

Poly(1,4-phenylene vinylene) Derivatives with Ether Substituents to Improve Polymer Solubility for Use in Organic Light-Emitting Diode Devices

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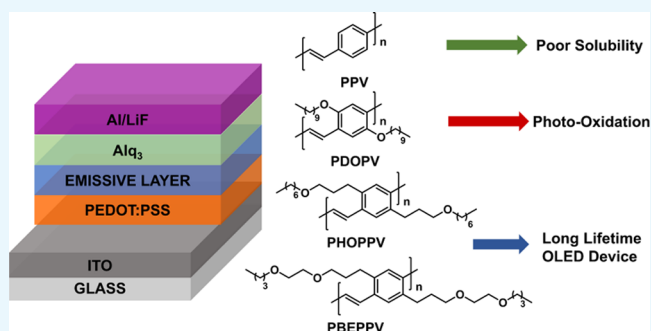
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Supporting Information

ABSTRACT: New ether-substituted poly(1,4-phenylene vinylene) (PPV) derivatives were synthesized via Horner–Emmons coupling. The structures of the monomers and the resultant oligomers were confirmed by ¹H and ¹³C NMR spectroscopies. The molecular weights of the oligomers were characterized by gel permeation chromatography, giving the number-average and weight-average molecular weights and the corresponding polydispersity indices. Measurements of UV–vis absorption and fluorescence were used to characterize the optical properties of the oligomers. Estimation of the highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels and other electrochemical characteristics of the oligomers were investigated by cyclic voltammetry. Dialkyl and dialkoxy PPV oligomers were also prepared and characterized following the same instrumental methods used for the ether-substituted oligomers, providing a known reference system to judge the performance of the new conjugated oligomers. Devices were fabricated to analyze the electroluminescent characteristics of the oligomers in organic light-emitting diodes.



INTRODUCTION

Conjugated semiconducting polymers have been the focus of much research since the first green electroluminescent (EL) device, generated from poly(phenylene vinylene) (PPV), was presented.^{1–5} Since then, many modifications have been made to improve polymer processability, device efficiency, emission wavelength, and turn-on voltage.^{6–10} However, unsubstituted PPV is known to be insoluble and infusible, and because the oft-cited advantage of polymeric materials over small molecules in electronic devices is ease of processability, the search for soluble conjugated polymers has been extensive. Methods to improve solubility include the introduction of solubilizing side groups on the PPV structure, introduction of soluble polymers to yield PPV copolymers, and introduction of flexible blocks.^{11–15} One of the most common methods used to improve PPV solubility is the incorporation of solubilizing long alkyl chains—linear, branched, or alkyl chains with polar functional groups—onto the phenyl rings, see Figure 1 for examples.^{16–25} Synthetically, the solubilizing moieties can easily be attached through a phenoxy precursor. The increased acidity of the phenolic hydrogen facilitates alkylation of the

aromatic ring, opening avenues for the synthesis of a variety of functionalized PPV derivatives.

Previous research by Lee and co-workers focused on improving device lifetime by eliminating the use of electron-donating alkoxy substituents on the aromatic ring.²⁶ This not only decreases the oxidation potential by lowering the energy of the highest occupied molecular orbital (HOMO) but also introduces radical scavenging benzylic positions associated with the replacement of a solubilizing substituent. The proposed mechanism of PPV degradation shows singlet oxygen cleaving the vinyl bonds, reducing the conjugation length, and also introducing carbonyl defects that have been shown to be fluorescence quenchers.^{27,28} On the other hand, cleavage of the solubilizing alkyl chains from the benzylic position does not have a significant impact on the optical properties of the polymer; cleavage at the benzylic position ensures that the

Received: July 29, 2019

Accepted: November 15, 2019

Published: December 16, 2019

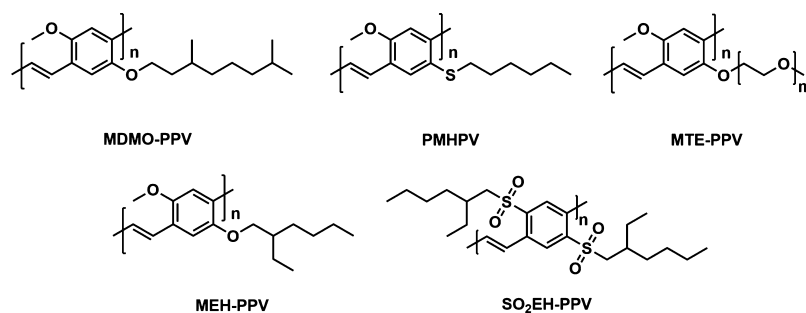


Figure 1. Common PPV derivatives with solubilizing side chains.

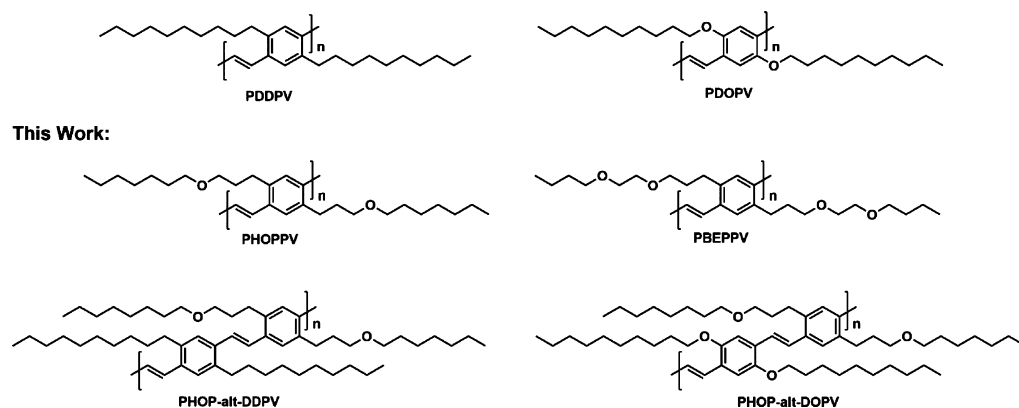


Figure 2. PPV derivatives targeted in this study.

polymer backbone remains intact, with no change in conjugation length.

However, in a previous study, removal of the oxygen atoms attached to the aromatic ring not only had the expected consequence of producing a blue shift in the emission spectrum (from orange to green), because of the replacement of the strong electron-donating oxygen with the weakly electron-donating alkyl group, but also produced a marked reduction in solubility from the dialkoxy PPV derivative—poly(2,5-didecyloxy-1,4-phenylene vinylene) (PDOPV)—to the new dialkyl PPV derivative—poly(2,5-didecyl-1,4-phenylene vinylene) (PDDPV), Figure 2.^{25,29} The decrease in solubility complicated comparisons in device performance because of the inability of PDDPV to form films of adequate thickness. While the oxygen present in PDOPV is detrimental to device lifetime, it appears to be necessary for improved device efficiency based on the role of solubility in device preparation. Apparent from the previous study, the presence of oxygen, directly attached to the aromatic ring, significantly affected the optical properties of the polymer. However, when the solubility-enhancing oxygen was not present, or in a position to donate electron density through resonance, the optical properties were less red-shifted, which is more amenable to realizing blue emitters. Therefore, herein we report the synthesis and characterization of new PPV derivatives in which the solubilizing chains are varied to study the effect on performance in organic light-emitting diode (OLED) devices. Meanwhile, because of the improved performance of the alternating copolymer poly(2,5-didecyl-*p*-phenylene vinylene-*alt*-2,5-didecyloxy-*p*-phenylene vinylene) (PDDPV-*alt*-DOPV) relative to the homopolymers in a previous study, the alternating copolymer incorporating the new heptyloxypropyl moiety was also studied.²⁶ The oligomers

prepared for this study include poly(2,5-didecyloxy-1,4-phenylene vinylene) (PDOPV) and poly(2,5-didecyl-1,4-phenylene vinylene) (PDDPV) and the new PPV derivatives poly(2,5-bis(3-(heptyloxy)propyl)-1,4-phenylene vinylene) (PHOPPV), poly(2,5-bis(3-(2-butoxyethoxy)propyl)-1,4-phenylene vinylene) (PBEPV), poly(2,5-bis(3-(heptyloxy)propyl)-1,4-phenylene vinylene-*alt*-2,5-didecyl-1,4-phenylene vinylene) (PHOP-*alt*-DDPV), and poly(2,5-bis(3-(heptyloxy)propyl)-1,4-phenylene vinylene-*alt*-2,5-didecyloxy-1,4-phenylene vinylene) (PHOP-*alt*-DOPV); the molecular structures of the oligomers used in this study are shown in Figure 2.

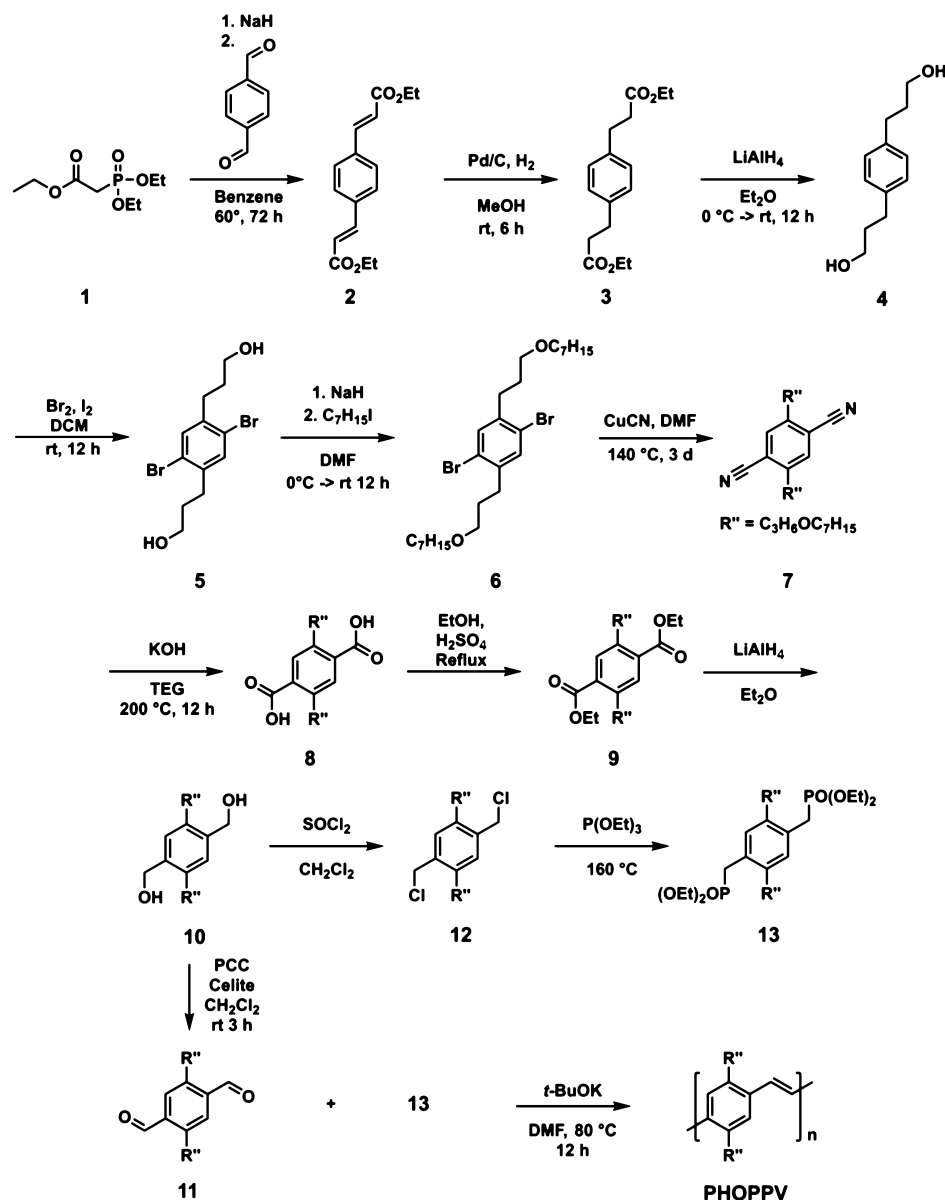
The incorporation of oxygen in the alkyl side chains should enhance the solubility of the new PPVs, leading to improved processing in the fabrication of OLED devices. To synthesize the targeted oligomers, the Horner–Emmons condensation was employed. This technique has been used to create polymers with no evidence of saturated defects, as can be seen with the Gilch polymerization.³⁰ Irregularities introduced in the polymer reduce the conjugation length and diminish the device efficiency by acting as charge traps.^{31,32} In addition, unlike the Wittig reaction, the Horner–Emmons condensation has been shown to produce no *cis*-defects, which can also reduce charge transfer by limiting conjugation.³³ Furthermore, unlike the Heck coupling or acyclic diene metathesis (ADMET) polymerization, the Horner–Emmons condensation does not rely on expensive metal catalysts.^{34,35}

EXPERIMENTAL SECTION

Details on instrumentation and device fabrication can be found in the Supporting Information.

Materials. 1,4-Dichlorobenzene, 1,3-bis-(diphenylphosphino)propane nickel(II) chloride

Scheme 1. Synthetic Route Followed to Obtain PHOPPV



[$\text{NiCl}_2(\text{dppp})$], 1-bromodecane, bromine, iodine, copper cyanide (CuCN), potassium *tert*-butoxide (*t*-BuOK), diisobutylaluminum hydride (DIBAL-H in toluene), paraformaldehyde, 33% hydrobromic acid in acetic acid, triethyl phosphite, 1,4-dihydroxybenzene, triethylphosphonoacetate, triethyl 2-phosphonopropionate, terephthalaldehyde, sodium hydride (NaH), 10% palladium on carbon (Pd/C), lithium aluminum hydride (LiAlH_4), 1-iodoheptane, pyridinium chlorochromate (PCC), thionyl chloride (SOCl_2), potassium iodide (KI), methanesulfonyl chloride (MsCl), 2-butoxyethanol, triethylamine, 9,10-diphenylanthracene, quinine sulfate, triethylene glycol, *ortho*-dichlorobenzene (ODCB), potassium *t*-butoxide, ammonium hydroxide, and Celite were purchased from either Acros or Sigma-Aldrich and used without further purification, unless otherwise noted. For synthetic preparations, diethyl ether, dichloromethane (CH_2Cl_2), and tetrahydrofuran (THF) were acquired from Sigma-Aldrich and dried by distillation from CaH_2 under nitrogen. Sulfuric acid (98.0%), anhydrous dimethyl sulfoxide, anhydrous benzene, and anhydrous

dimethylformamide (DMF) were purchased from Sigma-Aldrich and used as received. Column chromatography was performed using silica gel (Sorbent Technologies, 40–63 μm). Fused quartz microscope slides were purchased from AdValue Technology. For the preparation of the devices, Clevis PEDOT:PSS was purchased from Heraeus Precious Metals. Tris(8-hydroxyquinolino)-aluminum (Alq_3 ; sublimed) was acquired from Luminescence Technology Corp., and lithium fluoride (LiF ; anhydrous) was purchased from Sigma-Aldrich, while the 1.0 mm diameter aluminum wire (99.999%) was purchased from Kurt J. Lesker Co.

Synthesis of Monomers and Oligomers. The chemical structures of the targeted oligomeric products are illustrated in Figure 2. The synthetic routes used to prepare the monomers, oligomers, and alternating co-oligomers are outlined in Schemes 1, 2, 3.

*Poly(2,5-didecyl-p-phenylene vinylene) (PDDPV).*²⁶ The synthesis of PDDPV was conducted following the procedures from the literature. The final product was dried under vacuum

3,3'-(1,4-Phenylene)dipropan-1-ol (4).³⁶ In an oven-dried 500 mL round-bottomed flask (previously flushed with N₂ gas), lithium aluminum hydride (9.3 g, 0.25 mol) and freshly distilled diethyl ether (100 mL) were stirred and chilled in an ice bath. A solution of 3 (11.391 g, 40.925 mmol) in 300 mL of diethyl ether was slowly added. The reaction mixture was stirred at rt overnight. The reaction was then chilled in an ice bath before quenching with 20 mL of 2 M HCl. The mixture was filtered, the residual H₂O was removed with Na₂SO₄, followed by concentration and drying of the filtrate. The product was obtained as a white powder (8.93 g, quantitative). ¹H NMR (500 MHz, CDCl₃): δ 7.12 (s, 4H, aromatic), 3.67 (q, *J* = 6.25 Hz, *J'* = 5.75 Hz, 4H, γ-CH₂), 2.68 (t, *J* = 7.45 Hz, 4H, α-CH₂), 1.89 (quintet, *J* = 6.85 Hz, 4H, β-CH₂), 1.25 (t, *J* = 5.15 Hz, 2H, OH).

3,3'-(2,5-Dibromo-1,4-phenylene)dipropan-1-ol (5).²⁶ In a round-bottomed flask wrapped in foil, a solution of iodine (0.1374 g, 0.5414 mmol) and 4 (6.486 g, 33.39 mmol) in freshly distilled CH₂Cl₂ (25 mL) and bromine (13.255 g, 82.943 mmol) was added dropwise under rigorous exclusion of light. After 20 h at rt, a 20% KOH solution was added carefully until the red color of the solution disappeared. The mixture was filtered, and the solid was recrystallized in CH₂Cl₂. The product, 17, was obtained as a white powder (10.1737 g, 87%). ¹H NMR (500 MHz, CDCl₃): δ 7.40 (s, 2H, aromatic), 3.70 (q, *J* = 6.30 Hz, *J'* = 5.15 Hz, 4H, γ-CH₂), 2.76 (t, *J* = 8.05 Hz, 4H, α-CH₂), 1.86 (quintet, *J* = 8.00 Hz, 4H, β-CH₂), 1.33 (t, *J* = 5.15 Hz, 2H, OH).

1,4-Dibromo-2,5-bis(3-(heptyloxy)propyl)benzene (6).³⁸ Anhydrous DMF (10 mL) was added to a round-bottomed flask containing 60% NaH in mineral oil (2.0436 g, 85.150 mmol), which was previously washed three times with petroleum ether. A solution of 5 (3.5657 g, 10.128 mmol) in DMF (20 mL) was transferred by a syringe into the round-bottomed flask. After stirring for 1 h at rt, iodoheptane (15.0 mL, 91.5 mmol) was added. The mixture was heated to 120 °C overnight. After cooling to rt, the reaction was quenched with H₂O and extracted with CH₂Cl₂. After vacuum distillation at 100 °C, a purple oil was obtained. Column chromatography in a 24:1 ratio (hexanes/EtOAc) afforded a colorless oil (3.5132, 63%). ¹H NMR (400 MHz, CDCl₃): δ 7.38 (s, 2H, aromatic), 3.41 (t, *J* = 6.44 Hz, 4H, γ-CH₂), 3.38 (t, *J* = 6.88 Hz, 4H, OCH₂), 2.73 (t, *J* = 7.56 Hz, 4H, α-CH₂), 1.86 (quintet, *J* = 6.40 Hz, 4H, β-CH₂), 1.57 (quintet, *J* = 7.80 Hz, OCH₂CH₂), 1.22–1.38 (m, 16H, OCH₂CH₂(CH₂)₄), 0.88 (t, *J* = 6.30 Hz, 6H, O(CH₂)₆CH₃).

2,5-Bis(3-(heptyloxy)propyl)terephthalonitrile (7).²⁶ In a round-bottomed flask equipped with a stir bar and a condenser (oven-dried and flushed with nitrogen gas), 6 (1.0368 g, 1.8905 mmol) and CuCN (0.5910 g, 6.598 mmol) in anhydrous DMF (12 mL) were heated to 162 °C for 3 d. The solution was then cooled to rt and poured into a 25% NH₄OH solution (24 mL) to precipitate the product. The product was then washed with NH₄OH and water. The remaining material was extracted in a Soxhlet apparatus with acetone for 1 h. After evaporation of the solvent, a light brown solid was isolated (0.7789 g, 93%). ¹H NMR (500 MHz, CDCl₃): δ 7.58 (s, 2H, aromatic), 3.42 (t, *J* = 6.30 Hz, 4H, γ-CH₂), 3.41 (t, *J* = 6.85 Hz, 4H, OCH₂), 2.93 (t, *J* = 7.45 Hz, 4H, α-CH₂), 1.93 (quintet, *J* = 6.30 Hz, 4H, β-CH₂), 1.53 (m, OCH₂CH₂, obscured by H₂O), 1.21–1.32 (m, 16H, OCH₂CH₂(CH₂)₄), 0.88 (t, *J* = 6.30 Hz, 6H, O(CH₂)₆CH₃).

2,5-Bis(3-(heptyloxy)propyl)terephthalic Acid (8).³⁹ To a round-bottomed flask equipped with a condenser, 7 (0.8101 g, 1.838 mmol), KOH (1.2527 g, 22.328 mmol), and triethylene glycol (18 mL) were added. The mixture was heated to 200 °C overnight. After cooling to rt, the reaction mixture was poured into a 50% H₂SO₄ solution (600 mL) and then filtered. The solid was rinsed with H₂O and dried under vacuum to yield a brown solid (0.8083 g, 92%). ¹H NMR (500 MHz, CDCl₃): δ 7.80 (s, 2H, aromatic), 3.45 (t, *J* = 6.30 Hz, 4H, γ-CH₂), 3.38 (t, *J* = 6.90 Hz, 4H, OCH₂), 3.03 (t, *J* = 6.85 Hz, 4H, α-CH₂), 1.95 (quintet, *J* = 7.45 Hz, 4H, β-CH₂), 1.53 (m, OCH₂CH₂), 1.27 (m, 16H, OCH₂CH₂(CH₂)₄), 0.87 (t, *J* = 6.90 Hz, 6H, O(CH₂)₆CH₃).

Diethyl 2,5-Bis(3-(heptyloxy)propyl)terephthalate (9). In a round-bottomed flask, a solution of 8 (0.8831 g, 1.845 mmol), concentrated H₂SO₄ (1.41 mL), and absolute ethanol (14 mL) were heated to 88 °C for 12 h. After cooling the reaction mixture to rt, it was poured into H₂O. The solid was then filtered, washed with H₂O, and dried under vacuum to yield a dark brown solid (0.8957 g, 91%). ¹H NMR (500 MHz, CDCl₃): δ 7.71 (s, 2H, aromatic), 4.40 (q, *J* = 6.90 Hz, 4H, C(O)OCH₂), 3.42 (t, *J* = 6.85 Hz, 4H, γ-CH₂), 3.40 (t, *J* = 6.85 Hz, 4H, OCH₂CH₂), 2.98 (t, *J* = 8.00 Hz, 4H, α-CH₂), 1.87 (quintet, *J* = 6.30 Hz, 4H, β-CH₂), 1.57 (quintet, *J* = 6.85 Hz, OCH₂CH₂), 1.39 (t, *J* = 6.85 Hz, 6H, OCH₂CH₃), 1.24–1.35 (m, 16H, OCH₂CH₂(CH₂)₄), 0.87 (t, *J* = 6.85 Hz, 6H, O(CH₂)₆CH₃).

(2,5-Bis(3-(heptyloxy)propyl)-1,4-phenylene)dimethanol (10).³⁴ Lithium aluminum hydride (0.3772 g, 9.939 mmol) and dry diethyl ether (5 mL) were stirred in an oven-dried 50 mL round-bottomed flask (previously flushed with N₂ gas) at 0 °C. A solution of 9 (0.8957 g, 1.675 mmol) in dry diethyl ether (29 mL) was then added slowly. The reaction mixture was stirred at rt for 12 h and then chilled in an ice bath before quenching with 2 M HCl (4.5 mL). The mixture was filtered, the residual H₂O was removed with Na₂SO₄, followed by concentration and drying of the filtrate, and the product was obtained as a white powder (0.6668 g, 88%). ¹H NMR (400 MHz, CDCl₃): δ 7.18 (s, 2H, aromatic), 4.65 (s, 4H, CH₂OH), 3.39 (t, *J* = 6.88 Hz, 4H, γ-CH₂), 3.37 (t, *J* = 6.88 Hz, 4H, OCH₂), 2.75 (t, *J* = 7.36 Hz, 4H, α-CH₂), 1.90 (quintet, *J* = 6.88 Hz, 4H, β-CH₂), 1.55 (quintet, *J* = 6.88 Hz, OCH₂CH₂), 1.24–1.34 (m, 16H, OCH₂CH₂(CH₂)₄), 0.87 (t, *J* = 6.40 Hz, 6H, O(CH₂)₆CH₃).

2,5-Bis(3-(heptyloxy)propyl)terephthalaldehyde (11).⁴⁰ To a dry 25 mL flask, Celite (0.7337 g) and PCC (0.6403 g, 2.970 mmol) were added. A solution of 10 (0.3111 g, 0.6903 mmol) in freshly distilled CH₂Cl₂ (7 mL) was transferred to this suspension and stirred for 3 h at rt. The mixture was then filtered through a pad of Celite and rinsed with additional CH₂Cl₂. After removing the solvent, the product was obtained as a pale-yellow solid (0.2721 g, 88%). ¹H NMR (500 MHz, CDCl₃): δ 10.4 (s, 2H, C(O)H), 7.75 (s, 2H, aromatic), 3.41 (t, *J* = 6.30 Hz, 4H, γ-CH₂), 3.38 (t, *J* = 6.90 Hz, 4H, OCH₂), 3.14 (t, *J* = 8.05 Hz, 4H, α-CH₂), 1.90 (quintet, *J* = 6.30 Hz, 4H, β-CH₂), 1.57 (quintet, *J* = 6.90 Hz, OCH₂CH₂), 1.24–1.36 (m, 16H, OCH₂CH₂(CH₂)₄), 0.88 (t, *J* = 6.9 Hz, 6H, O(CH₂)₆CH₃).

1,4-Bis(chloromethyl)-2,5-bis(3-(heptyloxy)propyl)benzene (12).³⁰ Thionyl chloride (0.75 mL, 0.010 mol) was added to a solution of 10 (0.3121 g, 0.7216 mmol) in freshly distilled CH₂Cl₂ (7 mL) in a dry 50 mL flask. After stirring for 3 h, the reaction mixture was poured into H₂O (40 mL). The

aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were washed with H_2O and dried over Na_2SO_4 . After removal of the solvent, the product was obtained as a yellow oil (0.3612 g, quantitative). ^1H NMR (500 MHz, CDCl_3): δ 7.19 (s, 2H, aromatic), 3.14 (s, 4H, CH_2Cl), 3.43 (t, $J = 6.30$ Hz, 4H, $\gamma\text{-CH}_2$), 3.41 (t, $J = 6.90$ Hz, 4H, OCH_2), 2.77 (t, $J = 7.45$ Hz, 4H, $\alpha\text{-CH}_2$), 1.90 (quintet, $J = 6.30$ Hz, 4H, $\beta\text{-CH}_2$), 1.59 (quintet, $J = 6.90$ Hz, OCH_2CH_2), 1.24–1.38 (m, 16H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_4$), 0.88 (t, $J = 6.9$ Hz, 6H, $\text{O}(\text{CH}_2)_6\text{CH}_3$).

1,4-Bis(methylenediethylphosphonate)-2,5-bis(3-(heptyloxy)propyl)benzene (13). In a round-bottomed flask attached to a condenser, **12** (0.3612 g, 0.7408 mmol) and triethyl phosphite (0.85 mL, 5.0 mmol) were heated at 160 °C for 24 h. Excess triethyl phosphite was removed by vacuum distillation at 120 °C to give **13** as a brown solid (0.4389 g, 86%). ^1H NMR (500 MHz, CDCl_3): δ 7.11 (s, 2H, aromatic), 3.97 (q, $J = 6.85$ Hz, 8H, POCH_2), 3.41 (t, $J = 6.3$ Hz, 4H, $\gamma\text{-CH}_2$), 3.39 (t, $J = 6.85$ Hz, 4H, OCH_2), 3.14 (d, $J = 20.7$ Hz, 4H, CH_2P), 2.71 (t, $J = 8.0$ Hz, 4H, $\alpha\text{-CH}_2$), 1.83 (quintet, $J = 7.45$ Hz, 4H, $\beta\text{-CH}_2$), 1.58 (m, 4H, OCH_2CH_2) (obscured by H_2O), 1.20–1.36 (m, 16H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_4$), 1.21 (t, $J = 6.85$ Hz, 6H, OCH_2CH_3), 0.87 (t, $J = 6.85$ Hz, 6H, $\text{O}(\text{CH}_2)_6\text{CH}_3$).

Poly(2,5-bis(3-(heptyloxy)propyl)-1,4-phenylene vinylene) (PHOPPV). The dialdehyde **11** (0.1250 g, 0.2799 mmol), the diphosphonate **13** (0.1930 g, 0.2799 mmol), and potassium *t*-butoxide (0.1568 g, 1.397 mmol) were added to a 25 mL two-neck round-bottomed flask with a condenser that had been flame-dried, flushed with N_2 gas, and wrapped in aluminum foil. Anhydrous DMF (18 mL, purged 20 min with N_2 gas) was added via a syringe. The solution was stirred at 80 °C for 12 h and then cooled to rt. Methanol (24 mL) was added to precipitate the product. After transferring to a centrifuge tube, the suspension was chilled to promote precipitation. The sample was centrifuged and the supernatant was discarded. After adding a minimal amount of THF, additional reprecipitations were carried out using methanol (twice), isopropanol, and pentane. After vacuum-drying, the product was obtained as a yellow-green solid (0.0241 g, 19%). ^1H NMR (500 MHz, CDCl_3): δ 7.44 (s, 2H, aromatic), 7.22 (s, 2H, vinylene; the peak contains contributions from residual CHCl_3 in the NMR solvent), 3.47 (m, 4H, $\gamma\text{-CH}_2$), 3.39 (m, 4H, OCH_2), 2.87 (m, 4H, $\alpha\text{-CH}_2$), 1.93 (m, 4H, $\beta\text{-CH}_2$), 1.59 (m, 20H, CH_2), 1.27 (m, 6H, CH_3).

3,3'-(2,5-Dibromo-1,4-phenylene)bis(propane-3,1-diyl) Dimethanesulfonate (14). Diol **5** (10.0 g, 28.4 mmol) was introduced into a 500 mL round-bottomed flask containing 250 mL of THF, and then an aliquot of triethylamine (14.0 mL, 100 mmol) was slowly added into the solution. The reaction mixture was stirred at rt for 30 min. The reaction flask was placed in an ice bath, and methanesulfonyl chloride (8.0 mL, 100 mmol) was slowly transferred into the solution while stirring. The ice bath was then removed, and the reaction was stirred for 4 h at rt. After completion of the reaction, excess methanesulfonyl chloride was destroyed by addition of 100 mL of water. The mixture was extracted with diethyl ether (3 \times 100 mL). The combined organic layers were washed with 2.0 M HCl solution (100 mL) and water (2 \times 100 mL). The organic layer was dried over Na_2SO_4 , filtered, and concentrated in vacuo to produce **14** (11.0 g, 21.6 mmol), which was used in the next step without further purification (76% yield). ^1H

NMR (500 MHz, CDCl_3): δ 7.40 (s, 2H), 4.25 (t, $J = 5.7$ Hz, 4H), 3.03 (s, 6H), 2.80 (t, $J = 8.0$ Hz, 4H), 2.06 (m, 4H).

1,4-Dibromo-2,5-bis(3-iodopropyl)benzene (15). The crude mesylate **14** (11.0 g, 21.6 mmol) and KI (9.00 g, 54.1 mmol) were dissolved in reagent-grade acetone (250 mL) and refluxed for 12 h. The solvent was evaporated by rotary evaporation. Water (100 mL) and diethyl ether (50 mL) were added to dissolve the salts and the product. The mixture was extracted with diethyl ether (2 \times 100 mL). The combined organic layers were washed with brine (2 \times 100 mL), dried over Na_2SO_4 , filtered, and concentrated in vacuo to obtain the product (8.9 g, 16 mmol) as a brown solid (72% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.40 (s, 2H), 3.20 (t, $J = 6.9$ Hz, 4H), 2.78 (t, $J = 7.5$ Hz, 4H), 2.10 (m, 4H).

1,4-Dibromo-2,5-bis(3-(2-butoxyethoxy)propyl)benzene (16).³⁶ An aliquot of 2-butoxyethanol (6.0 g, 50 mmol) was added dropwise to a stirred solution of potassium hydride (2.00 g, 50.0 mmol) in THF (20 mL) at 0 °C under nitrogen. After 30 min, **15** (3.0 g, 5.3 mmol) in THF (10 mL) was added. The reaction mixture was refluxed for 24 h. After evaporation of the solvent, the crude product was purified by column chromatography (hexanes:ether = 9.8:0.2) to give 0.40 g (0.72 mmol) of **16** (13% yield). ^1H NMR (500 MHz in CDCl_3): δ 7.38 (s, 2H, aromatic), 3.59 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.49 (t, $J = 6.85$ Hz, 4H, $\gamma\text{-CH}_2$), 3.48 (t, $J = 6.30$ Hz, 4H, OCH_2), 2.73 (t, $J = 7.45$ Hz, 4H, $\alpha\text{-CH}_2$), 1.87 (quintet, $J = 7.45$ Hz, 4H, $\beta\text{-CH}_2$), 1.58 (quintet, $J = 6.3$ Hz, 4H, OCH_2CH_2), 1.58 (sextet, $J = 7.45$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 0.91 (t, $J = 7.45$ Hz, 6H, CH_3).

2,5-Bis(3-(2-butoxyethoxy)propyl)terephthalonitrile (17). 2,5-Bis(3-(2-butoxyethoxy)propyl)terephthalonitrile (**17**) was prepared following an analogous procedure used for the preparation of **7**: 0.1368 g, 65% yield. ^1H NMR (400 MHz in CDCl_3): δ 7.60 (s, 2H, aromatic), 3.58 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.49 (t, $J = 5.96$ Hz, 4H, $\gamma\text{-CH}_2$), 3.48 (t, $J = 6.88$ Hz, 4H, OCH_2), 2.93 (t, $J = 7.80$ Hz, 4H, $\alpha\text{-CH}_2$), 1.94 (quintet, $J = 5.92$ Hz, 4H, $\beta\text{-CH}_2$), 1.57 (quintet, $J = 4.56$ Hz, 4H, OCH_2CH_2), 1.36 (sextet, $J = 7.80$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 0.91 (t, $J = 7.36$ Hz, 6H, CH_3).

2,5-Bis(3-(2-butoxyethoxy)propyl)terephthalic Acid (18). 2,5-Bis(3-(2-butoxyethoxy)propyl)terephthalic acid (**18**) was prepared following an analogous procedure used for the preparation of **8**: 0.1489 g, quantitative yield. ^1H NMR (400 MHz in CDCl_3): δ 7.70 (s, 2H, aromatic), 3.62 (m, 4H, $\text{OCH}_2\text{CH}_2\text{O}(\text{CH}_2)_3\text{CH}_3$), 3.57 (m, 4H, $\text{OCH}_2\text{CH}_2\text{O}(\text{CH}_2)_3\text{CH}_3$), 3.52 (t, $J = 6.88$ Hz, 4H, $\gamma\text{-CH}_2$), 3.43 (t, $J = 5.96$ Hz, 4H, OCH_2), 3.07 (t, $J = 7.32$ Hz, 4H, $\alpha\text{-CH}_2$), 1.89 (quintet, $J = 6.40$ Hz, 4H, $\beta\text{-CH}_2$), 1.63 (quintet, $J = 7.76$ Hz, 4H, OCH_2CH_2), 1.38 (sextet, $J = 7.80$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 0.92 (t, $J = 7.32$ Hz, 6H, CH_3).

Diethyl 2,5-Bis(3-(2-butoxyethoxy)propyl)terephthalate (19). Diethyl 2,5-bis(3-(2-butoxyethoxy)propyl)terephthalate (**19**) was prepared following an analogous procedure used for the preparation of **9**: 0.1425 g, 86% yield. ^1H NMR (400 MHz in CDCl_3): δ 7.71 (s, 2H, aromatic), 4.35 (q, $J = 6.88$ Hz, 4H, $\text{C}(\text{O})\text{OCH}_2$), 3.58 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.49 (t, $J = 6.40$ Hz, 4H, $\gamma\text{-CH}_2$), 3.46 (t, $J = 6.84$ Hz, 4H, OCH_2), 2.98 (t, $J = 7.36$ Hz, 4H, $\alpha\text{-CH}_2$), 1.89 (quintet, $J = 7.32$ Hz, 4H, $\beta\text{-CH}_2$), 1.56 (quintet, $J = 6.84$ Hz, 4H, OCH_2CH_2), 1.39 (t, $J = 6.84$ Hz, 6H, CH_2CH_3), 1.37 (sextet, $J = 7.32$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 0.90 (t, $J = 7.36$ Hz, 6H, CH_3).

(2,5-Bis(3-(2-butoxyethoxy)propyl)-1,4-phenylene)-dimethanol (20). (2,5-Bis(3-(2-butoxyethoxy)propyl)-1,4-

phenylene)dimethanol (**20**) was prepared following an analogous procedure used for **10**: 0.1053 g, 88% yield. ^1H NMR (400 MHz in CDCl_3): δ 7.19 (s, 2H, aromatic), 4.66 (s, 4H, CH_2OH), 3.56 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.47 (t, $J = 6.88$ Hz, 4H, $\gamma\text{-CH}_2$), 3.45 (t, $J = 5.96$ Hz, 4H, OCH_2), 2.76 (t, $J = 7.45$ Hz, 4H, $\alpha\text{-CH}_2$), 1.92 (quintet, $J = 6.44$ Hz, 4H, $\beta\text{-CH}_2$), 1.57 (quintet, $J = 7.80$ Hz, 4H, OCH_2CH_2), 1.36 (sextet, $J = 7.32$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 0.91 (t, $J = 7.36$ Hz, 6H, CH_3).

2,5-Bis(3-(2-butoxyethoxy)propyl)terephthalaldehyde (21). **2,5-Bis(3-(2-butoxyethoxy)propyl)terephthalaldehyde (21)** was prepared following an analogous procedure used for **11**: 0.0346 g, 66% yield. ^1H NMR (500 MHz in CDCl_3): δ 10.3 (s, 2H, $\text{C}(\text{O})\text{H}$), 7.76 (s, 2H, aromatic), 3.57 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.48 (t, $J = 6.30$ Hz, 4H, $\gamma\text{-CH}_2$), 3.47 (t, $J = 6.30$ Hz, 4H, OCH_2), 3.14 (t, $J = 7.80$ Hz, 4H, $\alpha\text{-CH}_2$), 1.92 (quintet, $J = 6.30$ Hz, 4H, $\beta\text{-CH}_2$), 1.58 (quintet, $J = 6.30$ Hz, 4H, OCH_2CH_2), 1.37 (sextet, $J = 7.45$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 0.91 (t, $J = 7.45$ Hz, 6H, CH_3).

1,4-Bis(3-(2-butoxyethoxy)propyl)-2,5-bis(chloromethyl)benzene (22). **1,4-Bis(3-(2-butoxyethoxy)propyl)-2,5-bis(chloromethyl)benzene (22)** was prepared following an analogous procedure used for **12**: 0.0605 g, quantitative yield. ^1H NMR (500 MHz in CDCl_3): δ 7.19 (s, 2H, aromatic), 4.60 (s, 4H, CH_2Cl), 3.59 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.50 (t, $J = 5.95$ Hz, 4H, $\gamma\text{-CH}_2$), 3.48 (t, $J = 6.90$ Hz, 4H, OCH_2), 2.77 (t, $J = 7.80$ Hz, 4H, $\alpha\text{-CH}_2$), 1.92 (quintet, $J = 6.40$ Hz, 4H, $\beta\text{-CH}_2$), 1.58 (quintet, $J = 6.90$ Hz, 4H, OCH_2CH_2), 1.37 (sextet, $J = 7.80$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 0.91 (t, $J = 7.30$ Hz, 6H, CH_3).

1,4-Bis(methylenediethylphosphonate)-2,5-bis(3-(2-butoxyethoxy)benzene (23). **1,4-Bis(methylenediethylphosphonate)-2,5-bis(3-(2-butoxyethoxy)benzene (23)** was prepared following an analogous procedure used for **13**: 0.0745 g, 88% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.10 (d, $J = 1.36$ Hz, 2H, aromatic), 3.96 (dq, $J = 7.32$ Hz, $J' = 2.28$ Hz, 8H, POCH_2), 3.57 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.48 (t, $J = 6.4$ Hz, 4H, $\gamma\text{-CH}_2$), 3.46 (t, $J = 6.88$ Hz, 4H, OCH_2), 3.13 (d, $J = 20.6$ Hz, 4H, CH_2P), 2.70 (t, $J = 7.80$ Hz, 4H, $\alpha\text{-CH}_2$), 1.85 (quintet, $J = 7.80$ Hz, 4H, $\beta\text{-CH}_2$), 1.57 (quintet, $J = 7.76$ Hz, 4H, OCH_2CH_2), 1.35 (sextet, $J = 7.80$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.21 (t, $J = 6.88$ Hz, 6H, OCH_2CH_3), 0.90 (t, $J = 7.80$ Hz, 6H, CH_3).

Poly(2,5-bis(3-(2-butoxyethoxy)propyl)-1,4-phenylene vinylene (PBEPV)). Monomers **21** (0.0788 g, 0.175 mmol) and **23** (0.1226 g, 0.176 mmol) were used to prepare the oligomer **PBEPV** following an analogous procedure used for the preparation of **PHOPPV**: 0.0303 g, 43% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.43 (s, 2H, aromatic), 7.26 (s, 2H, vinylene; the peak contains contributions from residual CHCl_3 in the NMR solvent), 3.57 (m, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.44 (t, $J = 6.85$ Hz, 8H, $\gamma\text{-CH}_2$, OCH_2), 2.88 (m, 4H, $\alpha\text{-CH}_2$), 1.96 (m, 4H, $\beta\text{-CH}_2$), 1.55 (sextet, $J = 6.85$ Hz, 4H, OCH_2CH_2), 1.34 (sextet, $J = 7.45$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 0.89 (t, $J = 7.45$ Hz, 6H, CH_3).

1,4-Bis(methylenediethylphosphonate)-2,5-didecylbenzene (24). The synthesis of **24** was conducted following procedures from the literature.²³ A total of 3.60 g of white solid was obtained (99% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.07 (d, $J = 1.2$ Hz, 2H, aromatic), 3.89–4.10 (m, 8H, $-\text{OCH}_2\text{CH}_3$), 3.11 (d, 4H, $J = 20.1$, CH_2P), 2.59 (t, $J = 8.0$ Hz, 4H, $\alpha\text{-CH}_2$), 1.48–1.55 (m, 4H, $\beta\text{-CH}_2$), 1.20–1.37 (m, 28H, CH_2), 1.20 (t, $J = 6.9$ Hz, 12H, $-\text{OCH}_2\text{CH}_3$), 0.85 (t, $J = 6.9$ Hz, 6H, CH_3).

2,5-Bis(decyloxy)benzene-1,4-dialdehyde (25). The synthesis of **25** was conducted following procedures from the literature.⁴¹ The final product was obtained as a yellow solid (59% yield). ^1H NMR (400 MHz, CDCl_3): δ 10.51 (s, 2H, CHO), 7.42 (s, 2H, aromatic), 4.07 (t, $J = 6.4$ Hz, 4H, $\text{OCH}_2\text{R}''$), 1.82 (quintet, $J = 7.8$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{R}'$), 1.42–1.49 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{R}$), 1.21–1.39 (m, 24H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 0.87 (t, $J = 6.8$ Hz, 6H, CH_3).

Poly(2,5-bis(3-(heptyloxy)propyl)-1,4-phenylene vinylene-alt-2,5-didecyl-1,4-phenylene vinylene (PHOP-alt-DDPV)). Monomers **11** (0.0683 g, 0.165 mmol) and **24** (0.1006 g, 0.1671 mmol) were used to prepare the co-oligomer **PHOP-alt-DDPV** following an analogous procedure used for the preparation of **PHOPPV**: 0.0317 g, 12% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.42 (s, 8H, aromatic), 7.26 (s, 8H, vinylene; the peak contains contributions from residual CHCl_3 in the NMR solvent), 3.48 (m, 4H, $\gamma\text{-CH}_2$), 3.41 (m, 4H, OCH_2), 2.86 (m, 4H, $\alpha\text{-CH}_2$), 2.77 (m, 4H, $\alpha\text{-CH}_2$), 1.94 (m, 4H, $\beta\text{-CH}_2$), 1.65 (m, 4H, $\beta\text{-CH}_2$), 1.26 (m, 48H, CH_2), 0.87 (m, 12H, CH_3).

Poly(2,5-bis(3-(heptyloxy)propyl)-1,4-phenylene vinylene-alt-2,5-didecyloxy-1,4-phenylene vinylene (PHOP-alt-DOPV)). Monomers **11** (0.0502 g, 0.121 mmol) and **25** (0.0772 g, 0.112 mmol) were used to prepare the co-oligomer **PHOP-alt-DOPV** following an analogous procedure used for the preparation of **PHOPPV**: 0.0233 g, 12% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.42 (s, 8H, aromatic), 7.26 (s, 8H, vinylene; the peak contains contributions from residual CHCl_3 in the NMR solvent), 3.47 (m, 4H, $\gamma\text{-CH}_2$), 3.39 (m, 4H, OCH_2), 2.85 (m, 4H, $\alpha\text{-CH}_2$), 1.93 (m, 4H, $\beta\text{-CH}_2$), 1.86 (m, 4H, OCH_2CH_2), 1.26 (m, 48H, CH_2), 0.87 (m, 12H, CH_3).

RESULTS AND DISCUSSION

Monomer and Oligomer Synthesis. As outlined in Schemes 1, 2, 3 and detailed in the Experimental Section, the Horner–Emmons polycondensation was carried out in DMF to accomplish the polymerizations. All the investigated oligomers were isolated in modest yields with those formed from alkyl substituents as yellow-green solids and those including alkoxy substituents as red solids. The anticipated chemical structures of the oligomers were verified by analysis of their ^1H NMR spectra (Figures S1–S6).

For the synthesis of the diether precursors, our initial approach was to use the same Kumada coupling used to obtain didecylbenzene in the synthesis of **PDDPV**.⁴² However, coupling of the ether side chains onto 1,4-dichlorobenzene failed, and thus, the route seen in Scheme 1 was then developed to obtain the dibromobenzene, intermediate **5**, used in the synthesis of both diether precursors to **PHOPPV** and **PBEPV** in good yield. While the purification of the dibromobenzene with the ether side chains (**6**) in Scheme 1 was achieved in moderate yields, the route outlined in Scheme 2 was more successful for the **PBEPV** precursors, with substituents bearing two oxygen atoms. The increased solubility of **PBEPV** contributed to low yields in the polymerization step as significant portions of the product failed to precipitate during the purification process. Even with two glycol-like moieties per repeat unit, **PBEPV** still remained insoluble in water, a necessary characteristic for purification methods as well as for future device fabrication. Additionally, the ^1H NMR spectra for this series of oligomers/co-oligomers confirmed that the Horner–Emmons route led to PPV derivatives with no saturated defects.^{30,32,43} While

derivatives with benzylic hydrogens exhibit peaks below 3.0 ppm, and the hydrogens adjacent to oxygen are observed above 3.3 ppm, no saturated defects were observed at 3.1 ppm in the PPV oligomers prepared here (please see the ^1H NMR spectra in Figures S1–S4),³⁰ which is consistent with other reported syntheses of PPV derivatives using Horner–Emmons methods.^{32,43} We also note that a reduced signal-to-noise ratio was observed for PDDPV and to a lesser extent for PHOP-DDPV because of reduced solubility of the PDDV-containing derivatives; however, all other derivatives were readily soluble when analyzed by ^1H NMR spectroscopy.

Molecular Weight Measurements. The number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the polydispersity index (PDI) are shown in Table 1.

Table 1. Molecular Weight Data As Determined by GPC Relative to Polystyrene Standards for PPV Derivatives

oligomer	M_n^a	M_w^a	PDI ^b	DP ^c	yield (%)
PDDPV	5200	8800	1.7	21	65
PDOPV	3500	5700	1.6	13	84
PHOPPV	3300	5400	1.6	12	19
PBEPPV	4500	6900	1.5	15	43
PHOP- <i>alt</i> -DDPV	3200	5700	1.7	14	12
PHOP- <i>alt</i> -DOPV	4200	8000	1.9	19	12

^a M_n = number-average molecular weight; M_w = weight-average molecular weight. Molecular weights of THF-soluble materials determined by GPC. ^bPDI = M_w/M_n . ^cDP = number of monomer units per chain.

Because the oligomers were all synthesized under similar reaction conditions, the resultant molecular weights and PDIs are similar. PDDPV, the only oligomer in this series produced without oxygen incorporated in its side chains, produced oligomer chains with the highest degree of polymerization (DP). It is possible that with varying reaction conditions, such as time and concentration, larger molecular weights could be obtained for the more soluble oligomers.⁴⁴ The poor solubility of the oligomers is also a contributing factor to the low molecular weights obtained. Both PDDPV and PDOPV precipitated during the course of the reaction; however, the other derivatives, PHOPPV, PBEPPV, PHOP-*alt*-DOPV, and PHOP-*alt*-DDPV, precipitated upon cooling in methanol.

Limitations associated with the gel permeation chromatography (GPC) equipment used in this study also complicate the analysis of the results. The GPC sample preparation methods necessitated multiple filtrations, which only allowed lower molecular weight chains to be analyzed. Regardless, for the current set of polymers, all degrees of polymerization exceed the estimated theoretical limit for delocalization of excitons; therefore, the optical properties should be unaffected by chain length.⁴⁵

Absorption and Photoluminescence Spectra. The optical properties of the oligomers were measured for dilute solutions in THF and for thin films spin-coated onto quartz slides and are shown in Figures 3 and 4, respectively; a summary of the optical properties with numerical values is given in Table 2. The absorbance maxima in solution for PDDPV, PHOPPV, PBEPPV, and PHOP-*alt*-DDPV are all similar: 408, 410, 415, and 410 nm, respectively (see Figure 3). A similar trend is also observed for the spin-coated quartz slides, 385, 390, 400, and 375 nm, respectively. The similarity in the absorbance maxima for the aforementioned oligomers can be attributed to the nature of the alkyl linkage at the aromatic ring for the substituent chains. The slight red shift observed for PBEPPV in solution could be attributed to a more rodlike structure from improved solvation of the chains.⁴⁶ In contrast to all other oligomers, PDOPV exhibited a red shift in the solid state (485 nm) compared to solution (472 nm). This difference can perhaps be attributed to the presence of multiple strong electron-donating alkoxy groups in PDOPV and/or interactions of the multiple phenoxy moieties in PDOPV with the THF solvent and/or additional ordering of PDOPV in the solid state, which has been observed for certain organic semiconductors.⁴⁷

In both the film and solution photoluminescent (PL) spectra, secondary peaks can be observed, which correspond to vibronic coupling of the excitons.⁴⁸ All of the investigated oligomers exhibited a slight red shift in the film PL spectra (see Figures 3 and 4), compared to the solution-based samples, because of increased interchain interactions.⁴⁹ The optical properties for this set of oligomers and co-oligomers are summarized in Table 2, including the PL quantum yields (QYs). From all of the homo-oligomer derivatives, PDOPV exhibited the lowest QY, 34%, while PHOPPV exhibited the highest, 74%. Incorporation of the PHOPPV unit in the investigated co-oligomers led to a higher QY than the other

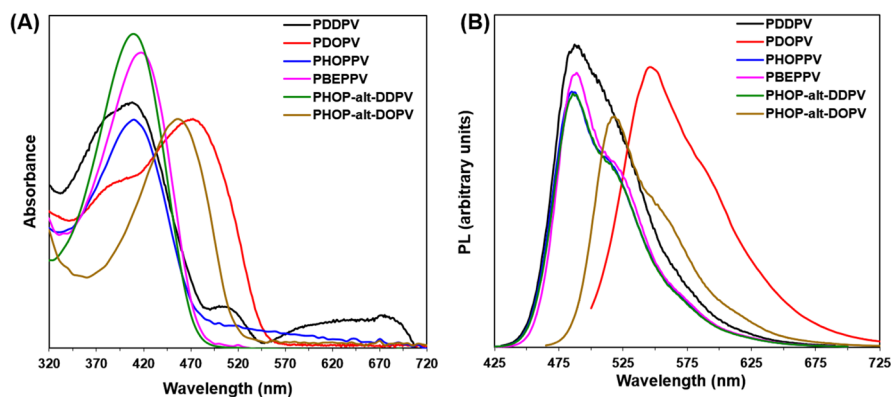


Figure 3. (A) UV–visible absorption and (B) fluorescence spectra for solutions of PDDPV (excitation at 408 nm), PDOPV (excitation at 472 nm), PHOPPV (excitation at 410 nm), PBEPPV (excitation at 415 nm), PHOP-*alt*-DDPV (excitation at 410 nm), and PHOP-*alt*-DOPV (excitation at 455 nm); oligomers were prepared by Horner–Emmons polymerization and examined in THF (1.5×10^{-5} M) at rt.

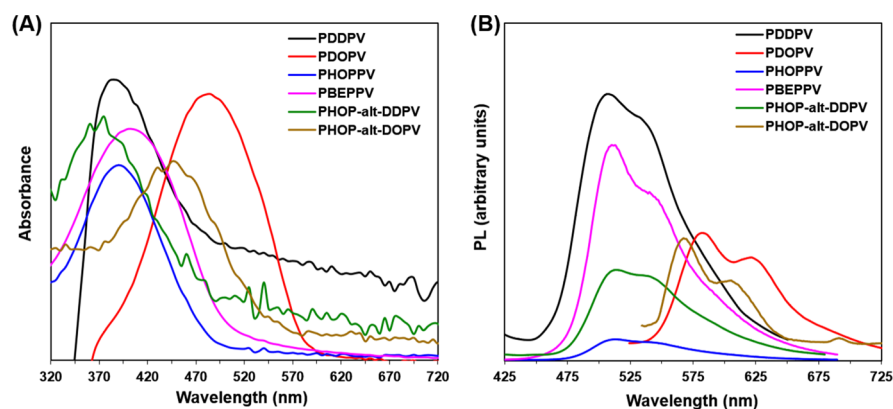


Figure 4. (A) UV–visible absorption and (B) fluorescence spectra for films of PDDPV (excitation at 385 nm), PDOPV (excitation at 485 nm), PHOPPV (excitation at 390 nm), PBEPV (excitation at 400 nm), PHOP-*alt*-DDPV (excitation at 375 nm), and PHOP-*alt*-DOPV (excitation at 445 nm); oligomers were prepared by Horner–Emmons polymerization, spin-coated onto quartz slides, and examined at rt.

Table 2. Summary of Optical Properties

oligomer	UV–vis λ_{max} (nm)	PL λ_{max} (nm)	QY ^a (%)
PDDPV	408 ^a , 385 ^b	487 ^a , 507 ^b	57
PDOPV	472 ^a , 485 ^b	546 ^a , 582 ^b	34
PHOPPV	410 ^a , 390 ^b	485 ^a , 513 ^b	74
PBEPV	415 ^a , 400 ^b	489 ^a , 510 ^b	56
PHOP- <i>alt</i> -DDPV	410 ^a , 375 ^b	486 ^a , 514 ^b	69
PHOP- <i>alt</i> -DOPV	455 ^a , 445 ^b	518 ^a , 567 ^b	78

^aAbsorption (UV–vis) and PL maxima on 1.5×10^{-5} M solutions in THF. ^bOn quartz slides spin-coated from 10 mg/mL solutions in THF. ^cPL QY in THF relative to 9,10-diphenylanthracene and quinine sulfate.

oligomers with alkyl linkages, PDDPV (57%), PDOPV (34%), and PBEPV (56%). In the alternating co-oligomers (PHOP-*alt*-DDPV and PHOP-*alt*-DOPV), the QY was improved significantly relative to the homo-oligomers without the heptyloxypropyl moiety (PDDPV and PDOPV). The higher QY values observed for derivatives containing the heptyloxypropyl moiety can plausibly be attributed to a reduction in the coiled nature of the pendant side chains in these derivatives, leading to an increase in their intrinsic persistence length.⁵⁰

Electrochemical Properties. Cyclic voltammetry (CV) is widely used in studying the electrochemical behavior of the investigated compounds. The HOMO and lowest unoccupied molecular orbital (LUMO) of the conjugated oligomers were estimated using methods from the literature to verify oligomer compatibility with device structures.⁵¹ The onset oxidation measured from thin-film cyclic voltammograms was used to estimate the HOMO, eq 1. Using the low-energy edge of the absorption spectra to calculate the band gap (E_g), eq 2, it is also simple to estimate the LUMO, eq 3.

$$\text{HOMO (eV)} = -4.8 \text{ eV} - (E_{\text{oxd},1} - E_{\text{oxd,ferrocene}}) \times 1 \text{ eV/V} \quad (1)$$

$$E_g \text{ (eV)} = 1240/\lambda \quad (2)$$

$$\text{LUMO (eV)} = \text{HOMO} + E_g \quad (3)$$

$E_{\text{oxd},1}$ is the first oxidation potential, which was obtained by CV from the oligomer thin film on a glassy carbon working electrode. $E_{\text{oxd,ferrocene}}$ is the onset oxidation potential of ferrocene (0.40 V vs Ag/AgNO₃) and was determined by CV in a 0.1 M solution of tetrabutylammonium perchlorate in

acetonitrile. E_g is the energy band gap estimated from the low-energy edge of the absorption spectra from the oligomer thin film. A summary of the electronic properties is shown in Table 3. The energy band gaps of the investigated oligomers are

Table 3. Summary of Electronic Properties of the Investigated Oligomers

oligomer	λ (nm)	E_g (eV)	$E_{\text{oxd},1}$ (V)	HOMO (eV)	LUMO (eV)
PDDPV	487	2.55	1.75	−6.15	−3.60
PDOPV	563	2.20	1.20	−5.60	−3.40
PHOPPV	480	2.58	1.48	−5.88	−3.30
PEBEPV	475	2.61	1.21	−5.61	−3.00
PHOP- <i>alt</i> -DDPV	475	2.61	1.48	−5.88	−3.27
PHOP- <i>alt</i> -DOPV	510	2.43	1.35	−5.75	−3.32

similar, ranging from 2.20 to 2.61 eV. The data of PHOP-*alt*-DOPV, PDDPV, and PDOPV are consistent with values from the previous research.²⁶ While the absence of oxygen in PDDPV increased the band gap relative to PDOPV, moving it to the δ position achieved the same result in PHOPPV, PEBEPV, and PHOP-*alt*-DDPV.

Device Studies. The OLED energy diagram shown in Figure 5 is a representative example of the devices fabricated for this report. The design consists of a glass substrate patterned with an indium tin oxide (ITO) anode, followed by a conducting layer of poly(3,4-ethylenedioxythiophene) poly-

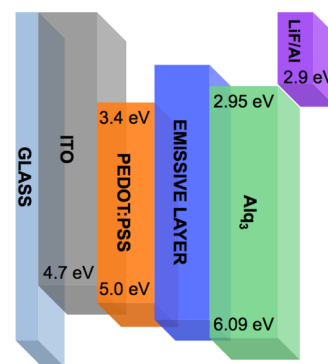


Figure 5. Energy diagram depicting the relative position of the band gaps for the components of an OLED device representative of those fabricated in this report.⁵⁴

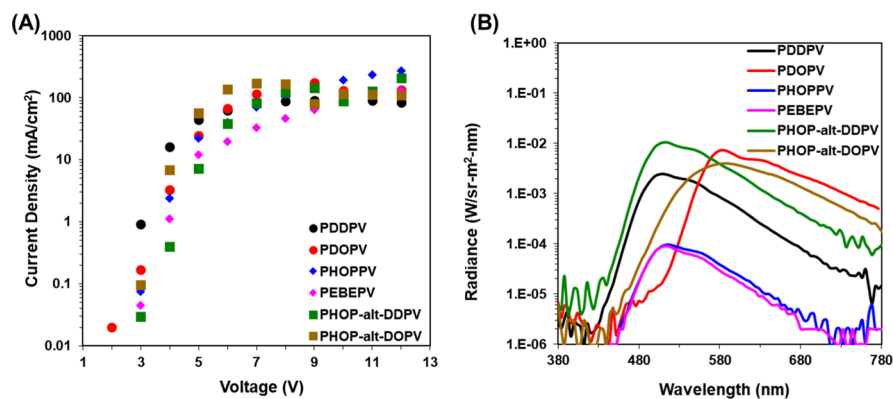


Figure 6. (A) Current density–voltage characteristics and (B) EL spectra of the investigated oligomers in OLED devices.

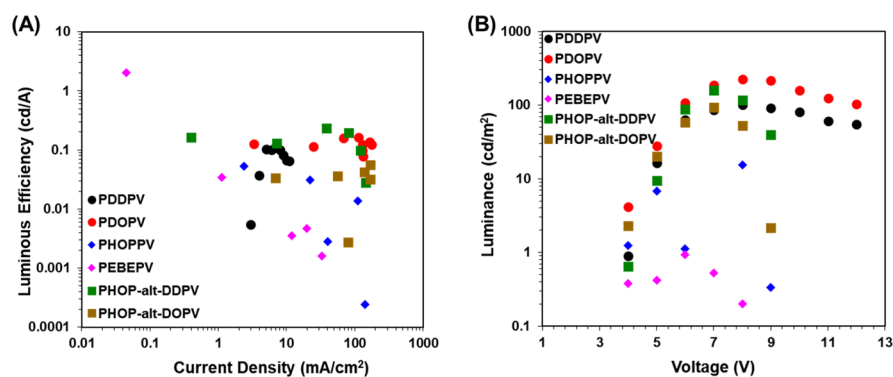


Figure 7. (A) Luminous efficiency and (B) luminance–voltage characteristics of the investigated oligomers in OLED devices.

(styrenesulfonate) (PEDOT:PSS) and then the emissive layer (active layer). Using thermal evaporation, tris(8-hydroxyquinolino)-aluminum (Alq_3), an electron transport layer, and a thin electron injection layer of lithium fluoride (LiF) were deposited prior to the aluminum (Al) cathode.⁵² The organic component (e.g., PDDPV) is utilized for the emissive layer. Conducting polymers often exhibit higher hole mobility caused by increased HOMO overlap, necessitating electron transport layers (e.g., Alq_3) to allow recombination of hole–electron pairs (excitons) to occur in the emissive layer. Energy is released in the form of photons at a wavelength corresponding to the band gap of the emissive material.⁵³ While the characteristics of the polymer are critical to device performance, the effectiveness of the device is also dependent on designing an architecture that has a good band gap overlap between layers.⁶

Previous studies showed marked improvement in the performance of PDOPV and PDDPV devices when using an electron injection layer of Alq_3 .²⁶ Not only did this promote exciton recombination in the emissive layer but it also increased efficiency by reducing shorts caused by defects in the polymer film. Because of low solubility, pinhole defects in devices without Alq_3 caused shorts and pixel burnout. The electronic properties of the new oligomers are within the range between those of PDDPV and PDOPV; therefore, Alq_3 was used as the electron injection layer in all of the devices. Based on the above conditions, we designed our device configuration as: ITO/PEDOT:PSS/Oligomer/ Alq_3 (30 nm)/LiF (8 nm)/Al (80 nm). The properties and performance of the OLED devices fabricated with the investigated oligomers are shown in Figures 6–8.

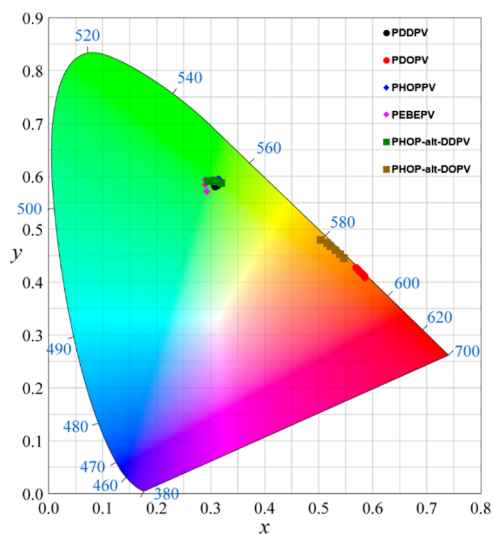


Figure 8. CIE chromaticity diagram of the OLED devices.

The current density–voltage characteristics and the EL spectra of the oligomers in the OLED devices are shown in Figure 6. The luminous efficiency and luminance–voltage characteristics of the OLED devices are shown in Figure 7. The maximum EL brightness of each OLED device obtained with the oligomers is summarized in Table 4. Note that all of the newly synthesized oligomers and co-oligomers exhibited improved solubility in 1,2-dichlorobenzene (ODCB) over PDDPV and PDOPV, allowing for thicker spin-coated films for the devices. Perhaps because of the solubility advantage, the device prepared from PHOP-alt-DDPV was able to outper-

Table 4. EL Characteristics of OLEDs Containing PPV Derivatives

oligomer	turn-on voltage ^a (V)	EL brightness max (cd/m ²)	maximum efficiency (cd/A)	$\lambda_{\text{max}}^{\text{EL}}$, fwhm (nm) at 8 V	1931 CIE chromaticity (x,y) at 8 V
PDDPV	5.0	101.0	0.116	508, 76	0.31, 0.58
PDOPV	4.0	210.0	0.725	560, 88	0.49, 0.51
PHOPPV	5.0	44.8	0.075	512, 88	0.31, 0.52
PEBEPV	4.0	14.6	0.061	516, 72 ^b	0.29, 0.59 ^b
PHOP- <i>alt</i> -DDPV	5.0	157.7	0.230	512, 76	0.30, 0.59
PHOP- <i>alt</i> -DOPV	4.0	94.0	0.056	588, 112	0.52, 0.47

^aWith EL at 1 cd/m². ^bMeasurement taken at 6 V.

form the device prepared with PDDPV in EL brightness, an oligomer with poor solubility characteristics, at 157.7 and 101.0 cd/m², respectively. The maximum efficiency of 0.230 cd/A, for the DDPV co-oligomer while modest, was twice that of the PDDPV homo-oligomer, 0.116 cd/A. Furthermore, the device produced with the alkoxy-substituted PDOPV oligomer had the best results, 210.0 cd/m², and a maximum efficiency of 0.725 cd/A. However, the most soluble oligomer, PBEPPV, produced a device with the lowest brightness, 14.6 cd/m². While all other samples produced light in a 0.2 cm² pixel, the PBEPPV device showed only pinpoints of light within the measured area. It is possible that the increased polarity of PBEPPV might cause unfavorable interactions with the ODCB solvent or the underlying PEDOT:PSS layer.^{16,55,56} Interestingly, although PBEPPV exhibited similar electronic properties to the other alkyl derivatives, it had a lower turn-on voltage, which allows for milder operating conditions. As expected, the lower energy PDOPV and DOPV co-oligomer exhibited lower turn-on voltages because of their smaller band gaps. The PHOPPV and the DDPV co-oligomer exhibited a similar turn-on voltage as PDDPV because they share correspondingly higher band gaps. The EL maxima are very similar to the film PL maxima and can be seen with a summary of other EL characteristics in Table 4. The observed broadening of the peaks in the EL spectra in Figure 6 when compared to the PL spectra in Figures 3 and 4 can plausibly arise from exciplex emission at the organic solid interface.⁵⁷

The chromaticity of all fabricated OLED devices is shown in Figure 8. The chromaticity coordinates of each OLED device are also summarized in Table 4. In addition, all of the investigated oligomers, with the exception of PHOP-*alt*-DOPV, exhibited similar CIE chromaticity coordinates across the measured voltage range and efficiency. The co-oligomer PHOP-*alt*-DDPV also exhibited twice the efficiency of the PDDPV homo-oligomer, with almost identical optical properties. This shows that the limited performance of PDDPV can be improved by introducing more soluble side chains. Unfortunately, these preliminary results do not clearly delineate the role the position or amount of oxygen atoms present on the side chains has on OLED performance requiring further investigations to determine parameters affecting film formation.

CONCLUSIONS

New poly(*p*-phenylene vinylene) derivatives, PHOPPV and PBEPPV, as well as co-oligomers, PHOP-*alt*-DDPV and PHOP-*alt*-DOPV, were synthesized through the well-known Horner–Emmons polycondensation procedure. This simple and inexpensive synthetic route afforded oligomers with low PDI and of sufficiently high molecular weight for use in OLED devices. The introduction of oxygen into the solubilizing alkyl

side chains increases the solubility of the oligomers (i.e., PHOPPV was more soluble than PDDPV). Furthermore, increasing the oxygen content in the side chains 2-fold (i.e., PBEPPV) further increases the solubility of the oligomer. The optical properties of these new soluble derivatives were studied using UV–visible absorption and fluorescence emission spectroscopy. The nearly identical optical properties of the oligomers, where oxygen is not attached directly to the ring, were expected because of the inability of the oxygen to participate in resonance. The synthesized oligomers demonstrated the capacity to perform color tuning, as demonstrated by the incorporation of the alkoxy phenylene units in PDOPV and PHOP-*alt*-DOPV as compared to PHOPPV and the corresponding shift from orange to green as alkoxy units were reduced or removed from the ring. Considering the modest performance of the OLED devices, it is clear that solubility is not the only factor affecting device performance, and film morphology is not totally dependent on good solubility. The study of the lifetime of devices prepared from these oligomers is currently in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.9b02396>.

Experimental details regarding the instrumentation used to characterize the oligomers, methods used to construct the LED devices, and ¹H NMR spectra of the oligomers (PDF)

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was generously supported by the Robert A. Welch Foundation (E-1320, T.R.L.), the Texas Center for Superconductivity (T.R.L.), and the University of Texas at Dallas (B.E.G.).

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