

Carbazole-Based Conjugated Polymers Incorporating Push/Pull Organic Dyes: Synthesis, Characterization, and Photovoltaic Applications

SO-LIN HSU, CHIA-MIN CHEN, KUNG-HWA WEI

Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan

Received 7 August 2010; accepted 12 August 2010

DOI: 10.1002/pola.24311

Published online 5 October 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: We have synthesized and characterized two new carbazole-based conjugated polymers, **PCDCN** and **PCDTA**, incorporating two strong light-absorbing organic dyes. These polymers exhibit relatively low band gaps (~ 1.5 eV) and broad absorption ranges (from 300 to 700 nm). We fabricated polymer solar cells incorporating these polymers as donors and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as the acceptor. At a blending ratio of 1:4, we

obtained power conversion efficiencies, under simulated AM 1.5 (100 mW/cm²) conditions, of 2.31% and 2.47% for the **PCDCN**- and **PCDTA**-based devices, respectively. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 5126–5134, 2010

KEYWORDS: blends; conjugated polymers; donor/acceptor; photovoltaic cells; polycarbazole; polycondensation

INTRODUCTION Harvesting energy directly from sunlight using photovoltaic cells is potentially one of the most efficient ways of solving future global energy crises and environmental pollution problems. Polymeric solar cells (PSCs) can be used to produce lightweight, large-area, flexible devices at low cost because they can be fabricated using solution coating or roll-to-roll processing.^{1–3} In recent years, many conjugated polymers have been developed and blended with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) to form the bulk heterojunction (BHJ)-type solar cells.³ Among these materials, poly(3-hexylthiophene) (P3HT) is the state-of-the-art *p*-type material, providing power conversion efficiencies (PCEs) of up to 5%.^{3–9} Unfortunately, the optical band gap of P3HT (~ 2 eV) is too large to absorb solar energy in the near-IR region. Furthermore, the energy offset between the highest occupied molecular orbital (HOMO) of P3HT and the lowest unoccupied molecular orbital (LUMO) of PC₆₁BM is relatively small; therefore, the open circuit voltage (V_{oc}) of the PSCs is limited.¹⁰ A conjugated polymer possessing a narrow optical band gap can be obtained by either rising its HOMO energy level or lowering its LUMO energy level. The latter approach will, however, inevitably decrease the LUMO energy difference between the donor and acceptor materials, thereby weakening the driving force of exciton dissociation.^{11–13} Moreover, a high-lying HOMO energy level might also decrease the magnitude of V_{oc} of a BHJ device, according to the semiempirical estimation equation proposed by Scharber et al.¹⁰ Consequently, molecular engineering of new conjugated polymers should be performed not only to reduce the band gap of the polymers but also to modulate their HOMO and LUMO energy levels to optimal values. One of the

most effective strategies toward this goal is to directly alternate a conjugated electron-rich donor (D) unit with a conjugated electron-deficient acceptor (A) unit in a polymer backbone.^{14–16} Following this approach, various donor–acceptor (D–A) conjugated polymers have exhibited promising performance, with PCEs as high as 4–6%.^{17–23}

Push/pull D- π -A organic compounds, comprising an electron-releasing donor unit, a π -conjugated bridge, and an electron-withdrawing acceptor unit, have been used extensively as active materials in the field of nonlinear optics.^{24–28} Because efficient intramolecular charge transfer (ICT) occurs from the donor unit to the acceptor unit on excitation, such chromophores are strong light-absorbing dyes possessing a broad absorption window extending to the near-IR region. More importantly, the band gap of D- π -A chromophores can be controlled simply by adjusting the electron-donating strength of the donor and the electron-withdrawing strength of the acceptor units in the dye. As a result, D- π -A chromophores have been used as effective photoactive materials in dye-sensitized solar cells.^{29–34} It is envisaged that incorporation of D- π -A organic dyes into *p*-type conjugated polymers might be a useful strategy for greatly enhancing the light-harvesting ability of solar cells. Recently, several new conjugated polymers with pendent D- π -A side chains have been synthesized for use in high-performance PSCs.^{35,36} By copolymerization with fluorene or silafluorene segments in an alternating manner, the diphenylamino groups in D- π -A organic dyes are embedded into the main chains of the polymers. We envisioned that utilization of other electron-rich conjugated building blocks in the main chain would allow further optimization of the intrinsic properties of this class of *p*-type conjugated polymer.

Correspondence to: K.-H. Wei (E-mail: khwei@mail.nctu.edu.tw)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 5126–5134 (2010) © 2010 Wiley Periodicals, Inc.

Because of its excellent thermal and photochemical stability, relatively high hole mobility, and good solubility in common organic solvents, the 2,7-carbazole unit has emerged as a promising electron-donating moiety for the construction of D-A polymers.^{37–41} For example, devices based on poly(2,7-carbazole)-*alt*-dithienylbenzothiadiazole, synthesized by Leclerc and coworkers,^{19,22,42,43} have exhibited values of V_{oc} as high as 0.89 V and PCEs of up to 6%.^{43,44}

In this article, we report the synthesis and characterization of two-dimensional conjugated polymers: **PCDCN** and **PCDTA**, denoted from 2,7-carbazole-based polymers using dicyanovinyl group (DCN) and diethyl thiobarbituric acid (DTA) as acceptors, respectively. Both alternating copolymers comprise 2,7-carbazole units and pendent D- π -A organic dye units. The D- π -A organic dye in **PCDCN** features a diphenylamino group as the donor unit, a styrylthiophene unit as the π -bridge, and a dicyanovinyl group as the acceptor unit; in contrast, the dye in **PCDTA** features a thiobarbital group as the acceptor unit. We fabricated BHJ PSC devices using the polymers as the electron donor and PC₇₁BM as the acceptor and investigated their photovoltaic properties.

EXPERIMENTAL

Materials

Malononitrile, 1,3-diethyl-2-thiobarbituric acid, phosphorus oxychloride, triphenylamine, *N*-bromosuccinimide (NBS), and tetrakis(triphenylphosphine)palladium [Pd(PPh₃)₄] were purchased in reagent grade from Aldrich, Acros, TCI, or Lancaster Chemical and used as received. [6,6]-Phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) was purchased from Nano-C. Tetrahydrofuran (THF), toluene, and *N,N*-dimethylformamide (DMF) were purified prior to use. All other solvents, including 1,2-dichlorobenzene and chloroform, were purchased from Aldrich, J. T. Baker, or Tedia and used as received.

Characterization Techniques

¹H and ¹³C NMR spectra were recorded using a Varian Unity-300 spectrometer. The molecular weights of the polymers were measured through gel permeation chromatography, using a Waters 2414 differential refractometer and a Waters Styragel column (polystyrene standards, THF as the eluent). UV-vis absorption spectra were recorded using an HP 8453 spectrophotometer. Photoluminescence spectra were recorded using a Hitachi F-4500 luminescence spectrometer. Thermogravimetric analysis (TGA) was performed under a N₂ atmosphere using a Du Pont TGA 2950 instrument (heating rate: 10 °C/min). Differential scanning calorimetry (DSC) was performed under a N₂ atmosphere using a Perkin-Elmer Pyris DSC1 instrument (heating rate: 10 °C/min). Cyclic voltammetry (CV) was performed using a BAS 100 electrochemical analyzer and a conventional three-electrode cell: a carbon glass electrode coated with the polymer thin film functioned as the working electrode, a Pt wire as the counter electrode, and Ag/Ag⁺ (0.01 M AgNO₃) as the reference electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile was the electrolyte for the CV measurements; the curves were calibrated using ferrocene as the standard (HOMO energy level of -4.8 eV with respect to the zero vacuum level). The topographies of the polymer/PC₇₁BM

films were measured through atomic force microscopy (AFM) in tapping mode, using a Digital Instruments Nanoscope IIIa apparatus under ambient conditions.

Synthetic Procedures

2-(2-{4-[*N,N*-Di(4-bromophenyl)amino]phenyl}ethenyl)thien-5-yl (**M1**)^{35,36} and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-*N*-9'-heptadecanilcarbazole (**M2**)⁴⁵ were prepared using reported procedures. The synthetic procedures for the preparation of the monomer **M1** and the copolymers **PCDCN** and **PCDTA** are presented in Scheme 1.

4-(Diphenylamino)benzaldehyde (**1**)^{46,47}

Phosphorus oxychloride (13.8 g, 89.7 mmol) was added dropwise to DMF (6.65 g, 89.7 mmol) cooled at 0 °C in a three-neck 100-mL round-bottom flask and then the mixture was stirred at 0 °C for 1 h. A solution of triphenylamine (20.0 g, 81.5 mmol) in 1,2-dichloroethane was added via syringe and then the mixture was heated at 90 °C for 2 h. After cooling to room temperature, the reaction mixture was washed sequentially with water (2 × 200 mL), saturated NaHCO₃ (1 × 200 mL), and water again (1 × 200 mL). Following extraction with CH₂Cl₂ (2 × 200 mL), the organic layer was dried (MgSO₄) and concentrated. The crude product was recrystallized (EtOH) to yield **1** (12.8 g, 57%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 9.81 (s, 1 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.34 (t, J = 7.5 Hz, 4 H), 7.19–7.17 (m, 6 H), 7.02 (d, J = 8.4 Hz, 2 H).

4-[*N,N*-Di(4-bromophenyl)amino]benzaldehyde (**2**)

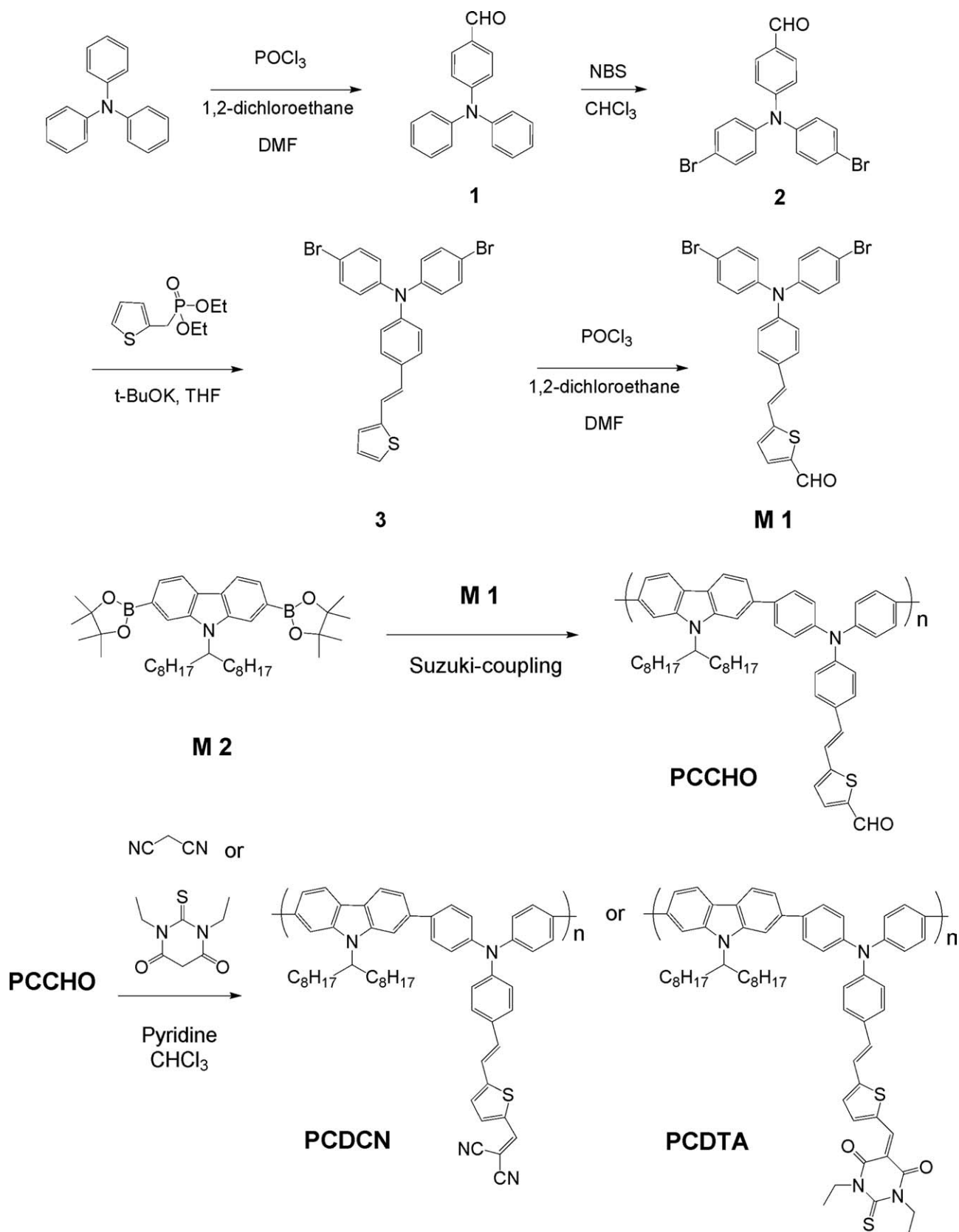
NBS (17.2 g, 96.6 mmol) was added portionwise to a solution of **1** (12.0 g, 43.9 mmol) in chloroform (110 mL) in an ice-water cooling bath (0 °C) and then the mixture was stirred for 1 h. After removing the ice bath, the mixture was heated under reflux for 16 h. The resulting mixture was extracted with CH₂Cl₂ and then the combined extracts were washed with water and brine. The organic phases were collected, dried (MgSO₄), and concentrated under reduced pressure. The crude product was recrystallized (MeOH) to yield **2** (15.6 g, 82%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 9.84 (s, 1 H), 7.71 (d, J = 8.8 Hz, 2 H), 7.46–7.43 (m, 4 H), 7.06–7.00 (m, 6 H).

2-(2-{4-[*N,N*-Di(4-bromophenyl)amino]phenyl}ethenyl)thiophene (**3**)

Diethyl (2-methylthiophene)phosphonate (1.41 g, 6.03 mmol) was added to a solution of potassium *tert*-butoxide (0.680 g, 6.03 mmol) in dry THF (15 mL) at 0 °C and then the mixture was stirred for 1 h. A solution of **2** (2.00 g, 4.64 mmol) in dry THF was added via syringe and the resulting mixture was then stirred at room temperature for 12 h. The reaction mixture was poured into water and extracted with CH₂Cl₂. The organic layer was washed with water, dried (MgSO₄), and concentrated under reduced pressure; the crude product was purified chromatographically (SiO₂; EtOAc/hexane, 1:10). Recrystallization (CH₂Cl₂/hexane) afforded **3** as a yellowish solid (0.96 g, 41%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.37–7.34 (m, 6 H), 7.19–7.11 (m, 2 H), 7.05–6.94 (m, 8 H), 6.89–6.84 (m, 1 H). Anal.



SCHEME 1 Syntheses of monomers and copolymers.

Calcd: C, 56.38; H, 3.35; N, 2.74. Found: C, 56.24; H, 3.72; N, 2.84.

2-(2-(4-[N,N-Di(4-bromophenyl)amino]phenyl)ethenyl)thien-5-yl (M1)

Phosphorus oxychloride (2.25 g, 14.7 mmol) was added dropwise to DMF (1.07 g, 14.7 mmol) in a two-neck 100-mL round-bottom flask at 0 °C and then the mixture was stirred for 1 h. A solution of **3** (3.00 g, 5.87 mmol) in 1,2-dichloroethane was added via syringe and then the mixture was heated at 90 °C for 12 h. After cooling to room temperature, the reaction was quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The combined organic phases were washed with water, dried (MgSO₄), and concentrated under reduced pressure. The crude product was purified chromatographically (SiO₂; EtOAc/hexane, 1:10) to yield **M1** as a brown solid (3.01 g, 95%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 9.85 (s, 1 H), 7.66 (d, *J* = 3.9 Hz, 1 H), 7.39 (d, *J* = 8.7 Hz, 6 H), 7.13–6.96 (m, 9 H). Anal. Calcd: C, 55.68; H, 3.18; N, 2.60. Found: C, 55.43; H, 3.49; N, 2.56.

PCCHO

A mixture of **M1** (164 mg, 0.30 mmol), **M2** (200 mg, 0.30 mmol), K₂CO₃ (221 mg, 1.6 mmol), H₂O (1 mL), and Aliquat 336 (36 mg) in toluene (5 mL) was degassed and then Pd(PPh₃)₄ (7 mg, 0.006 mmol) was added at 60 °C. The mixture was stirred and heated under reflux for 24 h under a N₂ atmosphere. Phenylboronic acid (37 mg, 0.03 mmol) was then added and the mixture was heated under reflux for a further 3 h; bromobenzene (0.03 mL, 0.03 mmol) was then added and the mixture was heated under reflux for another 3 h. The reaction mixture was poured into MeOH (100 mL) and the resulting orange precipitate was collected through filtration and then purified in a Soxhlet apparatus with MeOH, acetone, and hexane for 24 h to remove any residual oligomers and catalyst residues, to provide the purified polymer (182 mg, 76%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 9.83 (s, 1 H), 8.18–8.10 (m, 2 H), 7.75–7.12 (m, 20 H), 4.67 (s, 1 H), 2.38 (s, 2 H), 1.98 (s, 2 H), 1.23–1.12 (m, 24 H), 0.77 (t, *J* = 6 Hz, 6 H). Anal. Calcd: C, 82.82; H, 7.47; N, 3.58. Found: C, 81.64; H, 7.56; N, 3.81.

PCDCN

Pyridine (0.085 mL) was added to a solution of **PCCHO** (85 mg, 0.10 mmol) and malononitrile (250 mg, 3.78 mmol) in chloroform (8.5 mL) with a two-neck 25-mL round-bottom flask. The mixture was stirred at room temperature for 24 h and then poured into MeOH (100 mL). The black precipitate was filtered off and purified through repeated precipitation (twice) from THF solution into MeOH (71 mg, 79%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 8.18–8.10 (m, 2 H), 7.72–7.12 (m, 21 H), 4.67 (s, 1 H), 2.38 (s, 2 H), 1.98 (s, 2 H), 1.23–1.12 (m, 24 H), 0.77 (t, *J* = 6 Hz, 6 H). Anal. Calcd: C, 82.36; H, 7.03; N, 6.74. Found: C, 80.71; H, 7.70; N, 6.40.

PCDTA

Pyridine (0.085 mL) was added to a solution of **PCCHO** (85 mg, 0.10 mmol) and 1,3-diethyl-2-thiobarbituric acid (758

TABLE 1 Molecular Weights and Thermal Properties of the Polymers

Polymer	<i>M_n</i> (g/mol)	<i>M_w</i> (g/mol)	PDI	<i>T_d</i> (°C)	<i>T_g</i> (°C)
PCCHO	11,017	50,675	4.59	398	145
PCDCN	11,049	50,957	4.61	402	157
PCDTA	6,466	22,284	3.45	312	166

mg, 3.78 mmol) in chloroform (8.5 mL) in a two-neck 25-mL round-bottom flask. The mixture was stirred at room temperature for 24 h and then poured into MeOH (100 mL). The black precipitate was filtered off and purified through repeated (twice) precipitation from THF solution into MeOH (90 mg, 86%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 8.61 (s, 1 H), 8.18–8.10 (m, 2 H), 7.78–7.14 (m, 20 H), 4.62–4.56 (m, 5 H), 2.38 (s, 2 H), 1.98 (s, 2 H), 1.48–1.12 (m, 30 H), 0.77 (t, *J* = 6 Hz, 6 H). Anal. Calcd: C, 77.13; H, 7.10; N, 5.81. Found: C, 75.74; H, 7.68; N, 5.86.

Photovoltaic Device Fabrication

The current density–voltage (*J*–*V*) properties were determined for devices possessing the sandwich structure: indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) (PEDOT)/polymer:PC₇₁BM/Ca/Al. First, an ITO-coated glass substrate was etched with acid and cleaned using detergent, deionized water, acetone, and isopropyl alcohol, respectively. The cleaned substrate was treated with ozone plasma for 5 min and then a 30-nm-thick layer of PEDOT (Batron P AL 4083, HC Stark) was deposited through spin coating. The PEDOT-coated substrate was heated at 150 °C for 30 min to ensure that all of the solvents had been removed. The active layers of the devices were spin coated (1500 rpm) from 1,2-dichlorobenzene/chloroform (1:1, v/v) solutions containing a polymer and PC₇₁BM at mixed ratios ranging from 1:1 to 1:4 (w/w). The thickness of each polymer/PC₇₁BM layer was ~100 nm. After thermal annealing of the active layers at 120 °C for 10 min, a layer of Ca (35 nm) was vapor deposited as the cathode and then a layer of Al (100 nm) was deposited as a protecting layer under a base pressure of less than 1 × 10⁻⁶ torr. The effective area of each resulting device was 0.04 cm². Testing of the sample devices was performed under simulated AM 1.5 G illumination (100 mW/cm²) using a Xe lamp-based Newport 66902 150 W solar simulator equipped with an AM 1.5 filter as the white light source. An OPHIR thermopile 71964 instrument was used to determine that the optical power at the sample was 100 mW/cm². The *J*–*V* characteristics of all of the samples were measured under a N₂ atmosphere using a Keithley 236 source measurement meter. The external quantum efficiencies (EQEs) were measured using a Keithley 236 source measure unit coupled with an Oriel Cornerstone 130 monochromator; the light intensity at each wavelength was calibrated using an OPHIR 71580 diode.

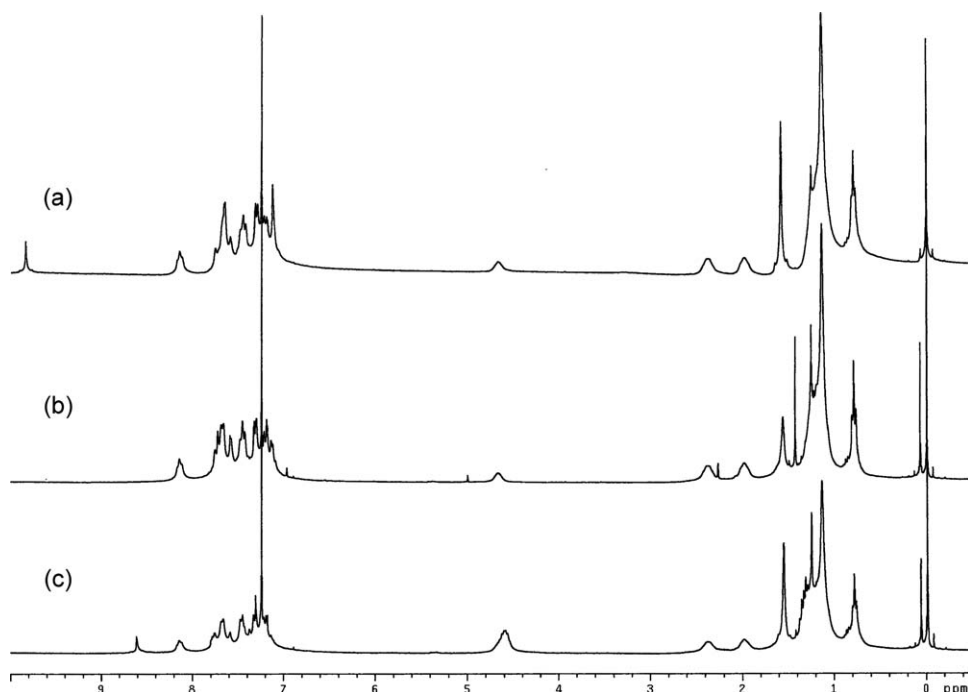


FIGURE 1 ^1H NMR spectra of the polymers: (a) **PCCHO**, (b) **PCDCN**, and (c) **PCDTA**.

RESULTS AND DISCUSSION

Synthesis and Characterization

Scheme 1 presents the chemical structures and synthetic routes toward the copolymers **PCDCN** and **PCDTA**. We copolymerized the monomers **M1** and **M2** through Suzuki cross-coupling polycondensation to afford the precursor polymer **PCCHO** in reasonable yield of 76%. After polymerization for 24 h, end-capping reactions were performed using bromobenzene and phenylboronic acid to increase the stability of the polymer. The final polymers, **PCDCN** and **PCDTA**, were obtained through Knoevenagel condensations by treating the aldehyde-functionalized precursor polymer with

malononitrile and diethylthiobarbituric acid, respectively. The reason to complete the targeted polymers via post-functionalization of the precursor polymer is that the final D- π -A organic dyes are subject to decomposition in the presence of base used in Suzuki cross-coupling condition. According to size exclusion chromatography experiments (monodisperse polystyrene standards, THF as the solvent), our purified **PCCHO** had a number-average molecular weight (M_n) of 11,017 g/mol and a polydispersity index (PDI) of 4.59. Table 1 summarizes the physical properties of our three polymers. The values of M_n of **PCDCN** and **PCDTA** are 11,049 g/mol and 6466 g/mol, respectively, with corresponding PDIs of

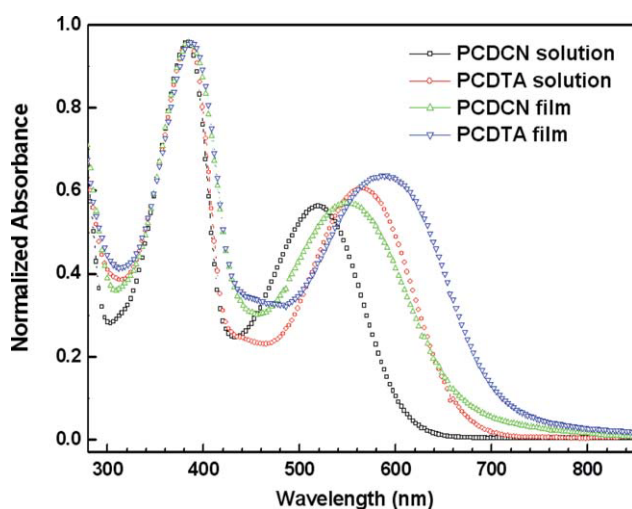


FIGURE 2 UV-vis absorption spectra of **PCDCN** and **PCDTA**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

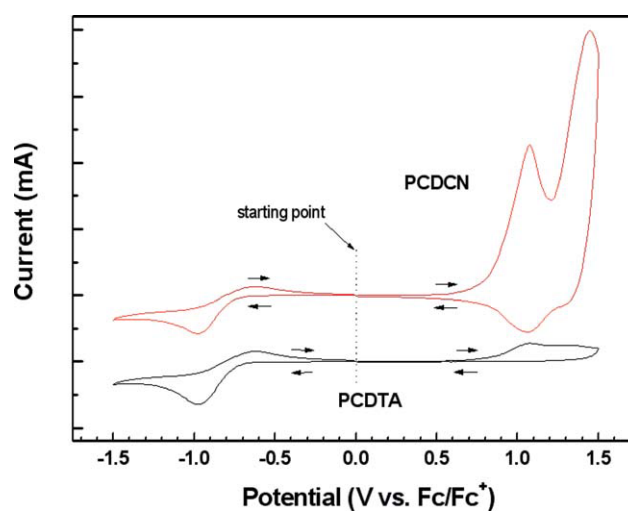


FIGURE 3 Cyclic voltammograms of the polymer films, measured from acetonitrile solutions containing 0.1 M Bu_4NPF_6 at a scan rate of 50 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 2 Optical and Electrochemical Properties of the Polymers

Polymer	λ_{\max} (nm) Solution	λ_{\max} (nm) Film	E_g^{opt} (eV) ^a	E_g^{EC} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
PCDCN	383, 519	385, 550	1.51	1.55	-5.22	-3.66
PCDTA	384, 567	388, 592	1.47	1.56	-5.24	-3.68

^a The value of E_g^{opt} was calculated from the edge of the absorption spectrum of the film.

4.61 and 3.45, respectively. Notably, **PCDTA** possessed a lower molecular weight than its precursor polymer, **PCCHO**, presumably because strong dipole-dipole interactions between the organic dye units led to packing of the side chains and, thereby, disturbed the GPC results. Hence, the molecular weight based on **PCCHO** ($M_n = 11,017$ g/mol) is more reliable for estimating the actual molecular weight of **PCDTA**. The chemical structures of both polymers were verified through ^1H NMR spectroscopic and elemental analyses. Figure 1 presents the ^1H NMR spectra of our three polymers. The signal of the aldehydic proton of **PCCHO** at 9.83 ppm is absent in the spectra of both **PCDCN** and **PCDTA**; meanwhile, signals of olefinic proton appear at 7.72 ppm for **PCDCN** and 8.61 ppm for **PCDTA**, confirming the transformation of the aldehyde units to the targeted acceptor groups. The solubilities of **PCDCN** and **PCDTA** are good in 1,2-dichlorobenzene, chloroform, and THF; therefore, we readily obtained uniform thin films of the polymers through spin coating for further study of PSC devices.

Thermal Properties

We performed DSC and TGA under a N_2 atmosphere to determine the thermal properties of **PCDCN** and **PCDTA** (Table 1). TGA indicated that both polymers exhibit good thermal stability, with 5%-weight-loss temperatures (T_d) of 402 °C for **PCDCN** and 312 °C for **PCDTA**. The glass transition temperatures (T_g) of **PCDCN** and **PCDTA** are 157 °C and 166

°C, respectively. Good thermal stability and high values of T_g are important parameters for polymers incorporated in PSC devices, because they provide resistance against the deformation or degradation of the active layers.

Optical Properties

The absorption spectra of all studied polymers were measured in both dilute THF and in the thin films (Fig. 2), and the correlated optical parameters were summarized in Table 2. Both polymers exhibit two characteristic bands in the absorption spectra; the first absorption peak at ~ 385 nm represents the π - π^* transition of their conjugated main chains, while the second absorption peaks at longer wavelengths are attributed to the ICT from the diphenyl amino groups in the conjugated main chains to the acceptor groups in the pendent side chains. The ICT absorption peak of **PCDTA** (at ~ 567 nm) is much red-shifted compared with that of **PCDCN** (at ~ 519 nm), indicating that the accepting strength of DTA unit is stronger than that of DCN unit. It is also noteworthy that the ICT bands of absorption spectra shift toward longer wavelengths from the solution to the solid states, whereas the π - π^* transition bands are essentially unchanged. This result suggests that strong packing between the D- π -A conjugated side chains due to electrostatic interactions occurs in the solid state, whereas the intermolecular interactions between the main chains of polymers are relatively weak. The optical band gaps (E_g^{opt}), calculated from the absorption onsets in their films, are 1.51 eV for **PCDCN** and 1.47 eV for **PCDTA**.

Electrochemical Properties

CV was used to estimate the HOMO and LUMO energy levels of our conjugated polymers (Figure 3). We calculated the HOMO energy levels of **PCDCN** and **PCDTA** to be -5.22 and -5.24 eV when using ferrocene (-4.8 eV below the vacuum)

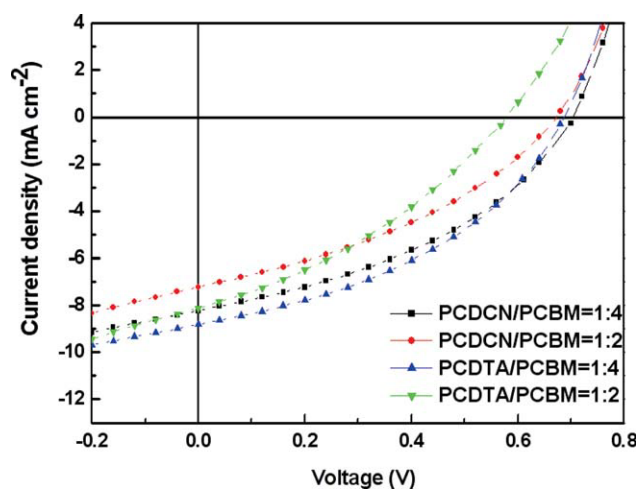


FIGURE 4 J - V characteristics of devices having the configuration ITO/PDOT:PSS/polymer:PC₇₁BM/Ca/Al. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 3 Photovoltaic Properties of Polymer Solar Cells

Polymer:PC ₇₁ BM (Weight Ratio)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
PCDCN:PC₇₁BM (1:1)	0.60	6.95	0.36	1.52
PCDCN:PC₇₁BM (1:2)	0.66	7.32	0.37	1.81
PCDCN:PC₇₁BM (1:3)	0.68	7.55	0.38	1.95
PCDCN:PC₇₁BM (1:4)	0.70	8.22	0.40	2.31
PCDTA:PC₇₁BM (1:1)	0.37	5.62	0.34	0.74
PCDTA:PC₇₁BM (1:2)	0.58	8.13	0.34	1.61
PCDTA:PC₇₁BM (1:3)	0.66	8.62	0.37	2.12
PCDTA:PC₇₁BM (1:4)	0.68	8.80	0.41	2.47

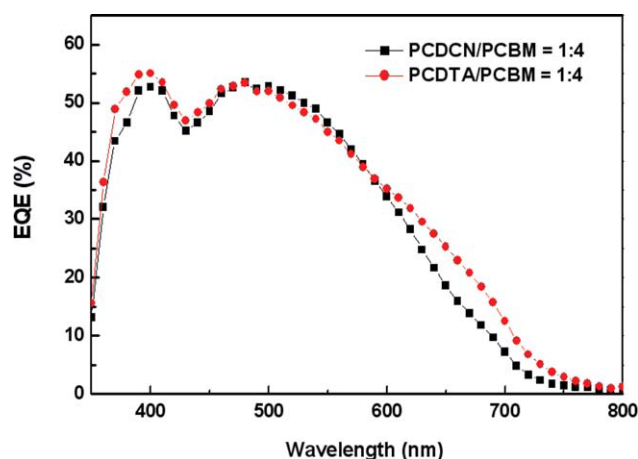


FIGURE 5 EQE spectra of **PCDCN**- and **PCDTA**-based solar cells illuminated under monochromatic light.

as the internal standard. The similar HOMO energy levels can be ascribed to the identical main chain structure of the polymers. The LUMO energy levels are approximately located at -3.66 eV for **PCDCN** and -3.68 eV for **PCDTA**, which are positioned 0.2 – 0.3 eV above the LUMO level of the PC_{71}BM acceptor (3.8 eV) to ensure energetically favorable electron transfer.

Photovoltaic Properties

To investigate the photovoltaic properties of **PCDCN** and **PCDTA**, we fabricated BHJ PSC devices having the structure of ITO/PEDOT:PSS/polymer: PC_{71}BM /Ca/Al. The copolymer: PC_{71}BM blend active layers, in which the copolymer was used as the donor and PC_{71}BM as the acceptor, were spin coated from 1,2-dichlorobenzene/chloroform (1:1, v/v) solutions at a concentration of 7.5 mg/mL. The PC_{71}BM was chosen as the acceptor because of its high absorption coefficient in the region from 440 to 530 nm, which could complement the absorption valley of the polymers.⁴⁸ Because the weight ratio between the copolymer and PC_{71}BM in the active layer affects the device performance, we studied PSC devices incorporating blending ratios ranging from 1:1 to 1:4 (polymer: PC_{71}BM). The optimal ratio was 1:4; Figure 4 presents the J - V characteristics of the resulting device measured under simulated AM 1.5 G (100 mW/cm^2) illumination conditions. A PCE of up to 2.47% with a value of V_{oc} of 0.68 V, a value of J_{sc} of 8.80 mA/cm^2 , and a fill factor (FF) of 0.41 was obtained for the device based on **PCDTA**: PC_{71}BM (1:4). In the **PCDCN** system, a best performance—a value of V_{oc} of 0.70 V, a value of J_{sc} of 8.22 mA/cm^2 , a FF of 0.40 , and a PCE of 2.31% —was also obtained at a polymer: PC_{71}BM ratio of 1:4. Table 3 summarizes the performances of devices prepared from the two polymers at different blending ratios. The values of V_{oc} were quite similar for the solar cells incorporating **PCDCN** and **PCDTA** because of the relatively

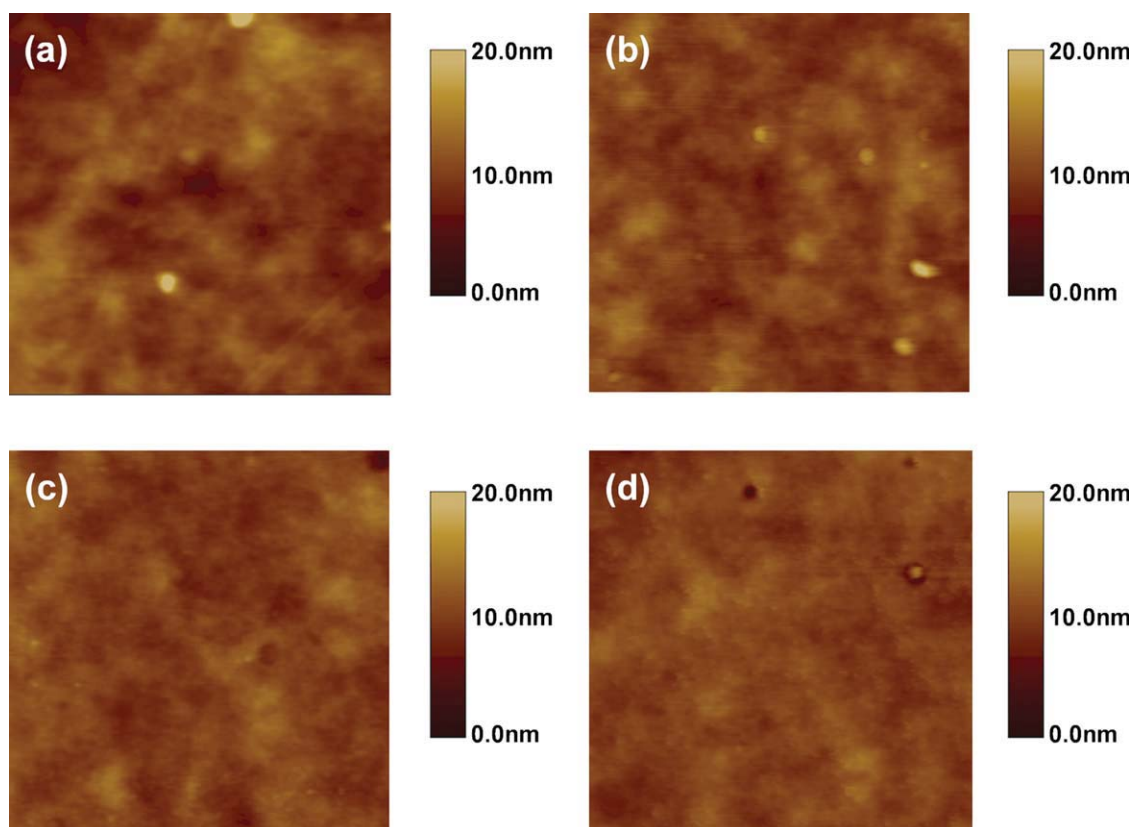


FIGURE 6 Topographic AFM images (scale: 2×2 μm^2) of devices incorporating **PCDCN**/ PC_{71}BM blends at weight ratios of (a) 1:1, (b) 1:2, (c) 1:3, and (d) 1:4. Their corresponding roughness are determined to be 1.92 , 1.45 , 1.25 , and 1.07 nm, respectively.

small difference in the HOMO energy levels of these two polymers; however, the higher value of J_{sc} for the device incorporating **PCDCN** might be ascribed to its broader absorption in the range 600–700 nm, as supported by the spectra of EQE in Figure 5. On increasing the amount of PC₇₁BM, the photocurrents (J_{sc}) of the devices incorporating either **PCDCN** or **PCDTA** increased. We attribute this phenomenon to the sufficient number of electron and hole percolation pathways that were formed to allow more efficient charge separation.^{22,49} Figure 5 presents the EQE spectra of the best two devices; the curves reveal great coherence with the absorptions of the active layers. Although relative to the **PCDCN** blended layer, the **PCDTA** blended layer exhibited lower absorption near 500 nm, it maintained slightly higher intensities in the range 620–720 nm so that the device based on **PCDTA** provided a higher photocurrent (8.80 mA/cm²) than that based on **PCDCN** (8.22 mA/cm²).

The morphology of the active layer in the device plays an important role in determining the device performance and was thus investigated using tapping-mode AFM. The topography images of **PCDCN**:PC₇₁BM blends are shown in the Figure 6. It is interesting to observe that as the blending ratio of PC₇₁BM increases from 1:1 to 1:4, the root-mean-square roughness decreases from 1.92 to 1.07 nm. Increasing the content of PC₇₁BM in the blend might prevent the polymer from severe aggregation by diluting the electrostatic interactions between the organic dyes, thereby decreasing the surface roughness. As a result, the improved photovoltaic performance of the PSC devices may be correlated to the decreased intermolecular packing between the organic dyes in the polymers.

CONCLUSIONS

We have used Suzuki coupling to synthesize two new carbazole-based conjugated polymers, **PCDCN** and **PCDTA**, incorporating strong acceptor groups linked through a triphenylamine backbone, for use in PSCs. These two polymers exhibit high solubility, adequate thermal stability, and the broadband absorptions from 300 to 700 nm. According to the CV measurements, **PCDCN** and **PCDTA** possessed very similar band gap energies (1.55 eV and 1.56 eV, respectively). The best performing devices incorporating **PCDCN**/PC₇₁BM and **PCDTA**/PC₇₁BM at the same blending ratio (1:4), exhibited promising PCEs of 2.31% and 2.47%, respectively, accompanied by values of J_{sc} of 8.22 mA/cm² and 8.80 mA/cm², respectively. To further optimize the optical and electrical properties, future molecular engineering of D- π -A dye-based polymers will be focused on selecting appropriate acceptor units for positioning at the ends of the side chains.

The authors thank the National Science Council for financial support.

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