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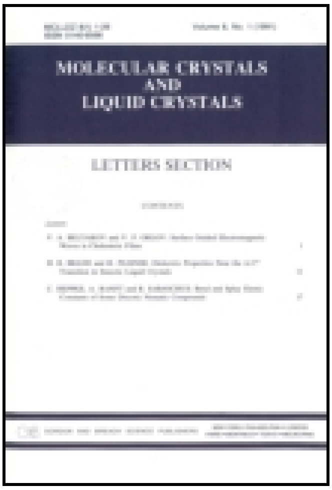

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Synthesis and Characterization of Benzodithiophene-Based Copolymers for Polymer Solar Cells

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Two novel thieno[3,4-b]pyrazine-based copolymers of the donor-acceptor type, poly[4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-alt-5,7-(2,3-bis-(4-octyloxy-phenyl)-thieno[3,4-b]pyrazine)] (P1) and poly[4,8-bis(5-((2-ethylhexylthiophene)-2-yl))benzo[1,2-b:4,5-b']dithiophene-alt-5,7-(2,3-bis-(4-octyloxy-phenyl)-thieno[3,4-b]pyrazine)] (P2), designed and synthesized by Stille polymerization for use in polymer solar cells. The synthesis, thermal stability, as well as the optical and photovoltaic properties of these polymers are systematically investigated. The polymers were thermally stable up to 290°C, and readily soluble in common organic solvent. Conventional polymer solar cells (PSCs) with the configuration ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al are fabricated. Under optimized conditions, the polymers display power conversion efficiencies (PCEs) for the PSCs in the range 0.28–1.46% under AM 1.5 illumination. Among the studied thienopyrazine-based copolymers, P2 displays a PCE of 1.46% with a short circuit current of 7.61 mA/cm^2, an open circuit voltage of 0.43 V, and a fill factor of 0.45 under AM 1.5 illumination.

Keywords conjugated polymers; polymer solar cells; thienopyrazine-based copolymers

Introduction

Over the last two decades, polymer solar cells based on blends of conjugated polymers and fullerene derivatives have attracted considerable attention because of their good processability, low cost fabrication, light weight, and flexibility [1–3]. To date, the power conversion efficiencies of PSCs have reached 7–8%, primarily due to the development of new conjugated polymers and better control over the nanoscale morphologies of the interpenetrating electron donor/acceptor networks [4]. Thus, enormous effort has been focused on improving the PCE of PSCs for future commercial applications. One of the main factors limiting the performance of PSCs is the mismatch of their absorption to the terrestrial solar

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spectrum [5]. The most successful approach to obtain low band gap structures uses a copolymerized donor-acceptor structure. Conjugated polymers that incorporate alternating donor and acceptor units provide significant decreases in the band gap due to the introduction of intramolecular charge transfer (ICT) structures [6, 7].

In this study, we report the use of thieno[3,4-b]pyrazine-based copolymers, poly[4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b’]dithiophene-alt-5,7-(2,3-bis-(4-octyloxy-phenyl)-thieno[3,4-b]pyrazine)] (P1) and poly[4,8-bis(5-((2-ethylhexylthiophene)-2-yl))benzo[1,2-b:4,5-b’]dithiophene-alt-5,7-(2,3-bis-(4-octyloxy-phenyl)-thieno[3,4-b]pyrazine)] (P2), which have the same polymer backbone but different side chains, in bulk heterojunction solar cells. The thieno[3,4-b]pyrazine derivatives were used as electron-deficient comonomers in the donor-acceptor system. We systematically investigated the synthesis, thermal stability, optical properties, and photovoltaic characteristics of the resulting polymers. Interestingly, two thieno[3,4-b]pyrazine-based copolymers show near infrared photovoltaic response in bulk heterojunction solar cells with PCBM as acceptor.

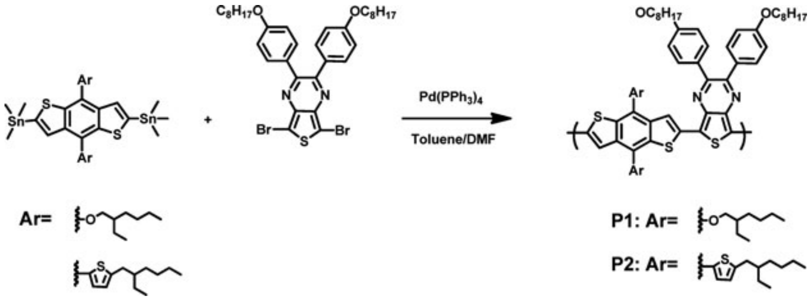
Experimental

The monomers, 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene [8], 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b’]dithiophene [9], and 5,7-dibromo-2,3-bis(4-(octyloxy)phenyl)thieno[3,4-b]pyrazine [10] were prepared with previously described methods.

UV-visible analysis was performed with a Lambda 20 (Perkin Elmer) diode array spectrophotometer. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC; Viscotek) equipped with TDA 302 detector and PL-gel (Varian) column, using chloroform as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10°C/min with a Dupont 9900 analyzer.

In this study, the devices were fabricated with the structure ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al. The procedure for cleaning the ITO surface included sonication and rinsing in deionized water, methanol, and acetone. The hole-transporting PEDOT:PSS layer was spin-coated onto each ITO anode from a solution purchased from H. C. Starck. Each polymer:$PC_{71}BM$ solution was then spin-coated onto the PEDOT:PSS layer. The polymer solution for spin-coating was prepared by dissolving the polymer (8 mg/mL) in chlorobenzene. Calcium and aluminum contacts were formed by vacuum deposition at pressures below 3×10^{-6} Torr, providing an active area of 0.09 cm^2. Solar cell efficiencies were characterized under simulated 100 mW/cm^2 AM 1.5G irradiation from a Xe arc lamp with an AM 1.5 global filter. Simulator irradiance was characterized using a calibrated spectrometer, and the illumination intensity was set using an NREL-certified silicon diode with an integrated KG1 optical filter. All device fabrication procedures and measurements were carried out in air at room temperature.

General procedure for the synthesis of polymers with the Stille reaction. Synthesis of poly[4,8-bis(5-((2-ethylhexylthiophene)-2-yl))benzo[1,2-b:4,5-b’]dithiophene-alt-5,7-(2,3-bis-(4-octyloxy-phenyl)-thieno[3,4-b]pyrazine)] (P2). This is presented in detail as a representative example. To 50 mL round bottom flask, 2,6-bis(trimethyltin)-4,8-bis (5-(2-ethylhexyl) thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (271 mg, 0.3 mmol) and 5,7-dibromo-2,3-bis(4-(octyloxy)phenyl)thieno[3,4-b]pyrazine (210mg, 0.3mmol) were mixed in 4 mL of toluene and 1 mL of DMF. After being purged with argon for 5 min, $Pd(PPh_3)_4$ (14 mg) was added as the catalyst, and the mixture was then purged with argon for 30 min. The reaction mixture was stirred at 105°C for 24 h. Then the reaction mixture



Scheme 1. Synthetic scheme for the copolymers.

was cooled to room temperature, and the polymer was precipitated by addition of 50 mL methanol, filtered and dried for 24 h at 40°C. Polymer was redissolved in chlorobenzene and precipitated in 50 mL methanol. The precipitate was then filtered and subjected to Soxhlet extraction with methanol, acetone, hexanes, and chloroform. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The dark green solid was dried under vacuum.

Poly[4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-alt-5,7-(2,3-bis-(4-octylloxy-phenyl)-thieno[3,4-b]pyrazine)] (P1) was synthesized with the procedure described for P2.

Results and Discussion

The synthetic routes for preparing the thienopyrazine-based copolymers are shown in Scheme 1. The synthesized copolymers are soluble in common organic solvent such as tetrahydrofuran (THF), chloroform, or toluene. The molecular weights were determined by using gel permeation chromatography (GPC) against polystyrene standards in a chloroform eluent and were found to be in the range of 10,000–12,000 with a polydispersity index of 2.0–2.1. As shown in Figure 1, the copolymers have good thermal stability up to ca. 290°C. The physical properties of the polymers are summarized in Table 1.

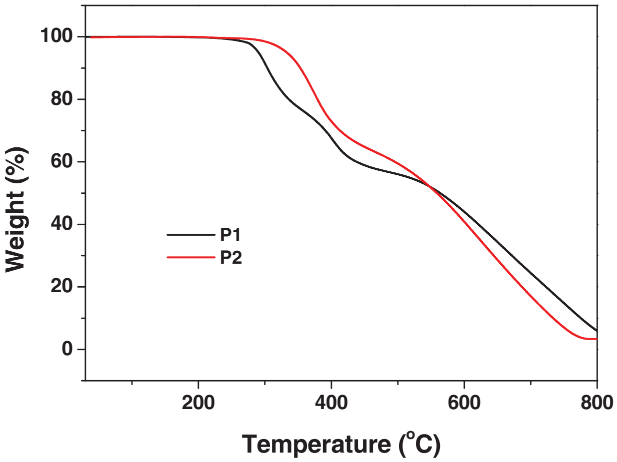


Figure 1. TGA traces for the copolymers.

Table 1. Physical and optical properties of the polymers

polymer	Mn[a]	PDI	Yield (%)	T_{5d} (°C)[b]	$\lambda^{abs,sol}$ (nm)[c]	$\lambda^{abs,film}$ (nm)[c]	E_g^{opt} (eV)[d]
P1	10,000	2.1	73	290	412,738,819	414, 851, 820	1.37
P2	12,000	2.0	70	330	354,437,755,840	356,440,764,844	1.34

[a] Number-average molecular weight were determined by using gel permeation chromatography (GPC) against polystyrene standards in chloroform eluent.

[b] Decomposition temperature determined by TGA in N_2 based on 5% weight loss.

[c] The UV-Vis absorption spectra of the polymers were measured in chloroform solution and thin film.

[d] The optical band gap was determined from the UV-Vis absorption onset in the solid state.

The UV-Vis absorption spectra of the polymers in chloroform solution and thin films are shown in Figure 2 and 3, respectively, and the corresponding absorption properties are summarized in Table 1. Both in solution and in the films, the polymers exhibited two distinct absorption bands: one at about 300–500 nm and the the other one in the range: 650–900 nm, which could be assigned to an intramolecular charge transfer (ICT) between the donor and the acceptor [11].

In comparison with the absorption spectrum of the P1 solution, the spectrum of the P2 solution showed a significantly red-shifted absorption band with a broad spectrum due to the extended $\pi-$conjugation length. The absorption maxima of the polymer films were slightly red-shifted relative to the corresponding maxima of the polymer solution. This indicated that chain packing among the polymers in the thin films was prevented due to the bulky side chains of the polymer backbone. The optical band gap obtained by extrapolating the absorption edges of the films increased in the order P2 (1.34 eV) < P1 (1.37 eV). This result can be ascribed to the extended conjugation of the alkylthienyl side chains for P2.

Bulk-heterojunction PSCs were fabricated with the structure ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al. The device fabrication process is described in detail in the

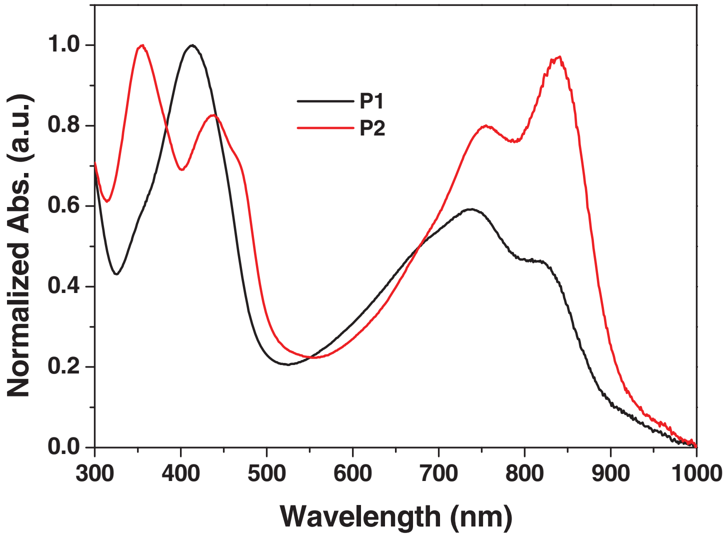


Figure 2. UV-Vis absorption spectra of the copolymers in chloroform solutions.

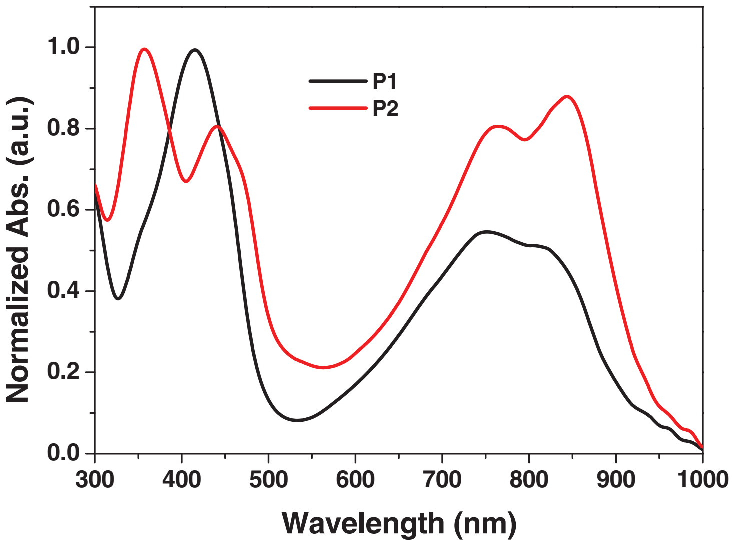


Figure 3. UV-Vis absorption spectra of thin films of the copolymers.

Experimental Section. The PSC performance was strongly affected by the processing parameters, such as the choice of solvent and blend ratio of the polymer and $PC_{71}BM$ [12]. Optimal fabrication conditions were obtained dissolving the polymer (8 mg/mL) in chlorobenzene solution at a 600 rpm spin-coating rate and a polymer :$PC_{71}BM$ ratio of 1:1.5 (w/w). The thicknesses of the layer were PEDOT:PSS (30 nm), active layer (80 nm), and Ca/Al (120 nm).

Figure 4 shows the current-voltage curves of the optimized devices based on blends of the thienopyrazine-based copolymers and fullerene. The output characteristics of the

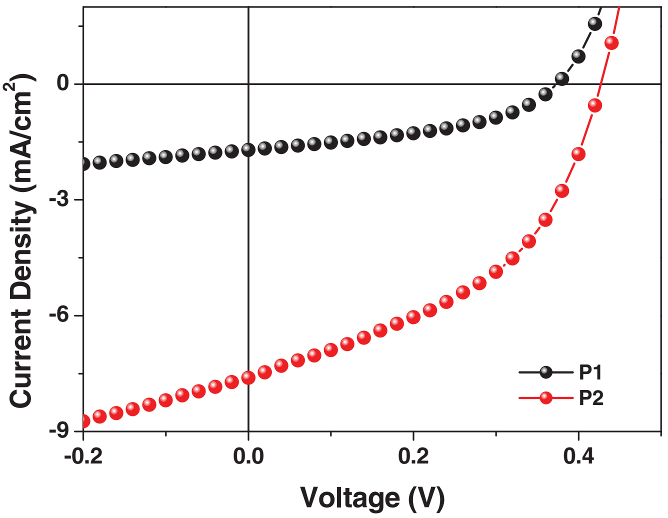


Figure 4. J-V characteristics of photovoltaic devices fabricated with P1:$PC_{71}BM$ (black) and P2:$PC_{71}BM$ (red) under AM 1.5G irradiation (100 mW/cm^2).

Table 2. PSC performances of the polymers

polymer	Voc [V]	Jsc [mA/cm^2]	FF	PCE (%)
P1	0.37	1.71	0.44	0.28
P2	0.43	7.61	0.45	1.46

resulting polymer-based devices are summarized in Table 2. Under optimized conditions, the polymers display power conversion efficiencies for the PSCs in the range 0.28–1.46% under AM 1.5 illumination. Among the studied thienopyrazine-based copolymers, P2, containing a alkylthienyl side chains, displays a PCE of 1.46% with a short circuit current of 7.61 mA/cm^2, an open circuit voltage of 0.43 V, and a fill factor of 0.45 under AM 1.5 illumination. These results are preliminary. Furthermore modifications to the polymer structure and/or the device structure are currently being tested in an effort to achieve even better performance.

Conclusion

We synthesized new conjugated thieno[3,4-b]pyrazine-based copolymers by Stille polymerization for use in polymer solar cells. Two low-band gap polymers, P1 and P2, show near infrared photovoltaic response in bulk heterojunction solar cells with PCBM as acceptor. Further modifications of the polymer structure and optimization of the device performance are in progress toward achieving even better performances.

Acknowledgments

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