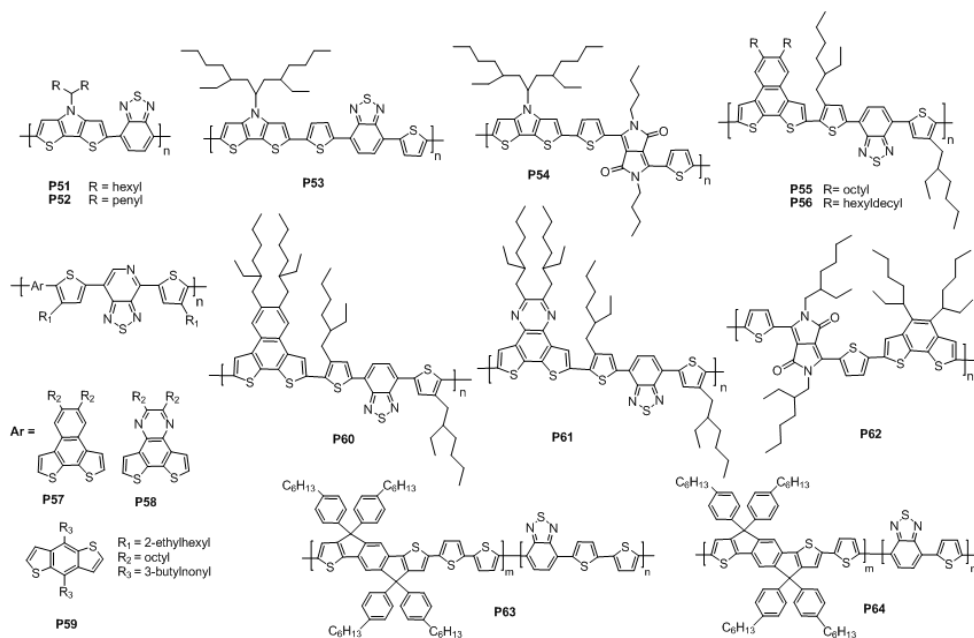


Chart 5. Fused Thiophene based narrow band gap polymers.

Recently, You (H. Zhou, 2010b) proposed a design strategy for narrow band gap polymers by alternating “weak donor” and “strong acceptor” to approach ideal polymers with both low HOMO energy level and small E_g in order to achieve both high V_{oc} and J_{sc} (H. Zhou, 2010e). By alternating DTBT or thiadiazolo[3,4-*c*]pyridine as strong acceptor, with naphtho[2,1-*b*:3,4-*b'*]-dithiophene (NDT), dithieno[3,2-*f*:2',3'-*h*]quinoxaline (QDT) or BDT as weak donor, polymers **P55-61** were developed (Yang, 2010; H. Zhou, 2009; H. Zhou, 2010b, 2010c). For NDT-containing **P55-56**, a 4-(2-ethylhexyl)thiophene unit in DTBT was used to reduce the steric hindrance of polymer backbone and hence to achieve near identical E_g and energy levels (H. Zhou, 2010a). It was believed that E_g and energy levels of a conjugated polymer were primarily determined by the molecular structure of conjugated backbone, while the solubilizing alkyl chains should have a negligible impact on these properties and hence a little impact on device's J_{sc} and V_{oc} . However, Yu's study showed variations of length and shape of alkyl chains in NDT had significant influence on device performance: long and branched side-chains would weaken the intermolecular interaction, benefiting for improvement of V_{oc} ; while short and straight side-chains would promote the intermolecular interaction, rendering a large J_{sc} . The desirable balance between V_{oc} and J_{sc} could be tuned through adopting suitable short and branched side-chains. **P55-56**:PCBM (1:1, w/w) devices showed a best PCE of 3.0% and 3.36%, respectively.

Polymer	λ_{max} nm	E_g eV	μ_h $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	HOMO/ LUMO, eV	Polymer: PCBM	J_{sc} mA/cm^2	V_{oc} V	FF	PCE
P51	764	1.42	-	-4.86/-3.07	1:3	11.1	0.43	0.43	2.06
P52	764	1.43	-	-4.81/-3.08	1:3	11.9	0.54	0.44	2.80
P53	697	1.46	-	-5.00/-3.43	1:1	9.47	0.52	0.44	2.18
P54	790	1.13	0.05	-4.90/-3.63	1:2 ^a	14.87	0.38	0.48	2.71
P55	547	-	-	-	1:1	10.93	0.59	0.46	3.00
P56	548	-	-	-	1:1	10.67	0.69	0.46	3.36
P57	580	1.53	-	-5.36/-3.42	1:1	14.16	0.71	0.62	6.20
P58	650	1.56	-	-5.50/-3.44	1:1	13.49	0.75	0.55	5.57
P59	675	1.51	-	-5.47/-3.44	1:1	12.78	0.85	0.58	6.32
P60	681	1.61	1.7×10^{-5}	-5.34/-3.29	1:0.8	14.20	0.67	0.54	5.10
P61	647	1.70	7.2×10^{-6}	-5.46/-3.28	1:1.2	11.38	0.83	0.46	4.3
P62	928	1.34	-	-5.21/-3.63	1:2 ^a	10.1	0.68	0.63	4.31
P63	520	1.76	7.0×10^{-4}	-5.46/-3.56	1:3 ^a	8.7	0.84	0.53	3.9
P64	590	1.70	3.4×10^{-3}	-5.43/-3.66	1:3 ^a	10.1	0.80	0.53	4.3

Definitions for all parameters are the same as those in Table 1.

Table 5. The optical, electrochemical, hole mobility, and PSC characteristics of **P51-64**

By replacing BT with a new stronger acceptor, thiadiazolo[3,4-c]pyridine, You (H. Zhou, 2010d) developed **P57-59** by adopting NDT, QDT or BnDT as donating unit. **P57-59** exhibit an E_g of 1.53eV, 1.56eV and 1.51eV, respectively, which is noticeably reduced (ca.0.09–0.19eV) compared with the band gaps of their BT counterparts (Price, 2010; H. Zhou, 2010c). The device with ITO/PEDOT:PSS/**P57-59**:PCBM/Ca/Al achieved a PCE of 6.20% for **P57**, 5.57% for **P58**, and 6.32% for **P59**. By alternating DTBT acceptor with NDT or QDT weak donor, You (H. Zhou, 2010e) developed **P60-61**, with an E_g of **P60-61** of 1.61eV and 1.70eV, respectively. The devices based on **P60-61**:PCBM achieved a PCE of 5.1% and 4.3%, respectively. The donor unit with electron-withdrawing atoms was demonstrated to lead to a lower HOMO level while have little impact on the LUMO level. You thought that future research should be focused on employment of even weaker donors and stronger acceptors via innovative structural modification in order to concurrently achieve a higher V_{oc} and a higher J_{sc} . By alternating DPP and benzo[1,2-*b*:4,5-*b'*]dithiophene, Yang (Huo et al., 2009) synthesized **P62**. Its device with the structure of ITO/PEDOT:PSS/**P62**:PC71BM(1:2 w/w)/Ca/Al achieved improved PCE from 4.31% to 4.45% after device annealing under 110°C for 30 min. **P62** was expected to a very promising candidate for highly efficient OSCs owing to relatively low E_g and suitable HOMO level.

Ladder-type coplanar thiophene-phenylene-thiophene (TPT) structure tends to lead to strong molecular π - π interaction and thus exhibits remarkable hole mobility (Wong et al., 2006). Poly(TPT)s demonstrated an $E_g \sim 2.1\text{eV}$ and hole mobility as high as $10^{-3}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ (Chan et al., 2008). By alternating TPT donor and DTBT acceptor, Ting (Chen et al., 2008) developed **P63-64**, which exhibited an E_g of 1.76eV and 1.70eV, and absorption band in the range of 350-700nm and 350-730nm, respectively. **P64** displayed a hole mobility up to $3.4 \times 10^{-3}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Both of them showed good solubility at room temperature in organic solvents. Using DCB as blending solvent, the devices ITO/PEDOT:PSS/**P63-64**:PCBM(1:3 w/w)/Ca/Al harvested a PCE of 2.0% and 2.5%, respectively, a little lower than that (3.9% PCE) of P3HT:PCBM(1:1 w/w) device under the same conditions. The optimized device

with **P63-64**:PC71BM (1:3 w/w) showed a PCE of 3.9% for **P63** and 4.3% for **P64**, higher than that of the device based on P3HT:PC71BM (1:1 w/w) (3.4%) under the same conditions.

5. Conclusions

Narrow band gap polymers **P1-P64** developed by alternating donor (ca. fluorene, carbazole and thiophene) and acceptor (ca. benzothiadiazole, quinoxaline and diketopyrrolopyrrole) units in recent 4 years are summarized, with their fullerene blend-based BHJ OSCs contributing PCE over 3%. The design criteria for ideal polymer donors to achieve high efficiency OSCs is: (1) a narrow E_g (1.2-1.9eV) with broad absorption to match solar spectrum; (2) a HOMO energy level ranging from -5.2 to -5.8 eV and a LUMO level ranging from -3.7 to -4.0eV to ensure efficient charge separation while maximizing V_{oc} ; and (3) good hole mobility to allow adequate charge transport. Besides, device structure and morphology optimizations of polymer:fullerene blend film have been extensively demonstrated to be crucial for PCE improvement in OSCs. The current endeavors boosted OSCs PCEs up to 7% would encourage further efforts toward a next target of efficiency in excess of 10%.

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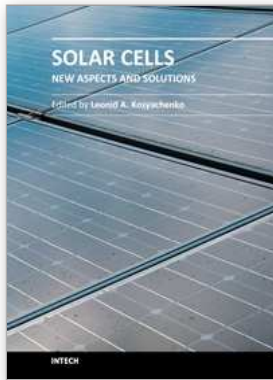
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The fourth book of the four-volume edition of 'Solar cells' consists chapters that are general in nature and not related specifically to the so-called photovoltaic generations, novel scientific ideas and technical solutions, which has not properly 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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中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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