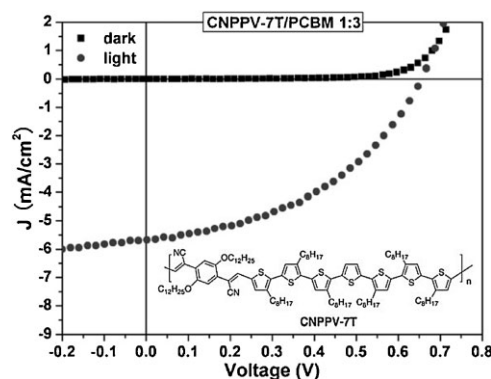


Synthesis of New Conjugated CNPPV Derivatives Containing Different Lengths of Oligothiophene Units for Organic Solar Cells

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A new series of CNPPV derivatives that contain oligothiophenes in the polymer backbone, have been synthesized by Knoevenagel polycondensation. Different lengths of oligothiophene units have been introduced to study the relationship between polymer structure and electronic properties. Thermal stability, UV-vis absorption spectra, and electrochemical properties of the copolymers were studied. The bandgaps estimated from UV-vis spectra varied from 1.77 to 1.83 eV. BHJ photovoltaic cells from different copolymers and a soluble fullerene derivative have been fabricated. The best PCE of 1.62% was obtained for the polymer CNPPV-7T, with a short-circuit current of $5.68 \text{ mA} \cdot \text{cm}^{-2}$, open-circuit voltage of 0.66 V, and fill factor of 43.2%.



Introduction

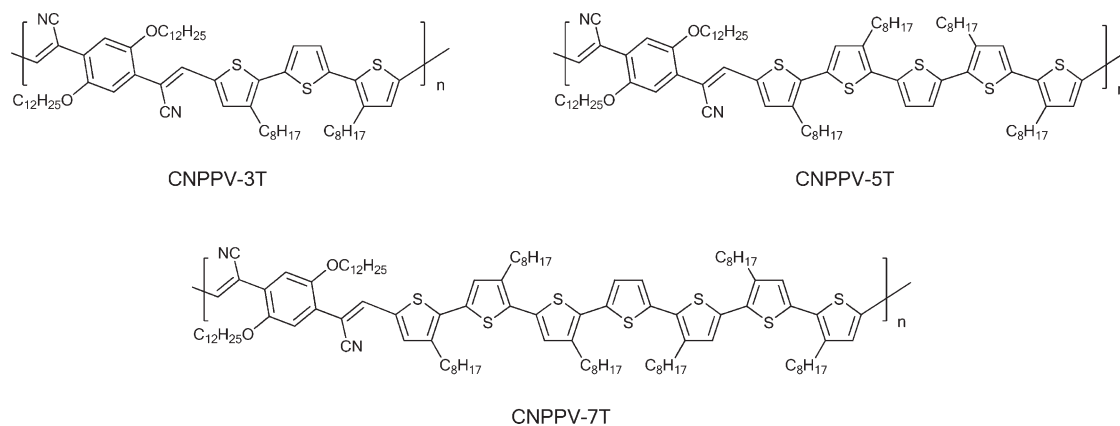
Organic solar cells based on conjugated polymer semiconductors have become increasingly feasible owing to projected advantages over their inorganic counterparts, including solution processability, light weight, low cost, and potential applications in flexible large-area devices.^[1–5] In recent years, considerable attention has been drawn to the research of organic solar cells, from the device structures and fabrication techniques, to new materials design.^[6–9] Bulk heterojunction (BHJ) structures based on intimate blends of polymeric donors and soluble fullerene derivative acceptors in particular have emerged as the most efficient to

date.^[10–15] So far, such devices based on polymer/fullerene blends have achieved high power conversion efficiencies (PCEs) of more than 7%.^[15]

In recent years, low-bandgap (< 2.0 eV) conjugated polymers have been promising materials for the development of organic solar cells because of the improved harvest of the solar photon flux.^[16] Many works have demonstrated that alternating the conjugated electron-rich donor (D) unit and conjugated electron-deficient acceptor (A) units in the same polymer backbone is an effective strategy for tuning the properties of polymers, especially to reduce the bandgap and broaden the absorption spectra.^[17]

Cyano-substituted poly[2,5-bis(dodecyloxy)-*p*-phenylenevinylene]s (CNPPV) with electron-deficient cyano groups on the vinyl units, display high electron affinities and electron-transport properties and have been used as electron acceptors in organic photovoltaic (OPV) devices.^[18–20] To effectively reduce the bandgap of CNPPV below 2 eV, electron-rich thiophene units with lower aromaticities have been incorporated into the main chain to form a D/A-type polymer. Vanderzande^[21,22] and co-

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■ Scheme 1. Structures of CNPPV-3T, CNPPV-5T, and CNPPV-7T.

workers reported a series of CNPPV derivatives with different alkyl or alkoxy side chains on the thiophene rings. One of the polymer blends with [6,6]-phenyl-C-61-butyric acid methyl ester (PCBM) as the active layer in BHJ devices achieved a PCE of 0.14%. Optimization of this device by thermal annealing showed a slight increase of PCE to 0.19%. Reynold^[23,24] and co-workers also reported synthesizing a range of CNPPV derivatives containing dioxithiophene moieties in the polymer backbone. The best photovoltaic device based on these polymer blends with PCBM as the active layer showed a PCE of $\approx 0.4\%$. Oligothiophenes possess extensive π -electron delocalization along the molecular backbone and are well known as high hole-transporting materials, but solution-processable CNPPV analogues of this class using different lengths of oligothiophene as repeat units in the polymer backbone are rarely studied.

In this work, we present a family of three conjugated polymers based on 1,4-bis(cyanomethyl)-2,5-bis(dodecyloxy)benzene (**1**) and oligothiophenes. By changing the lengths of oligothiophenes in the repeat donor moiety, we were able to tune the polymer's electronic and photophysical properties. An optical bandgap between 1.77 and 1.83 eV was found, which makes these polymers promising for solar cells. BHJ-type devices with PCBM as the acceptor were fabricated in order to investigate the photovoltaic properties of CNPPV-3T, CNPPV-5T, and CNPPV-7T (Scheme 1).

Experimental Part

Materials and Reagents

All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. Tetrahydrofuran (THF) was distilled over Na/benzophenone under argon atmosphere. All starting materials were purchased from commercial suppliers and used without further purification. The

starting materials, diformylterthiophene (**2**), diformylquinquethiophene (**3**), and diformylseptithiophene (**4**), were synthesized according to our reported literature procedures.^[25] 1,4-Bis(cyanomethyl)-2,5-bis(dodecyloxy)benzene (**1**) was obtained by a three-step synthetic path from hydroquinone as described elsewhere.^[23,26]

Instruments and Measurements

The ^1H NMR spectra were recorded on a Bruker AV400 Spectrometer. Gel permeation chromatography (GPC) analysis was conducted on a Waters 510 system using polystyrene as the standard and THF as eluent at a flow rate of $1.0\text{ mL} \cdot \text{min}^{-1}$ at 40°C . Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis curves were recorded on a Netzsch STA 409PC instrument under purified nitrogen gas flow with a $5^\circ\text{C} \cdot \text{min}^{-1}$ heating rate. UV-Vis spectra were obtained with a Jasco V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. CH_3CN was distilled from calcium hydride under dry nitrogen immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6 , 0.1 M) in CH_3CN was used as the supporting electrolyte, and the scan rate was $50\text{ mV} \cdot \text{s}^{-1}$.

Fabrication of Polymer Solar Cells

All the photovoltaic devices were fabricated by using a common process. The indium-tin oxide (ITO) coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 20 min each and subsequently dried in a vacuum oven at 60°C for 12 h. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P VP AI4083) was spin-coated (4000 rpm, ca. 40 nm thick) onto the ITO surface in air. After being baked at 150°C for 30 min, the ITO/PEDOT:PSS substrate was transferred into a nitrogen-filled glove box ($< 0.1\text{ ppm O}_2$ and H_2O). The active layer

was then spin-coated from a blend of a polymer (8 mg · mL⁻¹)/PCBM (1:1, w/w) solution in *o*-dichlorobenzene (ODCB) at 1500 rpm for 1 min onto the ITO/PEDOT:PSS substrate without further special treatment. Subsequently, the device was completed by depositing a 1 nm thick layer of LiF and an 80 nm thick layer of Al under < 10⁻⁶ Torr pressure. The active area of the device was ≈ 4 mm².

General Procedure of Polymerization

In a solution consisting of THF/*t*-butanol (1:1, v/v), compound **1**, and the corresponding oligothiophene derivatives (**2–4**) were dissolved at room temperature. Potassium *t*-butoxide (*t*-BuOK) was then added and the solution was heated to 70 °C for 2.5 h. The reaction mixture was then cooled to room temperature and poured into cold methanol acidified with 1 mL of acetic acid. The precipitate was then isolated by filtration and dried under vacuum. The polymer was purified by Soxhlet extraction with MeOH, hexane, and chloroform. The chloroform fraction was concentrated and precipitated into methanol to yield the polymer.

CNPPV-3T

Compound **2** (450 mg, 0.85 mmol), compound **1** (446 mg, 0.85 mmol), and *t*-BuOK (191 mg, 1.70 mmol) were used. Yield: 200 mg (23%) of a purple black solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.99 (s, 2H), 7.43 (br, 2H), 7.13 (br, 3H), 7.01 (br, 1H), 4.09 (m, 4H), 2.84 (m, 4H), 1.87 (m, 4H), 1.70 (m, 4H), 1.24 (m, 56H), 0.87 (m, 12H). GPC (THF): $\overline{M}_n = 16\ 700$; $\overline{M}_w = 24\ 800$; PDI = 1.48. (C₆₅H₉₂N₂O₂S₃)_n (1017.63)_n; Calcd. C 75.54, H 9.11, N 2.75. Found: C 74.97, H 9.01, N 2.69.

CNPPV-5T

Compound **3** (270 mg, 0.29 mmol), compound **1** (154 mg, 0.29 mmol), and *t*-BuOK (65 mg, 0.58 mmol) were used. Yield: 180 mg (44%) of a black solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (s, 2H), 7.40 (br, 2H), 7.13 (br, 6H), 4.09 (m, 4H), 2.81 (br, 8H), 1.87 (m, 4H),

1.70 (br, 8H), 1.26 (m, 76H), 0.87 (m, 18H). GPC (THF): $\overline{M}_n = 29\ 800$; $\overline{M}_w = 66\ 000$; PDI = 2.21. (C₈₈H₁₂₈N₂O₂S₅)_n (1406.30)_n; Calcd. C 75.16, H 9.17, N 1.99. Found: C 74.07, H 9.03, N 1.69.

CNPPV-7T

Compound **4** (320 mg, 0.25 mmol), compound **1** (129 mg, 0.25 mmol), and *t*-BuOK (56 mg, 0.50 mmol) were used. Yield: 300 mg (67%). ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (s, 2H), 7.39 (s, 2H), 7.12 (s, 6H), 7.02 (s, 2H), 4.09 (m, 4H), 2.81 (br, 12H), 1.88 (m, 4H), 1.70 (br, 4H), 1.29 (m, 96H), 0.88 (m, 24H). GPC (THF): $\overline{M}_n = 127\ 000$; $\overline{M}_w = 777\ 900$; PDI = 6.12. (C₁₁₂H₁₆₄N₂O₂S₇)_n (1794.97)_n; Calcd. C 74.94, H 9.21, N 1.56. Found: C 73.82, H 7.79, N 1.40.

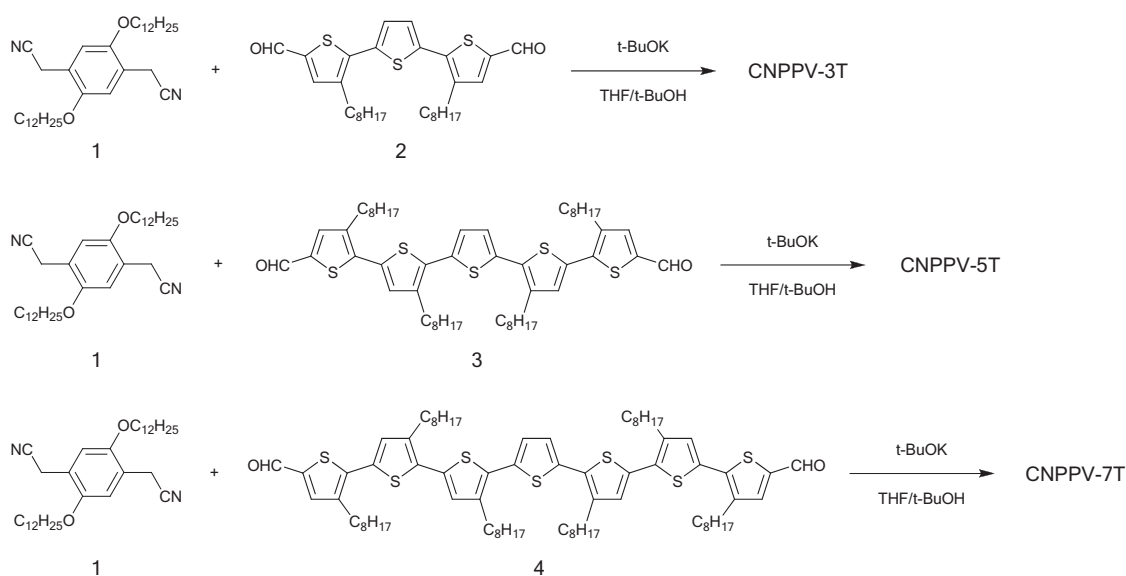
Results and Discussion

Synthesis

The synthesis of the polymers is depicted in Scheme 2. The starting material, 1,4-bis(cyanomethyl)-2,5-bis(dodecyloxy)benzene (**1**), was obtained by a three-step synthetic path from hydroquinone as described elsewhere.^[23,26] Diformylterthiophene (**2**), diformylquinquethiophene (**3**), and diformylseptithiophene (**4**) were prepared according to the literature procedures.^[25] The polymers CNPPV-3T, CNPPV-5T, and CNPPV-7T were obtained by Knoevenagel polycondensation of **1** with the corresponding dialdehydes. The polymers were isolated by precipitation into methanol and purified by Soxhlet extraction using methanol, hexane, and CHCl₃ as solvent.

Thermal Properties

The thermal stability of CNPPV-3T, CNPPV-5T, and CNPPV-7T were characterized by TGA at the heating rate of



■ Scheme 2. Synthesis of CNPPV-3T, CNPPV-5T, and CNPPV-7T.

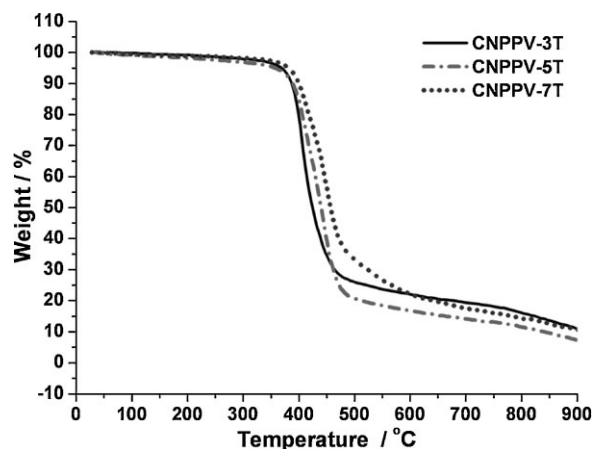


Figure 1. TGA plots of CNPPV-3T, CNPPV-5T, and CNPPV-7T with a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere.

$5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere (Figure 1). TGA analysis revealed that the onset degradation temperature of these three polymers are 385, 388, and 389 $^{\circ}\text{C}$, respectively. It is apparent that the polymers have good thermal stability for use in organic optoelectronic devices. No phase transition was observed for all polymers below the decomposition temperatures from DSC measurements.

Photophysical Properties

The UV-vis absorption spectra of CNPPV-3T, CNPPV-5T, and CNPPV-7T in dilute CHCl_3 solution and thin films are displayed in Figure 2, and the corresponding data are presented in Table 1. The absorption spectra show that the absorption peak of CNPPV-3T, CNPPV-5T, and CNPPV-7T in CHCl_3 solutions are observed at 510, 499, and 496 nm, respectively. Compared with solution absorption spectra, the absorption maxima of films of CNPPV-3T, CNPPV-5T, and CNPPV-7T exhibit a large bathochromic shift, which is 66, 88, and 84 nm, respectively. These bathochromic shifts can be ascribed to the aggregation and enhanced interchain

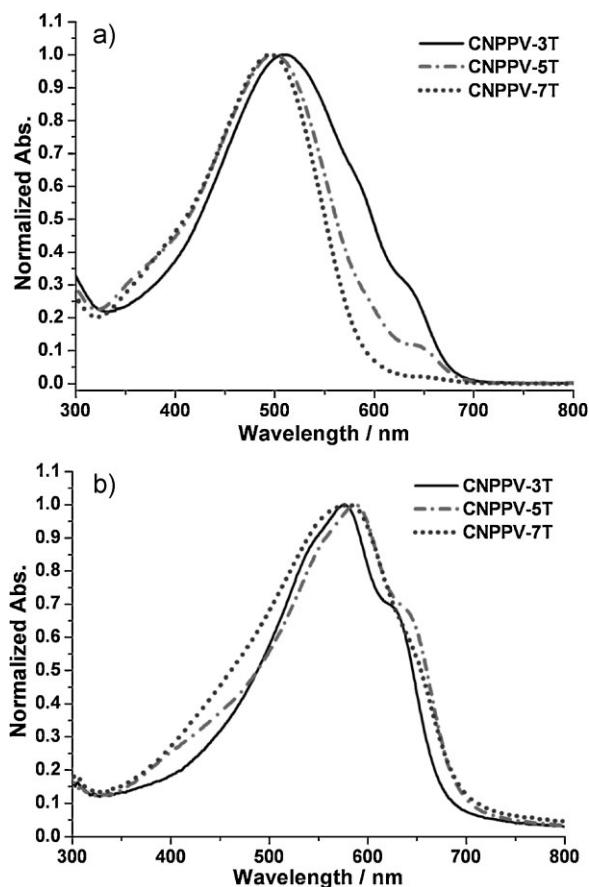


Figure 2. Normalized UV-vis absorption spectra of CNPPV-3T, CNPPV-5T, and CNPPV-7T a) in CHCl_3 and b) in thin films.

interactions of the polymers in the solid state. As shown in Figure 2b, all of the three polymers show a strong absorption between 400 and 700 nm. The optical bandgaps (E_g^{opt} , eV) of these polymers were approximated by extrapolation of the low-energy edge of each absorption spectrum.^[27] As anticipated, the alternation of electron-rich oligothiophene and electron-deficient cyanovinylene units

Table 1. Optical and electrochemical properties of CNPPV-3T, CNPPV-5T, and CNPPV-7T.

Polymer	$\lambda_{\text{max}}^{\text{abs}}$		E_g^{opt} a)	$E_{\text{onset}}^{\text{red}}$	$E_{\text{onset}}^{\text{ox}}$	Orbital energy		E_g^{CV}
	nm					eV		
	in CHCl_3	film		V	V	HOMO ^{b)}	LUMO ^{c)}	eV
CNPPV-3T	510	576	1.83	-0.86	1.05	-5.45	-3.54	1.91
CNPPV-5T	499	587	1.79	-0.81	1.02	-5.42	-3.59	1.83
CNPPV-7T	496	580	1.77	-0.74	0.93	-5.33	-3.66	1.67

a) Estimated from the onset absorption of the thin film; b) $\text{HOMO} = -e(E_{\text{onset}}^{\text{ox}} + 4.4\text{ V})$; c) $\text{LUMO} = -e(E_{\text{onset}}^{\text{red}} + 4.4\text{ V})$.

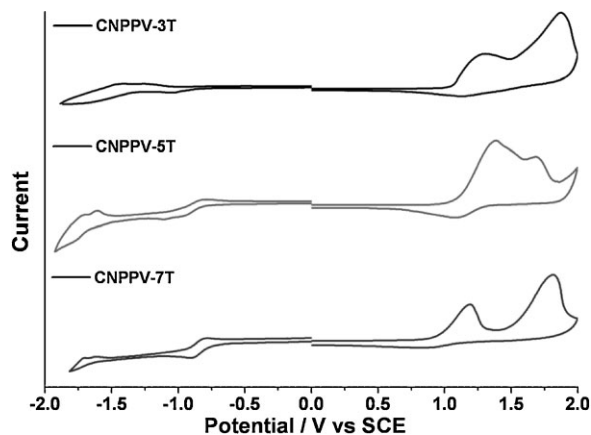


Figure 3. Cyclic voltammograms of CNPPV-3T, CNPPV-5T, and CNPPV-7T films on a glassy carbon electrode measured in a $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ Bu}_4\text{NPF}_6$ solution in acetonitrile at $50 \text{ mV} \cdot \text{s}^{-1}$.

along the conjugated backbone results in a low optical bandgap, which are 1.83, 1.79, and 1.77 eV, respectively. The results show that the optical bandgaps decrease with increasing the lengths of oligothiophenes in the repeating units.

Energy Levels

The energy levels of CNPPV-3T, CNPPV-5T, and CNPPV-7T were evaluated from the cyclic voltammogram (CV) of their thin films (Figure 3). The energy levels of the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) and the electrochemical bandgaps (E_g^{CV}) of the polymers calculated from the oxidation onsets ($E_{\text{onset}}^{\text{ox}}$) and the reduction onsets ($E_{\text{onset}}^{\text{red}}$) are listed in Table 1. From the onset of the oxidation, the HOMO energy level of CNPPV-3T, CNPPV-5T, and CNPPV-7T were estimated to be -5.45 , -5.42 , and -5.33 eV, respectively. These HOMO levels are lower than -5.2 eV, which indicates a higher stability against oxidation and thus an advantage for solar cell applications.^[23,28] The LUMO energy level of -3.54 eV for CNPPV-3T, -3.59 eV for CNPPV-5T, and -3.66 eV for CNPPV-7T were deduced from the onset of the reduction. These LUMO levels, which are higher (>0.3 eV) than the level of PCBM, can guarantee the formation of a downhill binding energy for the energetically favorable electron transfer and overcome the binding energy of the intrachain exciton.^[29–31] The low bandgap, relevant energy level positions, good solar spectrum match, and good solubility indicate that these polymers should be effective donors in BHJ devices. It is also worth noting that the difference between the electrochemical bandgap and the corresponding optical bandgap is 0.04–0.1 eV, which is reasonable and also observed in other polymers measured by similar methods.^[32–34]

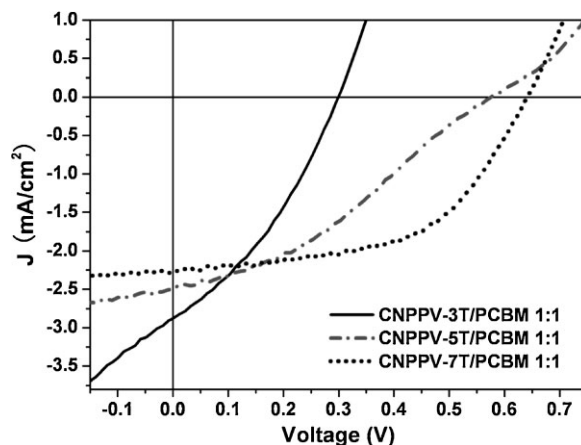


Figure 4. J/V characteristics of the device with the structure of ITO/PEDOT:PSS/polymer:PCBM (1:1 w/w)/LiF/Al under the illumination of AM 1.5G from a solar simulator ($100 \text{ mW} \cdot \text{cm}^{-2}$).

Photovoltaic Properties

BHJ solar cells with the structure of ITO/PEDOT:PSS/polymer:PCBM/LiF/Al using the polymer as the electron donor and PCBM as the electron acceptor were fabricated (Figure 4). After spin-coating a hole extraction/electron-blocking layer, a 40 nm layer of PEDOT:PSS, onto a pre-cleaned ITO-coated glass substrate, the polymer/PCBM (1:1, w/w) blends in ODCB were spin-coated. The thickness of the photoactive layer of all the devices was approximately 100 nm. After drying, the cells were then completed by sequential thermal vacuum deposition of LiF (1 nm) and Al (80 nm) as the cathode with an area of $\approx 4 \text{ mm}^2$.

Figure 4 shows the current density versus voltage (J/V) curves for devices of polymer (8 mg mL^{-1})/PCBM (1:1, w/w) under AM 1.5G simulated solar illumination at an intensity of $100 \text{ mW} \cdot \text{cm}^{-2}$. The photovoltaic properties are listed in Table 2. For devices using CNPPV-3T/PCBM as the active layer, the PCE, short-circuit current density (J_{sc}), open circuit voltage (V_{oc}), and fill factor (FF) are 0.30%, $2.88 \text{ mA} \cdot \text{cm}^{-2}$, 0.30 V, and 34.7%, respectively. When the number of

Table 2. Photovoltaic performance of the polymer solar cells based on CNPPV-3T, CNPPV-5T, and CNPPV-7T.

Polymer/PCBM (w/w)	J_{sc}	V_{oc}	FF	PCE
	$\text{mA} \cdot \text{cm}^{-2}$	V	%	%
CNPPV-3T/PCBM (1:1)	2.88	0.30	34.7	0.30
CNPPV-5T/PCBM (1:1)	2.48	0.58	34.1	0.49
CNPPV-7T/PCBM (1:1)	2.26	0.64	54.6	0.79
CNPPV-7T/PCBM (1:2)	4.84	0.66	41.3	1.32
CNPPV-7T/PCBM (1:3)	5.68	0.66	43.2	1.62
CNPPV-7T/PCBM (1:4)	3.18	0.67	44.6	0.95

thiophene rings in the repeating units of the polymer increases to five, the PCE increases to 0.49% from the device based on CNPPV-5T/PCBM as the active layer, combined with a V_{oc} of 0.58 V, a J_{sc} of $2.48 \text{ mA} \cdot \text{cm}^{-2}$, and an FF of 34.1%. The best PCE was obtained when CNPPV-7T was used, which has seven thiophene rings in the repeating units of the polymer main chain, as donor, and a J_{sc} of $2.26 \text{ mA} \cdot \text{cm}^{-2}$, a V_{oc} of 0.64 V, and a PCE of 0.79% were achieved with an FF of 54.6%. These values of the CNPPV-5T and CNPPV-7T-based devices excel those of other thiophene-containing CNPPV derivatives as donors in BHJ devices reported in the literature.^[21–24] It should be noted that the V_{oc} of these three polymer-based devices, as shown in Figure 4, are different although their HOMO levels are similar. This difference can be attributed to other factors that influence the V_{oc} , such as the exciton binding energy of the dissociated electron–hole pair,^[35] electronic coupling between donor and acceptor,^[36,37] the morphology of the donor/acceptor blend,^[38] and so on. The J/V curves, as shown in Figure 4 for the CNPPV-5T/PCBM-based device, show an inflection point (kink), which was attributed to a carrier transport problem.^[39–41]

To optimize the device performance of the most efficient polymer, CNPPV-7T, devices of various compositions incorporating the CNPPV-7T/PCBM blend were investigated. Figure 5 presents the J/V curves of the OPV devices using varied blend ratios (1:1, 1:2, 1:3, and 1:4, w/w) of CNPPV-7T and PCBM. Table 2 lists the photovoltaic properties of the devices. Increasing the concentration of PCBM in the blend has a strong impact on the J_{sc} , while the V_{oc} is much less dependent on the concentration of PCBM (Table 2) as it is related to the nature of the components. With increasing the donor/acceptor blend ratios from 1:1 to 1:4, the J_{sc} first increased and then decreased. In comparison with the blend ratio of 1:1, an increase in the PCBM weight

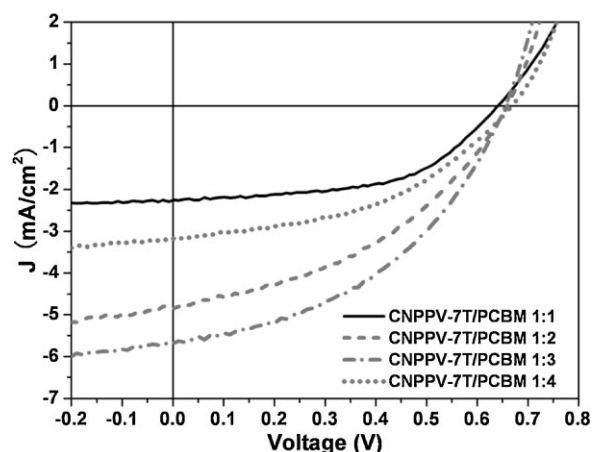


Figure 5. J/V characteristics of OPV devices based on CNPPV-7T/PCBM with different blend ratios (w/w) under the illumination of AM 1.5 G from a solar simulator ($100 \text{ mW} \cdot \text{cm}^{-2}$).

ratio to 1:2 led to a higher J_{sc} ($4.84 \text{ mA} \cdot \text{cm}^{-2}$) and a higher PCE (1.32%) with an FF of 41.3%. The best PCE was obtained when the ratio was 1:3, which gave a J_{sc} of $5.68 \text{ mA} \cdot \text{cm}^{-2}$, a V_{oc} of 0.66 V, and thus a PCE of 1.62% was achieved with an FF of 43.2%. The decrease of J_{sc} to $3.18 \text{ mA} \cdot \text{cm}^{-2}$ for the ratio of 1:3 to 1:4 is believed to be because saturating the active layer with PCBM leads to phase separation and unbalanced charge transporting properties between holes and electrons as reported in the literature.^[42,43] Combined with a V_{oc} of 0.67 V and an FF of 44.6%, the device using the 1:4 ratio yields a PCE of 0.95%.

Conclusion

In conclusion, a series of alternating donor/acceptor polymers based on 1,4-bis(cyanomethyl)-2,5-bis(dodecyloxy)benzene and oligothiophenes have been synthesized using a Knoevenagel polycondensation reaction. By changing the lengths of oligothiophenes in the repeat donor moiety, the optical bandgap of the polymers can be tuned. The photovoltaic properties of these polymers were investigated in BHJ devices using fullerene derivatives as electron acceptors. A PCE of 1.62% was obtained when using a CNPPV-7T/PCBM (w/w, 1:3) blend in OPV devices, with a J_{sc} of $5.68 \text{ mA} \cdot \text{cm}^{-2}$, a V_{oc} of 0.66 V, and a FF of 43.2%, under the illumination of AM 1.5 G ($100 \text{ mW} \cdot \text{cm}^{-2}$).

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