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New cyano-substituted copolymers containing biphenylenevinylene and bithienylenevinylene units: synthesis, optical, and electrochemical properties

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Abstract Two new cyano-substituted copolymers containing biphenylenevinylene and bithienylenevinylene moieties (DCN-PPV and DCN-PTV) were synthesized by a stille condensation reaction with $Pd(PPh_3)_4$ as catalyst. Their structures were confirmed by ^{1}H NMR, IR spectroscopy, and elemental analysis. The thermal, optical, and electrochemical properties of the polymers were investigated. The results show that the polymers possess high thermal decomposition temperature and reversible *n*-doping/dedoping processes. In addition, DCN-PTV has higher electron affinity with a low LUMO energy level of −3.84 eV and a relatively broader absorption band covering 300–780 nm, indicating that DCN-PTV could be a potential *n*-type conjugated polymer in optoelectronic devices.

Introduction

Great attention has been paid to the conjugated polymers due to their many applications in electronics such as polymer light emitting diodes [1–9], field effect transistors, polymer solar cells (PSCs), and sensors [10–19]. Among the various applications, PSCs represent a new kind of alternatives to the relative expensive inorganic solar cells. PSCs have in most cases been fabricated by blending conjugated polymers (as donor) with soluble C_{60} derivative PCBM (as acceptor) [20–25]. Solar cells convert absorbed light energy into electric energy, so the absorption ability of the materials is a very important aspect to be taken into account when choosing photovoltaic materials.

Fullerenes are excellent electron acceptors, but they have very limited absorption in the visible and near-infrared part of the spectrum which is the main part of the solar light energy. The conjugated polymers not only have strong absorption in the visible wavelength range, but their absorption and intensity can be further modified by changing the polymer backbone or simply by attaching various side groups [26–28]. From the absorption point of view, the use of the conjugated polymers as electron acceptors could improve the absorption ability of the photovoltaic devices. But only a few papers have been published on the PSCs with cyano-substituted PPV derivatives as electron acceptors [29–31], due to the absence of good acceptor polymers.

In this article, we describe the facile synthesis and properties of two novel cyano-substituted copolymers containing biphenylenevinylene and bithienylenevinylene moieties (DCN-PPV and DCN-PTV). The results demonstrate that DCN-PTV has high electron affinity, broad absorption, and excellent stability, which indicates that the

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polymer could be potentially used as electron acceptors in polymer solar cells.

Experimental part

Materials

$Pd(Ph_3)_4$, $(C_4H_9)_3SnCl$, BuLi (2.5 M in hexanes) were obtained from Alfa Asia Chemical Co, and they were used as received. Toluene was dried over Na/benzophenone ketyl and freshly distilled prior to use. The other chemical reagents were common commercial level and used as received.

Characterization

^1H NMR spectra were measured on a Bruker DMX-300 or Bruker DMX-400 spectrometer. Elemental analysis was measured on a Flash EA 1112 elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a BIO FTS-135 spectrometer by dispersing samples in KBr disks. Absorption spectra were taken on a Hitachi U-3010 UV–Vis spectrophotometer. The photoluminescence (PL) spectra were obtained with a Hitachi F-4500 Fluorescence spectrophotometer. The molecular weight of polymers was measured by GPC method, and polystyrene was used as a standard. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation. 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 electrode and the reference electrode, respectively. In these conditions, the oxidation potential (E_{ox}) of ferrocene was 0.09 V versus Ag/Ag^+. The HOMO and LUMO energy levels were determined from the oxidation and reduction onset from the CV spectra assuming ferrocene to be −4.8 eV from vacuum. Electrochemical onsets were determined at the position where the current starts to differ from the baseline.

Synthesis

Synthetic routes of the monomers and polymers are shown in Scheme 1.

*5-Bromo-2-thiopheneacetonitrile (**1**)*

This was synthesized by the literature procedure [32]. *N*-Bromosuccinimide(6.5 g, 36 mmol) was added to a solution of 2-thiophenacetonitrile (4.29 g, 34 mmol) in *N*,*N*-dimethylformamide (30 mL). The reaction mixture was stirred for 3 h at room temperature and for 2 h under 60 °C. The resulting mixture was extracted with methylene chloride and washed with water repeatedly. After the extraction, the solvent was evaporated and the pure colorless liquid was obtained by column chromatography using petroleum ether as an eluent (yield: 5.1 g, 77%) MS: $m/z = 202$ (M^+). ^1H NMR ($CDCl_3$, ppm, δ): 6.93(d, 1H, ThH), 6.81(d, 1H, ThH), 3.82(s, 2H, $–CH_2CN$). Anal. Calcd. For C_6H_2NSBr: C 35.60, H 0.99, N 6.93; Found: C 35.54, H 0.95, N 6.92.

*4-(Acetyloxymethyl)-5-octyloxyl-2-methoxylphenyl) methyl acetate (**3**)*

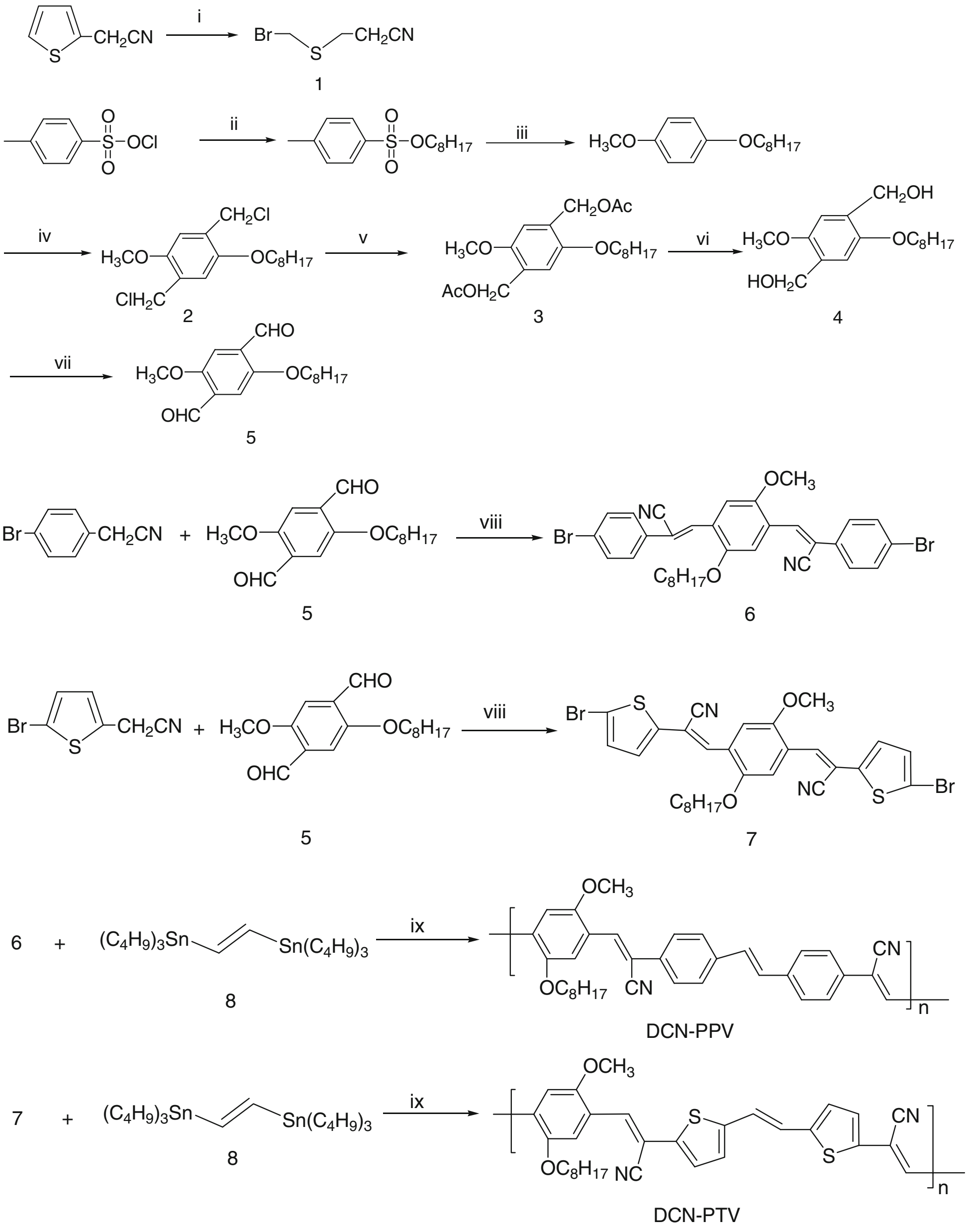
1,4-Bis(chloromethyl)-5-octyloxyl-2-methoxyl benzene (**2**) was prepared as described earlier [8]. A mixture of 10.26 g (30.8 mmol) of compound **2**, anhydrous sodium acetate (12.8 g, 154.4 mmol), acetic anhydride (8.7 mL, 92.4 mmol), and acetic acid (160 mL) was stirred at 90 °C for 3 h. After being cooled, the mixture was poured into the large amount of distilled water and extracted with methylene chloride, the solvent was evaporated to give the product and recrystallized from hexane to afford a white solid of **3** (yield: 11 g, 93%). MS: $m/z = 380$ (M^+). ^1H NMR ($CDCl_3$, ppm, δ): 6.92(s, 2H, ArH), 5.12(s, 4H, $–CH_2Ac$), 3.90(d, 2H, $–OCH_2–$), 3.82(s, 3 H, $–OCH_3$), 2.10(s, 6 H), 1.72–1.3(m, 12H, $–CH_2–$), 0.90(m, 3H, $–CH_3$). Anal. Calcd. For $C_{21}H_{32}O_6$: C 66.29, H 8.48; Found: C 66.12, H 8.40.

*[(4-Hydroxymethyl)-5-octyloxyl-2-methoxylphenyl] methyl-1-ol (**4**)*

A mixture of compound **3** (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 being cooled, it was poured into 300 mL of distilled water. And this was then neutralized with diluted aqueous hydrochloric acid solution, the solution was extracted with methylene chloride, and the evaporation of the organic layer under reduced pressure afforded white crystal-like solid. (Yield: 6.1 g, 95%). MS: $m/z = 296$(M^+). ^1H NMR ($CDCl_3$, ppm, δ): 6.87(s, 2H, ArH), 4.68(s, 4H, $–CH_2O$), 3.95(t, 2H, $–OCH_2$), 3.82(s, 3H, $–OCH_3$), 1.73–1.32(m, 12H, $–CH_2–$), 0.90(m, 3H, $–CH_3$). Anal. Calcd. For $C_{17}H_{28}O_4$: C 68.92, H 9.46; Found: C 68.88, H 9.37.

*5-Octyloxyl-2-methoxyl benzene-1,4-dialdehyde (**5**)*

This was synthesized by the literature procedure [33]. 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 pyridinum chlorochromate (PCC) (9.95 g, 46.12 mmol) was added in a portion wise manner over a period of half an hour. The reaction mixture was then



Scheme 1 Synthetic routes of the monomers and polymers. (i) NBS, DMF, rt, 3h, then 60 °C, 2h, 77%; (ii) $C_8H_{17}OH$, pyridine, 0–5 °C, 2h, rt, 6h; 83%; (iii) 4-hydroxyanisole, DMF, K_2CO_3, reflux, 4h; (iv) HCl, $(HCHO)n$, HCHO, reflux, 5h; (v) NaOAc, Ac_2O, HAc, 90 °C, 4h; (vi) NaOH, EtOH, 50 °C, 3h; (vii) CH_2Cl_2, PCC, rt, 8h; (viii) t-BuOK, EtOH, rt, 5h; (ix) $Pd(PPh_3)_4$, toluene, reflux, 12h

stirred for 8 h at room temperature until the oxidation process was completed (as monitored by thin layer chromatography). After a dark brown suspension has formed, the mixture was diluted with 200 mL diethyl ether and washed with diluted HCl solution. The solution was concentrated, and the remaining green solid was purified by column chromatography using petroleum ether as eluent under reduce pressure. The pure greenish yellow solid was obtained with a yield of 3.81 g (87%). MS: $m/z = 292(M^+)$. ^{1}H NMR ($CDCl_3$, ppm, δ):10.52(s, 1H, –CHO), 10.50(s, 1H, –CHO), 7.45(s, 2H, ArH), 4.07(t, 2H, $-OCH_2$), 3.89(s, 3H, $-OCH_3$), 1.81(t, 2H, $-CH_2$), 1.50–1.20(m, 10H, $-CH_2$), 0.87(t, 3H, $-CH_3$). Anal. Calcd. For $C_{17}H_{24}O_4$: C 69.86, H 8.22; Found: C 69.88, H 8.35.

*2,5-Bis{2-(4′-bromophenyl)-2-cyanovinyl}-2-octyloxyl-5-methoxylbenzene (**6**)*

This was synthesized by the literature procedure [32]. 4-Bromophenyl-acetonitrile (1.96 g, 10 mmol) and the compound **5** (1.46 g, 5 mmol) were dissolved in 80 mL of dry ethanol under nitrogen atmosphere in the flask. A mixture of 252 mg (2.25 mmol) of tert-butoxide potassium and 20 mL of ethanol was added drop wisely. The reaction mixture was stirred overnight; the precipitate was filtered out and washed with water and methanol. An orange red solid was obtained with a yield of 3.10 g (96%). MS: $648(M^+)$. ^{1}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, $-OCH_2$), 3.91(s, 3H, $-OCH_3$), 1.80(m, 2H, $-CH_2$), 1.54–1.28(m, 10H, $-CH_2$), 0.88(t, 3H, $-CH_3$). UV–Vis($CHCl_3$) $\lambda_{max} = 352$ nm, 438 nm. FL($CHCl_3$) $\lambda_{max} = 513$ nm.

2,5-Bis{2-(4′-bromothienyl)-2-cyanovinyl}-2-octyloxyl-5-methoxylbenzene (7)

This was synthesized by the literature procedure [32]. A mixture of 5-bromo-2-thiopheneacetonitrile (3.03 g, 15 mmol) and the compound **5** (1.46 g, 5 mmol) was stirred in 70 mL of ethanol at room temperature, 480 mg of tert-butoxide potassium in 20 mL ethanol was dropped into the reaction mixture under the protection of argon. The mixture was stirred overnight at room temperature, the red solid was filtered and washed with methanol and water successively, the final product was obtained by column chromatography using petroleum ether/ethyl acetate(10:1) as eluent with a yield of 2.9 g (88%). MS: 660(M^+). ^1H 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, $-OCH_2$), 3.93 (s, 3H, $-OCH_3$), 1.85(t, 2H, $-CH_2$), 1.52-1.25(m, 10H, $-CH_2$), 0.89(t, 3H, $-CH_3$). UV–Vis($CHCl_3$) $\lambda_{max} = 464$ nm, FL($CHCl_3$) $\lambda_{max} = 529$ nm.

(E)-1,2-bis (tributylstannyl) ethane (8)

This was synthesized by the literature procedure [34]. Tributylethynylstannane (3.16 g, 10 mmol) and tributyltin hydride (3.06 g, 10.5 mmol) were put into a flask, and 0.03 g 2,2′-azobis(2-methylpropionitrile) was added. Under the protection of nitrogen, the mixture was heated to 100 °C for 6 h, distillation (170 °C, 40 Pa) with a yield of 5.2 g (85%) of (E)-1,2-bis (tributylstannyl) ethane as a clear, colorless oil.

GC–MS: *m/z* 606. Purity (by GC/MS) > 97%. ^1H NMR ($CDCl_3$, ppm, δ): 6.82 (s, 2H), 1.49–1.65 (m, 12 H), 1.25–1.46 (m, 12 H), 0.80–1.0 (m, 30 H). Anal. Calcd. For $C_{26}H_{56}Sn_2$: C, 51.52; H, 9.31; Found: C, 51.32; H, 9.78.

DCN-PPV

$Pd(PPh_3)_4$ (50 mg, 0.043 mmol), compound **6** (0.648 g, 1 mmol), compound **8** (0.605 g, 1.0 mmol) were put into a three-neck flask. The mixture was flushed with argon for 10 min, and then 15 mL toluene was added. Under the protection of argon, the reactant was heated to reflux for 12 h. The mixture was cooled to room temperature and poured into 30 mL of methanol and then filtered into a Soxhlet thimble. Soxhlet extractions were performed with methanol, hexane, and chloroform. The polymer was recovered from the chloroform fraction by rotary evaporation. The solid was dried under vacuum overnight. Yield: 23%. ^1H NMR ($CDCl_3$, ppm, δ): 8.10–7.41(br, 12H), 7.20–6.90(br, 2H), 4.14–3.91 (br, 5H), 2.05–0.88 (br,15H). Anal. Calcd. For $(C_{35}H_{34}N_2O_2)n$: C 81.17, H 6.61, N 5.45; Found: C 79.23, H 6.31, N 5.33, Br 1.92. $M_n = 8695$, $M_W = 12782$; poly dispersity = 1.47. IR (KBr, cm^{-1}): 2961, 2923, 2852, 2208, 1636, 1541, 1458, 1260, 1092, 1215, 1092, 1018, 799, 595.

DCN-PTV

The synthetic process is similar to that of DCN-PPV but compound **7** instead of **6** was used as the monomer. Yield: 19%. ^1H NMR ($CDCl_3$, ppm, δ): 8.04–7.41(br, 8H), 7.22–6.87(br, 2H), 4.12–3.91(br, 5H), 1.97–0.88(br, 15H). Anal. Calcd. For $(C_{31}H_{30}N_2S_2O_2)n$: C 70.72, H 5.70, N 5.32; Found: C 69.16, H 5.62, N 5.27, Br 1.85. $M_n = 9453$, $M_W = 14370$; poly dispersity = 1.52. IR (KBr, cm^{-1}): 2957, 2921, 2857, 2213, 1546, 1505, 1306, 1260, 1211, 1092, 1024, 801, 598.

Results and discussions

Material synthesis

DCN-PPV and DCN-PTV were synthesized by Stille coupling polycondensation, the synthesis routes of monomers and polymers are illustrated in Scheme 1. The pure polymers were obtained after the precipitation from methanol and successive Soxhlet extraction with methanol, hexane, chloroform, and recovered from $CHCl_3$ solution. DCN-PPV is a red powder while DCN-PTV is a purple powder. They can be dissolved in conventional organic solvents such as methylene chloride, chloroform, and toluene, the solubility is attributed to the two unsymmetrical alkoxyl side chains on the benzene ring of the polymers. But the yield of the two polymers is low, due probably to insolubility of some crude polymers with too higher molecular weight or cross linking between dibromo monomer and the vinyl group of the other monomer.

The chemical structures of the two polymers DCN-PPV and DCN-PTV were confirmed by ^1H NMR, Infrared spectroscopy, and elemental analysis. The number of aromatic and aliphatic protons estimated from integration of the peaks is consistent with the expected repeating unit of the copolymers. The IR spectra show a sharp ($C\equiv N$) band around 2208 and 2213 cm^{-1} for DCN-PPV and DCN-PTV, respectively. The vinylene C=C band together with the aromatic C=C band appears as a broad peak at 1630 cm^{-1}. Because of the inducement effect on the vinylene double bonds of the cyano group, its band shifts to a higher wavenumber at 1018 and 1024 cm^{-1} for DCN-PPV and

DCN-PTV, respectively. The elemental analysis shows the content of carbon, hydrogen, and nitrogen slightly lower than that expected.

The thermal properties of DCN-PPV and DCN-PTV were analyzed by thermal gravimetric analysis (TGA) under a nitrogen atmosphere with a heating rate of 10 K/min. Typical TGA curves demonstrated that the polymers are highly thermostable. Thermal decomposition starts at around 360 and 345 °C, and 5% weight loss was recorded at 425 and 410 °C for DCN-PPV and DCN-PTV respectively.

Optical properties

The UV–Vis absorption spectra of the polymers are shown in Fig. 1. The absorption spectra of the DCN-PPV and DCN-PTV in $CHCl_3$ solution exhibit the absorption maxima at 466 and 552 nm, respectively. Corresponding to the difference of their absorption, the color of DCN-PPV and DCN-PTV chloroform solutions is obviously different: DCN-PPV is red, but DCN-PTV is dark purple. In solid film, the absorption maxima locate at 479 and 531 nm for DCN-PPV and DCN-PTV, respectively. In comparison with the absorption of the polymer solutions, the absorption peak position of DCN-PPV shifted to longer wavelength, while that of DCN-PTV blue shifted a little. The absorption band of DCN-PTV with bithienylenevinylene in its main chain red-shifted by more than 50 nm than that of DCN-PPV with biphenylenevinylene in the main chain. The absorption edge of DCN-PPV and DCN-PTV films are 675 and 780 nm, respectively, corresponding to the bandgap of 1.84 eV for DCN-PPV and 1.59 eV for DCN-PTV. Interestingly, DCN-PTV possesses a broad absorption from 450 to 780 nm, which should be beneficial to the application as photovoltaic material. The optical data are summarized in Table 1.

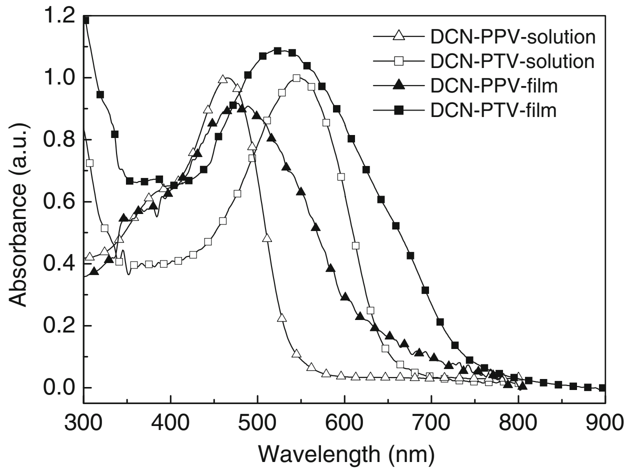


Fig. 1 UV–vis absorption spectra of DCN-PPV and DCN-PTV solutions in $CHCl_3$ and films on a quartz plate

Figure 2 shows the photoluminescence (PL) spectra of DCN-PPV and DCN-PTV in $CHCl_3$ solutions and films. In solution, DCN-PPV and DCN-PTV exhibit PL emission maxima at 538 and 630 nm, respectively. The PL peaks of DCN-PPV and DCN-PTV films locate at 643 and 720 nm, respectively.

Electrochemical properties

Cyclic voltammetry (CV) was employed to investigate the redox behavior of the polymers and to estimate their HOMO and LUMO energy levels. Figure 3 shows the cyclic voltammograms of the polymers. The two polymers show reversible *n*-doping/dedoping (reduction/re-oxidation) processes. The electrochemical *n*-doping (reduction) of DCN-PPV and DCN-PTV starts at about −1.15 and −0.87 V versus Ag/Ag^+, respectively. The electrochemical *p*-doping (oxidation) of DCN-PPV and DCN-PTV starts at about 0.85 and 0.65 V versus Ag/Ag^+, respectively.

It is well-known that the onset potentials of the *p*- and *n*-doping are corresponding to the HOMO and LUMO energy levels of the conjugated polymers [35, 36]. So we can get the HOMO and LUMO energy levels of DCN-PPV and DCN-PTV according to the equations [37]: $\mathrm{HOMO} = -e\left(E_{on}^{ox} + 4.71\right)(\mathrm{eV})$; $\mathrm{LUMO} = -e\left(E_{on}^{red} + 4.71\right)(\mathrm{eV})$. The energy levels calculated together with the electrochemical data are also listed in Table 2 for comparison with the optical data. The electrochemical bandgap $\left(E_g^{EC}\right)$ calculated from the LUMO and HOMO is slightly different with the optical bandgap $\left(E_g^{opt}\right)$ within the range of 0.2–0.5 eV. The lower LUMO and HOMO energy levels of the two

Table 1 The optical properties of DCN-PPV and DCN-PTV

Polymer	UV–vis absorption spectra				PL spectra	
	In $CHCl_3$	In film			In $CHCl_3$	In film
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	λ_{max}	λ_{max} (nm)
DCN-PPV	383, 465	477	675	1.84	538	643
DCN-PTV	531,550	530	780	1.59	630	720

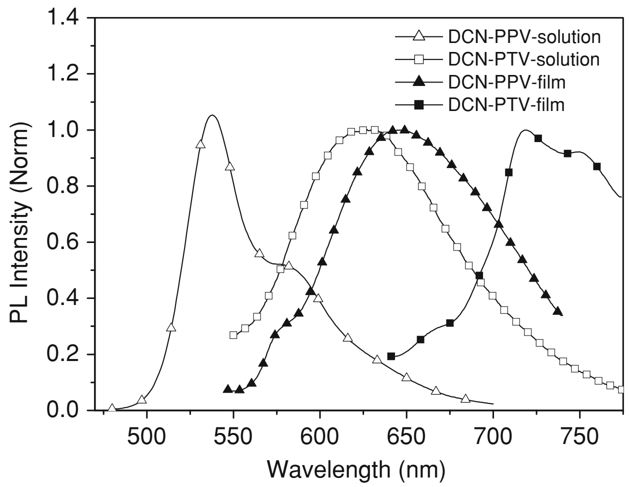


Fig. 2 PL spectra of DCN-PPV and DCN-PTV solutions in $CHCl_3$ and films on a quartz plate

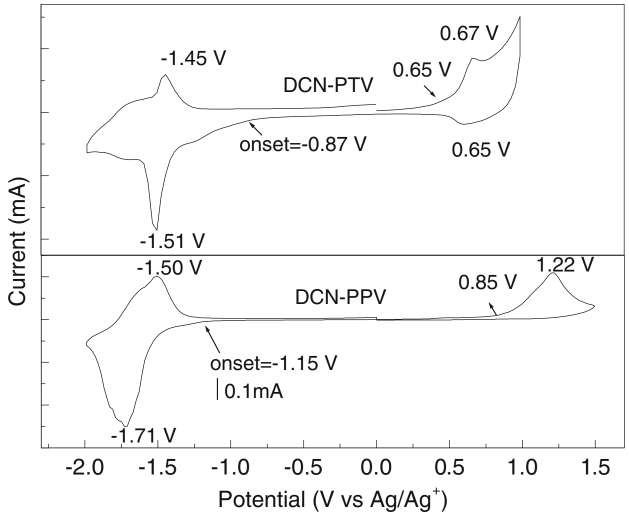


Fig. 3 Cyclic voltammograms of the polymer films on platinum plate electrode in an acetonitrile solution of 0.1 M $[Bu_4N]PF_6$ (Bu = butyl) with a potential scan rate of 50 mV/s

Table 2 The electrochemical properties of DCN-PPV and DCN-PTV

Polymer	Cyclic voltammograms				
	p-Doping		*n*-Doping		E_g^{EC} (eV)
	E_{on}^{ox} (V)	HOMO (eV)	E_{on}^{red} (V)	LUMO (eV)	
DCN-PPV	0.85	−5.56	−1.15	−3.56	2.0
DCN-PTV	0.65	−5.36	−0.87	−3.84	1.52

polymers suggest that the new polymers can act as *n*-type conjugated polymers. Combining with the broad absorption band, DCN-PTV could be a promising photovoltaic acceptor material used in PSCs [38].

Conclusions

Two cyano-substituted copolymers containing biphenylenevinylene and bithienylenevinylene moieties (DCN-PPV and DCN-PTV) were synthesized by the stille polycondensation. The polymers possess high thermal stability and reversible *n*-doping/dedoping processes. In addition, DCN-PTV has a higher electron affinity with a low LUMO energy level of −3.84 eV and a relatively broader absorption band covering 300–780 nm. The results indicate that the polymer DCN-PTV can act as an *n*-type material, especially for electron acceptors for photovoltaic cells due to its broad absorption and high electron affinity.

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