Design, Synthesis, and Characterization of a Novel c-Donor-nc-Bridge-c-Acceptor Type Block Copolymer for Optoelectronic Applications

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ABSTRACT: A novel conjugated block copolymer system containing a donor-type conjugated block (c-D) covalently connected to an acceptor type conjugated block (c-A) via a nonconjugated and flexible bridge chain (nc-B), also called a DBA type block copolymer, has been designed, synthesized, and characterized for potential cost-effective and high-efficiency optoelectronic applications such as solar cells. Specifically, D is a regio-regular para-2-ethylhexyloxy-substituted polyphenylenevinylene (or EH-RO-PPV), A is a regio-regular polyphenylenevinylene with sulfone (SO₂) acceptor moiety and a linear oxydecane ($-OC_{10}H_{21}$) group substituted on every phenylene unit, and B contains an aliphatic chain with two or four methylene units. The size of each block can be controlled via synthetic feed ratio of the monomer and the terminator. The measured average molecular weights of D, A, and DBA based on gel permission chromatography are in good agreements with the molecular weights calcu-

INTRODUCTION Polymer-based optoelectronic materials and devices are very attractive for future optoelectronic applications due to advantages such as cost effectiveness, lightweight, and flexibility in terms of both device shape and fabrications.¹⁻¹⁰ Development of organic and polymer based solar cells have advanced tremendously since the initial demonstration of organic donor/acceptor binary phase concept,¹ the ultrafast photo induced charge transfer between donor and acceptor,² the donor/acceptor large interface, or bulk heterojunction BHJ concept.³⁻⁵ Though the photoelectric power conversion efficiencies of the donor/acceptor conjugated polymer blend systems (also called "bulk heterojunction" systems) have reached about 10%,5 the blend systems, however, exhibit inherent disadvantages. For instance, due to the statistic distribution of domain sizes, it is hard to avoid the formation of very large or small domains, which are not desirable for organic or Frenkel type exciton dissociation as well as charge transport. To further minimize exciton and carrier losses, the donor/acceptor lated using the monomer:terminator synthetic feed ratios. Preliminary optoelectronic device studies revealed an order of magnitude better improvement in photoelectric power conversion efficiency of DBA over the corresponding D/A blend under identical fabrication and testing conditions. Such improvements could be attributed to more efficient photo induced charge separation and charge transport in DBA versus in D/A blends. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 1149–1160

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binary system solid-state morphologies are desirably consisted of two continuous phases or bi-continuous ordered nanostructures (BONS) with at least one dimension around 20 nm (the average exciton diffusion length for $PPVs^{6-11}$) in each phase. The BONS type morphologies appear ideal for both exciton diffusion and charge transport.⁶⁻¹¹

Block copolymers are known to self-assemble into a variety of BONS type morphologies at nanoscale,^{12–15} making it an attractive candidate for solar cell applications. There have been a number of efforts on the development of various block copolymer systems containing conjugated donor and acceptor blocks, since chemically different donor and acceptor blocks may undergo phase separation on the nanometer scale.^{7,10,11,16–28} When two different conjugated blocks are covalently connected directly, charge separated states appear not stable.^{20,27,28} Two popular approaches include, for example, (1) block copolymers where a conjugated electron-donating block is covalently linked to a nonconjugated flexible

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SCHEME 1 Scheme of potential solid-state stacking patterns of $(DBAB)_n$ and DBA type block copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

block with an electron acceptor as side chains,^{7,23,24} and (2) donor/acceptor block copolymers where **D/A**-conjugated blocks are separated by nonconjugated bridge units (**B**).^{7,10,11,16-22}

We have been working on the second approach and have earlier developed a (**DBAB**)_{*n*} type block copolymer earlier (shown in Scheme 1, top), where **D** is a conjugated donor block, **A** is a conjugated acceptor block, and **B** is a nonconjugated and flexible bridge chain.^{7,10,11,16-22} However, as Scheme 1 shows, the (**DBAB**)_{*n*} type block copolymer could suffer from poor solid-state phase separation when the sizes of the donor or acceptor blocks are not uniform. In contrary, as shown in Schemes 1 and 2, a c-Donor-nc-Bridge-c-Acceptor or **DBA** type block copolymer has a potential to form **D/A** phase separated nanostructures even if the polydispersity of the **D** or **A** are broad.²¹ Furthermore, as Scheme 1 bottom shows, the **DBA** phase separation may be further enhanced with addition of **D** and **A** as plasticizers.

Due to the rational discussed above, a **DBA** type block copolymer (Scheme 2) containing a conjugated donor block c-**D** covalently linked to a conjugated acceptor block c-**A** via a non-conjugated and flexible bridge unit nc-**B** was thus designed and developed. Photo induced charge separation in small molecular **DBA** system are known to be very effective.²⁹ As demonstrated in our earlier work, the sizes of the donor and acceptor blocks can be chemically controlled to be on the ranges of exciton diffusion lengths between 5 and 20 nm depending on the number of polymer repeat units. However, the synthesis of **DBA** turned out to be more challenging than (DBAB)_n mainly due to a need for unsymmetrically functionalized monomers and one-end (mono-end) functionalized **D** and **A** blocks as exhibited in Schemes (3 and 5).

EXPERIMENTAL

Starting Materials and Instrumentation

All starting materials, reagents, and solvents were purchased from commercial sources (mostly from Sigma-Aldrich and Fisher-Scientific) and used as received unless noted otherwise. NMR spectra were obtained from a Bruker Advance 300 MHz spectrometer with TMS as the internal reference. UV-vis absorption data were collected on a Perkin-Elmer Lambda-1050 spectrophotometer. Luminescence spectra were obtained from a Horiba Fluoromax-3 spectrofluorometer. Thermal analysis was performed on a Perkin-Elmer TGA6/DSC6 system. Polymer film thicknesses were measured with a Dektak-6M profilometer.

Gel Permeation Chromatography (GPC)

The polymer molecular weights were measured on a Viscotek T60A/LR40 triple-detector gel permeation chromatography (GPC) system at ambient temperature. Polystyrene standards were used for universal/conventional calibration. Although CHCl₃ is a better solvent than tetrahydrofuran (THF) for PPVs, its refractive index (RI = 1.446) is too high, leading to very weak RI detector signal. THF, with a RI of 1.405 is used for all materials measured by GPC.

Cyclovoltammetry

Electrochemical studies were performed on a Bioanalytical (BAS) Epsilon-100W tri-electrode cell system. Three electrodes include a Pt working electrode, an ancillary Pt electrode, and a silver reference electrode in a CH_3CN solution of 0.01 M AgNO₃ and 0.1 M tetrabutylammonium hexafluorophosphonate (TBA-HFP). The polymer samples were dissolved in hot o-dichlorobenzene and then coated onto the Pt working electrode. The measurements were performed in a N₂-purged 0.1 M TBA-HFP/acetonitrile solution at a scan rate of 100 mV/s. Between the experiments, the surface of the electrodes were cleaned or polished. Ferrocene (2 mM in 0.10 M TBA-HFP/CH₃CN solution) was used as an internal reference standard and its HOMO level of-4.80 eV was used in calculations.

Optoelectronic Device Fabrication and Testing

Preliminary polymer solar cell devices are fabricated and tested inside a custom built MBraum inert gas glove box system coupled with a vacuum thermal deposition chamber (vacuum up to 1×10^{-7} mbar), a solar simulator (providing a one-Sun or 100 mW/cm², 1.5 AM visible light radiation), and a current-voltage source-measure unit (Keithley SMU-237), and a data processing PC.

Donor Synthesis

1,4-Bis(2-ethyl-hexyloxy)benzene (2)

In an argon environment, a mixture of DMSO (300 mL), hydroquinone **1** (20 g, 182 mmol, 1 mol equiv), and 2-ethylhexyl bromide (97 g, 454 mmol, 2.5 mol equiv) were stirred and heated in a hot oil bath at 90 $^{\circ}$ C, afterwards a



SCHEME 2 Scheme of a **DBA** block copolymer, where **D** is a conjugated electron-donating block, **A** is a conjugated electron accepting block, and **B** is a non-conjugated and flexible bridge unit. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 3 Design and synthesis of a mono-end terminal functionalized donor block C8-RO-PPV (7, D).



SCHEME 4 Design and synthesis of a mono-end terminal functionalized acceptor block C10-SF-PPV (17, A).



SCHEME 5 Design and synthesis of an example **DBA** block copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]





FIGURE 1 Donor Monomer **5** (a) ¹H NMR and (b) ¹³C NMR Spectra in CDCl₃. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solution of 1:1 solution of NaOH (23 g) and water (23 mL) was slowly added dropwise to the stirred mixture over 10 min. The reaction mixture was diluted and neutralized with 100 mL of water and 100 mL of 10% NaHCO₃ solution, then the product was extracted with 250 mL of hexane, dried in MgSO₄, and condensed to give 44.15 g of a crude oil product to be used in the next step.

2-Bromomethyl-1,4-bis(2-ethyl-hexyloxy)benzene (3)

In an argon environment, a mixture of **2** (39.68 g, 118.5 mmol, 1 mol equiv), paraformaldehyde (5.4 g, 1.5 mol equiv), glacial acetic acid (50 mL, 7 mol equiv), and 30% HBr/HOAc (22 mL, 3 mol equiv) (11 mL added dropwise at start of rxn, the other 11 mL added in 2–3 mL increments ever 2 h over a 6-h period) was heated at 60 °C for 6.5 h. The heat was stopped and reaction allowed to continue for another 3 h. A mixture of **2** (minority component) and **3** (majority component) were obtained. The reaction mixture was diluted and neutralized with 10% NaHCO₃ solution, and then the product was extracted with hexane, dried in MgSO₄, and condensed into a crude product mixture to be used in the next step without purification.

[2,5-Bis(2-ethyl-hexyloxy)benzyl]phosphonic acid diethyl ester(4)

In an argon environment, a crude product of **3** (63.21 g, 1 mol equiv) was added with triethyl phosphite (40 mL, 1.5 mol equiv) in 2 mL \times 20 times increments within a 5-min period, and the reaction was then continued to be stirred in a hot oil bath at 140 °C for 3 h. The unreacted triethyl phosphite was removed using a vacuum pump. The remaining crude product residue was purified in a silica gel column to afford 15.5 g colorless oil pure product **4** (44% yield).

¹H NMR: δ (ppm) 6.82 (s, 1H); 6.76 (s, 1H); 4.13–3.93 (m, 8H); 3.79 (t, J = 6 Hz); 3.27 (d, J = 22 Hz); 1.72 (m, 2H); 1.6–1.2 (m, 16H), 0.92 (t, J = 7 Hz, 18H). Anal. Calcd.: C 66.91; H 10.19. Found: C 67.18; H 10.37.

[2,5-Bis(2-ethyl-hexyloxy) – 4-formyl-benzyl]phosphonic acid diethyl ester (5, donor monomer)

To an ice bath cooled reaction mixture containing **4** (4.85 g, 10 mmol, 1 mol equiv), methylene chloride (33 mL), and α,α -dichloromethyl ether (1.39 g, 12 mmol), titanium tetrachloride (7 mL, 35mmol) was added dropwise over 2 min. Immediately, the reaction mixture color changed to red. An hour later, the reaction mixture was treated with a stirred mixture of K₂CO₃ (8.42 g), H₂O (200 mL), and ice (50 g) in a 1 L beaker. The reaction mixture was diluted/neutralized with 10% NaHCO₃ solution and water, and then the product was extracted with hexane. Dried in MgSO₄ and condensed and purified in a silica gel column (2:1 hexane:ethylacetate eluent) to give 3.84 g (75% yield) of pure product.

¹H NMR in CDCl₃ [also shown in Fig. 1(a)]: δ (ppm) 10.45 (s, 1H); 7.29 (s, 1H); 7.10 (d, due to phosphorus, 1H); 4.10– 3.92 (m, 8H); 3.33 (d, J = 22 Hz, 2H); 1.72 (m, 2H); 1.6–1.2 (m, 16H), 0.92 (t, J = 7 Hz, 18H). ¹³C NMR in CDCl₃ [also shown in Fig. 1(b)]: δ 11.25, 14.16, 16.43, 23.12, 24.05, 26.23, 28.06, 29.20, 30.71, 39.61, 62.17, 71.45, 77.33 (t, chloroform), 108.94, 116.15, 123.92, 129.47, 150.94, 156.06, 189.33. Anal. Calcd.: C 65.60; H 9.63. Found: C 65.60; H 9.76.

(4-Fluoro-benzyl)phosphonic acid diethyl ester (6, the terminator)

The terminator **6** was synthesized following a literature procedure reported before.³⁰



The Donor Block C8-RO-PPV (7, D)

In a nitrogen glove box, and at room temperature, to a vigorously stirred mixture of donor monomer 5 (2.30 g, 4.49 mmol, 1 mol equiv) and terminator (4-fluoro-benzyl)-phosphonic acid diethyl ester 6 (45 mg, 0.183 mmol, 1/25 mol equiv), 55 mL THF was added in 10 mL increments until everything dissolved, t-BuOK (5.5 mL, 1.0 M in THF, 5.5 mmol) was added drop wise over 5 min, and the reaction was allowed to continue for another 5 min. The reaction mixture was taken out from the glove box and 150 mL of methanol was added to precipitate out the reddish polymer product. The suspension mixture was placed in the refrigerator for 1 h to catalyze precipitation of the polymer. Finally, the suspension was slowly filtered via a Buchner fine glass funnel, rinsed twice with MeOH and left to dry overnight to give 1.345 g (58% yield) of donor polymer block (D) or 7.

¹H NMR in CDCl₃ (also shown in Fig. 3): δ (ppm) 7.7–7.4 (m, br, PPV aromatic); 7.3–7.1 (m, br, PPV vinylenene); 3.9–4.1 (s, trans-OCH₂), 3.5 (s, cis-OCH₂), 2.0–1.1 (m, aliphatic CH and CH₂), 1.1–0.7 (m, aliphatic CH₃). GPC data are tabulated in Table 1. Other physical properties are listed in Discussion section.

Acceptor Synthesis

1-Decyloxy-4-decylsulfanyl-benzene (9)

A solution of 4-mercaptophenol **8** (12.62 g, 0.10 mol, 1 mol equiv), potassium hydroxide (12.9 g, 0.23 mol, 2.3 mol equiv), and deionized water (15 mL) in acetonitrile (400 mL) was heated to 90 °C. Next, 1-bromodecane (44.24 g, 0.20 mol, 2 mol equiv) was added. After reacting for 48 h, the reaction mixture was poured into deionized water (\sim 800 mL). The white colored solid was collected by filtration and then dissolved in a small amount of chloroform (\sim 20 mL), and then re-precipitated in cold methanol (\sim 800 mL). Solid was filtered again and dried yielding 36 g (yield: 88.5%) **9**.

¹H NMR (CDCl₃): δ 0.88 (t, 6H, J = 6.1 Hz), 1.27 (m, 28H), 1.57 (quintet, 2H, J = 7.0 Hz), 1.76 (quintet, 2H, J = 7.0 Hz), 2.80 (t, 2H, J = 7.3 Hz), 3.92 (t, 2H, J = 6.5 Hz), 6.82 (d, 2H, J = 8.3 Hz), 7.31 (d, 2H, J = 8.3 Hz). Anal. Calcd. for C₂₆H₄₆OS: C, 76.78; H, 11.40. Found: C, 76.76; H, 11.43.

2-Bromomethyl-1-decyloxy-4-decylsulfanyl-benzene (10)

In an inert gas environment, a mixture of **9** (38.5 g, 94.66 mmol, 1 mol equiv), paraformaldehyde (6.06 g, 201.8 mmol, 2.1 mol equiv), glacial acetic acid (22 mL, 23.1 g, 385 mmol, 4.07 mol equiv), acetic anhydride (3.5 mL, 3.78 g, 37 mmol, 0.39 mol equiv), and 30% HBr/HOAc (25 mL, 33.85 g, 126 mmol, 1.33 mol equiv) was stirred and heated in a hot oil bath at 90 °C for 3 h. The reaction mixture was diluted/neutralized with water and 10% NaHCO3 solution, then the product was extracted with hexane, dried in MgSO₄, and condensed to give a crude oil product **10** to be used directly in the next step. Product weight: 25.84 g (~80% mono-CH₂Br based on ¹H NMR analysis. Yield of mono-CH₂Br: ~43%).

TABLE 1 Gel Permeation Chromotography data of D and A

	D, 7	A, 17
M _n	9,300 Daltons	7,700 Daltons
M _w	21,700 Daltons	19,300 Daltons
PDI	2.34	2.51
Repeat unit weight	358 g/mol	462 g/mol
# of Repeat units (DP, measured)	25.2	16.1
# of Repeat units (DP, targeted/ calculated)	25	15

(2-Decyloxy-5-decylsulfanyl-benzyl)phosphonic Acid Diethyl Ester (11)

In an enclosed environment, 25.85 g of crude **10** (containing about 20.41 g or 40.9 mmol **10**) and triethyl phosphite (20 mL, 19.38 g, 116.6 mmol, 2.9 mol equiv) were vigorously stirred and heated in a hot oil bath at 140 °C for 18 h. Triethyl phosphite was removed by high vacuum at 100 mbar at 160 °C, the remaining product was purified using a silica gel column (1:2 hexane/ethyl acetate solution) to give a colorless oil pure product. Yield: ~40%.

¹H NMR: δ (ppm) 7.36 (s, 1H); 7.23 (s, 1H); 6.78 (s, 1H); 4.10–3.9 (m, 6H); 3.27 (d, J = 2 2Hz, 2H); 2.81 (t, J = 6 Hz, 2H); 1.85–1.15 (m, 32H); 0.88 (t, J = 4Hz, 12H). Anal. Calcd.: C 66.87; H 10.32. Found: C, 67.10; H, 10.58.

(4-Bromomethyl-2-decyloxy-5-decylsulfanylbenzyl)phosphonic Acid Diethyl Ester (12)

In an enclosed environment, a stirred solution containing **11** (23.87 g, 42.87 mmol, 1 mol equiv), paraformaldehyde (7.72 g, 257.22 mmol, 6 mol equiv), trifluoroacetic acid (33 mL, 428.7 mmol, 10 mol equiv), trifluoro acetic anhydride (12 mL, 18.13 g, 86.3 mmol, 2 mol equiv), and 30% HBr/HOAc (23 mL, 31.14 g, 115.5 mmol, 2.7 mol equiv) was stirred and heated in a hot oil bath at 60 °C for 5.5 h. The reaction mixture was diluted/neutralized with water and 10% NaHCO₃ solution, then the product was extracted with hexane. Dried in MgSO₄ and condensed to give 29.6 g of crude oil product directly used in the next step without purification.

(2-Decyloxy-5-decylsulfanyl-4-hydroxymethylbenzyl)phosphonic Acid Diethyl Ester (13)

In an enclosed environment, a mixture of crude **12** (29.6 g, 45.56 mmol, 1 mol equiv), sodium bicarbonate (11.5 g, 136.7 mmol, 3 mol equiv), water (62 mL, 3417 mmol, 75 equiv), and 1-methyl-pyrolidinone (549 mL, 5695 mmol, 125 mol equiv) was stirred and heated at 90 °C in a hot oil bath for 2.75 h. The reaction mixture was diluted/neutralized with water and 10% NaHCO₃ solution, then the product was extracted with hexane. Dried in MgSO₄ and condensed to give a crude oil product that was purified using a silica gel column (1:1 hexane/ethyl acetate solution) to give 15.92 g (~60% yield) of pure product **13**.





FIGURE 2 Acceptor Monomer 16 (a) ¹H NMR and (b) ¹³C NMR Spectra in CDCl₃. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

¹H NMR: δ (ppm) 7.4 (s, 1H); 6.93 (s, 1H); 4.76 (s, 1H); 4.10–3.9 (m, 6H); 3.25 (d, J = 22 Hz, 2H); 2.80 (t, J = 6 Hz, 2H); 1.85–1.15 (m, 32H); 0.88 (t, J = 6 Hz, 12H).

[5-(Decane-1-sulfonyl)-2-decyloxy-4-hydroxymethylbenzyl]phosphonic Acid Diethyl Ester (15)

In an enclosed environment, a mixture of 13 (15.92 g, 27.13 mmol, 1 mol equiv), 50% H₂O₂ (4.5 mL, 4.5 g, 66 mmol, 2.4 mol equiv), and acetic acid (22 mL, 352.69 mmol, 13 mol equiv) were stirred at room temperature for 25 min then stirred and heated in a hot oil bath at 90 °C for 35 min. The reaction mixture was allowed to cool to room temperature, diluted/neutralized with water and 10% NaHCO3 solution, then the product was extracted with hexane. Dried in MgSO4 and condensed to give a crude oil product mixture (14+15). This crude product mixture was treated with a mixture of KOH (12 g), water (50 mL), and EtOH (81 mL) at room temperature for 5 min. After 5 min, 14 g of NaHCO₃ was added and the mixture was condensed. The residue was extracted with ether or hexane, and the extract was dried in MgSO₄ and condensed to give 15.61 g crude product 15 to be used directly in the next step (60.8% yield).

¹H NMR: δ (ppm) 7.93 (s, 1H); 7.07 (s, 1H); 4.89 (s, 1H); 3.85-4.05 (m, 6H); 3.25 (d, J = 22 Hz, 2H); 3.13(t, J = 8 Hz, 2H); 1.9–1.18 (m, 32H); 0.88 (t, J = 4 Hz, 12H).

[5-(Decane-1-sulfonyl) – 2-decyloxy-4-formylbenzyl]phosphonic acid diethyl ester (16, acceptor monomer)

In an enclosed environment, a mixture of **15** (15.47 g, 25 mmol, 1 mol equiv), methylene chloride (72 mL, 95.4 g, 1123 mmol, 45 mol equiv), and pyridinium chlorochromate

PCC (6.52 g, 30.2 mmol, 1.2 mol equiv) was stirred at room temperature for 18 h. The reaction mixture was diluted with water and 10% NaHCO₃ solution, and the product was extracted with hexane, dried in MgSO₄, and condensed to give a sticky dark brown solution. The sticky solution was placed in the freezer for recrystallization overnight. The white crystal formed was filtered and dried to give 4.68 g of pure product **16** (45% yield).

¹H NMR in CDCl₃ [also shown in Fig. 2(a)]: δ (ppm) 10.8 (s, 1H); 7.99 (d, due to phosphonate group, 1H); 7.54 (s, 1H); 4.19-4.01 (m, 6H), 3.38 (d, *J* = 22 Hz, 2H); 3.18 (t, *J* = 8 Hz, 2H); 1.92-1.15 (m, 32H); 0.88 (t, *J* = 4 Hz, 12H). ¹³C NMR in CDCl₃ [also shown in Fig. 2(b)]: δ 14.09, 14.11, 16.36, 16.44, 22.65, 22.67, 25.36, 26.23, 28.07, 28.23, 28.99, 29.21, 29.24, 29.31, 29.33, 29.41, 29.54, 31.83, 31.89, 58.61, 62.18, 62.26, 69.49, 111.11 (d, 2.7 Hz), 127.38 (d, 9.4 Hz), 131.69 (d, 3.9 Hz), 133.78 (d, 4.9 Hz), 135.31 (d, 3.3 Hz), 160.71 (d, 6.1 Hz), 189.46. Anal. Calcd: C, 62.31; H, 9.31; S, 5.20. Found: C, 62.09; H, 9.25; S, 5.22.

The Acceptor Block (17, A)

In a glove box, and at room temperature, to a vigorously stirred mixture of acceptor monomer **16** (1.52 g, 2.46 mmol, \sim 15 mol equiv) and terminator (4-fluoro-benzyl)-phosphonic acid diethyl ester **6** (41 mg, 0.167 mmol, 1 mol equiv), 45 mL of anhydrous THF were added in 10 mL increments until everything dissolved. *t*-BuOK (3.2 mL, 1.0 M, 3.2 mmol, \sim 19 equiv) was added drop wise over 5 min, and the reaction was allowed to continue for another 5 min. The reaction mixture was taken out from the glove box and 150 mL of methanol was added to precipitate out the reddish polymer product. The polymer suspension solution was placed in the



refrigerator for 1 h to catalyze the precipitation of polymer. Finally, the polymer suspension was slowly filtered through a Buchner fine glass funnel, rinsed twice with methanol and left to dry overnight to give 0.63 g (40% yield) of acceptor polymer **17**.

¹H NMR in CDCl₃ (also shown in Fig. 3): δ (ppm) 8.5–8.1 (m, br, PPV aromatic); 7.3–7.1 (m, br, PPV vinylenene); 4.3–4.0 (m, br, trans-OCH₂), 3.2–3.1 (cis-OCH₂), 2.1–1.1 (m, aliphatic CH and CH₂), 1.1–0.7 (m, aliphatic CH₃). GPC data are tabulated in Table 1.

The Bridge Unit (18)

The synthesis of the bridge unit (in Scheme 5, where t = 2, 4) follows a literature procedure.³¹ Both two and four carbon-based bridge units were synthesized. Since properties of the polymer samples from either two or four carbon bridge unites are almost the same or similar, DBA data based mainly on the two carbon bridge unit are reported here unless noted otherwise.

Block Copolymer Synthesis

Phosphonate-Terminated C8-RO-PPV + Bridge (19, DB)

One example: In a glove box, a mixture of the donor polymer **D** (0.43g, 1 mol equiv of terminal phosphonate group), the bridge compound **B** (t = 2, 0.164 g, about 21 mol equiv aldehyde groups) and THF (7.5 mL) was heated until the polymer was fully dissolved. After being cooled for 5 min, t-BuOK (38 mg) in 1 mL THF was added over 10 s. After being stirred for 30 s, the reaction was quenched with 0.1 mL 30% acetic acid HOAc. The mixture was dropped into methanol MeOH and the polymer product was collected by filtration, yielding 0.415g (95% yield) **DB**.

¹H NMR in CDCl₃ (also shown in Fig. 3): δ (ppm) 9.9 (s, CHO), 7.9 (small, bridge aromatic), 7.7–7.4 (m, br, PPV aromatic); 7.4–7.2 (m, br, PPV vinylenene); 3.9–4.1 (s, br, trans-OCH₂), 3.5 (s, cis-OCH₂), 2.0–1.1 (m, aliphatic CH and CH₂), 1.1–0.7 (m, aliphatic CH₃).

Block Copolymer (20, DBA)

One example: In a glove box, to a stirred mixture of the **DB** (300 mg, 1 mol equiv), the acceptor polymer **A** (400 mg, about 1.6 mol equiv), and THF (13 g THF), 65.8 mg *t*-BuOK



(dissolved in 1 g THF) was added dropwisely. After being stirred for 5 min after the addition, the reaction mixture was dropped into a stirred 100-mL methanol MeOH. Polymer product was collected by filtration and dried at 60 $^{\circ}$ C in vacuum for two days.

Yield: 684 mg (98%). ¹H NMR in CDCl₃ (also shown in Fig. 3): δ (ppm) 8.5–8.1 (m, acceptor PPV aromatic); 7.9 (small, bridge aromatic), 7.7–7.4 (m, donor PPV aromatic); 7.4–7.2 (m, br, donor and acceptor PPV vinylenene); 4.3–4.1 (m, acceptor trans-OCH₂), 4.1–3.9 (s, donor trans-OCH₂), 3.5 (s, donor cis-OCH₂), 3.2–3.1 (acceptor cis-OCH₂), 2.1–1.1 (m, aliphatic CH and CH₂), 1.1–0.7 (m, aliphatic CH₃). GPC data are tabulated in Table 2, and RI signal curves of the GPC are shown in Figure 4. Other physical property data are listed in Discussion section.

Optoelectronic Solar Cell Device Fabrications and Characterizations

Polymer solar cells are fabricated and tested using following general protocols and procedures: (1) Polymer solution preparations: For DBA cells, 15 mg of synthesized DBA polymer sample are mixed with 15 mg PC₆₀BM (from Nano-C, batch # BJ100507) in 1 mL dichlorobenzene (DCB). For D/A blend cells, 8 mg donor block (D, 7) mixed with 7 mg acceptor block (A, 17) and 15 mg $PC_{60}BM$, also dissolved in 1 mL DCB. The sample solutions are gently heated to between 60 and 90 °C for at least 1 h and filtered through a 0.2-µm PTFE filter before spin coated on pretreated and patterned ITO glass slides. (2) ITO glass slides (from Delta Technologies, part # CG-50IN-S107, 25 \times 75 \times 0.7 mm, 8–12 Ω) patterning and treatments: Each ITO glass slide was cut in half and each cut slide was patterned into eight solar cells using a pattern mask, where each patterned solar cell has an effective size of 0.45 \times 0.45 $cm^2=0.2025~cm^2.$ Along the two long edges of the ITO side, about 0.5-cm ITO coating layer from the edge was etched away (for later electrode clamping positions) using hydrochloric acid (6N HCl for 15 min. Scotch tape is used to protect the nonetched part). The patterned ITO slides are then cleaned by detergent, DI water, acetone, and finally isopropanol each for 5 min in ultrasound. (3) Polymer film depositions: First PEDOT:PSS aqueous solution (Clevious PVPAI 4083, from H.C. Starck) was dropped onto the cut ITO slide using a 1-mL syringe and a 0.2-µm PTFE filter. The spin coating protocol include a key step of 5000 RPM for 30 s, tyically yielding a 30-40-nm thick PEDOT:PSS film. After PEDOT:PSS films are dried (60 °C under vacuum pump for at least 2 h, or 110 °C at room pressure for at least 30 min), the photovoltaic polymer DCB

TABLE 2 Gel Perm	eation Chromotogi	aphy data of DBA
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	DBA, 20
<i>M</i> _n (measured)	16,700 Daltons
M _w	38,900 Daltons
PDI	2.32
Mn (targeted/calculated)	16,700 Daltons



FIGURE 4 Normalized RI signal curves of **D**, **A**, and **DBA** from GPC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solutions were spun coated on top of dried PEDOT:PSS layer at a spin rate of 500-3000 RPM for 160 s (desired film thickness are between 100 and 200 nm). After the films are dried under vacuum, they are taken into the nitrogen-filled glove box for device fabrications. (4) Final solar cell device fabrications: Inside a high vacuum deposition chamber inside the glove box, polymer coated ITO slides are each covered and clamped with an eight-cell pattern mask, and are mounted facing downward on a rotary disk on top of the vacuum deposition chamber. At about 1×10^{-7} mbar vacuum level, Aluminum negative electrodes are thermally evaporated onto the mask covered cell slides to a thickness of about 100 nm. ITO positive electrode was exposed by scratching off a small area of polymer/PEDOT:PSS film at one terminal of the slide using a solvent such as THF. (5) Solar cell measurements: The light/photo incurred currentvoltage (IV) curves are measured by exposing the thin film cells in a measurement holder to a solar simulator generated one Sun (100 mW/cm²) 1.5 AM radiation from the top of the glove box. A voltage-current Source-Measure Unit (Keithley SMU-237) coupled with a PC were used to monitor and measure IV data on each cell.

RESULTS AND DISCUSSION

Materials Synthesis

General

DBA synthesis requires the synthesis of a mono-end functionalized conjugated donor block (Scheme 3 exhibits an example), a mono-end functionalized conjugated acceptor block (Scheme 4 exhibits an example), and a double-end functionalized bridge



FIGURE 5 Differential scanning calorimetry (DSC) curves of **D**, **A** and **DBA**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 6 Thermal gravimetric analysis (TGA) curves of **D**, **A**, and **DBA**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

unit that can connect the donor and acceptor blocks (Scheme 5 exhibits a specific **DBA** synthesis example). Horner–Emmons reaction is used to build individual donor or acceptor PPV blocks. Phosphonate instead of aldehyde is chosen as the terminal functional group of donor and acceptor blocks because it is more stable than the aldehyde group to the strong base (*e.g.*, t-BuOK), and it is used in excess in the polymerization reaction. The stability of the aldehyde group in the bridge unit is not a major concern as the coupling reaction time is very short and that the bridge compound is used in large excess.

Monomer Synthesis

The example synthesis of a PPV-based donor and acceptor monomers (5 and 16) and corresponding polymer blocks (7 and 17) are shown in Schemes 3 and 4. Both donor and acceptor monomers (5 and 16) are asymmetrically difunctionalized with an aldehyde and a phosphonate groups which can be polymerized into PPV via the Horner-Emmons reaction. In donor monomer synthesis, a branched 2ethylhexyl (C8) is used instead of a straight or linear alkyl group because a linear alkyl group substituent regio-regular PPV is more difficulty to dissolve. Interestingly, the acceptor block with linear side chains does not appear to have solubility problem. Presumably, the polar repeat units interact more strongly with the polar solvents used. The use of different side chains also facilitates donor and acceptor block phase separation. In the synthesis of 2-CH₂Br (methylene bromide) substituted 3 and 10, control of reaction temperature and



FIGURE 7 UV-vis absorption spectra of **D**, **A**, and **DBA** in THF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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FIGURE 8 Photoluminescence PL emission spectra of **D**, **A**, and **DBA** in 1 \times 10⁻⁷ M THF solutions of corresponding repeat units (in DBA case, concentration refers to acceptor repeat unit concentration). The excitation is at 400 nm which is optimal for the acceptor **A** block but not optimal for the donor **D** block (Donor block excitation is optimal at about 500 nm). The small peak spike at around 453 nm comes from the THF solvent used. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

time are very critical to avoid the undesirable 2,5-di-CH₂Br substitution. The light yellowish oil donor monomer **5** and the whitish solid acceptor monomer **16** were fully characterized by NMR (also shown in Figs. 1 and 2) and elemental analysis. The monomers can be further modified with different substituents for a variety of optoelectronic application needs.

Conjugated Block Synthesis

Synthesis of both donor and acceptor blocks requires the use of a block terminator (compound **6** in Scheme 3) to terminate one end of the block as well as to control the size of the blocks (Schemes 3 and 4). The choice of the terminator is very critical. For instance, compound **3** was initially tested as the terminator. However, when t-BuOK was added to the mixture of donor or acceptor monomer and compound **3** in THF, a high molecular weight PPV (judged by the way it precipitated in MeOH) was obtained. Presumably, the P-CH₂ group in **3** are not reactive (or acidic) enough to compete with the P-CH₂ group in monomer for *t*-BuOK added, and therefore, **3** does not participate in polymerization. There-



FIGURE 9 Photoluminescence PL emission spectra of **D** and **DBA** in 1×10^{-7} M donor repeat unit solutions. The excitation is at 500 nm which is optimal for the donor **D** block but it cannot excite the acceptor block (Acceptor block excitation needs 400 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 10 Cyclic voltammetry curves of Ferrocene (dotted line), **D** (solid line), and **A** (dashed line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fore, a terminator with higher P-CH₂ reactivity (or acidity) is required. When terminator 6 (with an electron-withdrawing fluorine substitution at the para position) was used, the size control in both donor and acceptor block synthesis worked well. For instance, since each PPV repeat unit has a straight length of about 0.65 nm along the conjugation chain, a donor monomer/terminator feed molar ratio of 25:1 is supposed to yield a chain length of 25 repeat unit (degree of polymerization, DP = 25).³² and it actually yielded a donor block of around 25.2 repeat units as measured from GPC (see Table 1 and Fig. 4). An acceptor monomer/terminator feed molar ratio of 15:1 is supposed to yield a chain size of 15 repeat units (DP = 15), and it actually yielded an acceptor block size of about 16.1 repeat units (see Table 1). ¹H NMR spectrum of the **D**, **DB**, **A**, and **DBA** are shown in Figure 3, where the monomer's characteristic aldehyde peak disappeared completely when the **D** or **A** blocks or **DBA** formed.

DBA Block Copolymer Synthesis

As shown in Scheme 5, when synthesizing donor-bridge or **DB** unit, the bridge **B** is in a large access amount (more than 20 mol equiv) of donor block **D** to minimize the chance of



FIGURE 11 Comparison of light JV curves of solar cells made of a **D/A** blend (dashed curve) versus a **DBA** block copolymer (solid curve). **DBA** cell exhibits an order of magnitude higher power conversion efficiency (PCE) then the **D/A** blend cell. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 12 Taping mode topographic AFM images for spincoated thin films of (a) **D/A** blend and (b) **DBA** block copolymer. Image dimensions are at 500 \times 500 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

forming **DBD** species, and to ensure that resulting polymer has one aldehyde group still available (see small aldehyde peak of **DB** in its NMR spectrum in Fig. 3). The available aldehyde group can further couple with the acceptor block forming the final **DBA** as indicated by the disappearance of the **DB** aldehyde peak and appearance of the NMR peaks associated with acceptor block (Fig. 3). The measured number average molecular weight of 16,700 Daltons matches nicely with the calculated molecular weight of 16,700 Daltons based on the individual donor and acceptor block average molecular weights (see Table 2 and Fig. 4). There could exist certain difference between polystyrene determined molecular weights versus actual PPV molecular weights due to polymer shape differences. If this indeed occurs, it would be a systematic error, that is, it would apply to all measured PPV samples including **D**, **A** and **DBA** blocks, but such systematic error would not affect summation relationship of D+A=DBA. Details of the synthetic procedures and data are described in the Experimental section.

Physical Properties Thermal Properties

Differential scanning calorimmetry (DSC) and thermal gravimetric analysis (TGA) scans of **D**, **A**, and **DBA** are shown in Figures 5 and 6. Thermal study results indicate that all three polymer samples exhibit no significant thermal induced transitions and/or degradations to about 300 °C.

Optoelectronic Properties

UV-vis absorption spectra of the D, A, and DBA in THF are shown in Figure 7. Donor block exhibits an absorption maximum at around 500 nm, and acceptor block exhibits an absorption maximum at around 420, the DBA exhibits a maximum absorption peak around 500 nm (reflecting the donor absorption maximum) and a relatively small but noticeable absorption peak at around 420 nm (reflecting the acceptor absorption maximum), confirming (1) DBA contains both **D** and **A**; and (2) **D** and **A** still maintain their electronic structures separately after connected by the bridge unit, and that there is no evidence of ground state charge transfer between D and A in DBA which is necessary for optoelectronic applications. The optical excitation absorption cut off (corresponding to optical excitation energy gaps) are 560 nm (2.21 eV) for the donor (D) and 530 nm (2.34 eV) for the acceptor (A) blocks. Due to an intramolecular electronic push-pull interaction within the acceptor block repeat units,²² the absorption peak maximum of the acceptor block is at higher energy (around 420 nm) and has lower intensity compared to the donor block (peak maximum around 500 nm).

The photoluminescence (PL) emission spectra of the D, A, and DBA in THF are shown in Figure 8. All three polymer samples were dissolved in THF at the same molar concentration of 1.0×10^{-7} M corresponding to their repeat units (in DBA case, concentration corresponds to acceptor repeat unit). Similar to what was observed in absorption, DBA emission spectrum exhibits two emission peaks corresponding to the emission peaks of the donor block (around 550 nm) and the acceptor block (around 500 nm). The excitation wavelength is set at 400 nm, which is optimal for the acceptor block but is not optimal for the donor block (Donor block excitation is at 500 nm). This explains why the donor emission intensity appears much weaker than the acceptor even if their concentrations are the same. The significant reduction of the emission peak of A at around 500 nm in DBA as compared to pristine A can be attributed to both charge transfer and energy transfer between the donor and the acceptor in DBA. Energy transfer is evidenced by the donor emission peak increase at around 550 nm from the pristine **D** to **DBA** in Figure 8. The small peak spike at around 453 nm comes from the THF solvent used. Charge transfer is evidenced by the donor block emission peak at 550 nm dropped significantly from the pristine **D** to **DBA** when the sample solutions were excited at 500 nm (Fig. 9). This is also another evidence of a close proximity of **D** block to the **A** block in the **DBA**.

The frontier orbitals (HOMOs and LUMOs) of the donor and acceptor blocks were analyzed using electrochemical cyclic voltammetry (CV) (shown in Fig. 10. A small bump at about -0.4 volt is from Ferrocene measurement and is therefore excluded in molecular frontier orbital determinations) combined with UV-vis absorption spectra (Fig. 7). Due to potential irreversible electrochemically incurred changes to polymer samples in CV negative (reduction) scan measurements, only the first oxidation onset potentials are used here to estimate HOMO values. Optical excitation energy gap data are used to estimate the LUMO values. Specifically, the HOMO and LUMO levels of donor and acceptor blocks are calculated as follows:

Frontier Orbital Calculations via Cyclic Voltammetry Measurements

 $D-HOMO \rightarrow -4.8eV - (1.05-0)eV = -5.85eV$ $A-HOMO \rightarrow -4.8eV - (1.22-0)eV = -6.02eV$

Frontier Orbital Calculations Using Optical Energy Gaps Combined with HOMOs

Optical excitation energy gap $(E_g) = (1240)/$ (UV-vis absorption cut off)

Donor optical energy gap = 1240/560 = 2.21eV (LUMO/ HOMO = -3.64eV/-5.85eV)

Acceptor optical energy gap = 1240/530 = 2.34 (LUMO/ HOMO = -3.68eV/-6.02eV)

The frontier orbital data indicate that the LUMO orbital offset (0.04 eV) is relatively small compared to the most desired or popular values (i.e., 0.3eV), this may explain the relatively low efficiency of photo induced charge transfer between **D** and **A** here (and therefore the potential optoelectronic device performance). Further optimizations of the frontier orbitals are necessary.

Preliminary Optoelectronic Device Studies

Figure 11 exhibit preliminary comparison between several cells fabricated from **DBA** (blue curve represents a best **DBA** cell in a particular measurement) versus several cells fabricated from **D/A** blends (red dashed curve represents a best **D/A** cell in a particular measurement). Based on measured JV data at AM 1.5 and one Sun intensity, the best **D/A** blend cell yielded a short circuit current density of 0.22 mA/cm², an open circuit voltage of 0.73 volt, a fill factor of 13%, and a power conversion efficiency of about 0.02%. The best **DBA** cell (not yet optimized), on the other hand, yielded a short

circuit current density of 0.92 mA/cm², an open circuit voltage of 0.65 volt, a fill factor of 26%, and a power conversion efficiency of about 0.2%. At the same cell fabrication and testing setup, the reference P3HT/PCBM best cell yielded a short circuit current density of 3.59 mA/cm², an open circuit voltage of 0.56 volt, a fill factor of 40%, and a power conversion efficiency of about 0.8%. The relatively lower efficiency for the new PPV based cells as compared to the reference P3HT/PCBM cells can be contributed to several obvious factors: (1) Energy gaps for these PPVs are typically over 2.2 eV, while P3HT has an energy gap of about 1.8 eV. Since most abundant sunlight photons are between 1 and 2 eV at AM 1.5, photon losses are expected to be more severe in PPV as in P3HT. (2) Regio-regular P3HT are known for its highly ordered solid-state morphology and corresponding high charge mobility, while the typical solid-state morphologies and charge transport in PPV are relatively poorer, thus, charge carrier losses are expected to be more severe in PPV as compared to P3HT. (3) The PPV thin film solar cell device fabrication protocol used here are from optimizations for the P3HT/PCBM reference cells, and that the optimal processing or morphologies of P3HT/PCBM cells are not necessarily the same or optimal for the PPV based solar cells. Even for our best P3HT/PCBM reference cell, a 0.8% PCE efficiency achieved is still much lower than the best or typical literature reported value of around 5%,5 that is, our device fabrication protocol still has room for further improvements. However, and most importantly, an order of magnitude better PCE improvement of the DBA cell over the D/A blend cell was clearly observed and demonstrated. Due to similarities of the frontier orbitals of DBA versus D/A blend, the significant PCE improvement should be attributed to the improvement on materials spatial regimes and not on energy regimes. For instance, there should be much less exciton and carrier transport losses in DBA than in D/A blend, as every exciton generated in DBA can easily reach its D/A interface within its life time, and every newly generated electron or hole can diffuse to their respective electrodes in their own domain or phases with much less interruptions in DBA than in D/A blend. Figure 12 exhibits preliminary atomic force microscopy (AFM) taping mode topographic images for spin coated thin films of (a) D/A blend and (b) DBA block copolymer. Image sizes are at 500 imes 500 nm. It appears certain phase domains on the 10-20 nm scales can be seen in the DBA block copolymer film but not in the D/A blend film. Systematic studies on polymer solid-state morphological optimizations and their effects to optoelectronic device performance are under way and will be reported in future.

CONCLUSIONS

A novel class of conjugated block copolymer system containing a donor type conjugated block c-**D** covalently connected to an acceptor type conjugated block c-**A** via a nonconjugated and flexible bridge unit nc-**B**, also called a **DBA** type conjugated block copolymer system, has been designed, synthesized, and characterized for potential cost effective and high efficiency optoelectronic applications. The **D** and **A**



block synthesis involve development of unsymmetrical difunctionalized donor or acceptor type monomers and a terminator unit, for instance, an aldehyde and a phosphonate functional groups are needed for Horner-Emmons coupling reaction, and that the size of each conjugated block can be controlled via synthetic feed ratio of the monomer and the terminator. The measured average molecular weights of D, A, and **DBA** based on gel permission chromatography (GPC) measurements are in good agreements with calculated values based on synthetic monomer feed ratios. Preliminary optoelectronic device studies revealed an order of magnitude better solar cell power conversion (PCE) efficiency improvement of DBA over the corresponding D/A simple blend under identical device fabrication and testing conditions. Such improvements are attributed to inherent improvement of DBA solid-state nanomorphology over the D/A blend resulting in more efficient photo induced charge separation and charge transport in DBA versus in D/A blend. Further improvement of DBA device efficiencies can be achieved via better matched frontier orbitals between the donor and acceptor blocks to enhance charge separation and transfer and minimize charge recombinations, better excitation energy gaps (to match the intended radiation energy range), optimal bridge length between the donor and the acceptor, better DBA solid-state morphologies (e.g., more ordered and self-assembled solid-state packing via stereo - or regioregular polymers to improve charge transports, more dissimilar donor or acceptor blocks for better phase separations), and improved device fabrications (e.g., optimal film thickness and post-treatments, improved electron, or hole blocking/ collecting layers and electrodes).

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