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New Polymers for Optimizing Organic Photovoltaic Cell Performances

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Konarka Technologies Inc., Lowell, MA

The performance of an organic solar cell critically depends on the materials used in the active layer. Desirable characteristics of active layer materials include an intense optical absorption covering broad range of the solar spectrum to maximize photon capture, the ability to effectively separate charges upon photo-excitation, high charge mobility to allow efficient charge transport to the electrodes, and suitable HOMO and LUMO levels to ensure a high device voltage. In order to optimize these properties simultaneously, we have designed and synthesized conjugated polymers containing alternating electron-donating and electron-accepting units. Based on one of the low band gap polymers we designed and synthesized previously, poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-b:3,4-b′]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)], we carried out both side chain and main chain modifications in order to improve performance even further. By incorporating fluorene repeating units into the main chain, it is possible to adjust the absorption characteristics of the polymers while maintaining a desirable HOMO level and good charge carrier mobility. The solubility profile of the polymer can be adjusted by modifying the side chains, and soluble polymer with mobility as high as 7×10^{-2} cm^2/Vs is realized when a combination of 2-ethylhexy and hexyl groups are used as side chains. These polymers should be promising candidates for high performance solar cells according to a recently published model (3).

Keywords: photovoltaic cell; low band gap polymers; modified polydithiophenes; alkyl side chains; carrier mobility

1 Introduction

Polymer/fullerene based organic bulk heterojunction solar cell represents one of the most promising emerging technologies that can provide carbon-neutral energy by harnessing and converting the freely available and abundant solar radiation (1). The essential element of this type of device consists of a thin layer of organic material, e.g., a conducting polymer/soluble fullerene derivative blend, with a thickness in the range of 0.1–0.25 μm, enclosed between two conductive electrodes, one of which is transparent. Configurations as simple as this allow the extremely light-weight, flexible devices to be fabricated resulting in products that are low-cost and can be easily integrated into many applications and architectures. Immense research effort has been made by many laboratories in this area and significant improvements have been achieved in the past few years. Presently power conversion efficiency up to 5% has been realized (2). However, this efficiency needs to be significantly increased in order for the organic solar cells to be sufficiently competitive with the conventional silicon technologies and to be incorporated into wider range of applications. One of the most straightforward avenues toward improved the cell efficiency has been to employ polymers that possess absorption spectra covering a wide range of the solar spectrum so that larger portions of solar influx can be converted into electricity. However, several additional parameters are also required. It was found that the difference between the HOMO of the electron-donating polymer and the LUMO of the electron-accepting fullerene derivative determines the open circuit voltage (3). Thus, a sufficiently low HOMO of the polymer is essential for better performance. Also high charge carrier mobility is needed for high external quantum efficiency and a good fill factor. The absorption characteristics, the HOMO level, and the charge carrier mobility of the polymer are determining factors for power conversion efficiency.

Increasing the absorption coverage of the conjugated polymers requires the reduction of the energy gap between their lowest unoccupied orbital (LUMO) and highest occupied orbital (HOMO). One of the most effective ways of decreasing the band gap has been the incorporation of both electron-accepting and electron donating units in the main chain (4). Several low-band-gap polymers have been prepared using the electron deficient 2,1,3-benzothiadiazole

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as an acceptor (Figure 1). A conjugated polymer consisting of alternating electron-rich *N*-dodecyl-2,5-bis(2′-thienyl) pyrrole and electron-deficient 2,1,3-benzothiadiazole units (PTPTB) was found to have a bandgap of approximately 1.6 eV. Bulk heterojunction photovoltaic cells prepared from PTPTB and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) gave power conversion efficiencies up to 1% under AM1.5 illumination (5). An alternating polyfluorene copolymer, poly(2,7-(9,9-dioctyl-fluorene)-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)) (APFO-3, Figure 1), was synthesized by a Suzuki coupling protocol. This class of polymer has an absorption maximum around 545 nm. Solar cells prepared from a mixture of APFO-3 and PCBM has an open circuit voltage as high as 1.03 V and power conversion efficiency as high as 2.84% (6).

Thieno[3,4-b]pyrazine is another successful acceptor used in the preparation of low-band-gap polymers. A polymer consisting of thiophene-thieno[3,4-b]pyrazine-thiophene repeating units (Figure 2, PB3OTP) was found to have an optical band gap of 1.3 eV. A bulk heterojunction solar cell made of a mixture of this material and [6,6]-phenyl-C61-butyric acid methyl ester (C60-PCBM) had a maximum IPCE of 6% at a wavelength of about 660 nm (7). An alternating polyfluorene containing 2,3-diphenyl-5,7-di-thiophen-2-yl-thieno [3,4-b]pyrazine and 9,9-dioctyl-9H-fluorene (APFO Green2, Figure 2) (8) was found to have a band-gap of 1.55. Cells fabricated from APFO-Green2 and PCBM have photo response at a long wavelength of 850 nm and external quantum efficiency as high as 10% at 650 nm. A short-circuit current of 3.0 mA/cm^2, an open circuit voltage of 0.78 V, and power conversion efficiency of 0.9% were obtained. One of the drawbacks of this polymer was that it had poor solubility. By attaching 2-ethyl-hexyloxy groups to the phenyls on 5,7-di-thiophen-2-yl-thieno[3,4-b]pyrazine, APFO Green5, (9) a polymer with much better solubility and high molecular weight was obtained. APFO Green5 has a higher hole mobility than APFO Green2 (c.a. 8×10^{-4} cm^2/Vs vs. 8×10^{-6} cm^2/Vs with APFO Green2), and power conversion efficiency as high as 2.2% was obtained. By attaching multiple solublizing side chains to thienyl or phenyl groups on 2,3-diphenyl-5,7-dithiophen-2-yl-thieno[3,4-b]pyrazine, soluble low-band-gap polymers without fluorene units (PBEHTT and PTBEHT, Figure 2) have also been recently synthesized. Solar cells that have photoresponse up to 1 mm and power conversion efficiency up to 1.1% have been constructed with these materials (10).

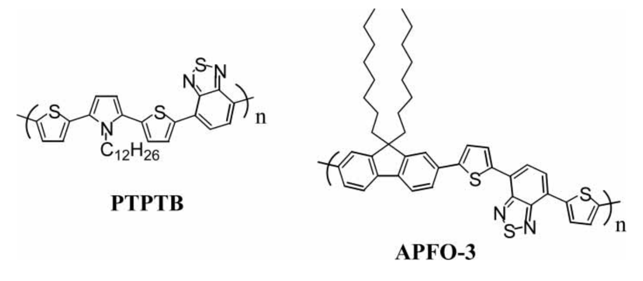


Fig. 1. Low-band-gap polymers with 2,1,3-benzothiadiazole electron-accepting units.

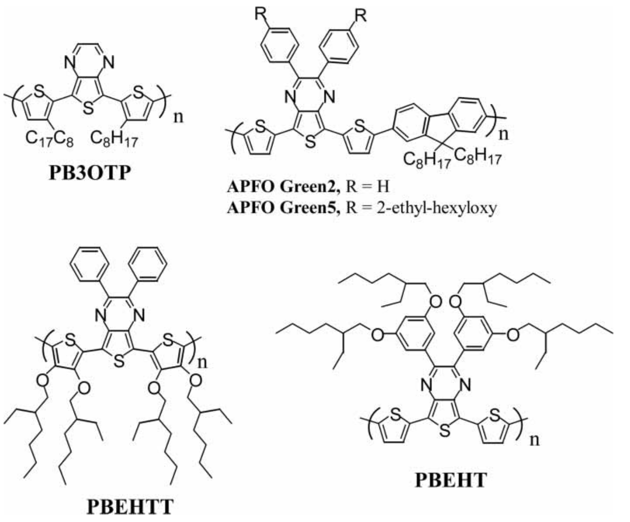


Fig. 2. Thieno[3,4-b]pyrazine-containing low-band-gap polymers.

6,7-Diphenyl-4,9-di-2-thienyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline provides another building block for low-band-gap polymers, such as APFO-Green1 (Figure 3). APFO-Green1 has an electrical band-gap of 1.3 eV, a HOMO of -5.3 eV and a LUMO of −4.0 eV. Due to its low LUMO level, which is very close to that of PCBM, a PCBM derivative with stronger electron affinity (and thus lower LUMO level), such as BRPF60 (Figure 1), is required for constructing working solar cells. A power conversion efficiency of 0.3% was obtained with blends of APFO-Green1:BTPF60, and was improved to 0.7% when a mixture of APFO-Green1:BTPF70 was used to increase the light absorption in the visible region (11).

Recently, we reported the synthesis and photovoltaic performance of a low-band-gap polymer containing alternating 4H-cyclopental[2,1-b:3,4-b′]dithiophene donor and 2,1,3-benzothiadiazole acceptor (PCPDTBT, Figure 4) (12). The two thienyl groups in 4*H*-cyclopenta[2,1-b:3,4-b′]dithiophene are forced to be planar by the additional 4-carbon that connects to the 3,3′-positions of the thiophenes. The 4-carbon also offers a convenient position for the attachment of alkyl and other types of solubilizing groups. Homopolymers of 4,4-dialkyl-4H-cyclopenta[2,1-b:3,4-b′]dithiophene (PCPDT, Figure 4) already possess much longer wavelength absorption than the regular polythiophenes (13). PCPDTBT has an even lower optical band gap of 1.4 eV, HOMO of −5.3 eV and a LUMO of −3.57 eV as determined by cyclic voltammetry. Cells prepared with this polymer gave a power conversion efficiency of 3.5%, which is significantly higher than those of other known low-band-gap polymers. We report here two of the directions we have taken in an effort to further improve this polymer. The first is the modification of side chains to improve charge carrier mobility and film morphology. Secondly, we incorporate fluorene into the main

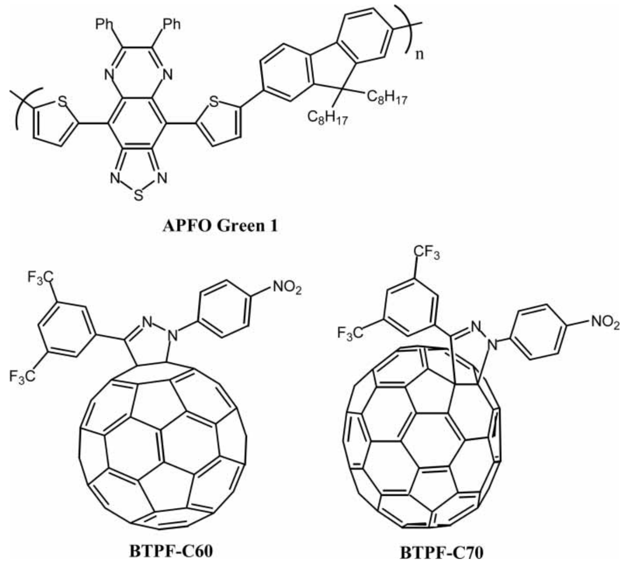


Fig. 3. Thieno[3,4-b]pyrazine-containing low-band-gap polymers.

chain to improve its light absorbing characteristics and decrease its HOMO level.

2 Experimental

2.1 General Methods

4,4-Dihexyl-2,6-bis-(trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene and 4,4-bis-(2-ethylhexyl)-2,6-bis(trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene were prepared as previously reported (12a). 4,7-Dibromo-2,1,3-benzothiadiazole was prepared following a literature procedure (14). 9,9-Di-(2′-ethylhexyl)-2,7-dibromofluorene, tris(dibenzylideneacetone)dipalladium, triphenylphosphine and all other starting materials were purchased from Sigma-Aldrich and used as received. NMR (^{1}H and ^{13}C) spectra were recorded on a Bruker 500 MHz spectrometer. Chemical shifts were recorded in parts per million (ppm), and splitting patterns are designated as s (singlet), d (doublet), and m (multiplet). Coupling constants, J, are reported in Hertz (Hz). The residual proton signal of the solvent was used as an internal standard for spectra recorded in chloroform-d (7.27 for ^{1}H, 77 for ^{13}C). The molecular weights of polymers were determined using a Plgel 5 μm Mixed-B (600 × 7.5 mm) column and a diode array detector at 300 nm at a flow rate of 1.0 mL/min. Polymer molecular weights are reported relative to polystyrene standards purchased from Aldrich.

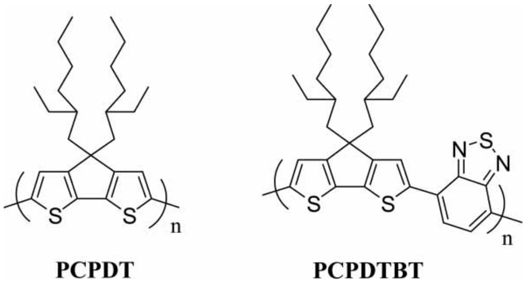


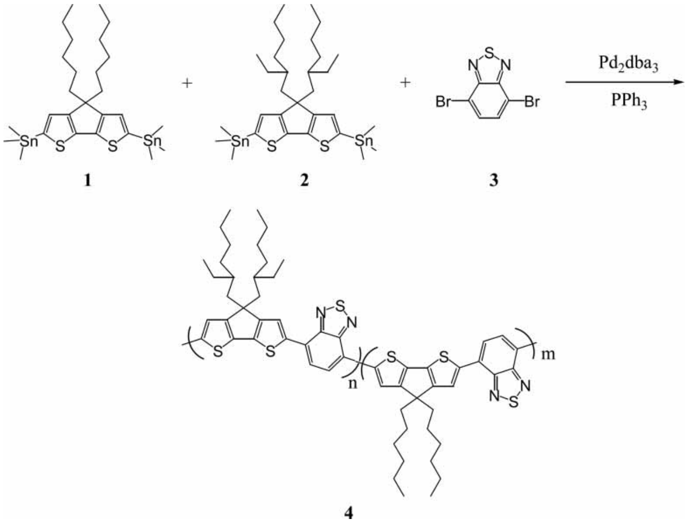
Fig. 4. 4*H*-cyclopenta[2,1-b:3,4-b′]dithiophene based low-band-gap polymers.

2.2 Copolymerization of 4,4-Dihexyl-2,6-bis-trimethyl stannanyl-4H-cyclopenta[2,1-b:3,4-b′]dithiophene, 4,4-Bis-(2-ethyl-hexyl)-2,6-bis-trimethylstannanyl-4H-cyclopenta[2,1-b:3,4-b′]dithiophene, and 4,7-Dibromo-2,1,3-benzothiadiazole

4,4-Dihexyl-2,6-bis(trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene (0.0863 g, 0.000128 mol), 4,4-bis-(2-ethylhexyl)-2,6-bis(trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene (0.187 g, 0.000257 mol), and 4,7-dibromo-2,1,3-benzothiadiazole (0.111 g, 0.000378 g) were dissolved in toluene (15 mL) and the solution was degassed and purged with N_2. Tris(dibenzylideneacetone)dipalladium (6.78 mg, 0.0074 mmol) and triphenylphosphine (15.5 mg, 0.0 593 mmol) was added. The reaction was purged with nitrogen for 30 min and heated to 120°C under nitrogen for 48 h. Solvent was removed under vacuum. The residue was dissolved in chloroform and added to methanol. The precipitates were collected and extracted with hexanes for 24 h. The polymer was extracted with chloroform for 8 h. The resulting blue solution was concentrated and added to methanol. The precipitates were collected to afford the polymer **1** (195 mg).

2.3 9,9-Bis-(2-ethylhexyl)-2,7-bis(trimethylstannanyl)-9H-fluorene

2,7-Dibromo-9,9-bis(2-ethylhexyl)-9H-fluorene (5.0 g) was dissolved in dry THF (45 mL) and the solution was cooled to − 72°C. *n*-Butyl lithium (2.5 M in hexanes, 11.67 mL, 0.0292 mol) was added dropwise. The reaction was stirred at this temperature for 5 h after completion of the addition. A solution of trimethyltin chloride (1 M in hexanes, 32.1 mL, 0.0321 mol) was added dropwise and the reaction was stirred at this temperature for 2 h and allowed to warm to room temperature and stirred overnight. Water was added and the reaction was extracted with dichloromethane. The combined organic layer was washed with water, dried over sodium sulfate, and filtered. Solvent was removed and the residue was dissolved in hexanes and passed through a silica gel column. Solvent was removed and the residue was dried under vacuum to afford the bisstannane as a colorless oil (4.2 g, 64%): ^{1}H NMR ($CDCl_3$, 500 MHz): 7.65 (d, $J = 7.7$ Hz, 2H), 7.48 (m, 2H), 7.41 (d, $J = 7.8$ Hz, 2H), 2.03 (m, 4H), 0.67–0.95 (m, 21H), 0.52 (m, 9H), 0.31 (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): 149.53, 141.61, 139.89, 133.75, 131.54, 119.04, 54.84, 44.01, 34.63, 34.25, 28.31, 27.10, 22.76, 14.00, 10.30, −9.60.



Sch. 1. Modification of the side chains of poly[4*H*-cyclopenta[2,1-b:3,4-b′]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)].

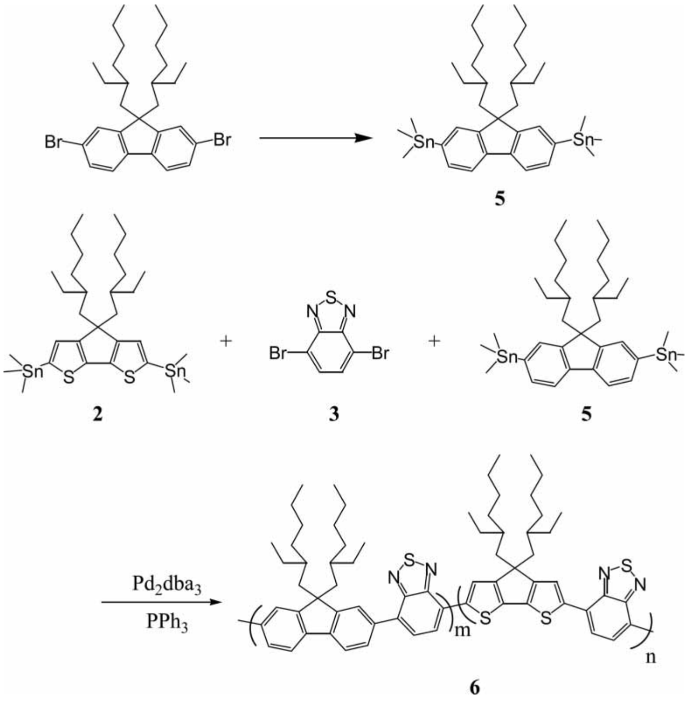
2.4 Random Polymer of 9,9-Bis-(2-ethylhexyl)-2,7-bis(trimethylstannanyl)-9H-fluorene, 2,6-Bis-(trimethylstannyl)-4,4-bis(2-ethylhexyl)-cyclopenta[2,1-b:3,4-b′]dithiophen and 4,7-Dibromo-2,1,3-benzothiadiazole

9,9-Bis-(2-ethylhexyl)-2,7-bis(trimethylstannanyl)-9H-fluorene (0.1609 g, 0.000225 mol), 2,6-bis(trimethylstannyl)-4,4-bis(2-ethylhexyl)-cyclopenta[2,1-b:3,4-b′]dithiophene (0.1636 g, 0.000225 mol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.127 g, 0.000432 mol) were dissolved in toluene (15 mL) and the reaction was degassed and purged with nitrogen. Tris(dibenzylideneacetone)dipalladium (7.9 mg, 0.00864 mmol), triphenylphosphine (18.1 mg, 0.0691 mmol) were added. The reaction was further purged with nitrogen and heated to 120°C for 24 h. The reaction was cooled to rt and the solvent was removed, the residue was dissolved in chloroform (30 mL) and methanol (400 mL) was added. The blue precipitates were collected and washed with methanol, and dried under vacuum to afford the polymer (220 mg, Mn = 5 kDa by GPC based on polystyrene standards).

3 Results and Discussions

Even though the power conversion efficiency realized with PCPDTBT (Figure 4) has reached 3.5%, which is among the highest for low-band-gap polymers, this polymer should exhibit efficiency of at least 7% based on the band gap, the HOMO/LUMO level and the charge carrier mobility, according to a previously published model (3). This lower-than-expected efficiency is mainly caused by a low fill factor (with a typical value of 0.40 for cells made of PCPDTBT and PCBM blends), which is most likely caused by non-ideal film morphology. Polymer-fullerene blends in which both the donor and acceptor segregate into bicontinuous phases (referred to as bulk-heterojuction) are the key to better performance. (15) One way to affect phase behaviour of the donor and acceptor would be to change their solubility profiles. It is known from our previous work that the poly[4*H*-cyclopenta[2,1-b:3,4-b′]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] with *n*-hexyl side chains is not soluble, while the polymer PCPDTBT, with 2-ethylhexyl side chains, is soluble in organic solvents such as chlorobenzene and *ortho*-dichlorobenzene. By employing both 2-ethylhexyl and *n*-hexyl side chains, it should be possible to tune the solubility of the polymer over a wide range. A synthesis of such a polymer, with a 2-ethylhexyl and *n*-hexyl ration of 2:1 is shown Scheme 1. The resulting polymer (**4**) was found to have a similar absorption characteristics as PCPDTBT but a higher hole mobility (7×10^{-2} cm^2/Vs). This high mobility promises a better fill factor, and the fabrication of more efficient solar cells is currently being pursued with this material.

One of the characteristics of PCPDTBT that might negatively influence cell performance is that it has a absorption minimum at ~500 nm that will cause less efficient photon harvesting in this region. By incorporating the less electron donating fluorene moieties into the polymer chain, it should be possible to shift the absorption maximum to mid-visible region, and to move the HOMO of the polymer to a more negative level. Polymerization of 9,9-bis-(2-ethylhexyl)-2,7-bis(trimethylstannanyl)-9H-fluorene (**5**), 2,6-bis(trimethylstannyl)-4,4-bis(2-ethylhexyl)-cyclopenta[2,1-b:3,4-b′]dithiophene (**2**), and 4,7-dibromo-2,1,3-



Sch. 2. Synthesis of random polymer of 9,9-bis-(2-ethylhexyl)-2,7-bis(trimethylstannanyl)-9H-fluorene, 2,6-bis(trimethylstannyl)-4,4-bis(2-ethylhexyl)-cyclopenta[2,1-b:3,4-b′]dithiophene and 4,7-dibromo-2,1,3-benzothiadiazole.

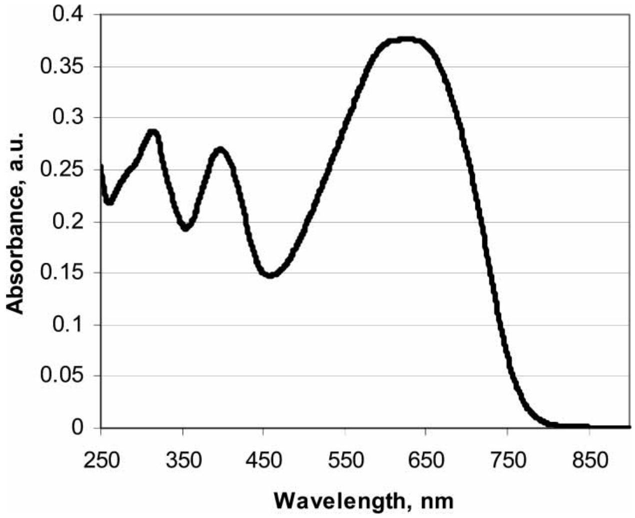


Fig. 5. The absorption spectrum of polymer **6**.

benzothiadiazole (**3**) to give random colopymer **6** (Scheme 2). And 9,9-bis-(2-ethylhexyl)-2,7-bis-trimethylstannanyl-9H-fluorene (**5**) was prepared by lithium-halogen exchange of 2,7-dibromo-9,9-bis-(2-ethylhexyl)-9H-fluorene with *n*-butyl lithium followed by treatment with trimethyltin chloride. Possibly due to the less reactivity of 9,9-bis-(2-ethylhexyl)-2,7-bis(trimethylstannanyl)-9H-fluorene, the resulting polymer had a Mn of about 5000 Da after precipitation and washing with methanol. A fraction with Mn $>$ 20 kDa was obtained by preparative GPC and its absorption spectrum was recorded. It has very nice absorption coverage over the visible region from 450 to 750 nm, with an absorption maximum at about 650 nm (Figure 5). Its HOMO and LUMO levels are found to be -5.37 eV (which is slightly lower than that of PCPDTBT) and -3.57 eV; these values are well within the desirable range for a high performance solar cell. Field effect transistors built with this material indicate a hole mobility of 1×10^{-4} cm^2/Vs, and it should be possible to improve the mobility even further by modification of side chains to induce closer interchain interactions.

4 Conclusions

We modified poly[2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b:3,4-b′]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) by both changing the side chains and incorporation of fluorene repeating units. Replacing part of the 2-ethylhexyl side chains with *n*-hexyl groups results in polymers with lower solubility but higher hole mobility. Incorporation of fluorene results in polymers with better absorption coverage of the mid-visible region of the solar spectrum. Both of these polymers possess desirable HOMO/LUMO level and good charge carrier mobility that promise good cell performance.

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