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Development of Novel Conjugated Donor Polymers for High-Efficiency Bulk-Heterojunction Photovoltaic Devices

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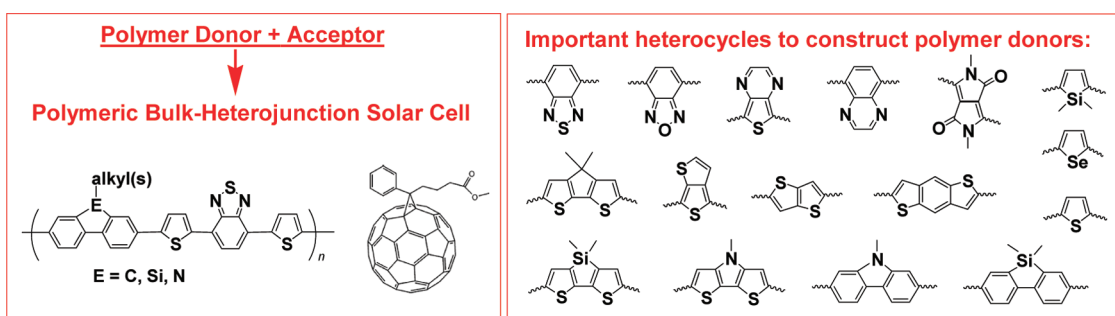
Solar cells are one attractive method for harnessing inexhaustible clean energy from the sun. Organic photovoltaic technology is emerging as a potential competitor to silicon-based photovoltaic cells (PVCs), and their power conversion efficiencies (PCE) can now exceed 6%. Polymeric bulk-heterojunction (BHJ) PVCs, whose photoactive layer is composed of a blend of bicontinuous and interpenetrating donors and acceptors, can maximize interfacial area between the donor and the acceptor.

Classic polymer donors, such as dialkoxy-substituted poly(*para*-phenylene vinylene)s (PPVs) and poly(3-hexylthiophene) (P3HT), have been widely investigated. However, advances in synthetic methodology provide new avenues for the development of novel conjugated polymer donors with improved power conversion efficiencies. Recently, researchers have achieved great advances in this area.

This Account primarily focuses on novel donor polymers that have shown power conversion efficiencies greater than 1%. 2,1,3-Benzothiadiazole, thiophene, thieno[3,4-*b*]pyrazine, quinoxaline, and silole have emerged as useful heterocycles for constructing a variety of conjugated polymers for photovoltaic applications. We summarize useful information, such as molecular weights, absorption, bandgap, energy levels, and their photovoltaic performances with detailed device parameters (see comparison tables), about these novel donor polymers. We use statistical summaries to evaluate several important parameter relationships among these polymer donors including open-circuit voltage versus HOMO, power conversion efficiency versus bandgap, and power conversion efficiency versus hole mobility. Further statistical analysis of the data listed in these tables may guide further structural design and evaluation of polymer donor materials.

1. Introduction

Photovoltaic cells (PVCs) or solar cells are one of the most attractive ways to use solar energy, an inexhaustible renewable clean energy. Organic photovoltaic technology, as a potential competitor to silicon-based PVCs, has undergone gradual progress with power conversion efficiency (PCE) over 6%.[1,2] Polymeric bulk-heterojunction (BHJ) PVCs, whose photoactive layer is composed of a blend of bicontinuous and interpenetrating donor and acceptor, can maximize interfacial area between the donor and the acceptor.[3−5] In addition, polymeric BHJ PVCs can be processed in solution, such as spin-coating or roll-to-roll print-

CHART 1. Chemical Structures of MEH-PPV, MDMO-PPV, and P3HT

MEH-PPV   MDMO-PPV   P3HT
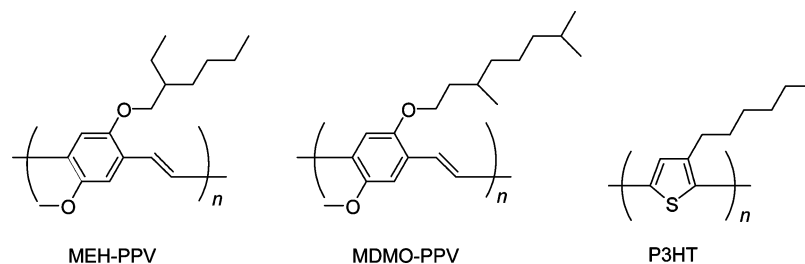
ing, thereby contributing several attractive advantages such as low-cost, lightweight, and flexible devices.

In a typical polymeric BHJ PVC, the photoactive blend layer, sandwiched between an indium tin oxide (ITO) positive electrode and a metal negative electrode, may be composed of a low band gap conjugated polymer donor and a soluble nanosized acceptor.[5−7] A fullerene derivative, [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), showing better solubility than C_{60} in common solvents, is a widely utilized acceptor. As a component in the active layer, a conjugated polymer donor serves as the main absorber to solar photon flux, as well as the hole transporting phase.[6−8] Thus a low band gap feature to match the solar spectrum and fast hole mobility are basic requirements to design an ideal polymer donor.

Dialkoxy-substituted poly(*para*-phenylene vinylene)s (PPVs), for example, poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) (Chart 1), show strong absorption in the visible light band.[9−12] Notable PCE values of 2−3% have been reproducibly achieved. Regioregular poly(3-hexylthiophene) (P3HT, Chart 1) is also a widely investigated polymer donor, from which repeatable PCE values of 3−5% have been reported.[9] Many optimization methods, such as using different solvents to fabricate the active layer, thermally annealing the active layer or the device, film forming speed, additives to the active layer, optical spacer, anode or cathode interfacial layer, and tandem structure, have been extensively carried out with P3HT, MEH-PPV, and MDMO-PVV as donors and have demonstrated significant improvements in the photovoltaic performance of BHJ PVCs.[2,4−9] Therefore, in some sense, MEH-PPV, MDMO-PPV, and P3HT could be attributed to classic polymer donors and have been well addressed in previous reviews.[4−7]

Despite the advances of PVC performance with the classic MEH-PPV, MDMO-PPV, and P3HT as the BHJ donor phase reaching PCE up to 5%, further significant enhancement of PCE is necessary in order to meet the requirements

for large scale commercialization as a renewable energy source. One of the routes for such improvements is the design of new polymer donors that have extended absorption edge to match solar terrestrial radiation, higher carrier mobility, and better energy alignment with acceptors to reach high open circuit voltage. This Account will mainly focus on novel polymer donors showing high efficiency (with PCE over an arbitrary 1%). Most approaches were achieved in the past five years. These studies have paved the pathway toward better understanding of the nature of BHJ solar cells, and some of them might be promising candidates for future commercial applications.

2. Benzothiadiazole-Containing Polymers

One of the most widely used strategies to make narrow band gap donor polymers is the synthesis of an alternating copolymer from electron-rich (donor) and electron-deficient (acceptor) units in their backbone. Although 2,1,3-benzothiadiazole (BT) is an electron-accepting (A) heterocycle that has been utilized to construct some n-type semiconducting polymers showing high electron mobility, BT has been recently used as acceptor unit in cooperation with varieties of electron-donating (D) units as low band gap donors in BHJ PVCs. High hole mobility and wide sunlight absorption band could be achieved for the D−A type BT-containing polymers. This category of polymer donors has been extensively studied and has shown outstanding photovoltaic performances.

P1 (Chart 2) derived from BT and 2,5-dithienylpyrrole showed an absorption peak (λ_{max}(abs)) at 510 nm in solution, but λ_{max}(abs) largely red-shifted to 608 nm for a spin-coated film (Table 1).[13] The absorption edge of the polymer film extended to the near-IR region (∼775 nm), corresponding to a low optical band gap (E_g) of 1.6 eV. The HOMO and LUMO levels of **P1** were −5.5 and −3.73 eV, respectively, because typically, the HOMO of the D−A polymer was determined by the HOMO of the donor unit, while the LUMO was controlled by the LUMO of the acceptor unit.

CHART 2. Chemical Structures of Benzothiadiazole-Containing Polymers **P1**−**P15**
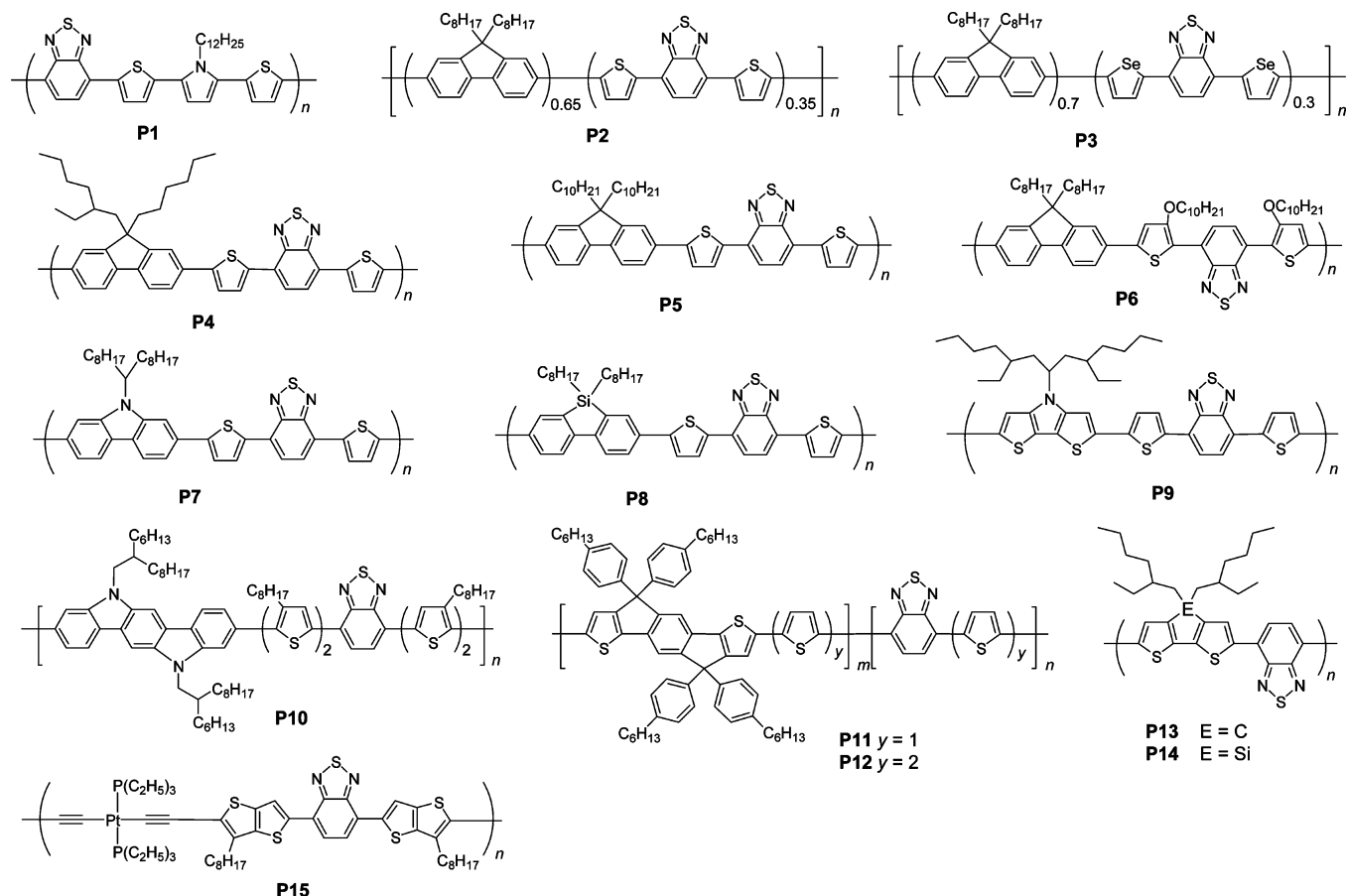
TABLE 1. Absorption Peak (λ_{max}(abs)), Optical Band Gap (E_g), and Energy Levels of **P1**−**P15** and PVC Device Performance from **P1**−**P15**/PCBM Blends

polymer	M_n (KDa) (M_w/M_n)	λ_{max}(abs) for solution (film) (nm)	E_g (eV)	electrochemical HOMO (LUMO) (eV)	donor/ PCBM ratio (w/w)	J_{sc}^b (mA/cm^2) @ P_{in}^c = 100 (mW/cm^2)	V_{oc}^d (V)	FF^e (%)	PCE (%)	ref
P1	a	510 (608)	1.60	−5.50 (−3.73)	1:3	3.10 @ 80	0.72	37.0	1.00	13
P2	11 (1.7)	545 (545)	2.01	−5.70 (a)	1:2	4.59 @ 78.2	0.95	35.0	1.95	16
P3	12 (1.8)	a (560)	1.85	−5.51 (−2.76)	1:4	2.53 @ 78.2	1.00	37.4	1.00	18
P4	4.8 (2.9)	545 (a)	a	a	1:4	4.66	1.04	46.0	2.20	21
P5	9.7 (3.6)	a	a	a	1:4	7.70	1.00	54.0	4.20	22
P6	68 (2.0)	a (580)	1.64	−5.14 (a)	1:4	4.31	0.76	48.6	1.60	23
P7	37 (2.0)	545 (576)	1.88	−5.50 (−3.60)	1:4	6.92 @ 90	0.89	63.0	3.60	24
P8	15 (1.3)	539 (576)	1.85	−5.70 (−3.81)	1:4	2.80 @ 90	0.97	55.0	1.60	25
					1:2	9.50 @ 80	0.90	50.7	5.40	17
P9	1.8 (3.4)	671 (697)	1.46	−5.00 (−3.43)	1:1	9.47	0.52	44.0	2.18	28
P10	20 (2.1)	538 (a)	1.89	−5.17 (−3.15)	1:2	9.17	0.69	57.0	3.60	29
P11	22 (1.7)	a (590)	1.70	−5.43 (−3.66)	1:3^f	10.1	0.80	53.0	4.30	30
P12	17 (1.6)	a (520)	1.76	−5.46 (−3.56)	1:3^g	8.70	0.84	53.0	3.90	30
P13	35 (1.3)	a (775)	1.40	−5.30 (−3.57)	1:1^h	11.0	0.70	47.0	3.16	31
					1:2−3^h	16.2	0.62	55.0	5.50	32
					1:3.6^h	15.7	0.61	53.0	5.12	33
P14	18 (1.2)	670 (740)	1.45	−5.05 (−3.27)	1:1^i	12.7	0.68	55.0	5.10	35
P15	12 (1.6)	596 (611)	1.81	−5.14 (a)	1:4^j	9.61	0.79	49.3	3.73	36

^{a} No data supplied. ^{b} Short-circuit current. ^{c} Incident radiation flux. ^{d} Open-circuit voltage. ^{e} Fill factor. ^{f} **P11**/PC$_{70}$BM. ^{g} **P12**/PC$_{70}$BM. ^{h} **P13**/PC$_{70}$BM. ^{i} **P14**/PC$_{70}$BM. ^{j} **P15**/PC$_{70}$BM.

Though a PVC device with a configuration of ITO/poly(3,4-ethylenedioxythiophene) (PEDOT)−poly(styrene sulfonate) (PSS)/(**P1**:PCBM = 1:1)/Al displayed a low PCE of 0.34% in their first report,[13] later the PCE was improved to 1% for an active layer of **P1**:PCBM = 1:3 (Table 1).[14] The open-circuit voltage (V_{oc}) of 0.72 V is lower than ~0.8 V for PVCs with PPV-type donors[10,11] but higher than ~0.6 V of P3HT.[9]

Hou et al. first synthesized BT-containing polyfluorenes by Suzuki coupling, initially for red light-emitting diode (LED) applications;[15] later it was applied as a donor phase of BHJ cells.[16] In the random copolymerized **P2**, the molar ratio of dithienyl-BT was 0.35 to make the polymer completely soluble at M_n of 11 000.[15] **P2** possessed a moderate E_g of 2.01 eV and a HOMO of -5.7 eV. A PVC device showed short-circuit current (J_{sc}) of 4.59 mA/cm^2, a high V_{oc} of 0.95 V, and fill factor (FF) of 35% under illumination of an AM 1.5 solar simulator (78.2 mW/cm^2), giving a PCE of 1.95%.[16] Some optimized devices displayed PCE values of 2.24% at the same light intensity.[16] The J_{sc} increased linearly with light intensity up to 500 mW/cm^2. The hole mobility of **P2** was later investigated with the polymer as the active layer in field-effect transistors (FETs),[17] giving a calculated hole mobility of $\sim 3 \times 10^{-4}$ cm^2 V^{-1} s^{-1}. The selenium atom has a much larger atomic size and less electronegativity compared with the S atom. Selenophene-incorporated **P3** showed a decreased E_g and an up-lying HOMO of **P3** in comparison with **P2**.[18] A PVC device displayed a PCE of 1.00% with a high V_{oc} of 1 V.[18] A recent report on a regioregular poly(3-hexylselenophene) showed low E_g of 1.6 eV, a reduction of 0.3 eV compared with P3HT.[19] Preliminary device results[20] produced a PCE of 2.7%, and this may attract more attention to selenium-containing donor copolymers in photovoltaic applications.

P4−**P6** are alternating copolymerized BT-containing polyfluorenes. The molecular weights of **P4** were specially controlled during the polymerization for its solubility.[21] For a 1 cm^2 active area PVC, an impressive PCE of 2.2% was realized, which was comparable to a PCE record of 2.5% with MDMO-PPV donor at that time.[10] The maximum incident-photon-to-collected-electron ratio (IPCE) was $\sim$40%. Later, **P5** with two longer decyl groups to improve the solubility showed a better PCE of 4.20% and a larger FF of 54%.[22] **P6** with 3-decyloxyl substitutions on thiophenes possessed decreased E_g of 1.64 eV and elevated HOMO of -5.14 eV compared with other BT-containing polyfuorenes.[23] This polymer showed a PCE of 1.6% and a lower V_{oc} of 0.76 V, possibly due to its up-lying HOMO level.

BT-containing poly(2,7-carbazole) **P7** possessed an E_g of 1.88 eV and a HOMO level of -5.5 eV.[24] A PVC device showed J_{sc} of 6.92 mA/cm^2, V_{oc} of 0.89 V, and FF of 63% under illumination at 90 mW/cm^2, giving a high PCE of 3.6%. The FET hole mobility of the polymer was 1×10^{-3} cm^2 V^{-1} s^{-1}. Recently, a UCSB group reported an improved PCE of 6% by using this **P7** polymer in combination with PC$_{70}$BM in the presence of a TiOx cathode interlayer,[25] suggesting a bright future for poly(2,7-carbazole)s.[26]

Boudreault et al. prepared BT-containing poly(2,7-dibenzosilole) **P8** with M_n = 15 000 and M_w = 20 000.[27] It was found that **P7** and **P8** possessed comparable E_g's despite the lower-lying HOMO and LUMO levels of **P8**. A PVC device with a configuration of ITO/PEDOT−PSS/(**P8**:PCBM = 1:4)/Al, displayed a J_{sc} of 2.80 mA/cm^2, V_{oc} of 0.97 V, and FF of 55% under illumination at 90 mW/cm^2, giving a PCE of 1.6%. Independent work by Wang et al. almost simultaneously reported **P8** with much higher molecular weights (M_n = 79 000 and M_w = 330 000), which provided much better photovoltaic performance of 5.4% PCE, from the same device configuration but with a different component ratio (**P8**:PCBM = 1:2).[17] The FET hole mobility for **P8**, measured under ambient conditions without any encapsulation, reached $\sim 1 \times 10^{-3}$ cm^2 V^{-1} s^{-1}.

P9 derived from dithienopyrrole and dithienyl-BT possessed a very low E_g of 1.46 eV and a HOMO level of -5.0 eV.[28] A **P9**-based PVC device showed a good PCE of 2.18% but with a low V_{oc} of 0.52 V.

Rigid coplanar fused aromatic rings would enhance intermolecular $\pi-\pi$ stacking and improve charge transport of conjugated polymers. Coplanar indolo[2,3-*b*]carbazole was incorporated in **P10**.[29] A **P10**-based PVC device showed a high PCE of 3.6%. Random copolymerized **P11** and **P12** comprised coplanar thiophene−benzene−thiophene units.[30] The E_g of **P11** was 1.7 eV, slightly lower than the 1.76 eV of **P12**. The FET hole mobilities for **P11** and **P12** were 3.4×10^{-3} and 7.0×10^{-4} cm^2 V^{-1} s^{-1}, respectively. With an active layer of **P11**:PC$_{70}$BM = 1:3, PVC devices showed typical PCE as high as 4.3%.[30] IPCE showed spectral response between 350 and 750 nm, with a maximum value of 55% at 470 nm. **P12** displayed a slightly lower PCE of 3.9%.

Compared with **P1**−**P12**, **P13** had a simple D−A resonant structure.[31] **P13** possessed a wide absorption band (λ_{max}(abs) at the near-IR position of around 750 nm) and low E_g of 1.4 eV. The HOMO and LUMO levels of **P13** were -5.3 and -3.57 eV respectively. With an active layer of **P13**:PC$_{70}$BM = 1:1, BHJ PVC devices showed a PCE of 3.16%, higher than the PCE of 2.67% for the PCBM acceptor.[31] The wide absorption band and high hole mobility of 2×10^{-2} cm^2 V^{-1} s^{-1} of **P13** suggested a wide scope for device optimizations. When 1,8-octanedithiol was introduced as an additive to the active layer, **P13**-based PVCs with **P13**:PC$_{70}$BM = 1:2−3 displayed repeatable high PCEs of 5.5%.[32] More possible additives were tried, and it was found that 1,8-dihalo-octanes were also excellent, giving high PCEs of 5.12%.[33] No indication of crystallization was found from the active layer before or after the addition of the 1,8-octanedithiol.[32] The enhanced PCE was attributed to increases of mobile-carrier-generation efficiency and mobile-

CHART 3. Chemical Structures of Thiophene-Based Polymers **P16–P22**
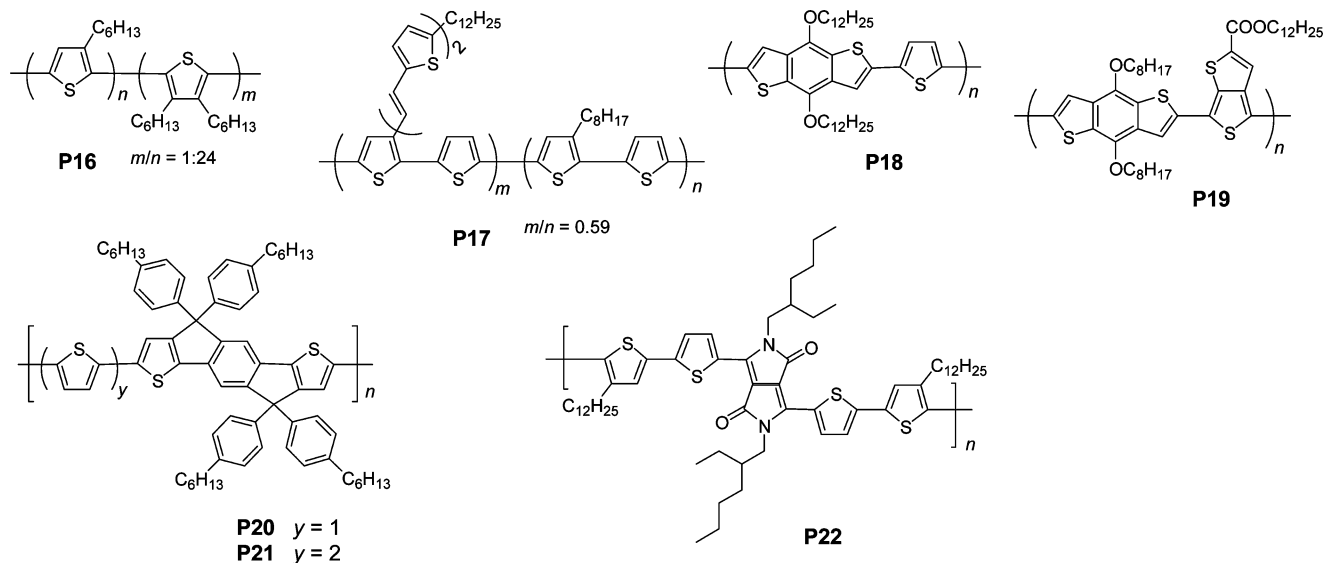
carrier lifetime. For the P3HT/PCBM system, a significant increase of P3HT crystallinity was found when devices were processed in the presence of trace oleic acid.[34]

A dithienosilole–BT alternating copolymer, **P14**, had structural similarity to **P13**.[35] The E_g of **P14** was 1.45 eV, slightly higher than that of **P13**. Polymer **P14** showed FET hole mobility of 3×10^{-3} cm^2 V^{-1} s^{-1}. With an active layer of **P14**: PC$_{70}$BM = 1:1, PVC devices showed an outstanding PCE of 5.1%. Within a broad response range covering 350–800 nm, average IPCE was about 43%, with a maximum value of 47% at 420 nm.

Baek et al. synthesized platinum metallopolyynes **P15** with a rigid-rod skeleton.[36] **P15** possessed a low E_g of 1.81 eV and FET hole mobility of 8.9×10^{-3} cm^2 V^{-1} s^{-1}, suitable for PVC application. With an active layer of **P15**:PC$_{70}$BM = 1:4, PVC devices showed an average PCE of 3.73%.

3. Thiophene-Based Polymers

Thiophene is a very important and popular heterocycle to construct semiconducting polymer donors for high-efficiency BHJ PVCs. However, some close analogues of P3HT such as poly(3-octylthiophene), poly(3-dodecylthiophene), and poly(3-decyloxythiophene) showed much lower photovoltaic performances than P3HT.[23] In order to achieve wider solar spectral response or better photovoltaic performance than P3HT, researchers have tried different structures for novel thiophene-based polymers, and the notable examples (**P16–P22**) are shown in Chart 3.

P16, introducing a small amount of 3,4-dihexylthiophene unit into P3HT, reduced regioregularity to 91% from >96% for the P3HT.[37] Thermal annealing of **P16**-based PVC devices

showed higher thermal stability than P3HT–PCBM devices for long-term performance. **P17**, by attachment of conjugated side chains to the polythiophene backbone, showed an increase of absorbance in the short-wavelength region (<500 nm) and lower E_g over P3HT.[38] **P17** displayed a good PCE of 3.18%, while under the same experimental conditions, P3HT only gave a PCE of 2.41% (Table 2).

Some fused coplanar heterocycles have been utilized for modification of polythiophenes. Hou et al. synthesized eight benzo[1,2-b:4,5-b′]dithiophene (BDT)-based low band gap polymers and a BDT–thiophene copolymer, **P18**, with E_g of 2.06 eV was the only product showing PCE over 1%.[39] BDT–thienothiophene copolymer **P19** with a lower E_g of ~1.62 eV showed largely improved PCE of 5.3% (5.6% after the spectral mismatch correction) for devices with an active layer of **P19**:PC$_{70}$BM = 1:1.2.[40] The high photovoltaic performances of **P19** were realized without special treatment like thermal annealing for high-efficiency P3HT–PCBM devices. The hole mobility of **P19** was ~4.5 × 10^{-4} cm^2 V^{-1} s^{-1}. Alternating copolymers **P20** and **P21** with the coplanar thiophene–benzene–thiophene unit possessed comparable E_g's of ~2.1 eV.[41] The FET hole mobilities for **P20** and **P21** were 8.3 × 10^{-4} and 3.0 × 10^{-3} cm^2 V^{-1} s^{-1}, respectively. **P20** displayed a PCE of 3.3%, higher than that of **P21**. For **P22**, diketo-pyrrolo-pyrrole was introduced in the backbone of polythiophene, which reduces band gap to 1.4 eV.[42] The polymer was soluble fully in chloroform but partially in *o*-dichlorobenzene. Using a mixture of the two solvents to dissolve **P22** and PC$_{70}$BM realized the best PVC performance of PCE = 4%.[42]

TABLE 2. Absorption Peak (λ_{max}(abs)), Optical Band Gap (E_g), and Energy Levels of **P16**–**P27** and PVC Device Performance from **P16**–**P27**/PCBM Blends

polymer	M_n (KDa) (M_w/M_n)	λ_{max}(abs) for solution (film) (nm)	E_g (eV)	electrochemical HOMO (LUMO) (eV)	donor/ PCBM ratio (w/w)	J_{sc}[b] (mA/cm^2) @ P_{in}[c] = 100 (mW/cm^2)	V_{oc}[d] (V)	FF[e] (%)	PCE (%)	ref
P16	22 (1.5)	a	a	a	1:1	9.77	0.61	62.0	3.73	37
P17	50 (1.6)	a (~500)	1.82	−4.93 (−2.96)	1:1	10.3	0.72	43.0	3.18	38
P18	47 (1.8)	a (511)	2.06	−5.05 (−2.69)	1:1[f]	3.78	0.75	56.0	1.60	39
P19	18 (1.25)	682 (690)	1.62	−4.90 (−3.20)	1:1.2[g]	15.0	0.56	63.3	5.30	40
P20	22 (2.2)	a (510)	2.08	−5.10 (−3.02)	1:3[h]	7.60	0.80	54.0	3.30	41
P21	16 (1.9)	a (508)	2.11	−5.18 (−3.07)	1:3[i]	7.00	0.79	49.0	2.70	41
P22	20 (3.35)	650 (660)	1.40	−5.10 (−3.40)	1:2[j]	11.3	0.61	58.0	4.00	42
P23	40 (2.25)	a (660)	a	−5.00 (−3.40)	1:3	8.88	0.59	42.0	2.20	43
P24	26 (35.4)	a	a	a	1:4	3.90	0.64	58.0	1.40	44
P25	20 (1.5)	628 (650)	1.57	−5.22 (−3.30)	1:1	10.7	0.67	33.0	2.37	45
P26	5.6 (4.8)	605 (694)	1.57	−5.29 (−3.36)	1:2	4.45	0.70	43.0	1.36	45
P27	52 (3.08)	a	1.20	a	1:4	3.10	0.56	58.0	1.10	46

[a] No data supplied. [b] Short-circuit current. [c] Incident radiation flux. [d] Open-circuit voltage. [e] Fill factor. [f] **P18**/PC$_{70}$BM. [g] **P19**/PC$_{70}$BM. [h] **P20**/PC$_{70}$BM. [i] **P21**/PC$_{70}$BM. [j] **P22**/PC$_{70}$BM.

CHART 4. Chemical Structures of Thieno[3,4-*b*]pyrazine-Containing Polymers **P23**–**P27**
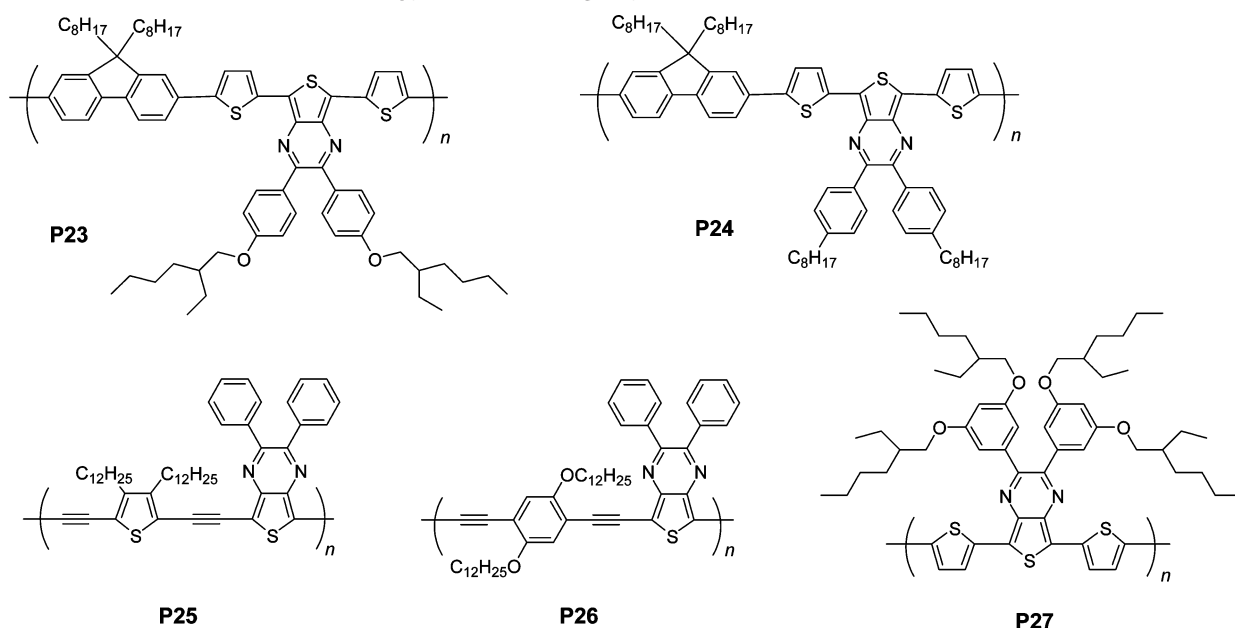

4. Thienopyrazine-Containing Polymers

Thieno[3,4-*b*]pyrazine (TP) is a narrow E_g heterocycle, which is useful in constructions of low E_g gap polymers. Alternating copolymer **P23** (Chart 4) derived from fluorene and 5,7-bis(thien-2-yl)thieno[3,4-*b*]pyrazine possessed HOMO and LUMO levels of −5.0 and −3.4 eV respectively, giving an electrochemical band gap of 1.6 eV (Table 2).[43] BHJ active layers with different **P23**:PCBM ratios and different thickness were investigated. A representative active layer (140 nm) of **P23**:PCBM = 1:3 showed the best PVC performance (PCE of 2.2%).[43] **P24**, an analogue of **P23**, had a very high polydispersity index of 35.4, and a **P24**-based device showed a lower PCE of 1.4%.[44] **P25** and **P26**, TP-incorporated poly-(arylene ethynylenes), had identical E_g's of 1.57 eV.[45] A **P25**-based device showed a higher PCE of 2.37%. TP-containing polymer **P27** had a much lower E_g of 1.2 eV, which showed wide spectral response from the UV throughout the visible region into the near infrared.[46] A PCE of 1.1% was realized for a **P27**-based device.

5. Quinoxaline-Containing Polymers

Quinoxaline is an n-type building block in semiconducting materials, and the electron-deficient *N*-heterocycle has been utilized to construct some donor polymers with typical D–A structure (Chart 5). Alternating copolymer **P28** derived from fluorene and 5,8-dithienylquinoxaline possessed an E_g of 1.94 eV and a very low-lying HOMO of −6.3 eV (Table 3).[47] **P28**-based PVC devices displayed high PCE's of 3.7%. **P29**, a close

CHART 5. Chemical Structures of Quinoxaline-Containing Polymers **P28**−**P33**

P28

P29

P30

P31

P32

P33
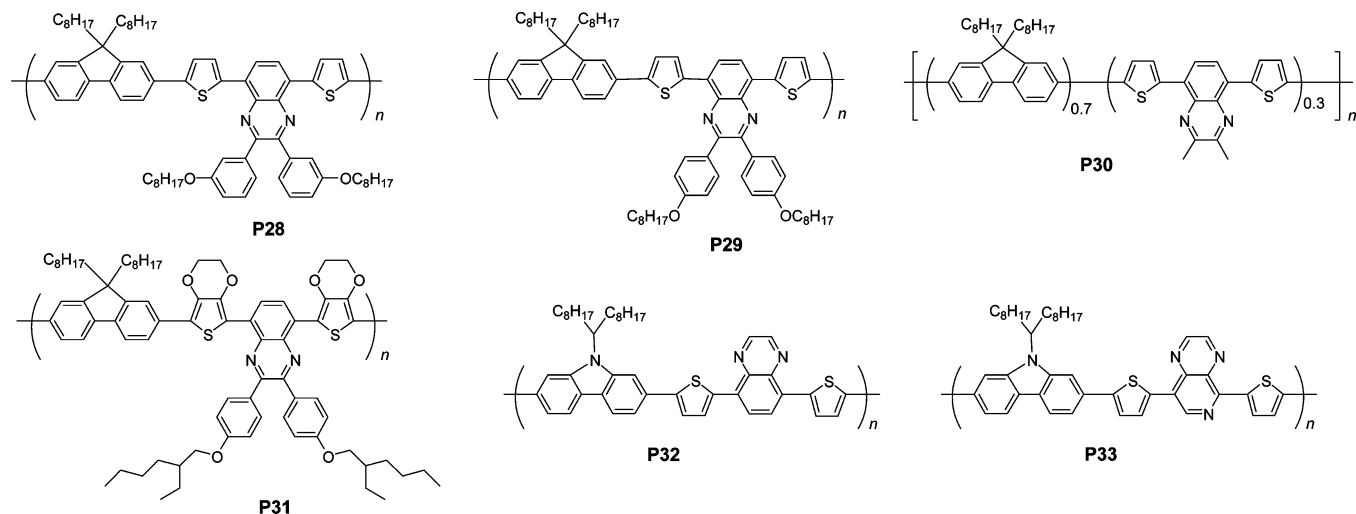
TABLE 3. Absorption Peak (λ_{max}(abs)), Optical Band Gap (E_g), and Energy Levels of **P28**−**P39** and PVC Device Performance from **P28**−**P39**/PCBM Blends

polymer	M_n (KDa) (M_w/M_n)	λ_{max}(abs) for solution (film) (nm)	E_g (eV)	electrochemical HOMO (LUMO) (eV)	donor/ PCBM ratio ($w{:}w$)	$J_{sc}^{\ b}$ (mA/cm^2) @ $P_{in}^{\ c}$ = 100 (mW/cm^2)	$V_{oc}^{\ d}$ (V)	FF^e (%)	PCE (%)	reference
P28	19 (2.1)	a (542)	1.94	−6.30 (−3.60)	1:3	6.00	1.00	63.0	3.70	47
P29	64 (1.6)	530 (540)	a	a	1:4	4.27	0.90	70.0	2.70	48
P30	47 (2.2)	a (503)	2.14	−5.43 (−3.28)	1:3	2.66	0.90	49.4	1.18	49
P31	15 (2.2)	a (555)	1.90	−5.60 (−3.40)	1:4	3.70	0.66	44.0	1.10	44
P32	9 (1.5)	a	2.02	−5.46 (−3.42)	1:4	3.00	0.95	56.0	1.80	50
P33	11 (1.7)	a	1.89	−5.52 (−3.67)	1:4	2.60	0.90	44.0	1.10	50
P34	32 (1.4)	510 (520)	2.08	−5.71 (−3.60)	1:4	8.67	0.65	35.8	2.01	52
P35	8 (1.5)	524 (a^d)	1.98	−5.09 (a)	1:4	3.27	0.70	44.4	1.10	53
P36	11 (1.5)	527 (a)	1.95	−5.20 (a)	1:4	4.57	0.75	48.6	1.67	53
P37	39 (1.7)	526 (535)	1.98	a	1:4	6.14	0.75	44.7	1.97	54
P38	55 (3.4)	526 (530)	2.00	a	1:4	4.68	0.75	44.5	1.51	54
P39	35 (2.4)	528 (532)	1.99	−5.13 (a)	1:4	4.55	0.75	39.0	1.33	54

^{a} No data supplied. ^{b} Short-circuit current. ^{c} Incident radiation flux. ^{d} Open-circuit voltage. ^{e} Fill factor.

analogue of **P28**, was utilized in an active layer of **P29**:PCBM = 1:4.[48] The PVC device showed a good PCE of 2.7% with high FF of 70%. A random quinoxaline-containing polyfluorene **P30** with 30% 5,8-dithienylquinoxaline had a slightly larger E_g of 2.14 eV, and a **P30**-based device showed a lower PCE of 1.18%.[49] **P31** comprising electron-donating 3,4-(ethylenedioxy)thiophene showed an E_g of 1.9 eV.[44] A **P31**-based device displayed a PCE of 1.1% with a low V_{oc} of 0.66 V.
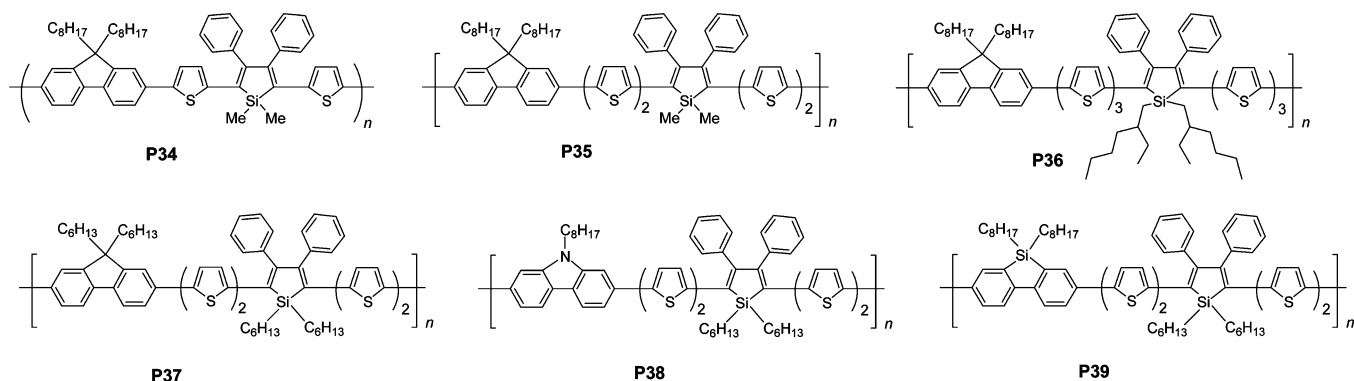
Alternating copolymer **P32**, derived from 2,7-carbazole and 5,8-dithienylquinoxaline, possessed an E_g of 2.02 eV.[50] The polymer displayed a FET hole mobility of 3 × 10^{-4} cm^2 V^{-1} s^{-1}. A **P32**-based device showed a PCE of 1.8%. Structural variation was also studied with pyrido[3,4-*b*]pyrazine to replace the quinoxaline, which generated poly(2,7-carbazole) analogue **P33** with a decreased E_g of 1.89 eV.[50] A **P33**-based

device showed a lower PCE of 1.1%. A lower hole mobility of 2 × 10^{-5} cm^2 V^{-1} s^{-1} for **P33** may be responsible for the falling of PCE.

The most notable feature of the quinoxaline-containing polymers **P28**−**P33**, except **P31**, is the high V_{oc} of 0.9−1.0 V for the resulting PVC devices (Table 3).

6. Substituted Silole-Containing Polymers

Siloles, or silacyclopentadienes, are a group of conjugated five-membered silacyclics.[51] Silole−BT copolymers **P8** and **P14**, where *coplanar siloles* (dibenzosilole and dithienosilole) were used as donor units in the D−A type of polymers, showed outstanding photovoltaic performances[18,35] and had been described in the section 2. Here we focus on non-D−A-type copolymers **P34**−**P39** derived from narrow band gap *substituted siloles* and wide band gap moieties (Chart 6).

CHART 6. Chemical Structures of Substituted Silole-Containing Polymers **P34**−**P39**

Alternating copolymer **P34** derived from fluorene and 2,5-dithienylsilole showed an E_g of 2.08 eV (Table 3).[52] The measured FET hole mobility of **P34** was 4.5×10^{-5} cm^2 V^{-1} s^{-1}. A **P34**-based PVC device showed a PCE of 2.01% with a V_{oc} of 0.65 V. More thiophene units were attached, as shown in **P35** and **P36**, which decreased the E_g's of **P35** and **P36** to 1.98 and 1.95 eV, respectively.[53] However, PVC devices of **P35** and **P36** did not show higher PCE over **P34**, despite the good tendencies of V_{oc} and FF.

Alternating polymers **P37**−**P39** with different wide band gap units (2,7-fluorene, 2,7-carbazole, and 2,7-dibenzosilole) were synthesized for a comparison study.[54] **P37**−**P39** had comparable E_g's of 1.99 eV. PVC devices of the polymers showed identical V_{oc} of 0.75 V. **P37**, a silole-containing polyfluorene, displayed the highest PVC performance (PCE = 1.97%).

7. Summary and Outlook

Polymers **P1**−**P39** with PCEs over 1%, as already described in this Account, contributed the majority of promising candidates for PVC applications. Further statistical analysis of the data listed in Tables 1−3 may give some guidance for further structure design and evaluation of polymer donor materials.

The PCE has linear relationship with V_{oc} according to the formula PCE = (FF × J_{sc} × V_{oc})/P_{in}.[7] Brabec et al. indicated that the V_{oc} of a polymer donor−acceptor BHJ cell is related directly to the energy difference between the HOMO level of the donor and the LUMO level of the acceptor.[55] Thus a low-lying HOMO of a donor would help to achieve a higher V_{oc}. A statistical summary of the V_{oc}−HOMO relationship of **P1**−**P39** is shown in Figure 1. Two arbitrary lines, a horizontal line at V_{oc} of 0.8 V and a vertical line at HOMO of −5.4 eV, were inserted to form a cross line, from which four zones were divided. It is well-known that PPV derivatives normally have V_{oc}'s of ∼0.8 V. Only two high probability zones, zone-11 and

zone-14, can be found from Figure 1. Comparison of zone-11 with zone-12 demonstrates that a polymer with a HOMO below −5.4 eV tends to have a higher possibility to realize V_{oc} > 0.8 V, while the comparison of zone-13 with zone-14 may imply that a polymer with HOMO above −5.4 eV would have less probability to show V_{oc} > 0.8 V. Significant scattering from linear correlation of V_{oc} with HOMO levels indicates that factors other than difference between donor HOMO and acceptor LUMO levels may play important role in some systems.

Extending the absorption edge or decreasing the band gap of a polymer donor to match solar terrestrial radiation is a main concern for use of a low band gap donor polymer. Figure 2 summarizes the PCE−E_g relationship of **P1**−**P39**, and four zones were divided similarly. A horizontal line at a PCE of 3% is arbitrarily assigned as the boundary of high and low efficiency, and a vertical line is arbitrarily chosen at 1.97 eV, close to the E_g of P3HT. Except almost no data falling into zone-23, data in the three other zones have almost equal probability. This fact indicates that a low band gap of a polymer is a necessary condition for high PCE (no high PCE for zone-23) but is not sufficient for a high-efficiency PVC (equal probability falling to zones 21 and 22).
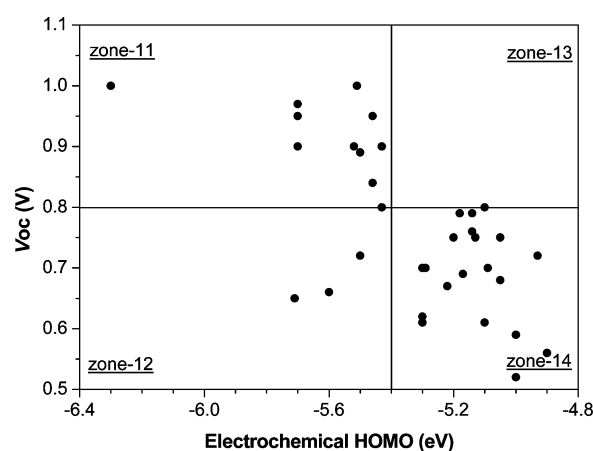

FIGURE 1. Statistical summary of open-circuit voltage vs. electrochemical HOMO of **P1**−**P39** (data from Tables 1−3).
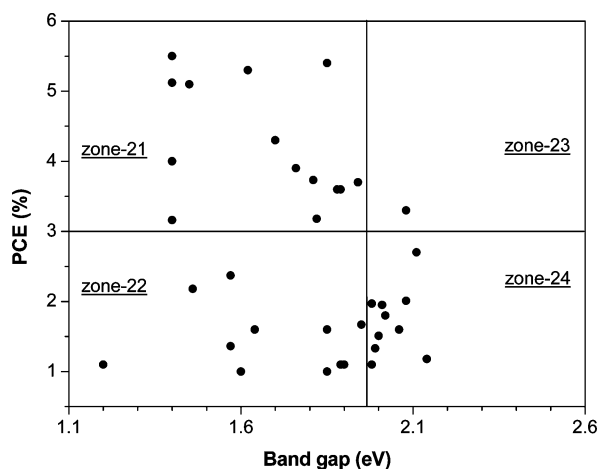
FIGURE 2. Statistical summary of power conversion efficiency vs. optical band gap of **P1**−**P39** (data from Tables 1−3).
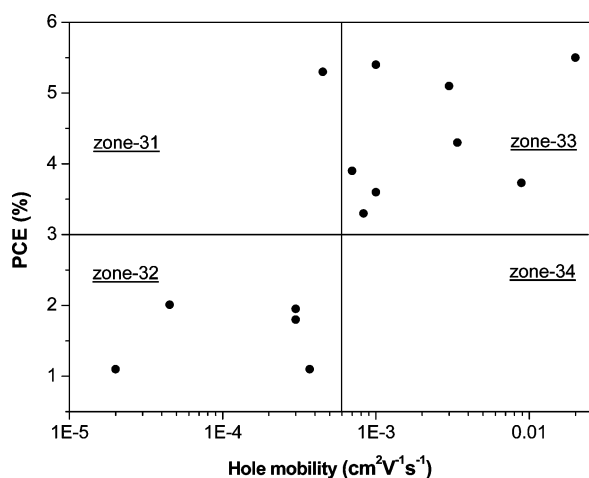

FIGURE 3. Statistical summary of power conversion efficiency vs. hole mobility.

Another basic requirement for a polymer donor is high hole mobility. Figure 3 summarizes the PCE−hole mobility relationship of a small portion of polymers among **P1**−**P39** for which mobility data are available. A vertical line is arbitrarily chosen at 6×10^{-4} cm^2 V^{-1} s^{-1}. Data in zone-32 and zone-33 clearly indicate that high mobility is absolutely necessary to reach high PCE.

Device and morphology optimizations have been extensively demonstrated to be important for PCE improvement in the case of P3HT-based PVCs. Recent progress in high PCE devices with donors of new structures other than P3HT indicates the importance of chemical optimizations of polymer donors, such as structure design (energy level, absorption band or band gap, charge carrier transport, etc.), polymerization (molecular weight and distribution), and purification. The endeavors have boosted PCEs of BHJ PVCs up to 5−6%,

which would encourage further efforts toward a next target of efficiency in excess of 10%.

BIOGRAPHICAL INFORMATION

Junwu Chen received his B.S. degree in 1989 and his Ph.D. degree in polymer materials from South China University of Technology (SCUT) in 1998. After postdoctoral research with Prof. B. Z. Tang at HKUST, he held an associate professor position in 2002 and a full professor position in 2007 at Institute of Polymer Optoelectronic Materials & Devices, SCUT. His research interests focus on synthesis of optoelectronic materials, their photophysical properties, and their optoelectronic device applications.

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FOOTNOTES

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