

Conjugated Copolymers of Cyanosubstituted Poly(*p*-phenylene vinylene) with Phenylene Ethynylene and Thienylene Vinylene Moieties: Synthesis, Optical, and Electrochemical Properties

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ABSTRACT: Three alternating conjugated copolymers of cyanosubstituted poly(*p*-phenylene vinylene) (CN-PPV) with phenylene ethynylene and thienylene vinylene moieties, **P1**, **P2**, and **P3**, were synthesized via cross-coupling polycondensation with Pd(PPh₃)₂Cl₂ as a catalyst. Their structures were confirmed by ¹H-NMR, IR spectroscopy, elemental analysis, and gel permeation chromatography, and the thermal, photophysical, and electrochemical properties of the copolymers were also investigated. The incorporation of a triple bond into the CN-PPV backbone led to higher reduction potentials, which corresponded to lower lowest unoccupied molecular orbital energy levels.

The three copolymers possessed broader absorption spectra, especially copolymer **P3** with its polymerization units containing two thiophene rings, which showed the broadest absorption spectrum, from 300 to 710 nm. Their high electron affinities, broad absorptions, and relatively higher oxidation potentials make the copolymers potentially good electron-acceptor material for use in photovoltaic devices. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1480–1488, 2010

Key words: fluoropolymers; luminescence; photophysics; solution properties; UV-vis spectroscopy

INTRODUCTION

Polymer solar cells (PSCs) have been recognized as part of the worldwide effort toward renewable energy resources. The advantage of their easy fabrication into flexible devices, their low cost, and their light weight have made PSCs a potential alternative to conventional silicon solar cells.^{1–4} Since the Santa Barbara group⁵ and Osaka group⁶ reported the ultrafast reversible metastable photoinduced electron transfer from conjugated polymers to C₆₀ in solid films in 1992, great attention has been paid to this field. Chemists have synthesized many kinds of conjugated polymers for application in PSCs, and much effort has been made by physicists to improve the performance of these devices.^{7–14}

PSCs have, in most cases, been fabricated by the blending of conjugated polymers (donor) with fullerene or its soluble derivatives (acceptor).^{15,16} The absorption ability is a very important aspect that must be taken into account when photosensitive materials are chosen for the fabrication of PSCs. Conjugated polymers mostly possess a strong absorption band in the visible wavelength range, and their absorption band can be modified by a change in the polymer backbone or simply by the attachment of various side groups.^{17–19} Currently, studies of photovoltaic conjugated polymers have mainly focused on the donor materials of the conjugated polymers. Li and coworkers^{20–24} have synthesized a series of polythiophene and poly(thienylene vinylene) derivatives as donors with conjugated side chains for extending their absorption spectra to cover a broader wavelength range in the visible region. The absorption spectrum of the branched poly(thienylene vinylene) covers the whole visible region from 350 to 750 nm.²³ The power conversion efficiency of the PSC based on the bi(thienylene vinylene)-substituted polythiophene as a donor material and [6,6]-phenyl-C61 butyric acid methyl

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ester (PCBM) as an acceptor reached 3.18% under an illumination of AM 1.5, 100 mW/cm².^{22(b)}

As we know, the main acceptor material used in PSCs at present is PCBM. However, PCBM has a very limited absorption in the visible and near-infrared region where solar light energy is mostly concentrated. From an absorption point of view, the use of conjugated polymers as electron acceptors could improve the absorption ability of PSCs. The main obstacle that has to be overcome for this type of PSC with a polymer donor and polymer acceptor is the lack of polymer acceptors with high electron affinities, high electron mobilities, and broad absorption bands. Only a few publications have reported PSCs with a polymer acceptor.²⁵ Kietzke et al.²⁶ reported the use of CN-ether-PPV as the polymer acceptor in a polymer blend solar cell and reached a power conversion efficiency of 1.7% under white illumination (100 mW/cm²). However, in their device, the polymer blend film only absorbed the light between 300 and 550 nm; the longer wavelength light in the visible region was not used.

In this study, we synthesized a new series of copolymers containing cyanosubstituted poly(*p*-phenylene vinylene) (CN-PPV) with phenylene ethynylene and thienylene vinylene (TV) moieties to obtain conjugated polymer acceptors with broad absorptions in the visible region and high electron affinities. The electron-withdrawing cyano units and triple bond were expected to give the polymers a high electron affinity and good photooxidative stability,²⁷ whereas the TV units could give the polymers absorption at longer wavelengths. The results indicate that the three copolymers obtained did possess high electron affinities and broad absorption spectra in the visible region.

EXPERIMENTAL

Materials

All of the solvents used in this study were purified according to standard methods before use. All other chemicals were reagent grade from Aldrich (Beijing, China) or Alfa Asia Chemical Co. (Tianjin, China), and were used as purchased without further purification. The following compounds were synthesized according to a literature procedure: 1,4-bis(octyloxy)-2,5-diiodobenzene and Pd(PPh₃)₂Cl₂.²⁸

Characterization

¹H-NMR spectra were recorded with a Bruker AM-300 spectrometer, and chemical shifts were recorded in parts per million. Elemental analysis was measured on a Flash EA 1112 elemental analyzer. Fourier transform infrared spectra were recorded on a BIO FTS-135 spectrometer by the dispersion of sam-

ples in KBr disks. The molecular weights and polydispersities of the polymers were determined by gel permeation chromatography analysis relative to polystyrene calibration [Waters 515 high pressure liquid chromatograph (HPLC) pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4)] with tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min at 35°C. Thermogravimetric analysis (TGA) was conducted on a PerkinElmer 7 thermogravimetric analyzer at a heating rate of 10°C/min under a nitrogen atmosphere. The ultraviolet-visible (UV-vis) absorption spectra were recorded on a Hitachi UV-3010 spectrometer. The photoluminescence (PL) spectra were obtained with a Hitachi F-4500 fluorescence (FL) spectrophotometer.

The cyclic voltammograms were recorded with a computer-controlled Zahner IM6e electrochemical workstation (Germany) with polymer film on a Pt plate as the working electrode, Pt wire as the counter electrode, and Ag/Ag⁺ (0.1M) as the reference.

Synthesis of the monomers and polymers

The synthetic routes of the monomers and copolymers are shown in Scheme 1. Detailed synthetic procedures are as follows.

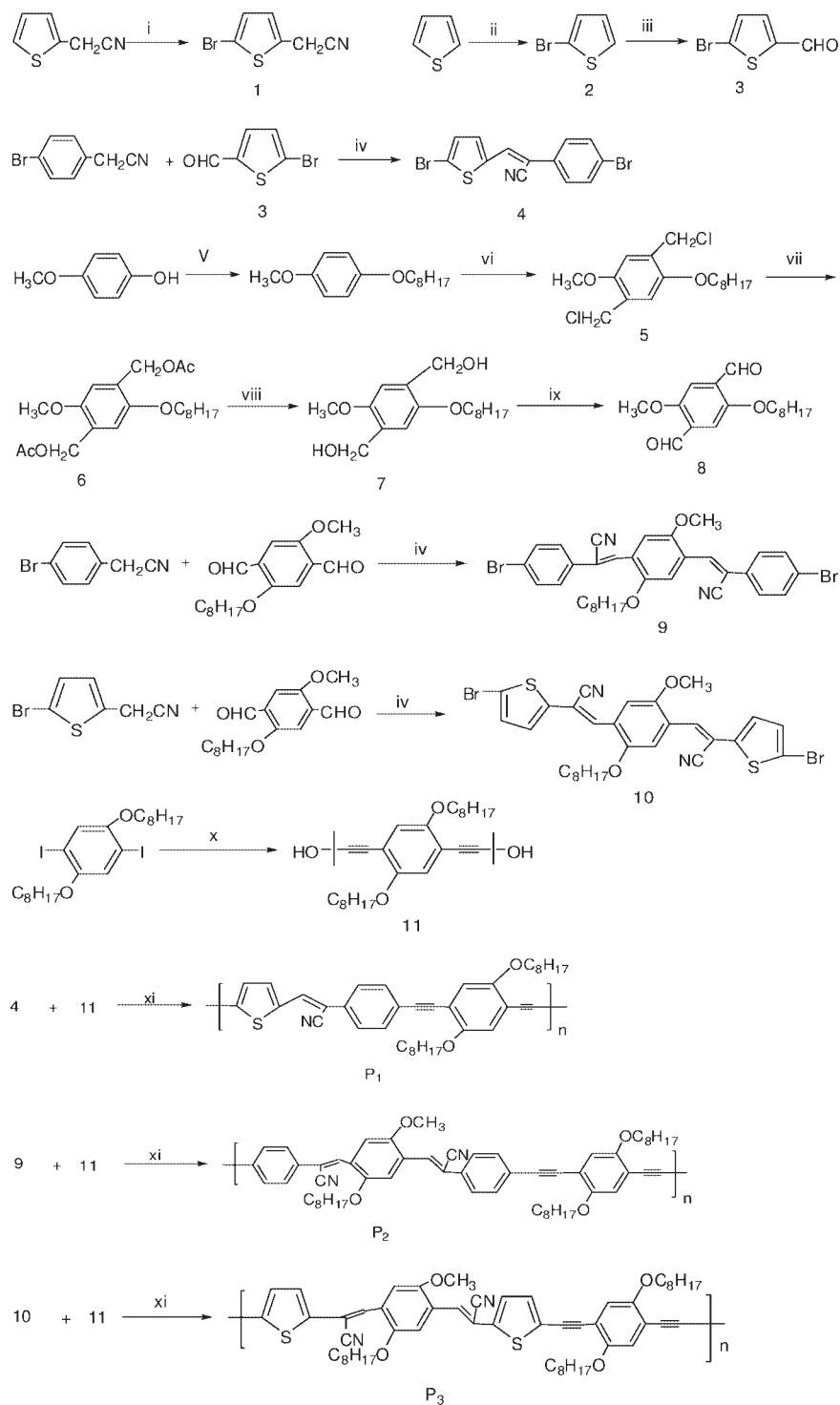
5-Bromo-2-thiopheneacetonitrile (1)

1 was synthesized by a literature procedure.²⁹ *N*-Bromosuccinimide (NBS; 6.5 g, 36 mmol) was added to a solution of 2-thiophenacetonitrile (4.29 g, 34 mmol) in *N,N*-dimethylformamide (DMF; 30 mL). The reaction mixture was stirred for 3 h at room temperature (RT) and for 2 h at 60°C. The resulting mixture was extracted with methylene chloride and washed with water repeatedly. The solvent was evaporated, and the pure colorless liquid was obtained by column chromatography with petroleum ether as an eluent (yield = 5.1 g, 77%).

Mass spectrometry (MS): *m/z* = 202 (M⁺). ¹H-NMR (CDCl₃, ppm, δ): 6.93 (d, 1H, thiophene H (ThH)), 6.81 (d, 1H, ThH), 3.82 (s, 2H, -CH₂CN). ANAL. Calcd for C₆H₂NSBr: C, 35.60%; H, 0.99%; N, 6.93%. Found: C, 35.54%; H, 0.95%; N, 6.92%.

2-Bromothiophene (2)

Thiophene (32 g, 0.38 mol) was dissolved in chloroform and acetic acid (50 mL: 50 mL, v/v) in a 250-mL, three-necked flask; bromine (62 g, 0.39 mol) was added to the solution dropwise for 5 h at 0°C. The mixture was then stirred for 24 h at RT. Then, the solution was extracted with diethyl ether; the organic extracts were washed with water three times and with KOH (aqueous) twice. The organic layer was dried over anhydrous MgSO₄, and the removal



Scheme 1 Synthetic route of the monomers and copolymers: (i) NBS, DMF, RT, 3 h, then 60°C, 2 h, 87%; (ii) Br₂, CHCl₃, CH₃COOH, RT, 24 h, 82%; (iii) POCl₃, DMF, 80°C, 4 h; (iv) EtOH, potassium tert-butoxide (*t*-BuOK), RT, 4 h; (v) Na, CH₃OH, C₈H₁₇Br, 50°C, 6 h; (vi) HCl, (HCHO)_{*n*}, HCHO, reflux, 5 h; (vii) CH₃COONa (CH₃CO)₂O, HAc, 90°C, 4 h; (viii) NaOH, EtOH, 50°C, 3 h; (ix) CH₂Cl₂, PCC, RT, 8 h; (x) 3-methyl-3-hydroxybut-1-yne, triethylamine, toluene, Pd(PPh₃)₂Cl₂, CuI, 60°C, 24 h; and (xi) Pd(PPh₃)₂Cl₂, CuI, toluene, triethylamine, NaOH, 90°C, 48 h.

of solvent gave a light yellow crude product. Distillation afforded 50.7 g (0.31 mol, yield = 82%) of a colorless liquid.

Gas chromatography–mass spectrometry (GC–MS): *m/z* = 162. ¹H-NMR (CDCl₃, ppm, δ): 6.69 (s, 1H), 6.91 (s, 1H), 7.09 (s, 1H).

5-Bromothiophene-2-carbaldehyde (3)

POCl₃ (35 mL) was dropped into the DMF (27 mL) dropwise under an iced bath; the solution turned red, and then, the mixture was stirred for 0.5 h. Then, **2** (25.7 g, 0.158 mol) was added to the mixture, and the reaction solution was heated to 80°C for 4 h. After the solution was cooled to RT, 50 mL of water was added to hydrolyze the reaction mixture. Then, the solution was extracted with chloroform, and the organic extracts were washed with water four times and with KOH (aqueous) twice. The colorless liquid was afforded by column chromatography with petroleum ether/ethyl acetate (10 : 1) as an eluent (22.33 g, 0.12 mol, yield = 74%).

GC-MS: *m/z* = 191.

¹H-NMR (CDCl₃, ppm, δ): 9.61 (s, 1H -CHO), 7.34 (s, 1H-ThH), 7.01 (s, 1H, -ThH).

2-(4-Bromophenyl)-3-(5-bromothiophen-2-yl) acrylonitrile (4)

4 was synthesized by a literature procedure.²⁹ To a solution of 4-bromophenyl acetonitrile (3.92 g, 20 mmol) at RT, 100 mL of ethanol and compound **3** (3.82 g, 20 mmol) were added. The mixture was then stirred for 30 min; *t*-BuOK (1.0 g, 9 mmol) in 40 mL of ethanol was added to the reaction mixture dropwise. The mixture was stirred for 4 h at RT. The yellow precipitate was filtered out and washed with water and methanol (yield = 6.91 g, 93.6%).

GC-MS: *m/z* = 369; ¹H-NMR (CDCl₃, ppm, δ): 7.57–7.47 (m, 5H), 7.33 (d, 1H), 7.11 (s, 1H). UV-vis (CHCl₃) λ_{max} = 364 nm; FL (CHCl₃) λ_{max} = 430 nm, where λ_{max} is the maximum absorption wavelength.

4-[(Acetyloxymethyl)-5-octoxyl-2-methoxyphenyl] methyl acetate (6)

1,4-Bis(chloromethyl)-5-octoxyl-2-methoxy benzene (**5**) was prepared as described earlier.³⁰ A mixture of 10.26 g (30.8 mmol) of compound **5**, anhydrous sodium acetate (12.8 g, 154.4 mmol), acetic anhydride (8.7 mL, 92.4 mmol), and acetic acid (160 mL) was stirred at 90°C for 3 h. After it was cooled, the mixture was poured into a large amount of distilled water and extracted with methylene chloride, evaporated to give the product, and recrystallized from hexane to afford white solids of **6** (yield = 11 g, 93%).

MS: *m/z* = 380 (M⁺). ¹H-NMR (CDCl₃, ppm, δ): 6.92 (s, 2H), 5.12 (s, 4H, -CH₂Ac), 3.90 (d, 2H, -OCH₂-), 3.82 (s, 3H, -OCH₃), 2.10 (s, 6H), 1.72–1.3 (m, 12H, -CH₂-), 0.90 (m, 3H, -CH₃). ANAL. Calcd for C₂₁H₃₂O₆: C, 66.29%; H, 8.48%. Found: C, 66.12%, H, 8.40.

[[4-Hydroxymethyl)-5-octoxyl-2-methoxyphenyl] methyl-1-ol (7)

A mixture of compound **6** (5.85 g, 15.4 mmol) and sodium hydroxide (7.62 g, 78.15 mmol) in 110 mL of ethanol was stirred at 55°C for 3 h; after it was cooled, it was poured into 300 mL of distilled water. This was then neutralized with a diluted aqueous hydrochloric acid solution, the solution was extracted with methylene chloride, and the evaporation of the organic layer under reduced pressure afforded a white crystal-like solid (yield = 6.1 g, 95%).

MS: *m/z* = 296 (M⁺). ¹H-NMR (CDCl₃, ppm, δ): 6.87 (s, 2H, ArH), 4.68 (s, 4H, -CH₂O), 3.95 (t, 2H, -OCH₂), 3.82 (s, 3H, -OCH₃), 1.73–1.32 (m, 12H, -CH₂), 0.90 (m, 3H, -CH₃). ANAL. Calcd for C₁₇H₂₈O₄: C, 68.92%; H, 9.46%. Found: C, 68.88%; H, 9.37%.

5-Octoxyl-2-methoxy benzene-1,4-dialdehyde (8)

8 was synthesized by a literature procedure.³¹ A solution of compound **4** (4.3 g, 15 mmol) in 150 mL of methylene chloride was stirred and cooled with an ice bath while pyridinium chlorochromate (PCC; 9.95 g, 46.12 mmol) was added in a portionwise manner over a period of 0.5 h. The reaction mixture was then stirred for 8 h at RT until the oxidation process was complete (as monitored by thin-layer chromatography). After a dark brown suspension formed, the mixture was diluted with 200 mL of diethyl ether and washed with a dilute HCl solution. The solution was concentrated, and the remaining green solid was purified by column chromatography with petroleum ether as an eluent under reduced pressure. The pure greenish yellow solid was obtained with a yield of 3.81 g (87%).

MS: *m/z* = 292 (M⁺). ¹H-NMR (CDCl₃, ppm, δ): 10.52 (s, 1H, -CHO), 10.49 (s, 1H, -CHO), 7.43 (s, 2H, ArH), 4.07 (t, 2H, -OCH₂), 3.93 (s, 3H, -OCH₃), 1.81 (t, 2H, -CH₂), 1.50–1.20 (m, 10H, -CH₂), 0.87 (t, 3H, -CH₃). ANAL. Calcd for C₁₇H₂₄O₄: C, 69.86%; H, 8.22%. Found: C, 69.88%; H, 8.35%.

2,5-Bis[2-(4'-bromophenyl)-2-cyanovinyl]-2-octoxyl-5-methoxybenzene (9)

9 was synthesized by a literature procedure.²⁹ 4-Bromophenyl acetonitrile (1.96 g, 10 mmol) and **8** (1.46 g, 5 mmol) were dissolved in 80 mL of dry ethanol under a nitrogen atmosphere in a flask. A mixture of 252 mg (2.25 mmol) of *tert*-butoxide and 20 mL of ethanol was added dropwise. The reaction mixture was stirred overnight, and the precipitate was filtered out and washed with water and methanol. An orange-red solid was obtained in a yield of 3.10 g (96%).

GC-MS: $m/z = 648$ (M^+). $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 7.86 (s, 1H, ArH), 7.93 (s, 1H, ArH), 7.89 (s, 1H, -vinyl), 7.83 (s, 1H, -vinyl), 7.60–7.52 (m, 8H, -ArH), 4.05 (d, 2H, $-\text{OCH}_2$), 3.91 (s, 3H, $-\text{OCH}_3$), 1.80 (m, 2H, $-\text{CH}_2$), 1.54–1.28 (m, 10H, $-\text{CH}_2$), 0.88 (t, 3H, $-\text{CH}_3$). UV-vis (CHCl_3) $\lambda_{\text{max}} = 352$ and 438 nm. FL (CHCl_3) $\lambda_{\text{max}} = 513$ nm.

2,5-Bis[2-(4'-bromothieryl)-2-cyanovinyl]-2-octyloxy-5-methoxybenzene (**10**)

10 was synthesized similar to the procedure used for compound **9**.²⁹

GC-MS: $m/z = 660$ (M^+). $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 7.83 (s, 1H, -ArH), 7.79 (s, 1H, -ArH), 7.75 (s, 1H, -vinyl), 7.70 (s, 1H, -vinyl), 7.15 (d, 2H, -ThH), 7.05 (d, 2H, -ThH), 4.10 (t, 2H, $-\text{OCH}_2$), 3.93 (s, 3H, $-\text{OCH}_3$), 1.85 (t, 2H, $-\text{CH}_2$), 1.52–1.25 (m, 10H, $-\text{CH}_2$), 0.89 (t, 3H, $-\text{CH}_3$). UV-vis (CHCl_3) $\lambda_{\text{max}} = 464$ nm, FL (CHCl_3) $\lambda_{\text{max}} = 529$ nm.

1,4-Bis(3-methyl-3-hydroxybut-1-ynyl)-2,5-dioctoxybenzene (**11**)

1,4-Bis(octoxy)-2,5-diiodobenzene (2.93 g, 5 mmol) and 3-methyl-3-hydroxybut-1-yne (2 mL) were dissolved in 30 mL of dry triethylamine and 30 mL of toluene; the mixture turned gray. A gentle stream of argon was bubbled into the mixture for 15 min. After the addition of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.2 g, 0.28 mmol) and copper(I) iodide (CuI; 0.12 g), the mixture was heated to 60°C under an inert atmosphere, and it remained at that temperature for 24 h; it was then cooled to RT. Appropriate toluene was added to the reaction solution. After filtration, the solvent was evaporated under reduced pressure to give an orange oil; then, a pale yellow solid was obtained by column chromatography eluted from petroleum ether to petroleum ether/ethyl acetate (10 : 1) with a 78% yield.

IR: 3294 (vs, OH), 2916, 2858, 2205 (w, $\text{C}\equiv\text{C}$). $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 6.85 (s, 2H), 3.92 (t, 4H), 2.0 (s, 2H), 1.62 (s, 12H), 1.80–1.25 (m, 24H), 0.88 (t, 6H). ANAL. Calcd for $\text{C}_{32}\text{H}_{50}\text{O}_4$: C, 77.11; H, 10.04; O, 12.85. Found: C, 77.52; H, 10.21. UV-vis (CHCl_3) $\lambda_{\text{max}} = 344$ nm, FL (CHCl_3) $\lambda_{\text{max}} = 373$ nm.

Copolymer P1

Under an Ar atmosphere, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.0615 g, 0.0876 mmol), CuI (0.0634 g, 0.333 mmol), triphenylphosphine (PPh_3 ; 0.1259 g, 0.48 mmol), and tetrabutylammonium chloride (0.5 mL) were added to a stirred mixture solution of 15 mL of toluene, 5 mL of 5.5 mol/L NaOH, and 3 mL of triethylamine. After it was degassed at RT for 20 min, monomer **4** (0.369 g, 1 mmol) and monomer **11** (0.498 g, 1 mmol) were added. The reaction mixture was then stirred

at 90°C for 2 days. The reaction mixture was cooled to RT, poured into some amount of methanol, and then filtered into a Soxhlet thimble. Soxhlet extractions were successively performed with methanol, hexane, and CHCl_3 . The polymer was recovered from the CHCl_3 fraction by rotary evaporation. The black-purple solid was obtained after drying *in vacuo* overnight. The yield, elemental analysis, molecular weight, $^1\text{H-NMR}$, and optical data of the polymer were as follows.

Yield = 47%. Weight-average molecular weight (M_w) = 16235, M_w /number-average molecular weight (M_n) = 1.94. IR (KBr, cm^{-1}): 2926, 2855, 2353, 2208, 1669, 1579, 1467, 1262, 1217, 1092, 1024, 981, 801, 728, 565, 542. $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 7.72–7.40 (br, 7H); 7.02–6.93 (br, 2 H); 4.04 (br, 4H); 1.87–1.29 (m, 24H); 0.87 (s, 6H). ANAL. Calcd for $\text{C}_{39}\text{H}_{43}\text{NSO}_2$: C, 79.45%; H, 7.30%; N, 2.38%; S, 5.43%; O, 5.43%. Found: C, 76.25%; H, 7.29%; N, 2.35%; Br, 2.1%. UV-vis (CHCl_3) $\lambda_{\text{max}} = 453$ nm, FL (CHCl_3) $\lambda_{\text{max}} = 534$ nm.

Copolymer P2

This polymer (red-black solid) was synthesized with the same procedure used for **P1**, but monomer **9** was used instead of **4**.

Yield = 42%. IR (KBr, cm^{-1}): 2957, 2925, 2209, 1666, 1603, 1516, 1417, 1260, 1218, 1020, 931, 692. $M_w = 8911$, $M_w/M_n = 1.56$. $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 8.09 (d, 1H), 7.91 (d, 1H), 7.71–7.34 (br, 8H), 7.04 (m, 2H), 4.14–3.91 (br, 9H), 1.87–1.26 (br, 36H), 0.88 (br, 9H). ANAL. Calcd for $\text{C}_{59}\text{H}_{68}\text{N}_2\text{O}_4$: C, 81.57%; H, 7.83%; N, 3.23%; O, 7.37%. Found: C, 77.23%; H, 7.45%; N, 3.18%; Br, 2.3%. UV-vis (CHCl_3) $\lambda_{\text{max}} = 441$ nm, FL (CHCl_3) $\lambda_{\text{max}} = 540$ nm.

Copolymer P3

Copolymer **P3** (purple solid) was synthesized with the same procedure as that used for **P1**, but monomer **10** was used instead of **4**.

Yield = 38%. IR (KBr, cm^{-1}): 2928, 2213, 1583, 1423, 1221, 1018, 678. $M_w = 15836$, $M_w/M_n = 1.62$. $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 7.98–7.22 (br, 10H), 4.12–3.96 (br, 9H), 1.88–1.23 (br, 36H), 0.87 (br, 9H). ANAL. Calcd for $(\text{C}_{56}\text{H}_{64}\text{N}_2\text{SO}_4)_n$: C, 78.14%; H, 7.44%; N, 3.26%; O, 7.44%. Found: C, 74.38%; H, 7.38%; N, 3.20%; Br, 1.84%. UV-vis (CHCl_3) $\lambda_{\text{max}} = 511$ nm, FL (CHCl_3) $\lambda_{\text{max}} = 591$ nm.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic routes for the preparation of the monomers and polymers are depicted in Scheme 1.

TABLE I
Molecular Weights and Thermal Properties of the Polymers

Polymer	Yield (%)	M_w	M_w/M_n	T_d^a
P1	47	16,235	1.94	405
P2	42	8911	1.56	240
P3	38	15,836	1.62	367

^a T_d measured by TGA under N_2 .

Monomer **1** was obtained from 2-thiopheneacetonitrile and NBS by a bromination reaction. Monomer **4** was prepared from (4-bromophenyl) acetonitrile and compound **3** through a Knoevenagel condensation with about an 80% yield. The synthesis of **8** was based on **5** and proceeded in a multistep process via the bis(acetoxymethyl) derivative **6**, which was converted to the bis(hydroxymethyl) derivative **7** and finally oxidized with PCC to give **8** in an overall yield of 77%. Monomers **9** and **10** were synthesized from bromoaryl acetonitrile, and compound **8** was synthesized with the same method as **4**. Monomer **11** was synthesized from 1,4-bis(octoxy)-2,5-diiodobenzene and 3-methyl-3-hydroxybut-1-yne by a Pd-catalyzed Heck coupling reaction. The three copolymers were prepared by a cross-coupling polycondensation of **11** and **4**, **9**, and **10**, respectively, with a catalyst of $Pd(PPh_3)_2Cl_2$ and a phase-transfer catalyst of tetrabutylammonium chloride, and the polymers were obtained after the removal of the protective isopropyl alcohol groups during the polymerization.

The chemical structures of the copolymers were confirmed by 1H -NMR spectroscopy, Fourier transform infrared spectroscopy, and elemental analysis. The IR spectra showed a sharp band around 2210 cm^{-1} ($C\equiv N$) and a very weak band around 2300 cm^{-1} ; however, no absorption from the terminal hydroxyl function group expected around 3294 cm^{-1} was observed. Because of the inducement effect on the vinylenic double bonds of the cyano group, the IR band of the double bond shifted to a higher wave number around 1018 cm^{-1} , which confirmed the all-

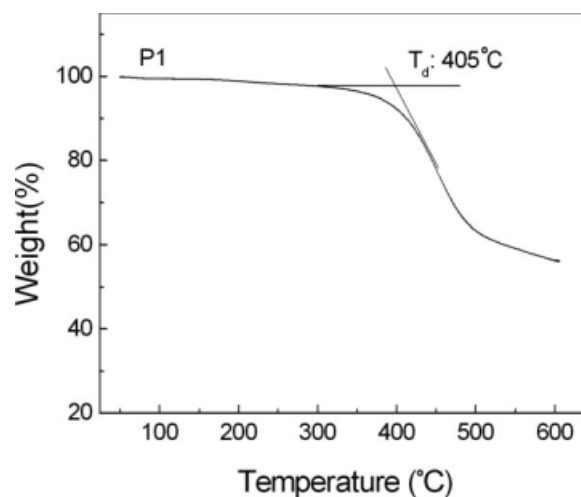


Figure 1 TGA curve of copolymer **P1**.

trans configuration of the vinylenic double bonds. The elemental analysis showed slightly lower carbon, hydrogen, and nitrogen contents than expected. All of the copolymers had good solubility in common solvents such as tetrahydrofuran, CH_2Cl_2 , $CHCl_3$, and toluene, which resulted from the long side chains attached to the repeating units.

The molecular weights of the copolymers were measured by gel permeation chromatography with reference to polystyrene standards. As listed in Table I, these copolymers had M_w values of 8911–15,836 with polydispersity indices (M_w/M_n) of 1.56–1.94. The thermal properties of the copolymers were determined from TGA. Figure 1 gives the TGA curve of copolymer **P1** with an onset decomposition temperature (T_d) of 405°C under nitrogen, which revealed the good thermal properties of the polymer **P1**. As shown in Table I, the thermal stability sequence was **P1** > **P3** > **P2**. A decrease in the thermal stability from **P1** to **P3** to **P2** may have resulted from the greater number of alkoxy chains introduced into the polymer backbone. The stability of these polymers is adequate for the fabrication of photovoltaic devices.

TABLE II
Optical Properties of the Polymers

Polymer	UV-vis absorption spectra				PL spectra		
	In $CHCl_3$	In the film		In $CHCl_3$	In the film		
	λ_{max} (nm)	$\lambda_{max}/\text{absorbance}$ ($\text{nm } 10^{-2} \text{ nm}^{-1}$) ^a	λ_{onset} (nm)	E_g^{opt} (eV) ^b	λ_{max} (nm)	λ_{max} (nm)	Φ_{PL}^c solution (%)
P1	453	474/0.55	611	2.03	534	625	4
P2	441	478/0.40	614	2.02	540	638	50
P3	511	512/1.14	706	1.75	591	—	8

^a This value was obtained from dividing the maximum absorbance in the visible region by the thickness of the film.

^b Band gap estimated from the onset wavelength of the optical absorption.

^c The quantum efficiency with FL as the standard.

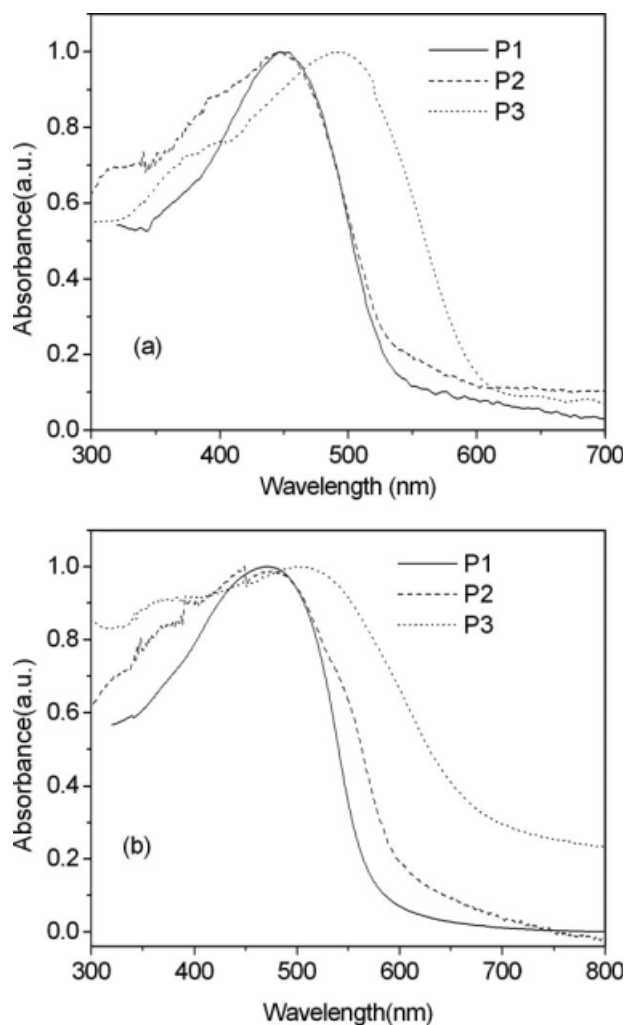


Figure 2 Absorption spectra of (a) the polymer dilute solutions in chloroform and (b) the polymer films on quartz plates.

Photophysical properties

The photophysical characteristics of the polymers were investigated in solution and in the solid state. The absorption spectral data for the polymer solutions and films are summarized in Table II. Figure 2(a) shows the absorption spectra of the copolymer solutions in chloroform. P1 and P2 exhibited absorption maxima at 453 and 441 nm, respectively. The absorption maximum of P3 showed an obvious bathochromic shift of 70 nm compared to that of P2, which indicated that the replacement of two benzene rings by two thiophene rings in the copolymers reduced the bandgap of the polymers effectively. The absorption spectra of the polymer films are shown in Figure 2(b). The absorption bands of the polymer films broadened obviously in comparison with those of the polymer solutions. Particularly, the absorption band of the P3 film covered a very broad wavelength range from 300 to 700 nm, which would be very desirable for application in

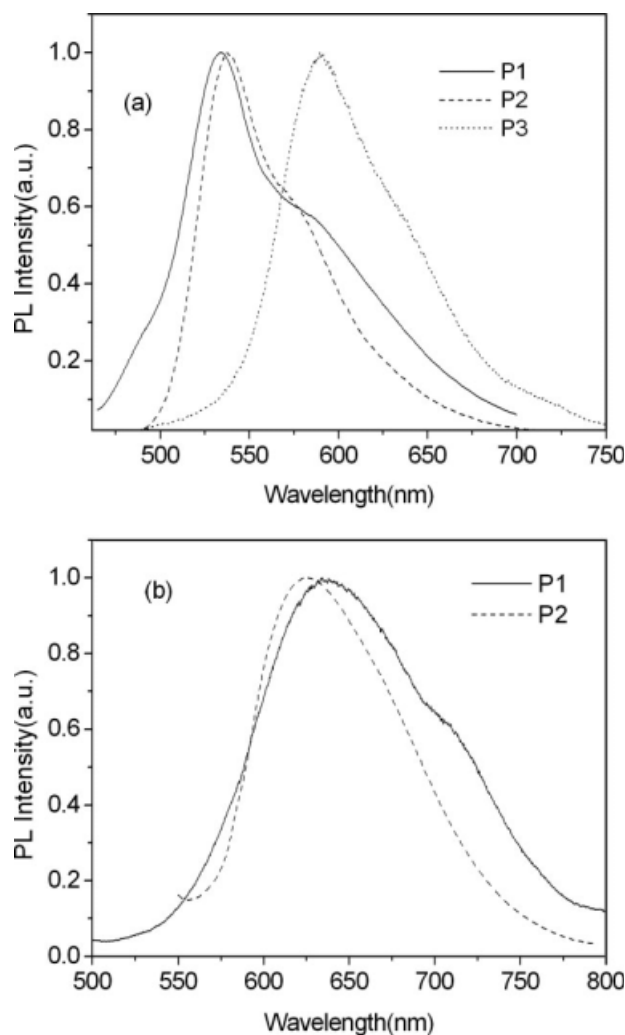


Figure 3 PL spectra of (a) the polymer dilute solutions in chloroform and (b) the polymer films on quartz plates.

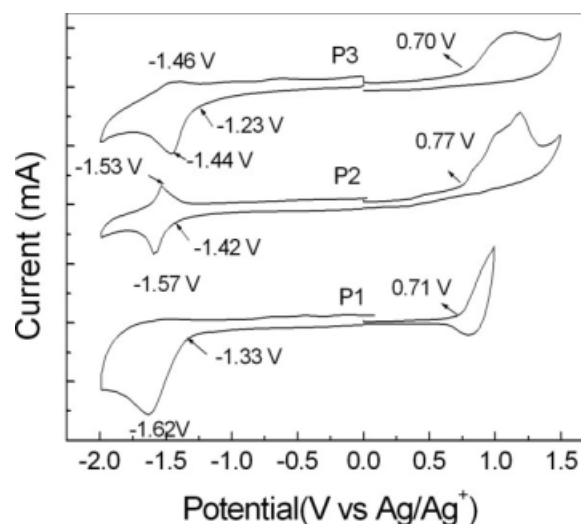


Figure 4 Cyclic voltammograms of the polymer films on platinum plates in an acetonitrile solution of 0.1 mol/L $[\text{Bu}_4\text{N}]\text{PF}_6$ (Bu = butyl) with a scan rate of 50 mV/s.

TABLE III
Optical and Electrochemical Properties of the Polymers

Polymer	Cyclic voltammograms				E_g^{EC} (eV)
	<i>p</i> doping		<i>n</i> doping		
	E_{on}^{ox} (V)	HOMO (eV)	E_{on}^{red} (V)	LUMO (eV)	
P1	0.71	-5.42	-1.33	-3.38	2.04
P2	0.77	-5.48	-1.42	-3.29	2.19
P3	0.70	-5.41	-1.23	-3.48	1.93

E_g^{EC} , electrochemical band gap.

PSCs. The absorption band edges of the **P1**, **P2**, and **P3** films were 611, 614, and 710 nm, respectively, which corresponded to band gaps of 2.03, 2.02, and 1.74 eV, respectively. To investigate the light harvest ability of the polymer films for application in PSCs, we calculated the peak absorbance for 1 nm thick film of the polymers, and the results are also listed in Table II. The absorbance of the **P3** film was much higher than that of **P1** and **P2**, which indicated that **P3** possessed better light-harvesting ability than the other two polymers.

Figure 3 shows the PL spectra of the polymer solutions and films. The **P1**, **P2**, and **P3** solutions exhibited emission peaks around 534, 540, and 591 nm, respectively [see Fig. 3(a)] with the excitation at the maximum absorption wavelength. While in the solid state, **P1** and **P2** both exhibited intense red emission peaks at about 625 and 638 nm, whereas the emission of **P3** was very weak, probably because of the introduced thienylene-vinylene units in the polymer because poly(thienylene vinylene)s is a nonluminescent polymer.³²

Electrochemical properties

The electrochemical behavior of the copolymers was investigated by cyclic voltammetry in an acetonitrile solution of 0.1M [Bu₄N]PF₆ (Bu = butyl) at a sweep rate of 50 mV/s at RT under the protection of argon. A Pt plate coated with a thin polymer film was used as the working electrode. A Pt wire and an Ag/Ag⁺ electrode were used as the counter and reference electrodes, respectively.

Figure 4 shows the cyclic voltammograms of the polymers. **P2** and **P3** showed reversible *n*-doping/dedoping processes but irreversible *p*-doping processes. The onset oxidation potentials of **P1**, **P2**, and **P3** were 0.71, 0.77, and 0.70 V versus Ag/Ag⁺, respectively, which was obviously higher than that of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) (0.41 V)²⁰ and P3HT (0.05 V).^{22(b)} The onset reduction potentials of **P1**, **P2**, and **P3** occurred at about -1.33, -1.42, and -1.23 V versus Ag/Ag⁺, respectively, which was greatly higher than that of MEH-PPV (-2.01 V)¹⁷ and P3HT (-2.16

V).^{22(b)} The results indicate that the three copolymers possessed high electron affinities, which could be attributed to the cyanosubstitution and the incorporation of triple bonds into the polymer main chains.

It is well known that the onset potentials of *p* and *n* doping correspond to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of conjugated polymers.^{33,34} So we obtained the HOMO and LUMO energy levels of the copolymers from the following equations:³⁵

$$\text{HOMO} = -e(E_{on}^{ox} + 4.71) \text{ (eV)} \quad (1)$$

$$\text{LUMO} = -e(E_{on}^{red} + 4.71) \text{ (eV)} \quad (2)$$

where the unit of the onset potential is volts versus Ag/Ag⁺, E_{on}^{ox} is the onset potentials of the oxidation, and E_{on}^{red} is the onset potentials of the reduction. From the onset potentials of the oxidation and reduction processes, the band gaps of **P1**, **P2**, and **P3** were estimated to be about 2.04, 2.19, and 1.93 eV, respectively. The electrochemical data are also listed in Table II for comparison with the optical properties. From Table III, the LUMO and HOMO energy levels of **P1**, **P2**, and **P3** were estimated to be -3.38, -3.29, and -3.48 eV and -5.42, -5.48, and -5.41 eV, respectively. It was obvious that the copolymers had lower LUMO and HOMO energy levels, which indicated that the copolymers could be potentially used as electron acceptors in PSCs.

CONCLUSIONS

Three alternating copolymers of CN-PPV with phenylene ethynylene and TV moieties were synthesized by a palladium-catalyzed cross-coupling reaction. The optical and electrochemical properties were characterized in detail. The incorporation of triple bonds into the CN-PPV backbone led to higher reduction potentials that corresponded to lower LUMO energy levels. The insertion of thienylene-vinylene units in the copolymers resulted in broader absorption spectrum covering the range from 300 to 710 nm. High electron affinity, broad absorption,

and relatively higher oxidation potential values make the copolymers potentially good electron-acceptor materials for use in PSCs.

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