New Conjugated Copolymers Based on Benzo[1,2-b; 3,4-b′]dithiophene and Derivatives of Benzo[g]quinoxaline for Bulk Heterojunction Solar Cells

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ABSTRACT: A series of new low-band gap copolymers based on dioctyloxybenzo[1,2-b;3,4-b′] dithiophene and bis(2-thienyl)-2,3-diphenylbenzo[g]quinoxaline monomers have been synthesized via a Stille reaction. The effect of different functional groups attached to bis(2-thienyl)-2,3-diphenylbenzo[g]quinoxaline was investigated and compared with their optical, electrochemical, hole mobility, and photovoltaic properties. Polymer solar cell (PSC) devices of the copolymers were fabricated with a configuration of ITO/ PEDOT: PSS/copolymers: PCBM (1:4 wt ratio)/Ca/Al. The best performance of the PSC device was obtained by using PbttpmobQ as the active layer. A power conversion efficiency of 1.42% with an open-circuit voltage of 0.8 V, a short-circuit current (JSC) of 5.73 mA cm^{-2}, and a fill factor of 30.9% was achieved under the illumination of AM 1.5, 100 mW cm^{-2}. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 662–670, 2011

KEYWORDS: benzodithiophene; benzoquinoxaline; conjugated polymers; copolymerization; monomer; polymer; solar cell; synthesis

INTRODUCTION

In recent years, polymer solar cells (PSCs) have attracted great attention as a new generation of renewable energy sources due to flexibility, low cost, light weight, and easy manufacturing.[1–4] The bulk heterojunction solar cells that are composed of an electron-donating conjugated polymer blended with an electron acceptor have played a major role in reaching high efficiencies.[5–7] At present, the most widely investigated PSCs are based on blends of regioregular poly(3-hexylthiophene) (P3HT) with 6.6-phenyl C_{61}-butyric acid methyl ester ($PC_{61}BM$), which have achieved a power conversion efficiency (PCE) of 4 to 6%.[8–10] However, the PCE of a $P3HT/PC_{61}BM$ blended system is limiting, because its absorption wavelength is less than 650 nm. To improve device performance, many researches have developed conjugated polymers with low-band gap, high mobility, and broader absorption of the solar spectrum.[11–18]

Internal charge transfer (ICT) from an electron donor (D) to electron acceptor (A) has been used to synthesize low-band gap conjugated polymers.[19,20] Several new D–A polymers were developed, which exhibited good performance. Conjugated copolymers containing 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione were applied to PSCs, and a high PCE of 4.45% was achieved.[21] Biniek et al.[22] reported [3,2-b]thienothiophene-*alt*-benzothiadiazole copolymer for photovoltaic applications with PCE up to 5.2%.

In this work, we developed a series of copolymers based on dioctyloxybenzo [1,2-b;3,4-b′]dithiophene and bis(2-thienyl)-2,3-diphenylbenzo[g]quinoxaline. Benzo[1,2-b;3,4-b′]dithiophene exhibits a large planar conjugated structure, and its copolymers have a high hole mobility.[23] Bis(2-thienyl)-2,3-bis-(4-phenyl)-benzo[g]quinoxaline is a monomer with a D–A molecular structure, and can be used to lower the band gap of copolymers. We will discuss the properties of the copolymers with different electron-withdrawing and electron-donating functional groups.

EXPERIMENTAL

Materials

8-Dihydrobenzo[1,2-b:4,5-b′]dithiophen-4,8-dione (**1**) was prepared according to the published method.[24] Trimethyltin chloride, and 2-(tributylstannyl)-thiophene (**8**) were obtained from Aldrich Chemicals. 1-Bromooctane, bromine, 2,3-diaminonaphthalene (**4**), 4,4′-dimethoxybenzil (**6a**), benzil (**6b**), 4,4′-difluorobenzil (**6c**), tetrakis(triphenylphosphine) palladium [Pd(PPh$_3$)$_4$], N-bromosuccinimide (NBS), and bis(triphenylphosphine)palladium(II) dichloride [PdCl$_2$(PPh$_3$)$_2$] were purchased from Acros Organics. Tetrabutylammonium bromide (TBAB) was obtained from TCI. *n*-Butyllithium was obtained from Strem Chemicals. Toluene, dichlorobenzene, and N,N-dimethylformamide (DMF) were obtained from TEDIA. All reagents were used as received.

Measurements and Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Brucker Advance 600 spectrometer, and the deuterated CDCl$_3$, and DMSO were used as solvents, and the chemical shifts were reported in ppm. The molecular weights and distributions of the polymers were obtained by using a Waters GPC 2414 in

tetrahydrofuran (THF) via a calibration curve of polystyrene standards. Thermal stability was analyzed using a TA instrument thermogravimetric analyzer (TGA) Q500 at a heating rate of 10 °C min^{-1} under nitrogen. The glass transition temperature (T_g) was determined on a Perkin Elmer Instruments Model 4000 differential scanning calorimeter (DSC) at a heating rate of 10 °C min^{-1} under nitrogen. UV–vis absorption spectra were recorded on a Hitachi U-2001 spectrophotometer. The voltage–current was controlled by a Keithley 2400 power source. Cyclic voltammetry (CV) was carried out on a potentiostat/galvanostat Autolab PGSTAT30 with a platinum electrode at a scan rate of 50 mV s^{-1} against an Ag/AgCl reference electrode with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The films of the copolymer/PC$_{71}$BM were placed on a 200 mesh copper grid, and examined with a JEOL JEM-1200EX TEM using an acceleration voltage of 200 KV. Hole mobility was investigated by fitting dark J–V curves to the space-charge-limited current (SCLC) model[25] with a device structure of ITO/PEDOT:PSS/copolymers:PC$_{61}$BM (1:4 wt ratio)/Au, where the SCLC is described by

$$J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer, μ is the hole mobility, V is the voltage drop across the device, and L is the thickness of the active layer.

Monomer Synthesis

4,8-Dioctyloxybenzo[1,2-b;3,4-b′]dithiophene (2)[23]

The synthetic route of the monomers is shown in Scheme 1. Compound (**1**) (2.2 g, 10 mmol) and zinc powder were suspended in 25 mL of water, and, then, 6 g of NaOH was added into the mixture under nitrogen. The mixture was heated to reflux and stirred for 1 h. During the reaction, the color of the mixture changed from yellow to red, and then to orange. Subsequently, 1-bromooctane (5.8 g, 30 mmol) and a catalytic amount of TBAB were added into the mixture, and the reaction solution was refluxed for 12 h. The reaction mixture was poured into cold water and extracted by diethyl ether three times. The organic layer was dried over anhydrous MgSO$_4$, and then the solvent was removed. The crude product was recrystallized from alcohol to obtain compound (2). The yield was 67%.

^{1}H NMR (600 MHz, CDCl$_3$): 7.48 (d, 2H), 7.36 (d, 2H), 4.30 (t, 4H), 1.89 (m, 4H), 1.55 (m, 4H), 1.41~1.29 (m, 16H), 0.90 (t, 6H).

2,6-Bis(trimethyltin)-4,8-dioctyloxybenzo[1,2-b;3,4-b′]dithiophene (3)[23]

Compound 2 (2.68 g, 6 mmol) and 100 mL of THF were added into a flask under an inert atmosphere. n-Butyllithium (13.2 mmol, 1.6 M in n-hexane) was added dropwise into the solution at room temperature, and after being stirred for 1 h at room temperature, a great deal of white solid precipitate appeared in the flask. Then, 14 mmol of trimethyltin chloride (14 mL, 1 M in n-hexane) was added in one portion, and the reactant turned clear rapidly. The cooling bath was

removed, and the reaction was stirred at ambient temperature for 2 h. Then, it was poured into 200 mL of cool water and extracted by ether three times. The organic layer was washed with water two times, and then dried by anhydrous MgSO$_4$. After removing the solvent under vacuum, the residue was recrystallized from ethyl alcohol three times. The yield was 62%.

^{1}H NMR (600 MHz, CDCl$_3$): 7.52 (s, 2H), 4.30 (t, 4H), 1.89 (m, 4H), 1.59 (m, 4H), 1.42~1.31 (m, 16H), 0.90 (t, 6H), 0.45 (s, 18H). ELEM. ANAL. (%) calcd: C, 49.76; H, 7.05; Found: C, 50.11; H, 7.20; MS (FAB): m/z 772 (M+) (calcd. 772.3).

1,4-Dibromonaphthalene-2,3-diamine (5)

Compound (**4**) (1 g, 6.32 mmol) was dissolved in 35 mL of glacial acetic acid. Bromine (0.8 mL, 14.5 mmol) in 30 mL of glacial acetic acid was added slowly, and the mixture was stirred for 2 h at room temperature. The precipitate was filtered and washed with aqueous K$_2$CO$_3$ solution and water. The yield was 85%.

^{1}H NMR (600 MHz, DMSO): 7.79 (d, 2H), 7.26 (d, 2H), 5.65 (s, 4H).

5,10-Dibromo-2,3-bis-(4-methoxyphenyl)benzo[g]quinoxaline (7a)

A mixture of compound (**5**) (0.954 g, 3 mmol), compound (**6a**) (0.81 g, 3 mmol), and ethanol (30 mL) was refluxed under nitrogen for 12 h. The precipitate was collected by filtration, washed with ethanol, and then vacuum dried. The yield was 65%.

^{1}H NMR (600 MHz, DMSO): 8.56 (d, 2H), 7.82 (d, 2H), 7.61 (d, 4H), 7.01 (d, 4H), 3.82 (s, 6H).

5,10-Dibromo-2,3-diphenylbenzo[g]quinoxaline (7b)

The synthetic route of compound (**7b**) was similar to compound (**7a**). The difference was that the compound (**6a**) was replaced by compound (**6b**). The yield was 68%.

^{1}H NMR (600 MHz, DMSO): 8.62 (d, 2H), 7.88 (d, 2H), 7.62 (d, 4H), 7.48 (t, 2H), 7.43 (t, 4H).

5,10-Dibromo-2,3-bis-(4-fluorophenyl)benzo[g]quinoxaline (7c)

The synthetic route of compound (**7c**) was similar to compound (**7a**). The difference was that the compound (**6a**) was replaced by compound (**6c**). The yield was 64%.

^{1}H NMR (600 MHz, DMSO): 8.26 (d, 2H), 7.88 (d, 2H), 7.68 (d, 4H), 7.30 (d, 4H).

5,10-Di-2-thienyl-2,3-bis-(4-methoxyphenyl)benzo[g]quinoxaline (9a)

Compound (**7a**) (1.1 g, 2 mmol) and compound (**8**) (1.8 g, 4.8 mmol) were dissolved in 70 mL of DMF, and PdCl$_2$(PPh$_3$)$_2$ was added into the solution. The reaction mixture was heated to 120 °C for 48 h under nitrogen atmosphere. After removing the solvent under reduced pressure, the crude product was washed with methanol three times. The yield was 56%.
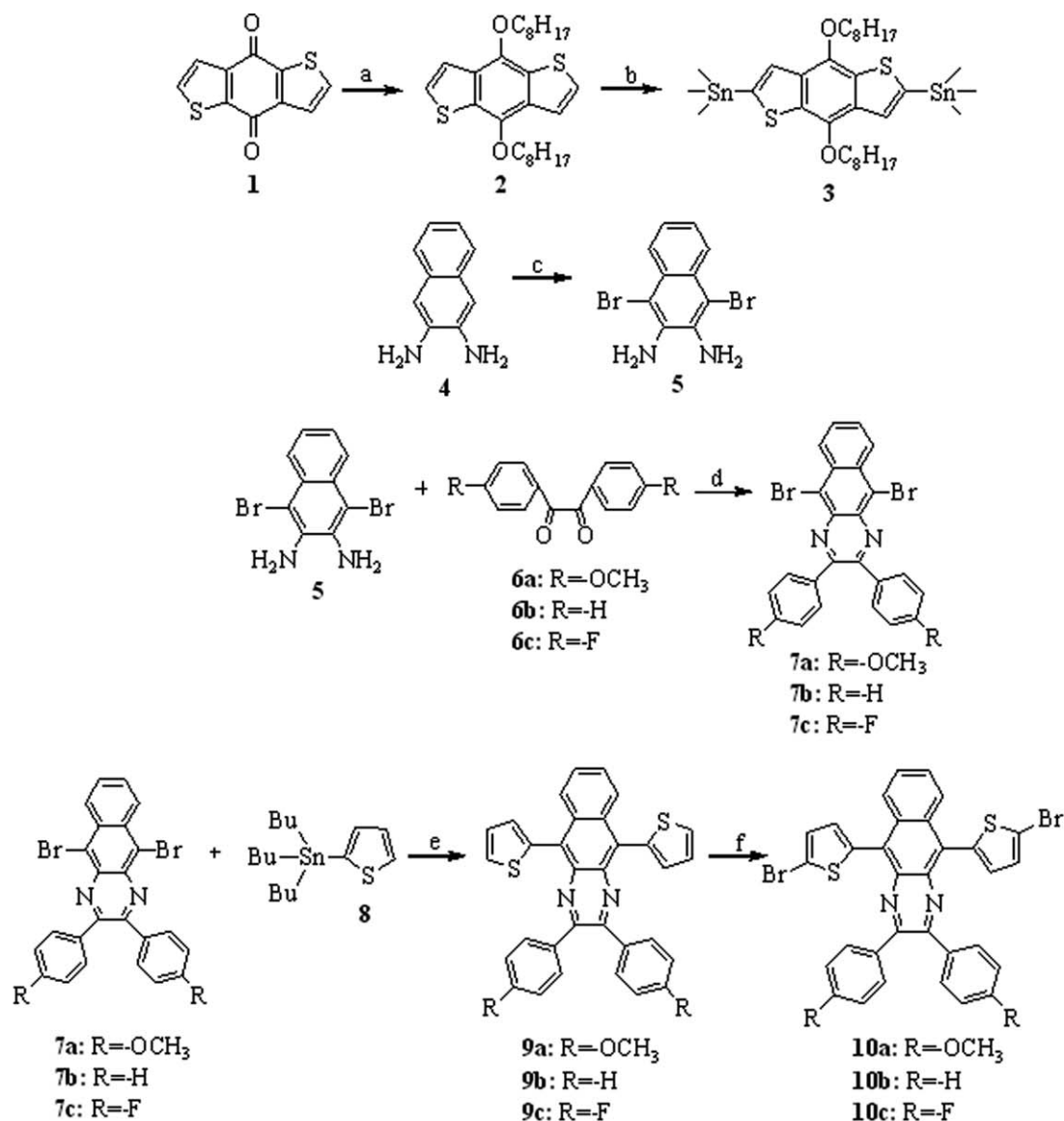
Reagents and conditions: (a) Zn, NaOH, H$_2$O, reflux, 1h; then 1-bromooctane, TBAB, reflux 12h; (b) n-butyllithium, room temperature, 1h; then trimethyltin chloride, room temperature, 2h; (c) bromine, room temperature, 2h; (d) ethanol, reflux; (e) PdCl$_2$(PPh$_3$)$_2$, DMF, 120 °C, 48h; (f) NBS, DMF, room temperature, overnight.

SCHEME 1 Synthesis of monomers.

^{1}H NMR (600 MHz, DMSO): 8.22 (d, 2H), 7.94 (d, 2H), 7.63 (d, 2H) 7.47 (d, 4H), 7.41 (d, 2H), 7.36 (t, 2H), 6.92 (d, 4H), 3.77 (s, 6H).

5,10-Di-2-thienyl-2,3-diphenylbenzo[g]quinoxaline (9b)

The synthetic route of compound (**9b**) was similar to compound (**9a**). The difference was that the compound (**7a**) was replaced by compound (**7b**). The yield was 59%.

^{1}H NMR (600 MHz, DMSO): 8.23 (t, 2H), 7.93 (d, 2H), 7.65 (t, 2H), 7.48 (d, 4H), 7.42 (d, 2H), 7.39–7.32 (m, 8H).

5,10-Di-2-thienyl-2,3-bis-(4-fluorophenyl)benzo[g]quinoxaline (9c)

The synthetic route of compound (**9c**) was similar to compound (**9a**). The difference was that the compound (**7a**) was replaced by compound (**7c**). The yield was 58%.

^{1}H NMR (600 MHz, DMSO): 8.22 (d, 2H), 7.93 (d, 2H), 7.65 (t, 2H), 7.52 (d, 4H), 7.41 (d, 2H), 7.35 (d, 2H), 7.20 (d, 4H).

5,10-Bis(5-bromo-2-thienyl)-2,3-bis-(4-methoxyphenyl) benzo[g] quinoxaline (10a)

Compound (9a) (0.834 g, 1.5 mmol) was dissolved in 40 mL of DMF under nitrogen atmosphere, and NBS (0.54 g, 3 mmol) was added in one portion. The mixture was stirred overnight at room temperature. After removing the solvent under reduced pressure, the solid was washed with methanol several times. Finally, the precipitate was recrystallized from a mixture of dichloromethane and methanol at room temperature. The yield was 60%.

^{1}H NMR (600 MHz, DMSO): 8.24 (d, 2H), 7.65 (d, 2H), 7.46 (m, 6H), 7.25 (d, 2H), 6.94 (d, 4H), 3.79 (s, 6H). ELEM. ANAL. (%) calcd.: C, 57.15; H, 3.10; N, 3.92; Found: C, 56.49; H, 3.02; N, 4.00. MS (FAB): m/z 714 (M+) (calcd. 714.5).

5,10-Bis(5-bromo-2-thienyl)-2,3-diphenylbenzo[g] quinoxaline (10b)

The synthetic route of compound (10b) was similar to compound (10a). The difference was that the compound (9a) was replaced by compound (9b). The yield was 55%.

^{1}H NMR (600 MHz, DMSO): 8.25 (d, 2H), 7.66 (d, 2H), 7.47–7.44 (m, 6H), 7.39 (d, 2H), 7.34 (t, 4H), 7.25 (d, 2H). ELEM. ANAL. (%) calcd.: C, 58.73; H, 2.77; N, 4.28 Found: C, 57.98; H, 2.74; N, 4.31. MS (FAB): m/z 654 (M+) (calcd. 654.4).

5,10-Bis(5-bromo-2-thienyl)-2,3-bis-(4-fluorophenyl) benzo[g] quinoxaline (10c)

The synthetic route of compound (10c) was similar to compound (10a). The difference was that the compound (9a) was replaced by compound (9c). The yield was 62%.

^{1}H NMR (600 MHz, DMSO): 8.25 (d, 2H), 7.69 (d, 2H), 7.51 (d, 4H), 7.45 (d, 2H), 7.22–7.27 (m, 6H). ELEM. ANAL. (%) calcd.: C, 55.67; H, 2.34; N, 4.06 Found: C, 54.96; H, 2.31; N, 3.97. MS (FAB): m/z 690 (M+) (calcd. 690.4).

General Procedure of Copolymer Synthesis

The synthetic route is shown in Scheme 2. The synthesis of copolymer PbtmobQ is taken as an example. Compound (3) (0.386 g, 0.5 mmol) and compound (10a) (0.357 g, 0.45 mmol) were dissolved in toluene (8 mL) and DMF (2 mL), and purged under a nitrogen atmosphere for 30 min. Subsequently, Pd(PPh$_3$)$_4$ (25 mg) was added into the flask, and the reaction mixture was stirred at 120 °C for 24 h. After being cooled to room temperature, the reaction mixture was poured into methanol. The collected solid was re-dissolved in chloroform and filtered to remove the metal catalyst. Then, the copolymer solution was concentrated and precipitated in a large amount of methanol. The solid was further purified by a Soxhlet extractor for 24 h using acetone as a solvent, and dried in a vacuum oven at 80 °C overnight. The yield was 60%.

^{1}H NMR (600 MHz, CDCl$_3$): 8.50 (s), 7.72–7.67 (broad), 7.58 (broad), 7.40 (m), 6.88 (broad), 4.41–4.34 (broad), 3.81 (s), 1.99 (broad), 1.66–1.26 (broad), 0.82–0.91 (broad). ^{13}C NMR (600 MHz, CDCl$_3$): 160.69, 151.95, 144.08, 139.76, 137.51, 135.34, 132.98, 131.7, 131.43, 129.86, 127.18, 126.86, 125.01, 116.05, 113.71, 74.10, 55.29, 31.86, 30.64, 29.35, 26.15, 22.67, 14.07.

PbtbQ

Monomer feed ratio: compound (3) (0.386 g, 0.5 mmol) and compound (10b) (0.327 g, 0.5 mmol). The yield was 72%.

^{1}H NMR (600 MHz, CDCl$_3$): 8.54 (s), 7.74–7.58 (broad), 7.44–7.35 (broad), 4.34–4.41 (broad), 1.99 (broad), 1.66–1.30 (broad), 0.84–0.91 (broad). ^{13}C NMR (600 MHz, CDCl$_3$): 152.45, 144.10, 139.95, 138.80, 137.22, 135.33, 133.22, 132.69, 131.80, 130.34, 129.82, 128.18, 127.12, 125.01, 116.14, 74.10, 31.87, 30.65, 29.36, 26.15, 22.68, 14.09.

PbtFbQ

Monomer feed ratio: compound (3) (0.386 g, 0.5 mmol) and compound (10c) (0.345 g, 0.5 mmol). The yield was 63%.

^{1}H NMR (600 MHz, CDCl$_3$): 8.53 (s), 7.70–7.58 (broad), 7.50–7.40 (broad), 7.05 (broad), 4.38–4.34 (broad), 1.97 (broad), 1.64–1.29 (broad), 0.91–0.84 (broad). ^{13}C NMR (600 MHz, CDCl$_3$): 164.38, 162.71, 151.10, 144.08, 140.01, 137.07, 136.81, 135.24, 134.68, 133.30, 132.66, 131.83, 130.31, 129.56, 128.99, 127.28, 126.56, 125.02, 116.19, 115.37, 74.06, 31.86, 30.62, 29.34, 26.13, 22.67, 14.07.

PbttpmobQ

Monomer feed ratio: compound (3) (0.386 g, 0.5 mmol), compound (10a) (0.179 g, 0.25 mmol), and compound (11) (0.061 g, 0.25 mmol). The yield was 68%.

^{1}H NMR (600 MHz, CDCl$_3$): 8.50 (s), 7.70–7.41 (broad), 6.87 (broad), 4.34 (broad), 3.82 (s), 1.96 (broad), 1.65–1.29 (broad), 0.92–0.83 (broad). ^{13}C NMR (600 MHz, CDCl$_3$): 160.68, 151.91, 144.08, 137.04, 136.05, 135.34, 132.95, 132.69, 132.39, 131.79, 129.58, 126.86, 125.02, 116.04, 113.70, 74.06, 55.28, 31.90, 30.64, 29.37, 26.15, 22.69, 14.17.

Fabrication and Characterization of Solar Cell Devices

Patterned indium tin oxide (ITO) slides were cleaned with detergent, deionized water, acetone, and 2-propanol in an ultrasonic bath and dried on a hot plate at 150 °C for 30 min, and then treated with UV-ozone for 30 min before use. A 50–60 nm layer of poly(styrene sulfonic acid)-doped poly(ethylene dioxythiophene) [PEDOT: PSS] (Baytron P VP AI 4083) was spin-coated on the ITO, and baked for 30 min at 150 °C. The copolymer blended with PCBM (1:4 by weight) solution in dichlorobenzene was spin coated on top of PEDOT: PSS, and dried on a hot plate. Finally, a thin layer of calcium (10 nm) was deposited by thermo-evaporation under a vacuum of 10^{-5} torr, and followed by a layer of Al (100 nm). The voltage–current characteristics were analyzed using a Keithley 2400 sourcemeter under one sun illumination of AM 1.5 (100 mW cm^{-2}) from a solar simulator (Model Class A 91160A, Newport-Oriel Instruments). The solar-simulator illumination intensity was measured using a standard monocrystalline silicon photovoltaic calibrated by

R=-OCH$_3$: **Pbtmob Q**

R=-H : **Pb tb Q**

R=-F : **PbtFb Q**

Pb ttp mob Q
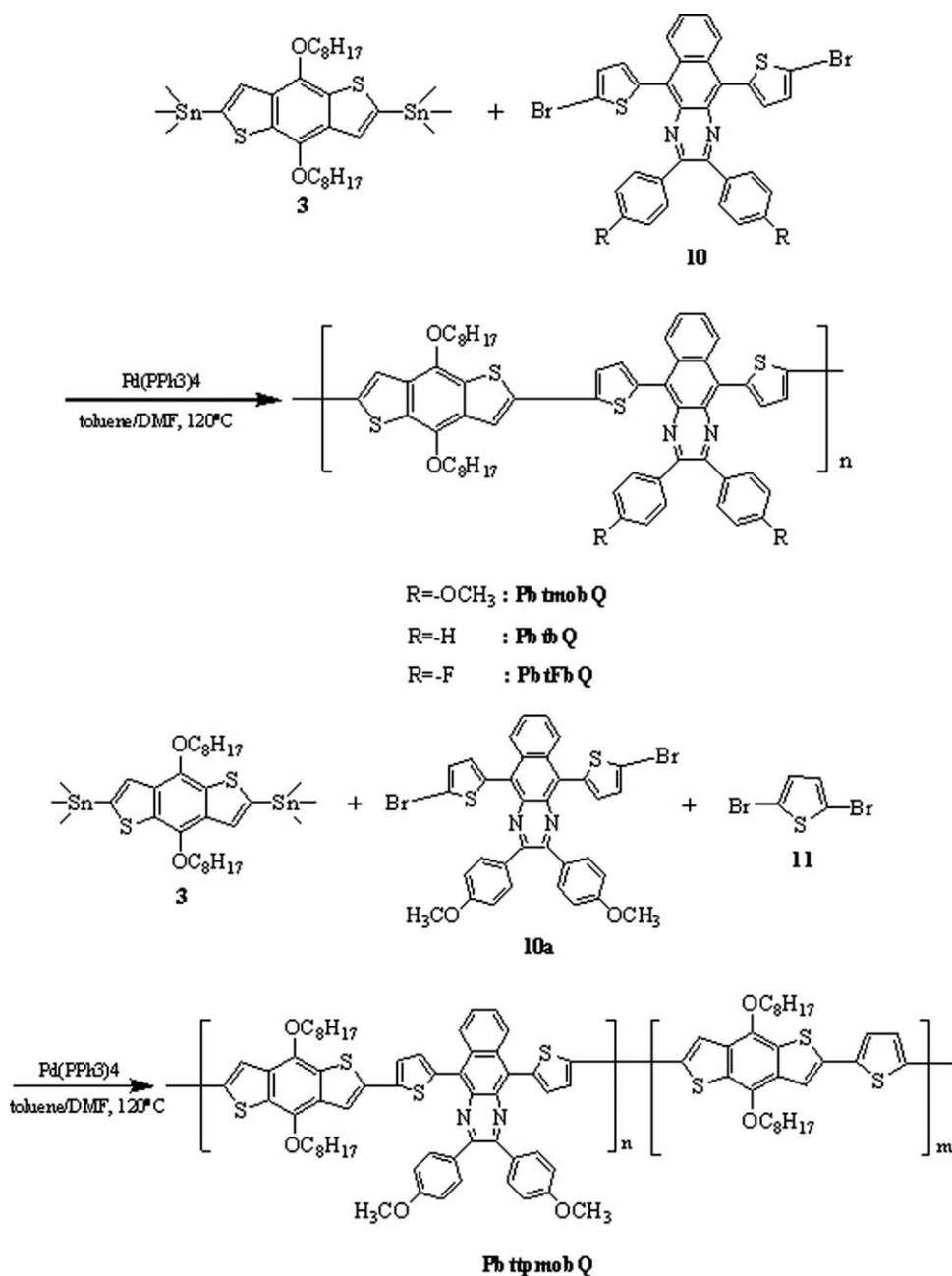
SCHEME 2 Synthesis of copolymers.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic route of the copolymers via palladium catalyzed Stille reaction[26,27] is shown in scheme 2. The colors of the resulting alternating copolymers are dark. The weight-average molecular weights (M_w), number-average molecular weights (M_n), and polydispersity index (PDI) of the copolymers were determined by gel permeation chromatography (GPC) against polystyrene standard in THF are listed in Table 1. The methoxy group in PbtmobQ and PbttpmobQ was introduced to increase the electron donating ability and solubility of the polymers. PbtmobQ and PbttpmobQ have higher molecular weights than PbtmobQ and PbttpmobQ, which could be due to their better solubility in the polymerization

TABLE 1 Polymerization Results and Thermal Properties of the Copolymers

Copolymer	M_n	M_w	PDI	T_d (°C)[a]
PbtmobQ	24,600	47,500	1.93	341
PbtbQ	12,600	25,900	2.05	337
PbtFbQ	12,000	22,800	1.90	334
PbttpmobQ	20,100	41,100	2.04	349

[a] Temperature of 5% weight loss measured by TGA in nitrogen.

the National Renewable Energy Laboratory. The device measurement was carried out in air at room temperature.
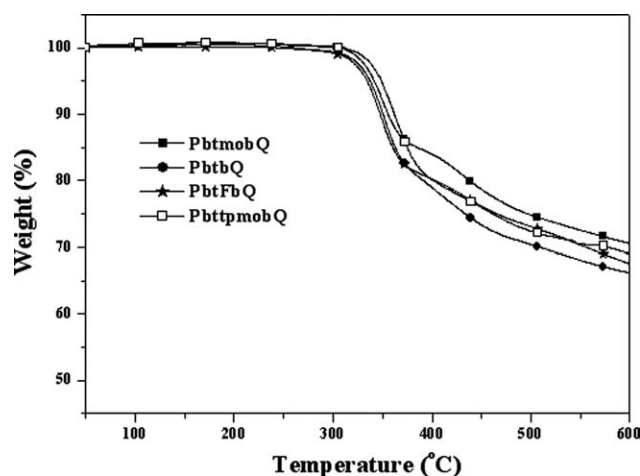
FIGURE 1 TGA curves of copolymers.

solvents. The thermal stability of the copolymers was investigated by TGA under a nitrogen atmosphere as shown in Figure 1. The thermal decomposition temperatures (T_{ds}, 5% weight loss) of PbtmobQ, PbtbQ, PbtFbQ, and PbttpmobQ are 341, 337, 334, and 349 °C. The result indicates that all copolymers have good thermal stability.
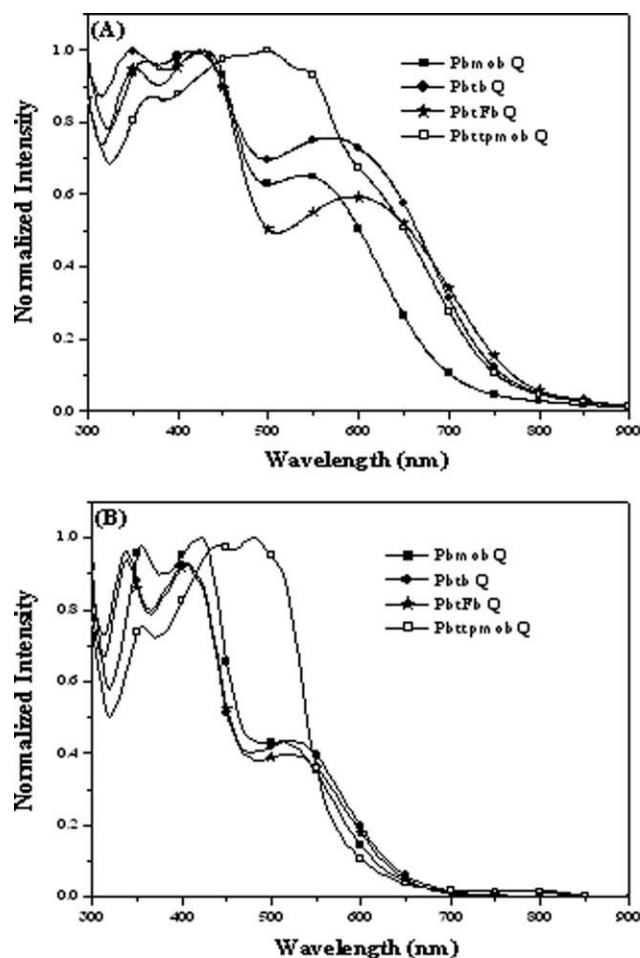

FIGURE 2 UV–vis spectra of copolymer in solid state (A) and in solution (B).

TABLE 2 Electrochemical Properties of Copolymers

Copolymer	E_{onset} (ox) (V)	E_{onset} (re) (V)	HOMO (eV)	LUMO (eV)	E_g (elec)[a] (eV)	E_g (opt)[b] (eV)
PbtmobQ	0.61	−0.92	−4.92	−3.39	1.53	1.78
PbtbQ	0.65	−0.86	−4.96	−3.45	1.51	1.65
PbtFbQ	0.70	−0.78	−5.01	−3.53	1.48	1.59
PbttpmobQ	0.79	−0.64	−5.1	−3.67	1.43	1.64

[a] Eg (elec) = −(HOMO − LUMO).
[b] Optical band gaps are estimated from the onset of absorption, Eg (opt) = 1240/λ_{onset}.

Optical Properties

The UV–vis absorption spectra of the copolymers as spin coated films on quartz and in dichlorobenzene are shown in Figure 2. PbtmobQ, PbtbQ, and PbtFbQ exhibited two absorption regions, which is a common phenomenon on donor–acceptor copolymers.[28] It can be observed that the absorption peaks of PbtFbQ show red shift in comparison with PbtmobQ and PbtbQ at long wavelength region (500~900 nm), due to the electron-withdraw effect of fluorine. The spectrum of PbttpmobQ shows broad and strong absorption peaks ranging from 300 to 800 nm because of copolymerization with three monomers. The absorption peaks of the
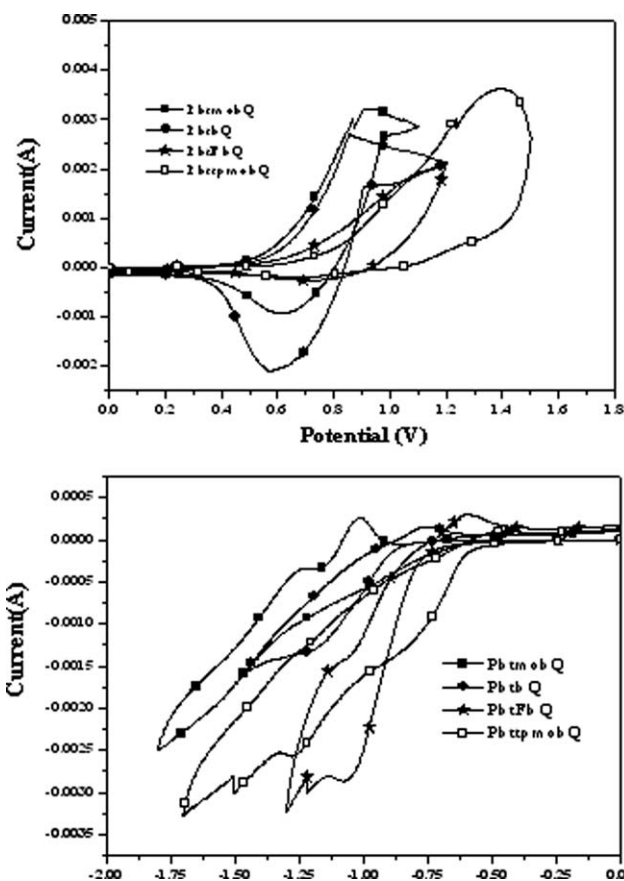

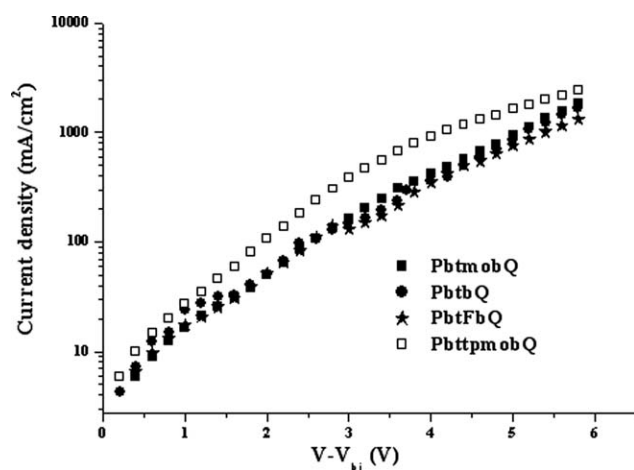FIGURE 3 Cyclic voltammograms of copolymers.

FIGURE 4 Dark J–V curves of the hole-only devices with copolymers:$PC_{61}BM$ (1:4 wt ratio)-blended films.

copolymer films [Fig. 2(A)] were similar to the spectra in solution [Fig. 2(B)] with red shifts. The higher absorption at long wavelength (450~700 nm) was attributed to the strong
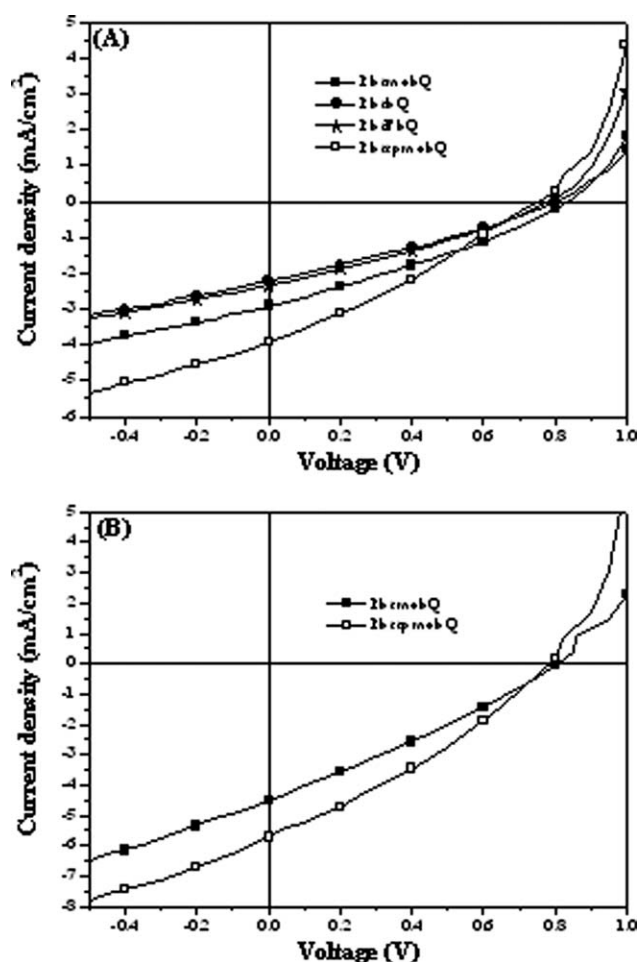

FIGURE 5 Current density–voltage characteristics of the PSCs based on copolymesr:$PC_{61}BM$ (A) and copolymers:$PC_{71}BM$ (B) under the illumination of AM 1.5, 100 mW cm^{-2}.

intermolecular interactions in the solid state. The optical band gaps (Eg^{opt}) of the copolymers (Table 2), derived from the absorption edge, range from 1.59 to 1.78 eV.

Electrochemical Properties

The redox behaviors of the copolymers were investigated by CV, and their cyclic voltammograms are showed in Figure 3. The highest occupied molecular orbital (HOMO) and the LUMO energy values of the copolymers are listed in Table 2. Comparing PbtmobQ, PbtbQ, and PbtFbQ, the introduction of the electron-withdrawing fluorine and electron-donating methoxy groups changed the energy levels of the copolymers slightly. Comparing PbttpmobQ and PbtmobQ, less electron-withdrawing benzoquinoxaline groups in the polymer backbone led to the lowering of the HOMO level.

Hole Mobility

Figure 4 shows the J–V curves of the devices with the copolymers:$PC_{61}BM$ (1:4 wt ratio) blended films. The hole mobilities of PbtmobQ, PbtbQ, PbtFbQ, and PbttpmobQ blends were 4.18×10^{-5}, 4.04×10^{-5}, 3.07×10^{-5}, and 8.05×10^{-5} cm^2 V^{-1} s^{-1}, respectively. PbttpmobQ exhibits the best hole mobility, because intermolecular packing may be enhanced when planar thiophene segments replaced large bis(2-thienyl)-2,3-bis-(4-phenyl)benzo[g]quinoxaline units in the copolymer backbone.

Photovoltaic Properties

The bulk heterojunction PSCs with configuration of ITO/ PEDOT: PSS/copolymers: PCBM (1:4 wt ratio)/Ca/Al were fabricated. Figure 5 shows the J–V curves of the devices. The open-circuit voltage (VOC), short-circuit current (JSC), fill factor (FF), and PCE are summarized in Table 3. The PCEs of $PC_{61}BM$ based devices are 0.73 (PbtmobQ), 0.53 (PbtbQ), 0.56 (PbtFbQ), and 0.87 (PbttpmobQ), respectively. As listed in Table 3, the VOC and FF of devices are close, but the Isc increases from 2.21 (PbtbQ) to 3.92 mA cm^{-2} (PbttpmobQ). The device with PbttpmobQ exhibits the highest value of Isc. This is because PbttpmobQ has a broader absorption spectrum, which can harvest more sunlight, and higher hole mobility. To improve PCE, $PC_{71}BM$ was used to replace $PC_{61}BM$. The PCEs of PbtmobQ and PbttpmobQ were achieved at 1.04 and 1.42%. The significantly higher Isc is due to the higher absorption of $PC_{71}BM$ in the visible region.[29]

TABLE 3 Photovoltaic Performances of the PSCs Based on the Copolymers

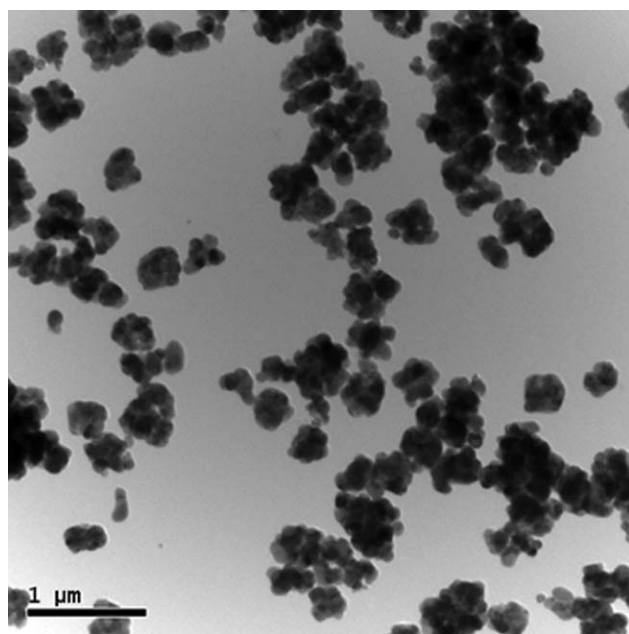| Copolymer/ $PC_{61}BM$ (1:4)	VOC (V)	Isc (mA cm^{-2})	FF (%)	PCE (%)
PbtmobQ	0.85	2.9	29.7	0.73
PbtbQ	0.8	2.21	30.1	0.53
PbtFbQ	0.8	2.34	29.8	0.56
PbttpmobQ	0.75	3.92	29.7	0.87
PbtmobQ[a]	0.8	4.50	28.9	1.04
PbttpmobQ[a]	0.8	5.73	30.9	1.42

[a] $PC_{71}BM$.

FIGURE 6 TEM image of PbttpmobQ:PC$_{71}$BM (1:4 wt ratio) film.

The dispersion state of the active layer is important to photovoltaic performance. Figure 6 shows the TEM bright-field image of the PbttpmobQ:PC$_{71}$BM (1:4 wt ratio)-blended film. A phase separation between the PC$_{71}$BM (dark areas) and polymer matrix can be observed. The agglomerations of PC$_{71}$BM are connected to each other and become pathways in the polymer films. The continuous pathways provide both charges to reach the respective electrodes for effective charge collection.[30,31] The PC$_{71}$BM domains exhibit a broad-size distribution (500~1500 nm), and the large scale of phase separation reduces the donor–acceptor interface for excitons to dissociate.[32,33]

CONCLUSIONS

In this article, we have developed four new low-band gap copolymers based on dioctyloxybenzo[1,2-b;3,4-b']dithiophene and bis(2-thienyl)-2,3-diphenylbenzo[g]quinoxaline. The band gaps of the copolymers are 1.78, 1.65, 1.59, and 1.64 eV, respectively. The energy levels of the copolymers were changed slightly by substituting different side chains of bis(2-thienyl)-2,3-diphenylbenzo[g]quinoxalines. The solar cell device based on PbttpmobQ:PC$_{71}$BM (1:4 wt ratio) exhibits the best PCE of 1.42% with a VOC of 0.8V, JSC of 5.73 mA cm^{-2}, and FF of 30.9% under the illumination of AM 1.5, 100 mW cm^{-2}. The results indicate that the four copolymers are promising candidates for PSCs.

REFERENCES AND NOTES

1 Padinger, F.; Rittberger, R. S.; Sariciftci, N. S. Adv Funct Mater 2003, 13, 85–88.

2 Coakley, K. M.; McGehee, M. D. Chem Mater 2004, 16, 4533–4542.

3 Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. Adv Funct Mater 2005, 15, 1617–1622.

4 Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dante, M.; Heeger, A. J. Science 2007, 317, 222–225.

5 Winder, C.; Sariciftci, N. S. J Mater Chem 2004, 14, 1077–1086.

6 Mihailetchi, V. D.; Koster, L. J. A.; Blom, P. W. M.; Melzer, C.; Boer, B. D.; Duren, J. K. J. V.; Janssen, R. A. J. Adv Funct Mater 2005, 15, 795–801.

7 Riedel, I.; Hauff, E. V.; Parisi, J.; Martin, N.; Giacalone, F.; Dyakonov, V. Adv Funct Mater 2005, 15, 1979–1987.

8 Reyes, M. R.; Kim, K.; Carroll, D. L. Appl Phys Lett 2005, 87, 083506.

9 Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. Nat Mater 2005, 4, 864–868.

10 Kim, K.; Liu, J.; Namboothiry, M. A. G.; Carroll, D. L. Appl Phys Lett 2007, 90, 163511.

11 Hou, J.; Tan, Z.; Yan, Y.; He, Y.; Yang, C.; Li, Y. J Am Chem Soc 2006, 128, 4911–4916.

12 Becerril, H. A.; Miyaki, N.; Tang, M. L.; Mondal, R.; Sun, Y. S.; Mayer, A. C.; Parmer, J. E.; McGehee, M. D.; Bao, Z. J Mater Chem 2009, 19, 591–593.

13 Liang, Y.; Wu, Y.; Feng, G.; Tsai, S. T.; Son, H. J.; Li, G.; Yu, L. J Am Chem Soc 2009, 131, 56–57.

14 Gedefaw, D.; Zhou, Y.; Hellström, S.; Lindgren, L.; Andersson, L. M.; Zhang, F.; Mammo, W.; Inganäs, O.; Andersson, M. R. J Mater Chem 2009, 19, 5359–5363.

15 Ahmed, E.; Kim, F. S.; Xin, H.; Jenekhe, S. A. Macromolecules 2009, 42, 8615–8618.

16 Song, S.; Jin, Y.; Park, S. H.; Cho, S.; Kim, I.; Lee, K.; Heeger, A. J.; Suh, H. J Mater Chem 2010, 20, 6517–6523.

17 Song, J.; Zhang, C.; Li, C.; Li, W.; Qin, R.; Li, B.; Liu, Z.; Bo, Z. J Polym Sci Part A: Polym Chem 2010, 48, 2571–2578.

18 Song, S.; Park, S. H.; Jin, Y.; Park, J.; Shim, J. Y.; Kim, I.; Lee, H.; Lee, K.; Suh, H. J Polym Sci Part A: Polym Chem 2010, 48, 4567–4573.

19 Zhang, Q. T.; Tour, J. M. J Am Chem Soc 1998, 120, 5355–5362.

20 Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletete, M.; Duricher, G.; Tao, Y.; Leclerc, M. J Am Chem Soc 2008, 130, 732–742.

21 Huo, L.; Hou, J.; Chen, H. Y.; Zhang, S.; Jiang, Y.; Chen, T. L.; Yang, Y. Macromolecules 2009, 42, 6564–6571.

22 Biniek, L.; Chochos, C. L.; Leclerc, N.; Hadziioannou, G.; Kallitsis, J. K.; Bechara, R.; Leveque, P.; Heiser, T. J Mater Chem 2009, 19, 4946–4951.

23 Hou, J.; Park, M. H.; Zhang, S.; Yao, Y.; Chen, L. M.; Li, J. H.; Yang, Y. Macromolecules 2008, 41, 6012–6018.

24 Sloocum, D. W.; Gierer, P. L. J Org Chem 1976, 41, 3668–3673.

25 Chang, Y. T.; Hsu, S. L.; Su, M. H.; Wei, K. H. Adv Mater 2009, 21, 2093–2097.

26 Liang, Y.; Feng, D.; Wu, Y.; Tsai, S. T.; Li, G.; Ray, C.; Yu, L. J Am Chem Soc 2009, 131, 7792–7799.

27 Hou, J.; Chen, T. L.; Zhang, S.; Huo, L.; Sista, S.; Yang, Y. Macromolecules 2009, 42, 9217–9219.

28 Wang, E.; Wang, M.; Wang, L.; Duan, C.; Zhang, J.; Cai, W.; He, C.; Wu, H.; Cao, Y. Macromolecules 2009, 42, 4410–4415.

29 Chen, C. P.; Chan, S. H.; Chao, T. C.; Ting, C.; Ko, B. T. J Am Chem Soc 2008, 130, 12828–12833.

30 Yang, X.; Duren, J. K. J. V.; Janssen, R. A. J.; Michels, M. A. J.; Loos, J. Macromolecules 2004, 37, 2151–2158.

31 Yang, X.; Loos, J.; Veenstra, S. C.; Verhees, W. J. H.; Wienk, M. M.; Kroon, J. M.; Michels, M. A.; Janssen, R. A. J. Nano Lett 2005, 5, 579–583.

32 Sivula, K.; Ball, Z. T.; Watanabe, N.; Frechet, M. J. Adv Mater 2006, 18, 206–210.

33 Günes, S.; Neugebauer, H.; Sariciftci, N. S. Chem Rev 2007, 107, 1324–1338.