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Synthesis and Characterizations of Poly(9,10-bisarylethynyl-2,6-anthrylene)s and Poly(9,10-bisalkynyl-2,6-anthrylene)

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ABSTRACT: A poly(9,10-bisalkynyl-2,6-anthrylene) (**P1**) and five poly(9,10-bisarylethynyl-2,6-anthrylene)s (**P2**−**P6**) as soluble conjugated polymers have been synthesized and characterized. All polymers exhibit two-dimensional conjugated characteristics as indicated by absorption spectra comprising multibands in the range of 300−600 nm. Compared with **P1**, polymers **P2**−**P5**, which contain phenylethynyl substituents with the longer conjugation than alkynyl groups, exhibit a ∼60 nm red shift of absorption edge. However, further increasing the conjugation length of the arylethynyl substituents (longer than phenylethynyl) has only a negligible effect on the conjugation of the polymer chains, while comparing the absorption spectra of **P6** with those of **P2**−**P5**. All polymers show absorption spectra with a noticeable red shift from solutions to films, indicative of stronger intermolecular interaction in solid state. The highest occupied molecular orbital (HOMO) energy levels are −5.32 eV for **P1** and around −5.20 eV for phenylethynyl-substituted polymers. Bulk heterojunction polymer solar cells (PSCs) of the polymers were fabricated with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as the acceptor material. Polymer **P1** exhibits the highest power conversion efficiency (PCE) of 1.60% with an open-circuit voltage (V_{oc}) of 0.96 V, a short-circuit current density (J_{sc}) of 3.18 mA/cm^2, and a fill factor (FF) of 0.53.

Introduction

Conjugated polymers have received growing attention due to their intriguing electronic and optoelectronic properties for application in a variety of optoelectronic devices, such as polymer light-emitting diodes (PLEDs),[1] organic thin film transistors (OTFTs),[2] and polymer solar cells (PSCs).[3] These applications, however, encourage the incessant exploration of conjugated polymers with new structures. To date, numerous soluble conjugated polymers based on simple aromatic units such as phenylene and thiophene have been reported.[4] Meanwhile, several ladder-type conjugated polymers and polymers based on fused aromatic units, e.g., polyfluorenes (PFs),[5] polyindonenfluorenes (PIFs),[6] and polyphenanthrylenes (PPAs),[7,8] have been developed as shown in Chart 1, which exhibit promising optoelectronic properties.

Because of its promising light-emitting properties and charge carriers transport properties, anthracene has been proved as an important building block for light-emitting small molecules.[9−12] Some anthracene-based oligomers and polymers have also been reported.[13−19] However, most of them are based on 9,10-linked anthracene derivatives for easy synthesis.[20] In this case, the main chain of the oligomers and polymers is strongly twisted, and thereby the conjugation is severely limited because of high steric hindrance. For example, Müllen et al. reported the synthesis and properties of oligo(9,10-anthrylene)s.[13a−d] They found that the dihedral angle between neighboring repeating units is about 81.5°.[13e] The first poly(2,6-anthrylene) as an insoluble polymer was reported by Hodge through a precursor approach.[16] Oligo(2,6-anthrylene)s up to trimers were also demonstrated by Ito et al.[15] The OTFT devices with mobility above 0.18 cm^2/(V s) have been realized by the vacuum deposition technique. Recently, we and others reported the synthesis and properties of soluble poly(2,6-anthrylene) (PBPA as shown in Chart 1) and poly(2,6-anthrylenevinylene) carrying alkylphenyl or alkoxyphenyl solubilizing groups.[21,22] We also demonstrated soluble oligo(9,10-bisalkynyl-2,6-anthrylene)s up to pentamer that could be used for fabrication of OTFTs with mobility up to 2.9×10^{-3} cm^2/(V s).[23] Further increase of the molecular length was unsuccessful due to a dramatic decrease of solubility as the molecular length increased. Considering that 9,10-bis(phenylethynyl)anthracene and its derivatives have been widely used as chemiluminescent species,[24] molecular probes,[25] electroluminescent materials,[26] and semiconducting materials for OSCs,[27] and the introduction of arylethynyl and alkylnyl substituents at 9,10-positions can afford poly(2,6-anthrylene)s with two-dimensional structures, which may render the polymers unique photophysical properties, in the current paper, we report the synthesis and characterizations of a series of anthracene-based conjugated polymers, as shown in Chart 2. Various arylethynyl substituents were introduced to 9,10-positions of the anthracene unit in order to study the effect of the substituents on the solubility and photophysical properties of the polymers.

Experimental Section

Materials. Tetrahydrofuran (THF), diethyl ether, and toluene was distilled over sodium/benzophenone. *N*,*N*-Dimethylformamide (DMF) was distilled over CaH_2 under reduced pressure. Other reagents were used without further purification unless otherwise stated. 2,6-Dibromoanthraquinone, 1-bromo-4-dodecylbenzene, 4-bromo-1,2-bis(octyloxy)benzene, and 1,2-bis(2-ethylhexyloxy)-4-bromobenzene were prepared following

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Chart 1. Structures of PFs, PIFs, PPAs, and PBPA

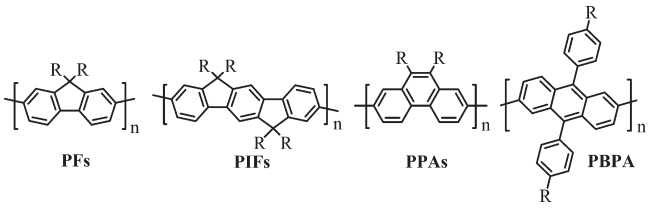
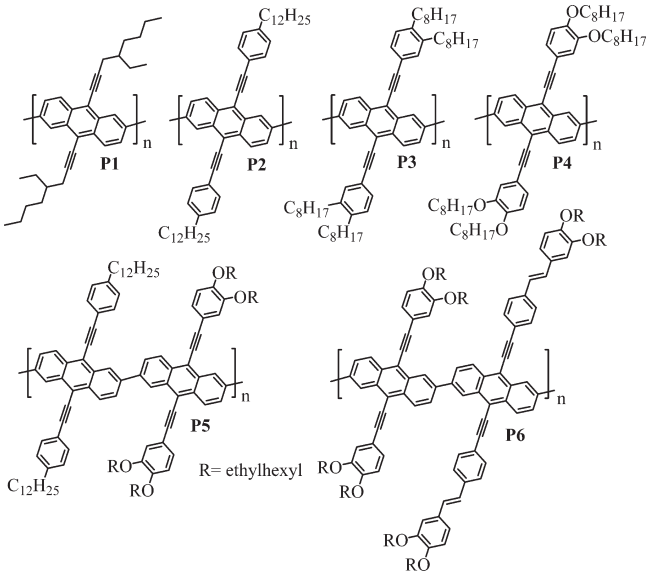


Chart 2. Chemical Structures of the Anthracene-Based Conjugated Polymers P1−P6



the reference procedures.[23,28] Details for the synthesis of intermediates are outlined in the Supporting Information (SI).

2,6-Dibromo-9,10-bis(4-ethyloct-1-ynyl)anthracene (14a). To a solution of **1b** (0.800 g, 5.79 mmol) in dry THF (25 mL) was added *n*-butyllithium (2.5 M in hexane, 2.20 mL, 5.53 mmol) at 0 °C. After 1 h, 2,6-dibromoanthraquinone (0.921 g, 2.52 mmol) was added, and then the mixture was stirred at room temperature under dry argon for 5 h. The mixture was poured into water and extracted with petroleum ether (PE). The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After the solvent being evaporated, the residue was dissolved in THF (30 mL) and then added dropwise into $SnCl_2 \cdot 2H_2O$ (2.85 g, 12.6 mmol) in 50% acetic acid (30 mL). The mixture was stirred at room temperature overnight and poured into water for extraction with diethyl ether. The organic extracts was washed with brine and dried over anhydrous $MgSO_4$. Solvent was removed, and the crude product was purified with column chromatography on silica gel with PE as eluent and then recrystallized from PE to yield **14a** (0.94 g, 61%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.93−0.97 (m, 6H), 1.00−1.05 (m, 6H), 1.38−1.43 (m, 12H), 1.58−1.65 (m, 4H), 1.71−1.75 (m, 2H), 2.74−2.75 (m, 4H), 7.60 (dd, J_1 = 9.15 Hz, J_2 = 2.1 Hz, 2H), 8.39 (d, J = 9.3 Hz, 2H), 8.6z9 (d, J = 1.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.30, 14.17, 23.06, 24.10, 26.48, 29.20, 33.23, 39,12, 103.20, 118.25, 121.14, 129.14, 129.31, 130.24, 130.84, 132.98. Anal. Calcd for $C_{34}H_{40}Br_2$: C, 67.11; H, 6.63. Found: C, 66.73; H, 6.48. *m*/*z* [MALDI-TOF]: 608.1.

2,6-Dibromo-9,10-bis((4-dodecylphenyl)-1-ethynyl)anthracene (14b). Compound **14b** was synthesized from **3b** following the procedure for preparation of **14a** as an orange solid in a yield of 77.0%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.85−0.91 (m, 6H), 1.21−2.33 (m, 36H), 1.63−1.66 (m, 4H), 2.67 (t, J = 7.65 Hz, 4H), 7.27 (d, J = 8.22 Hz, 4H), 7.64−7.68 (m, 8H), 8.54 (d, J = 9.15 Hz, 2H), 8.78 (d, J = 1.74 Hz, 2H). Anal. Calcd for $C_{54}H_{64}Br_2$: C, 74.30; H, 7.39. Found: C, 74.70; H, 8.18. *m*/*z* [MALDI-TOF]: 872.3.

2,6-Dibromo-9,10-bis((3,4-dioctylphenyl)-1-ethynyl)anthracene (14c). Compound **14c** was synthesized from **8b** following the procedure for preparation of **14a** as an orange solid in a yield of 64.0%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.87−0.91 (m, 12H), 1.30−1.37 (m, 32H), 1.49−1.55 (m, 8H), 1.84−1.91 (m, 8H), 4.05−4.13 (m, H), 6.94 (d, J = 8.37 Hz, 2H), 7.23 (d, J = 1.83 Hz, 2H), 7.33 (dd, J_1 = 8.28 Hz, J_2 = 1.86 Hz, 2H), 7.66 (dd, J_1 = 9.15 Hz, J_2 = 2.01 Hz, 2H), 8.49 (d, J = 9.12 Hz, 2H), 8.77 (d, J = 1.83 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.11, 22.69, 29.30, 29.53, 29.76, 29.83, 31.17, 31.26, 31.92, 32.66, 32.78, 84.57, 103.76, 118.03, 120.00, 121.77, 129.20, 129.31, 129.49, 130.60, 132.33, 132.73, 141.19, 142.33. Anal. Calcd for $C_{62}H_{80}Br_2$: C, 75.59; H, 8.19. Found: C, 75.68; H, 7.99. *m*/*z* [MALDI-TOF]: 984.4.

2,6-Dibromo-9,10-bis((3,4-dioctyloxyphenyl)-1-ethynyl)anthracene (14d). Compound **14d** was synthesized from **9b** following the procedure for preparation of **14a** as an orange solid in a yield of 71%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.87−0.90 (m, 12H), 1.30−1.55 (m, 40H), 1.85−1.91 (m, 8H), 4.05−4.13 (m, 8H), 6.94 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 1.8 Hz, 2H), 7.34 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 2H), 7.67 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 2H), 8.50 (d, J = 9.3 Hz, 2H), 8.78 (d, J = 1.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.10, 22.68, 26.34, 26.07, 29.22, 29.30, 29.40, 31.84, 69.25, 69.54, 84.05, 103.67, 113.41, 114.89, 116.77, 117.96, 121.73, 125.46, 129.18, 129.33, 130.57, 132.72, 149.03, 150.55. Anal. Calcd for $C_{62}H_{80}Br_2O_4$: C, 70.98; H, 7.69. Found: C, 70.69; H, 7.27. *m*/*z* [MALDI-TOF]: 1048.4.

2,6-Dibromo-9,10-bis((3,4-di(2-ethylhexyloxy)phenyl)-1-ethynyl)anthracene (14e). Compound **14e** was synthesized from **10b** following the procedure for preparation of **14a** as an orange solid in a yield of 63%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.90−1.00 (m, 24H), 1.34−1.55 (m, 32H), 1.81 (m, 4H), 3.90−3.99 (m, 8H), 6.94 (d, J = 8.22 Hz, 2H), 7.24 (d, J = 10.2 Hz, 2H), 7.33 (d, J = 8.31 Hz, 2H), 7.67 (d, J = 9.18 Hz, 2H), 8.51 (d, J = 9.15 Hz, 2H), 8.80 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.20, 11.24, 14.10, 23.08, 23.93, 23.97, 29.15, 30.60, 30.64, 39.53, 39.60, 71.57, 71.76, 83.99, 103.75, 113.13, 114.70, 116.35, 117.95, 121.68, 125.28, 129.17, 129.32, 130.52, 130.57, 132.69, 149.37, 150.87. Anal. Calcd for $C_{62}H_{80}Br_2O_4$: C, 70.98; H, 7.69. Found: C, 70.46; H, 7.19. *m*/*z* [MALDI-TOF]: 1048.4.

2,6-Dibromoanthracene-9,10-bis(2-(4-((*E*)-3,4-di(2-ethylhexyloxy)styryl)phenyl)ethynyl) (14f). Compound **14f** was synthesized from **13b** following the procedure for preparation of **14a** as a red solid in a yield of 55%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.92−1.00 (m, 24H), 1.34−1.39 (m, 16H), 1.42−1.59 (m, 16H), 1.78−1.81 (m, 4H), 3.89−3.96 (m, 8H), 6.87 (d, J = 8.31 Hz, 2 H), 6.97−7.17 (m, 8H), 7.58 (d, J = 8.31 Hz, 4H), 7.68 (dd, J = 9.20 Hz, J = 1.88 Hz, 2H), 7.72 (d, J = 8.22 Hz, 4H), 8.49 (d, J = 9.18 Hz, 2H), 8.78 (d, J = 1.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.20, 11.24, 23.10, 23.97, 29.15, 29.19, 30.61, 30.64, 39.59, 39.67, 71.72, 71.69, 86.32, 103.72, 111.25, 113.39, 117.82, 120.34, 121.18, 121.84, 125.57, 126.32, 128.96, 129.20, 129.93, 130.14, 130.45, 130.59, 132.06, 132.53, 138.47, 149.70, 149.97. Anal. Calcd for $C_{78}H_{92}Br_2O_4$: C, 74.75; H, 7.40. Found: C, 74.63; H, 7.05. *m*/*z* [MALDI-TOF]: 1252.5.

2,6-Bis(4,4,5,5-tetramethyl[1,3,2]dioxaborolane)-9,10-bis(4-ethyl-octy-1-ynyl)anthracene (15a). To a solution of **14a** (0.650 g, 1.07 mmol) in dry THF (30 mL) was added *n*-BuLi (2.5 M in hexane, 0.94 mL, 2.35 mmol) at −78 °C. After 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.540 mL, 2.57 mmol) was added dropwise. The mixture was stirred at room temperature overnight, poured into water, and extracted with dichloromethane (DCM). The organic layer was washed with brine and dried over anhydrous $MgSO_4$. On removal of the solvent, the residue was purified with column chromatography on silica gel (PE:DCM = 4:1) to afford **15a** (0.40 g, 53%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): 0.90−0.95 (m, 6H), 1.02−1.07 (m, 6H), 1.33−1.40 (m, 36H), 1.58−1.75 (m, 6H), 2.78−2.81

(m, 4H), 7.85 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 2H), 8.53 (d, $J = 8.7$ Hz, 2H), 9.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.36, 14.17, 22.98, 24.04, 24.96, 26.42, 29.28, 33.16, 39.07, 78.30, 83.89, 102.42, 119.51, 126.40, 130.12, 132.10, 133.34, 136.12. Anal. Calcd for $C_{46}H_{64}B_2O_4$: C, 78.63; H, 9.18. Found: C, 78.30; H, 8.66. *m/z* [MALDI-TOF]: 702.5.

2,6-Bis(4,4,5,5-tetramethyl[1,3,2]dioxaborolane)-9,10-bis((4-dodecylphenyl)-1-ethynyl)anthracene (15b). A mixture of **14b** (0.90 g, 1.0 mmol), bis(pinacolato)diboron (0.58 g, 2.3 mmol), $Pd(dppf)Cl_2$ (45 mg), potassium acetate (0.61 g, 6.2 mmol), and toluene/DMF (22.5 mL/45 mL) was stirred at 90 °C for 24 h under an argon atmosphere. The resulting mixture was poured into water and extracted with chloroform. The organic extracts were washed with brine and dried over anhydrous $MgSO_4$. On removal of the solvent, the residue was purified by recrystallization with acetone to yield **15b** (0.31 g, 32%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.86−0.90 (m, 6H), 1.27−1.34 (m, 44H), 1.56 (m, 4H), 1.63−1.70 (m, 4H), 2.69 (t, $J = 7.65$ Hz, 4H), 7.29 (d, $J = 8.1$ Hz, 4H), 7.74 (d, $J = 7.8$ Hz, 4H), 7.93 (d, $J = 9.0$ Hz, 2H), 8.64 (d, $J = 8.4$ Hz, 2H), 9.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.11, 22.69, 25.01, 29.35, 29.52, 29.67, 31.34, 31.92, 36.05, 84.03, 86.24, 103.18, 119.29, 120.84, 126.36, 128.65, 130.60, 131.73, 131.94, 133.19, 136.05, 143.91. Anal. Calcd for $C_{66}H_{88}B_2O_4$: C, 81.97; H, 9.17. Found: C, 81.53; H, 8.98. *m/z* [MALDI-TOF]: 966.7.

2,6-Bis(4,4,5,5-tetramethyl[1,3,2]dioxaborolane)-9,10-bis((3,4-dioctylphenyl)-1-ethynyl))anthracene (15c). Compound **15c** was synthesized from **14c** following the procedure for preparation of **15b** as an orange solid in a yield of 40%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.87−0.90 (m, 12H), 1.30 (m, 24H), 1.43 (m, 40H), 1.58−1.70 (m, 8H), 2.65−2.71 (m, 8H), 7.24 (d, $J = 8.1$ Hz, 2H), 7,57 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.5$ Hz, 2H), 7.61 (s, 2H), 7.93 (dd, $J_1 = 8.4$ Hz, $J_2 = 0.9$ Hz, 2H), 8.65 (d, $J = 8.4$ Hz, 2H), 9.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.11, 22.68, 25.02, 29.30, 29.54, 29.77, 29.89, 31.22, 31.32, 32.73, 32.80, 84.00, 85.94, 103.43, 108.44, 109.10, 119.33, 120.86, 126.41, 129.15, 129.38, 130.54, 131.95, 132.52, 133.18, 136.09, 140.99, 141.76. Anal. Calcd for $C_{47}H_{104}B_2O_4$: C, 82.35; H, 9.71. Found: C, 81.80; H, 9.18. *m/z* [MALDI-TOF]: 1078.8.

2,6-Bis(4,4,5,5-tetramethyl[1,3,2]dioxaborolane)-9,10-bis((3,4-dioctyloxyphenyl)-1-ethynyl))anthracene (15d). Compound **15d** was synthesized from **14d** following the procedure for preparation of **15b** as an orange solid in a yield of 56%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.87−0.92 (m, 12H), 1.30−1.37 (m, 32H), 1.48−1.53 (m, 8H), 1.84−1.92 (m, 8H), 4.06−4.14 (m, 8H), 6.95 (d, $J = 8.37$ Hz, 2H), 7.31 (d, $J = 1.83$ Hz, 2H), 7.39 (dd, $J_1 = 8.23$ Hz, $J_2 = 1.84$ Hz, 2H), 7.93 (dd, $J_1 = 8.61$ Hz, $J_2 = 0.99$ Hz, 2H), 8.64 (d, $J = 8.28$ Hz, 2H), 9.21 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.10, 22.68, 25.02, 26.03, 26.10, 29.29, 29.39, 31.83, 69.28, 69.32, 83.98, 85.36, 103.28, 113.48, 115.83, 116.84, 119.20, 125.26, 126.39, 130.54, 131.87, 133.12, 136.04, 148.96, 150.11. Anal. Calcd for $C_{47}H_{104}B_2O_8$: C, 77.74; H, 9.17. Found: C, 77.33; H, 8.52. *m/z* [MALDI-TOF]: 1142.7.

2,6-Bis(4,4,5,5-tetramethyl[1,3,2]dioxaborolane)-9,10-bis((3,4-di(2-ethylhexyloxy)phenyl)-1-ethynyl))anthracene (15e). Compound **15e** was synthesized from **14e** following the procedure for preparation of **15b** as an orange solid in a yield of 60%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.87−0.91 (m, 12H), 1.30−1.37 (m, 40H), 1.46−1.53 (m, 8H), 1.55 (s, 4H), 1.85−1.92 (m, 8H), 4.06−4.14 (m, 8H), 6.95 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 1.8$ Hz, 2H), 7.39 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.8$ Hz, 2H), 7.93 (dd, $J_1 = 8.4$ Hz, $J_2 = 0.9$ Hz, 2H), 8.64 (d, $J = 8.7$ Hz, 2H), (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.20, 11.25, 14.09, 23.08, 23.97, 25.02, 29.15, 19.18, 30.61, 30.68, 39.56, 39.70, 71.52, 83.98, 85.24, 103.35, 113.18, 115.62, 116.40, 119.23, 125.14, 126.41, 130.53, 131.85, 133.16, 136.05, 149.32, 150.47. Anal. Calcd for $C_{47}H_{104}B_2O_8$: C, 77.74; H, 9.17. Found: C, 77.37; H, 7.19. *m/z* [MALDI-TOF]: 1142.7.

P1. A mixture of **14a** (0.315 g, 0.517 mmol), **15a** (0.400 g, 0.569 mmol), $NaHCO_3$ (2.00 g, 23.8 mmol), 4-bromododecylbenzene (**2**) (18 mg, 0.053 mmol), THF (22 mL), and H_2O (12 mL) in a 100 mL Schlenk tube was degassed followed by adding $Pd(PPh_3)_4$ (7 mg, 6.06×10^{-3} mmol) in THF (2 mL) under argon flow. The mixture was stirred at refluxed for 24 h and then dropped into methanol to precipitate. After being filtered and dried, the precipitation was Soxhlet extracted with methanol, acetone, hexane, and chloroform in succession. The chloroform solution was concentrated and reprecipitated in methanol. The solid was filtered and dried to yield **P1** (0.10 g, 22%) as a dark-red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.89−0.93 (m, 6H), 1.05−1.11 (m, 6H), 1.36−1.45 (m, 8H), 1.67−1.78 (m, 10H), 8.12−8.15 (broad, 2H), 8.66−8.74 (broad, 2H), 9.01 (broad, 2H).

P2. A mixture of **14b** (0.15 g, 0.17 mmol), **15b** (0.18 g, 0.18 mmol), $NaHCO_3$ (0.71 g, 8.45 mmol), THF (17 mL), and H_2O (7 mL) in a 100 mL Schlenk tube was degassed followed by adding $Pd(PPh_3)_4$ (2 mg, 1.73×10^{-3} mmol) dissolved in THF (2 mL) under argon flow. After the mixture was stirred at reflux for 24 h, end-capper *p*-iodotoluene (4 mg, 0.018 mmol) dissolved in THF (2 mL) was added. After another 12 h, the resulting mixture was dropped into methanol to precipitate. The solid was collected and Soxhlet extracted with methanol, acetone, hexane, and chlorobenzene in succession. The chlorobenzene solution was concentrated and reprecipitated in methanol. The solid was filtered and dried to yield **P2** (0.20 g, 82%) as a red-brown solid. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C): δ (ppm) 0.81 (m, 6H), 1.23−1.35 (m, 36H), 2.57 (m, 4H), 7.10−7.18 (m, 4H), 7.60−7.66 (m, 6H), 8.05 (br, 2H), 8.60 (br, 2H).

P3. The procedure for preparation of **P2** was followed to synthesize **P3** from **14c** and **15c** as a red solid in a yield of 76%. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C): δ (ppm) 0.75−0.83 (m, 12H), 1.14−1.24 (m, 40H), 1.54 (br, 8H), 2.56 (br, 8H), 7.07 (br, 2H), 7.49−7.57 (m, 4H), 8.15 (br, 2H), 8.79 (br, 2H), 9.18−9.21 (m, 2H).

P4. The procedure for preparation of **P2** was followed to synthesize **P4** from **14d** and **15d** as a red solid in a yield of 60%. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C): δ (ppm) 0.76−0.83 (m, 12H), 1.20−1.42 (m, 40H), 1.66−1.79 (m, 8H), 3.93−4.00 (m, 8H), 6.72−6.80 (m, 2H), 7.19−7.30 (m, 4H), 8.09−8.16 (m, 2H), 8.76−8.84 (m, 2H), 9.11−9.19 (m, 2H).

P5. The procedure for preparation of **P2** was followed to synthesize **P5** from **14b** and **15e** as a red solid in a yield of 76%. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C): δ (ppm) 0.77−0.93 (m, 36H), 1.20−1.32 (m, 62H), 1.60 (m, 8H), 1.96 (m, 4H), 3.83−3.93 (m, 8H), 6.77−6.80 (m, 2H), 7.11−7.12 (m, 2H), 7.18−7.23 (m, 2H), 7.29−7.31(m, 2H), 7.63−7.65 (m, 4H), 8.13 (br, 2H), 8.65−8.82 (m, 4H), 9.16 (br, 2H).

P6. The procedure for preparation of **P2** was followed to synthesize **P6** from **14f** and **15e** as a red solid in a yield of 84%. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 °C): δ (ppm) 0.84−0.86 (m, 48H), 1.10−1.37 (m, 64H), 1.66 (br, 8H), 3.67−3.92 (m, 16H), 6.77−6.80 (m, 4H), 6.82 (m, 2H), 6.90−6.96 (m, 6H), 7.18−7.33 (m, 4H), 7.39−7.70 (m, 8H), 8.17 (br, 2H), 8.69 (br, 2H), 8.84 (br, 2H), 9.17 (br, 2H).

General Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 M Hz spectrometer or a 400 MHz spectrometer in $CDCl_3$ or CD_2Cl_4 with tetramethylsilane (TMS) as the internal standard. Elemental analysis was carried out on an Eager 300 elemental analyzer. MALDI-TOF mass spectra were recorded on a Kratos AXIMA-CFR Kompact MALDI mass spectrometer with dithranol as the matrix. Gel permeation chromatography (GPC) measurements were conducted on a Waters 510 system using polystyrene as standard. Electronic absorption spectra were obtained on a PerkinElmer Lambda35 UV/vis spectrometer. Photoluminescence spectra were recorded in $CHCl_3$ with a PerkinElmer LS50B luminescence spectrometer. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA7 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} at a nitrogen flow. Differential pulse voltammety were performed on a CHI660a electrochemical

analyzer in a three-electrode cell with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as supporting electrolyte in methylene chloride or *o*-dichlorobenzene at a scan rate of 80 mV/s. A Pt disk, a Pt wire, and an Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. The potential was calibrated by the ferrocene/ferrocenium standard. HOMO energy levels were estimated by the equation HOMO = $-(4.80 + \Delta E_{oxd}^{onset})$.[29]

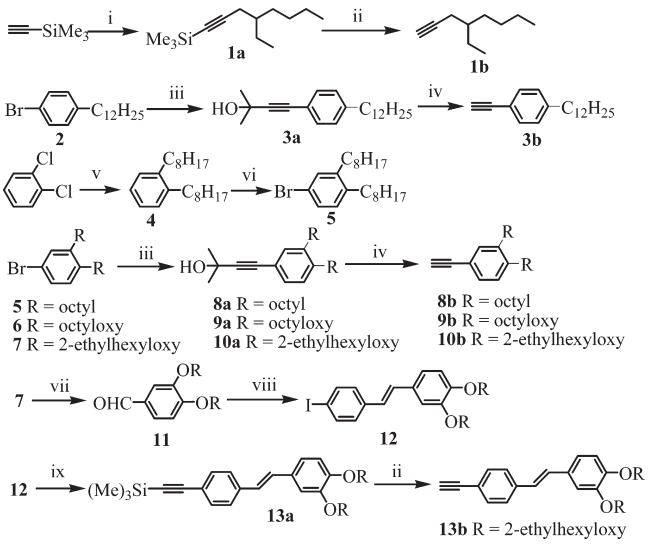
Device Fabrication and Measurements. PSCs were fabricated with the structure of ITO/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS)/polymer:PCBM/Al. ITO substrate was precleaned and modified by a 30 nm PEDOT:PSS (Baytron P4083) layer. The active layer was prepared by spin-coating chlorobenzene solution of the polymers and PCBM (1:2, w/w) with the polymer concentration of 10 mg /mL for **P1** and 8 mg/mL for **P3**−**P6**. The thickness of the active layer was controlled to ca. 80−100 nm by adjusting the rotating speed of the spin-coating. Al cathode with a thickness of 100 nm was deposited at a vacuum level of 4×10^{-4} Pa. The effective area of the unit cell is 12 mm^2. The current−voltage ($I-V$) dependence of the devices was measured on a computer-controlled Keithley 236 source measure unit. A xenon lamp (500 W) was used as the white light source, and the optical power at the sample was 100 mW/cm^2. The external quantum efficiency (EQE) was measured using a Model SR830 DSP lock-in amplifier coupled with a SBP500 monochromator, a DSC102 data acquisition system, and a Model SR540 chopper controller. The light intensity at each wavelength was calibrated with a standard single-crystal Si photodiode.

Results and Discussion

Scheme 1 shows the synthesis of intermediates with experimental details included in Supporting Information. The compound 4-ethyloct-1-yne (**1b**) was synthesized in two steps with a total yield of 50%. Bromophenyl derivatives **2**, **6**, and **7** were synthesized according to the reported procedures.[28] The compound 4-bromo-1,2-dioctylbenzene (**5**) was synthesized by means of Kumada coupling reaction of octylmagnesium bromide and 1,2-dichlorobenzene followed by bromination. Phenyl alkynes **3b** and **8b**−**10b** were prepared by Sonogashira coupling reaction of **2** and **5**−**7** with 2-methylbut-3-yn-2-ol followed by deprotection with NaOH in refluxing THF. Intermediate **12** was synthesized by Honner−Wadsworth−Emmons reaction of 3,4-bis(2-ethylhexyloxy)benzaldehyde (**11**) and diethyl (4-iodophenyl)methylphosphonate. Coupling of **12** with trimethylsilylacetylene followed by deprotection afforded arylethynyl derivative **13b** in good yield.

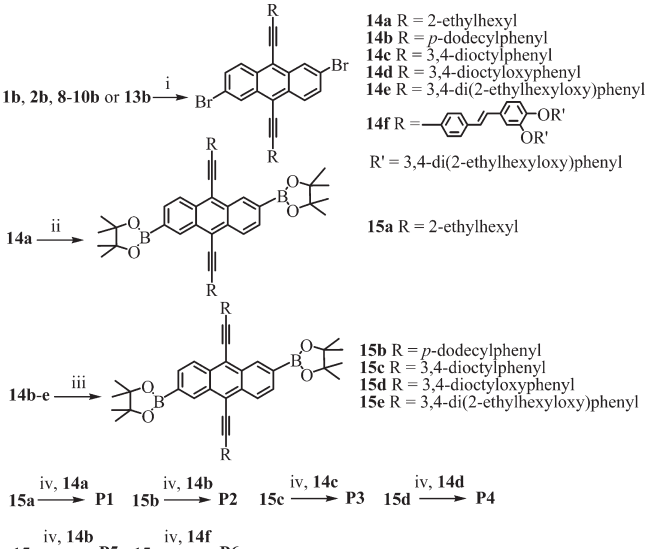
Scheme 2 outlines the synthesis of monomers **14** and **15** and polymers **P1**−**P6**. To synthesize **14**, alkynyl or arylethynyl derivatives were first treated with *n*-BuLi. Then the resulting lithium salts reacted with 2,6-dibromoanthraquinone followed by reduction with $SnCl_2$ to afford target compounds in yields of 55−77%. Monomer **15a** was prepared through treating **14a** with *n*-BuLi followed with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Since solubility of **14b**−**e** in THF at low temperature is too low to allow effective debromination by *n*-BuLi, organoboron reagents **15b**−**e** were synthesized by coupling reactions of **14b**−**e** and bis(pinacolato)diboron at the existence of Pd(dppf)Cl_2 and KOAc. Polymers **P1**−**P6** were synthesized by the typical Suzuki polymerization reaction in yields of 22%−84%. All polymers were purified by Soxhlet extraction and multiple precipitations prior to characterization. The rather low yield of **P1** (22%) is ascribed to its low solubility, and we only collected the product soluble in chloroform for characterization. Polymer **P2** exhibits the poorest solubility and only has limited solubility in chlorobenzene at room temperature. Polymers **P3**−**P6** possess two alkyl or alkoxyl substituents in the repeating units, which render them good solubility in organic solvents, such as chloroform and chlorobenzene. All polymers were characterized by ^{1}H NMR spectrometer and gel permeation chromatography (GPC). ^{1}H NMR spectra of the polymers in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) at 80 °C are depicted in Figure 1. Polymer **P2** showed strong aggregation as featured by rather broad and featureless signals, which is consistent with its low solubility. For **P1** and **P3**−**P6**, three groups of signals corresponding to protons in anthracene rings (numbered with 1, 2, and 3 in Figure 1) were observed. The signals related to anthracene

Scheme 1. Synthetic Route of Intermediates[a]



[a] Reagents and conditions: (i) *n*-BuLi, HMPT, 2-ethylhexyl bromide, THF, 0 °C to room temperature; (ii) K_2CO_3, MeOH, room temperature; (iii) Pd(PPh_3)$_2Cl_2$, CuI, 2-methylbut-3-yn-2-ol, Et_3N, reflux; (iv) NaOH, THF, reflux; (v) $C_8H_{17}MgBr$, Ni(dppp)Cl_2, Et_2O, reflux; (vi) Br_2, $FeCl_3$, $CHCl_3$, 0 °C to room temperature; (vii) (1) *n*-BuLi, THF, −78 °C and (2) DMF, −78 °C to room temperature; (viii) diethyl(4-iodophenyl)methylphosphonate, *t*-BuOK, THF, 0 °C to room temperature; (ix) trimethylsilylacetylene, Pd(PPh_3)$_2Cl_2$, CuI, THF/Et_3N, room temperature.

Scheme 2. Synthetic Route of Monomers and Polymers[a]



[a] Reagents and conditions: (i) (1) *n*-BuLi, THF, 0 °C; (2) 2,6-dibromoanthraquinone, 0 °C to room temperature and (3) $SnCl_2$, 50% HOAc, THF, room temperature. (ii) (1) *n*-BuLi, THF, −78 °C and (2) 2-isopropoxy-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane, −78 °C to room temperature; (iii) Pd(dppf)Cl_2, KOAc, bis(pinacolato)diboron, toluene/DMF, 90 °C; (iv) Pd(PPh_3)$_4$, $NaHCO_3$, THF, reflux.

units in **P3**−**P6** shifted to the downfield compared to those in P1, which indicates that arylethynyl substituents at 9,10-positions contribute to the conjugation of the polymers. The number-average molecular weights (M_ns) of **P1** and **P3**−**P6** are in the range of 0.67×10^4−1.54×10^4 g/mol relative to polystyrene standard, as shown in Table 1. Solubility of **P2** at room temperature is not enough for GPC measurements. Thermal properties of the polymers were investigated by thermal gravimetric analysis (TGA) in a N_2 atmosphere. As shown in Figure 2, the decomposition temperatures of the polymers are all above 300 °C (**P1**: 338 °C; **P2**: 307 °C; **P3**: 363 °C; **P4**: 326 °C; **P5**: 329 °C; **P6**: 321 °C).

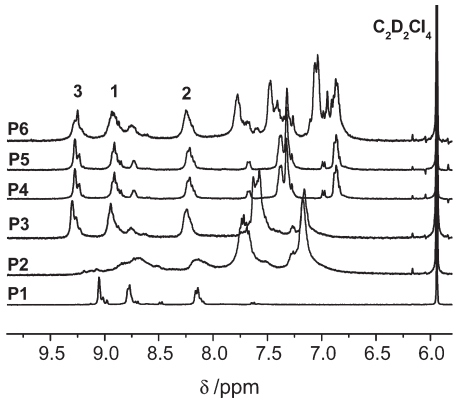


Figure 1. ^{1}H NMR spectra of polymers **P1**−**P6** in $C_2D_2Cl_4$ at 80 °C.

Table 1. Number-Average Molecular Weights (M_ns), Polydispersity Indices (PDIs), Absorption Edges (λ_{edge}^{abs}), Photoluminescence Maximum (λ_{max}^{PL}), and HOMO Energy Levels of Polymers P1−P6

			λ_{edge}^{abs} (nm)		λ_{max}^{PL} (nm)		
polymer	M_n[a]	PDI[a]	solution[b]	film	solution[b]	film	HOMO[c] (eV)
P1	6 700	1.51	513	564	515	560	−5.32
P2			578	620	551	681	
P3	15 400	2.62	568	588	561	636	−5.21
P4	10 000	2.51	570	625	580	680	−5.22
P5	14 300	2.18	570	618	575	650	−5.25
P6	11 900	1.88	578	624	575	665	−5.19

[a] Measured in chloroform for **P1** and in THF for **P3**−**P6**; M_n and PDI of **P2** could not be measured due to its poor solubility in chloroform and THF. [b] Measured in chloroform with a concentration of 10^{-5} M of the repeating unit. [c] Estimated by the equation HOMO = −(4.80 + ΔE_{oxd}^{onset}); electrochemical properties of **P2** could not be measured due to its poor solubility.

Solution (10^{-5} M of the repeating unit in chloroform) and film UV−vis absorption and photoluminescence (PL) spectra of the polymers are displayed in Figure 3. All polymers exhibit very broad absorption spectra in both solutions and films, probably due to the contribution of multiabsorption bands as like in two-dimensional conjugated small molecules.[30] In solution, the long wavelength absorption maximum of **P1** is at 489 nm, a 6 nm red-shift compared to that of the previously reported penta(9,10-bisalkynyl-2,6-anthrylene).[23] Its optical bandgap is 2.42 eV as calculated from the absorption edge (513 nm). Compared to **P1**, the absorption edges of **P2**−**P5** red-shift to about 570 nm, which is attributed to the extended conjugation of the polymers as the substituents are changed from alkynyl to phenylethynyl. It was found that the number of alkyl or alkoxy groups in phenyl ring had negligible effect on the optical bandgap but noticeably

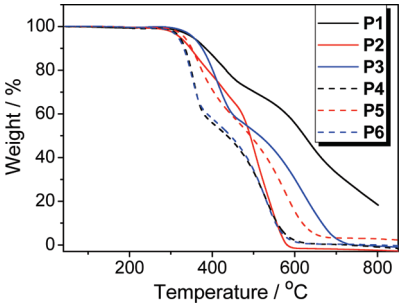


Figure 2. TGA curves of polymers **P1**−**P5** in a N_2 atmosphere with a heating rate of 10 °C min^{-1}.

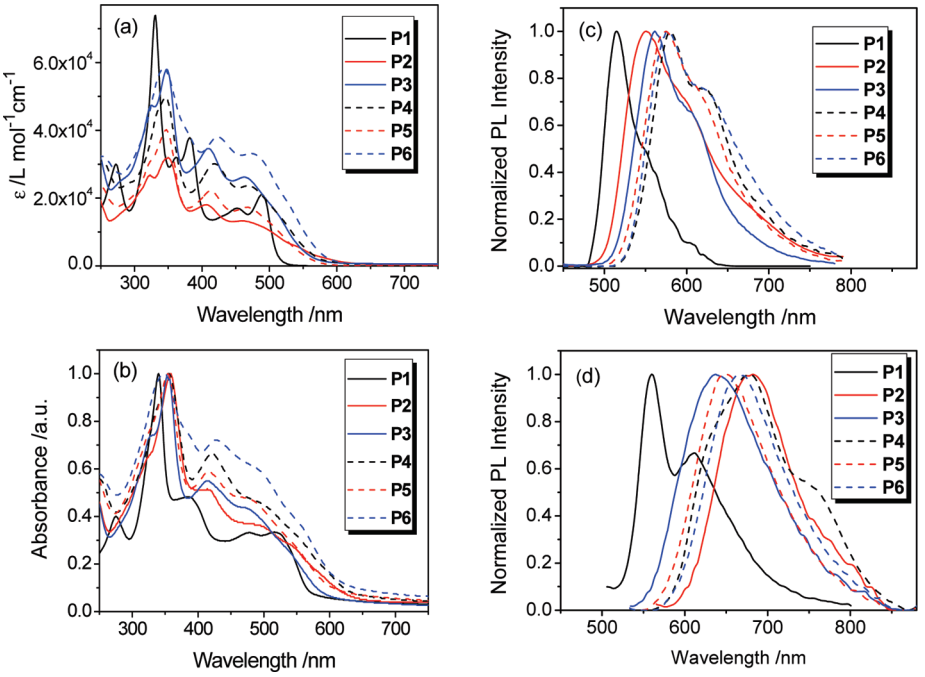


Figure 3. Solution (a and c, 10^{-5} M of the monomer units in chloroform) and film (b and d) UV−vis (a and b) and PL (c and d) spectra of **P1**−**P6**. The films were prepared by spin-coating their chloroform or chlorobenzene solutions (5 mg/mL in chloroform for **P1**, 3 mg/mL in chloroform for **P3**−**P6**, and 3 mg/mL in chlorobenzene for **P2**) at 1000 rmp onto quartz substrates.

affected the absorption coefficient of the polymers. Polymers **P2** and **P5**, which contain the anthracene units with one straight dodecyl alkyl chain in each phenyl ring, exhibit much smaller absorption coefficients than polymers **P3** and **P4**. Polymer **P6**, which carries arylethynyl groups with the longest conjugation length, exhibits a small red-shift of the absorption edge but the strongest absorption in the long wavelength region compared to **P2**−**P5**. This indicates that further increasing the conjugation length of the substituents at 9,10-positions will not contribute to the delocalization of the polymer chains. Unlike 9,10-diphenyl-substituted polymer PBPA, the absorption edges of polymers **P1**−**P6** in solid state show a bathochromic shift of 20−55 nm while comparing with those in dilute solution, indicating enhanced intermolecular interaction in solid state.

As shown in Figure 3c,d, similar to the phenomenon in absorption spectra, extension of the conjugation of the monomers renders the polymers red-shifted PL spectra. In dilute solution, **P1**−**P6** exhibit PL maxima at 515, 551, 561, 580, 575, and 575 nm, respectively. Introduction of more alkyl chains and exchange of alkyl chains with alkoxyl ones can also induce a 10−20 nm red-shift. From solution to film, PL spectra of **P1**−**P6** show a pronounced red-shift of 75−130 nm, which is consistent with the strong aggregation tendency of the polymers. The red-shift for **P2** is as large as 130 nm, which implies that the molecules can form aggregates with strong intermolecular interaction. This phenomenon is consistent with the poorest solubility of the polymer. In contrast, both absorption and PL spectra of poly-[9,10-di(*p*-dodecylphenyl)anthracen-2,6-diyl] (PBPA) display a small red-shift of 5 nm.[21] All above results indicate that the introduction of aryl substituents to the anthracene unit through a triple bond not only can extend the conjugation of the monomers for modulation of the bandgap of poly(2,6-anthrylene)s but also can avoid the steric-hindrance-induced twist of the aryl substituents form anthracene plane for increasing intermolecular interaction in solid state.

The electrochemical properties of the polymers were investigated by differential pulse voltammetry (DPV) in *o*-dichlorobenzene (**P1**) or methylene chloride (**P3**−**P6**) in a three-electrode electrochemical cell with Bu_4NPF_6 (0.1 M) and Ag/AgCl as the electrolyte and reference electrodes, respectively, as shown in Figure 4. The HOMO energy levels of **P1** and **P3**−**P6** were estimated to be −5.32, −5.21, −5.22, −5.25, and −5.19 eV, respectively. DPV characterization could not be accomplished for **P2** due to its poor solubility in employed solvents. However, the HOMO level of **P2** should be also around −5.2 eV, identical to that of **P3**−**P6**.

The broad absorption spectra of **P1**−**P6** should favor the harvesting of solar energy for application in PSCs.[31] Therefore, bulk heterojunction PSCs were fabricated with the device structure of ITO/PEDOT:PSS(30 nm)/polymer:PCBM(1:2)/Al-(100 nm). Preparation of the homogeneous films from **P2** was rather difficult due to its poor solubility. Therefore, devices were only prepared based on **P1** and **P3**−**P6**. Current density−voltage curves of the devices under the illumination of white light (100 mW/cm^2) are shown in Figure 5a. The devices show the open-circuit voltage (V_{oc}) of 0.86−1.03 V, the short-circuit current density (J_{sc}) of 1.36−3.18 mA/cm^2, the fill factor (FF) of 0.43−0.54, and the power conversion efficiency (PCE) of 0.56−1.60%, as in Table 2. The polymer **P1** exhibits the highest PCE of 1.60% with a V_{oc} of 0.96 V, a J_{sc} of 3.18 mA/cm^2, and a FF of 0.53. Figure 5b depicts the external quantum efficiency (EQE) curves of the devices based on **P1** and **P3**−**P5**. The response wavelength region of all polymers is well consistent with their absorption spectra as shown in Figure 3b. Polymer **P1** exhibits the highest EQE of 35% at 466 nm. This is consistent with its highest PCE.

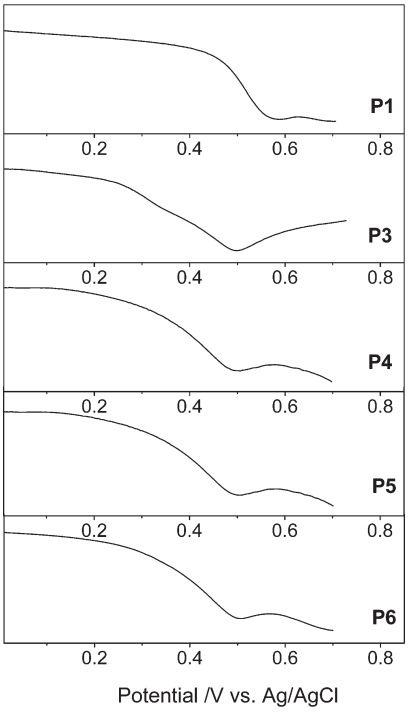


Figure 4. Differential pulse voltammograms (DPV) of the polymers (**P1** in *o*-dichlorobenzene, **P3**−**P6** in methylene chloride).

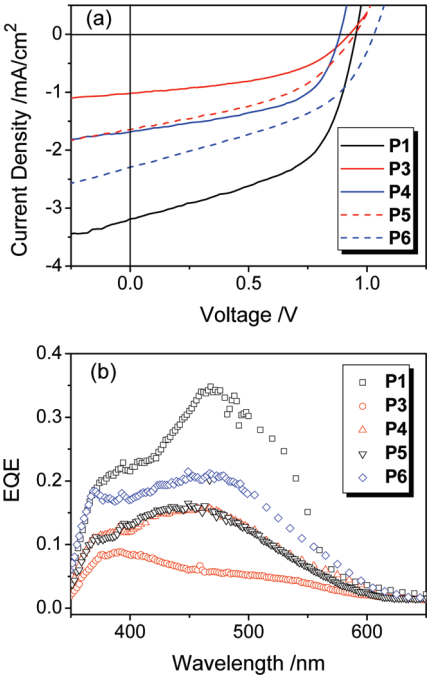


Figure 5. $I-V$ curves under the illumination of 100 mW/cm^2 white light (a) and external quantum efficiency (EQE) curves (b) of the polymer solar cells based on **P1** and **P3**−**P5**.

Table 2. Device Properties of the Polymers P1 and P3−P6 with the Device Structure of ITO/PEDOT:PSS/Polymer:PCBM(1:2)/Al

polymer	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
P1	0.96	3.18	0.53	1.60
P3	0.86	1.36	0.48	0.56
P4	0.88	1.67	0.54	0.80
P5	0.91	1.73	0.45	0.71
P6	1.03	2.30	0.43	1.03

Conclusions

A series of novel soluble conjugated polymers **P1**−**P6** with 9,10-bisarylethynylanthracene and 9,10-bisalkynylanthracene as the repeating units have been synthesized by typical Suzuki polymerization. The solubility and photophysical properties of the resulting polymers can be modified successfully through tuning the substituents at 9,10-positions of anthracene. All polymers are featured with broad absorption spectra due to their two-dimensional conjugated backbones. Comparing with poly-(9,10-bisalkynylanthracene), the introduction of phenylethynyl substituents with longer conjugation facilitates red-shifted absorption spectra. The HOMO energy levels of the polymers are −5.32 eV for **P1** and around −5.20 eV for **P3**−**P6**. Polymer solar cells (PSCs) were fabricated with the device structure of ITO/PEDOT:PSS/polymer:PCBM(1:2)/Al. Polymer **P1** exhibits the best device performance with a V_{oc} of 0.96 V, a J_{sc} of 3.18 mA/cm^2, and a FF of 0.53 to afford a PCE of 1.60%.

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Supporting Information Available: Experimental details for synthesis of intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

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