Macromolecules **2005,** *38,* 10667−10677

Synthesis and Electrooptical Properties of Copolymers Derived from Phenol-Functionalized Telechelic Oligofluorenes

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Received August 19, 2005; Revised Manuscript Received October 10, 2005

ABSTRACT: This paper describes the synthesis, characterization, and electrooptical properties of a series of phenol-capped, discrete oligofluorenes with 2, 3, 5, and 7 fluorene units and a statistical oligomer with an average of about 10 fluorene units. Polymers were prepared from the oligomers by various linking reactions through the phenol groups. High molecular weight polycarbonate polymers derived from these oligomers were prepared using BPA−bis-chloroformate (BPABCF) as the linking group. Trends in the optical and electrical properties as a function of oligomer length are reported. Device data for this family of emissive copolymers indicates that charge mobility increases with conjugation length and can be better than that of an analogue homopolymer. A surprising shift in LUMO values due to CF_3 substitution at the ends of the oligomers was observed.

Introduction

Significant advances in the performance of polymer-based light-emitting diodes have been made since the first demonstration of electroluminescence in conjugated polymers more than a decade ago.[1,2] The lure of polymer-based devices compared to small molecule LED's is the possibility of using low-cost fabrication methods, such as roll-to-roll processing or other printing methods suitable for large area or pixilated displays. Polymers that emit blue light efficiently are of special interest, as they are needed for production of full color displays and for white light illumination devices. Among the blue-light-emitting polymers currently available, polyfluorenes have emerged as the most promising due to a combination of high luminescence efficiency, good film-forming properties, and good thermal stability.[3−7]

Efforts to improve the performance of polyfluorenes in OLED devices, particularly with regard to minimizing their tendency to aggregate in the solid state, often focus on structural modification of substituents in the bridging 9-position. Bulky substituents in this position are thought to diminish interchain association in the solid state that leads to inefficient aggregate or excimer emission in polyfluorenes.[4,5,8−10] However, it is the nature of the conjugated backbone, more specifically, the conjugation length of segments in these polymers that defines the band gap, HOMO−LUMO energy levels, charge transport character, fluorescence quantum yield, and the singlet/triplet exciton population split, all of which are critical to efficient OLED device performance. Polyfluorenes are prepared by aryl−aryl coupling reactions of suitably functionalized monomers. The conjugation length in these polymers is determined, not by the average number of repeat units per chain (DP_{ave}) but by solid state morphology, which determines the distance between fluorene segments twisted out of conjugation and by chain defects arising either from impurities in the starting monomers or those introduced during the polymerization process. For these polymers, therefore, there is a conjugation length polydispersity, not easily controlled, that leads to a spread in the energy levels, carrier transport properties, and other photophysical properties that can affect OLED efficiency. In such disperse systems broadened emission may result or exciton energy transfer from high- to low-energy states may lead to red-shifted emission emanating from a very small population of conjugated segments.[11]

An approach that circumvents these conjugation length dispersity effects is to prepare monodisperse oligomers bearing functionality that enables linking of the oligomers to form a polymer. In this way, the integrity of the conjugated segment is maintained in the polymerization process and is decoupled from the molecular weight polydispersity and from defects associated with the polymerization process. This approach offers the possibility of tuning not only the electronic properties by variation of the conjugated segment but also the physical characteristics, such as morphology and solubility, by varying the linking segment. Also, by introducing comonomers it should be possible to tailor the charge carrier transport properties of these materials. These considerations are particularly important for the fabrication of multilayer devices. Finally, the method allows for rigorous purification of the oligomeric segments by chromatography or crystallization prior to polymerization and should thus afford high molecular weight polymers with good film-forming properties and good thermal stability.

The synthesis and characterization of monodisperse oligofluorenes with various substituents at the 9-position have been described in a number of publications.[12−23] In general, optical and photophysical properties of these polymers have been reported but very little device data is available. Several studies have examined the use of discrete terfluorene or related oligomeric molecules as emissive materials in small molecule devices (SMOLEDs).[24−26] Evaporated terfluorene films have been shown to exhibit good carrier mobilities for both holes and electrons in solid-state devices.[27−28]

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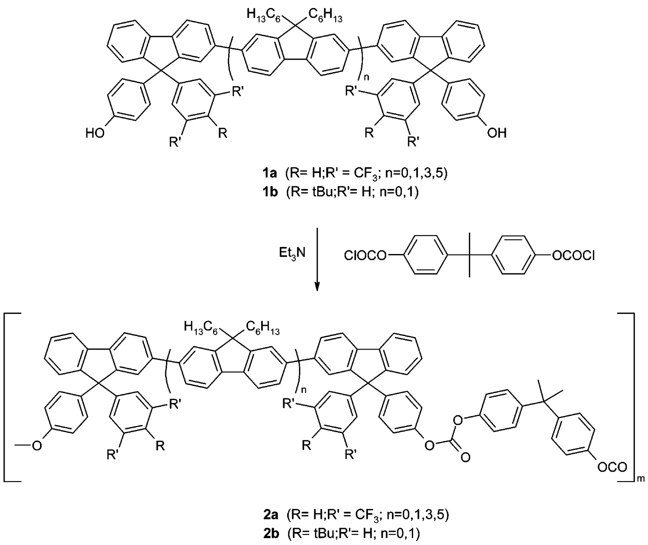
10.1021/ma0518353 CCC: $30.25

To systematically evaluate the effect of conjugated segment length on optical and photophysical properties of polyfluorenes and to obtain data from working OLED devices, discrete fluorene oligomers **1a** ($n = 0, 1, 3, 5$) and **1b** ($n = 0, 1$) bearing phenol functionality at the termini were prepared. The purified oligomers were polymerized by reaction with BPA−bis-chloroformate (BPAPCF) to obtain perfectly alternating BPA−oligofluorene copolycarbonates **2a** and **2b**. The synthesis and optical, photophysical, and charge transport properties of these materials were determined, and the trends observed as a function of oligomer length are reported in this paper. The synthesis and characterization of a range of condensation polymers derived from phenol-functionalized terfluorenes and various difunctional linkers are also described (Supporting Information).



1a (R= H;R' = CF_3; n=0,1,3,5)
1b (R= tBu;R'= H; n=0,1)

2a (R= H;R' = CF_3; n=0,1,3,5)
2b (R= tBu;R'= H; n=0,1)

Experimental Section

Measurements. ^{1}H NMR spectra were recorded on a Bruker 500 MHz instrument. UV spectra were recorded on a Varian-Cary 300 Scan UV−vis spectrophotometer. Gel permeation chromatography was carried out using a Perkin-Elmer Series 200 pump and a Perkin-Elmer 235 diode array detector. Chloroform was used as the eluant at a flow rate of 1.0 mL/min through a MetaChem Technologies, 5 μm linear 300 × 7.8 mm column. Liquid chromatography was carried out using a Perkin-Elmer Series 200 pump and UV−vis detector on a Whatman Partisil 5 ODS-3 10 × 4.5 mm column eluted with a water−acetonitrile (AN) linear gradient (50%−95% AN) at a flow rate of 1.5 mL/min.

Materials. 9,9-Dihexyl-2,7-dibromofluorene, 9,9-dihexylfluorene-2,7-bis(trimethyleneboronate), fluorenone, palladium acetate, tetraethylammonium hydroxide (20% aqueous solution), and *N*-bromosuccinimide were purchased from Aldrich and used without further purification.

Tetrakis(triphenylphosphine)palladium(0) was either purchased from Aldrich or prepared fresh according to the literature.[29]

n-Butyllithium (∼1.2 M) in hexane was obtained from Aldrich and titrated prior to use using *N*-pivaloyl-*o*-toluidine.[30]

2-Bromofluorenone, 3. Fluorenone (41 g, 0.228 mol) was dissolved in 225 mL of methanesulfonic acid and treated portionwise at room temperature with solid *N*-bromosuccinimide (NBS) (38.55 g, 0.217 mol). The mixture became dark and warm and the temperature was maintained below 60 °C by controlling the rate of NBS addition. Upon completion of the NBS addition, the mixture was allowed to cool to room temperature and was poured into 1 L of ice water. The yellow solid that separated was collected by filtration, washed with copious quantities of water, air-dried, and then recrystallized from about 1.5 L of ethanol. The yield was 40 g (71%) and the product contained 5−10% of 2,7-dibromofluorenone as indicated by LC analysis. A small sample was purified by column chromatography, but in general, the contaminated material was carried on in subsequent steps.

2-Bromo-9-[3,5-bis(trifluoromethyl)phenyl]-9-(4-hydroxyphenyl)fluorene, 5a. Solid 2-bromofluorenone (42 g, 161.5 mmol), dried in a vacuum oven overnight at 65 °C to remove excess ethanol from crystallization, was added via a solid addition funnel in portions to the Grignard reagent prepared from 3,5-bis(trifluoromethyl)bromobenzene (50 g, 170 mmol), 1,2-dibromoethane (7.36 mL, 85 mmol), and magnesium (6.223 g, 256 mg-atom) in a three-neck 1-L flask filled with 400 mL of anhydrous ether. After 30 min, the mixture was quenched by adding an excess of saturated ammonium chloride solution. The organic phase was washed three times with equal volumes of water and saturated NaCl and was passed through a cone of anhydrous $MgSO_4$. Solvent was removed on a rotary evaporator to afford a light brown solid (**4a**). The total mass was dissolved in 800 mL of methylene chloride in a one-neck 1-L flask along with phenol, (24 g, 256 mmol, 1.5 excess). Methanesulfonic acid (21.5 mL) was added and the mixture was stirred at ambient temperature for 18 h. When the reaction was complete, the organic phase was washed with water and saturated NaCl. Evaporation of solvent yielded an off-white solid. The product was further purified by trituration with a minimal amount of methylene chloride and hexanes (20/80) to give a final yield of 58.9 g (63.6%): MS (FAB$^+$) *m*/*e* 549 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 7.82−7.2 (m, 10, ArH), 7.0 and 6.78 (AB doublet, 4, phenol-ArH), 4.78 ppm (s, 1, OH).

2-Bromo-9-(4-*tert*-butylphenyl)-9-(4-hydroxyphenyl)fluorene, 5b. Solid 2-bromofluorenone (5.18 g, 20 mmol) was added in portions to the Grignard reagent prepared from 4-bromo-*tert*-butylbenzene (4.47 g, 21 mmol), 1,2-dibromoethane (1.88 g, 10 mmol), and magnesium (0.753 g, 31 mg-atom) in 75 mL of anhydrous ether. The reaction mixture was refluxed for 1 h after all the solids had been added. The cooled mixture was quenched by adding 50 mL of saturated ammonium chloride. The organic phase was washed with equal volumes of water and saturated NaCl and was passed through a cone of anhydrous $CaSO_4$. Solvent was removed on a rotary evaporator to afford 10 g of an amber oil that was chromatographed on silica gel (∼300 g) eluted with hexanes−ethyl acetate to afford 5.64 g (72%) of the carbinol **4b** as a colorless oil: GC−MS (EI mode) (*m*/*e*) 392 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 7.7−7.3 (m, 11, ArH), 1.3 ppm (s, 9, *tert*-butyl).

The carbinol **4b** (6.0 g, 15 mmol) and phenol (2.2 g, 23.25 mmol) were dissolved in 10 mL of methylene chloride. Methanesulfonic acid (200 μL, 3.08 mmol) was added, and the mixture was stirred at ambient temperature. When the reaction was complete (∼5 min), the organic phase was washed with water and saturated NaCl. Evaporation of solvent afforded an oil that was chromatographed on 200 g of silica gel (hexanes−ethyl acetate gradient) to afford 4.4 g (61%) of the product as a colorless oil. The oil could be crystallized by slow evaporation of an ether−hexane solution: MS (EI mode) *m*/*e* 470, 468 (M$^+$)

^{1}H NMR ($CDCl_3$) δ 7.8−6.7 (m, 15, ArH), 5.0 (s, 1, OH) and 1.3 ppm (s, 9, *tert*-butyl).

2-(1,1,2,2-Tetramethylethyleneboronato)-9-[3,5-bis(trifluoromethyl)phenyl]-9-(4-hydroxyphenyl)fluorene, 6a. A mixture of bromide **5a** (5.5 g, 10 mmol), bis-pinacolatodiboron (3.0 g, 12 mmol), potassium acetate (2.9 g, 30 mmol), and palladium(II) acetate (0.075 g, 0.3 mmol) in 25 mL of DMF was stirred in a 75 °C bath for 3 h. The cooled mixture was poured into 250 mL of water made slightly acidic with HCl. The dark solids that separated were collected by filtration, washed with water, and stirred with 150 mL of ethyl acetate. The resulting slurry was filtered through Celite and the filtrate was washed successively with water and brine then passed through a cone of anhydrous $CaSO_4$. Removal of solvent afforded a dark residue that was chromatographed on 150 g of silica gel eluted with 10−20% ethyl acetate in hexane to afford **6a** as a colorless oil: MS (FAB$^+$) *m/e* 596 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 7.9−7.2 (m,10, ArH), 7.0 and 6.7 (AB doublets, 4, phenol ArH), 1.35 ppm (s, 12, boronate CH$_3$'s).

2-(1,1,2,2-Tetramethylethyleneboronato)-9-(4-*tert*-butylphenyl)-9-(4-hydroxyphenyl)fluorene, 6b. A mixture of **5b** (0.469 g, 1.0 mmol), bis(pinacolato)diboron (0.279 g, 1.1 mmol), potassium acetate (0.294 g, 3.0 mmol), palladium(II) acetate (0.0075 g, 0.03 mmol), and DMF (10 mL) was stirred at 80 °C under a positive nitrogen pressure for 5 h. Additional bis(pinacolato)diboron (0.075 g) and palladium(II) acetate (0.002 g) was added, and heating and stirring were continued for an additional 1.5 h. The mixture was poured into 100 mL of cold water made slightly acidic with HCl. Solids were collected by filtration and stirred with ethyl acetate (50 mL). The solution was filtered through Celite, washed with brine, and dried by passage through a cone of anhydrous CaSO$_4$. Evaporation of solvent afforded a residue that was chromatographed on 50 g of silica gel eluted with 10−20% ethyl acetate/hexanes. The main fractions crystallized slowly from an ether−hexane solution: MS (FAB$^+$) *m/e* 516 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 7.8−7.2 (m, 11, ArH), 7.15 and 6.7 (AB doublets, 4, phenol-ArH), 4.8 (br-s, 1 OH), 1.3 (s, 12, pinacol-CH$_3$), 1.25 ppm (s, 9, *tert*-butyl CH$_3$'s).

Phenol-Functionalized Bifluorene 1a (*n* = 0). A mixture of phenol borate **6a** (0.596 g, 1.0 mmol), bromophenol **5a** (0.549 g, 1.0 mmol), toluene (15 mL), and tetraethylammonium hydroxide (0.275 g, 1.4 g of a 20% aqueous solution) was degassed with argon for about 20 min and then tetrakis(triphenylphosphine)palladium(0) (0.0035 g, 0.022 mmol) was added and the mixture was stirred under a positive nitrogen pressure at 75 °C for 18 h. The cooled mixture was diluted with ethyl acetate (25 mL) and 1.0 N HCl (25 mL), stirred briefly, and then filtered through Celite. The organic phase was washed with water (2×) and brine (1×) and then passed through a funnel containing Drierite on top of a 1 cm layer of 3-(diethylenetriamino)propyl-functionalized silica gel (SiliCycle) (200−400 mesh). Removal of solvent in vacuo afforded a white powder: MS (FAB$^+$) *m/e* 938 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 8.0−6.75 (m, 28, ArH) and 5.05 ppm (s, 2, OH).

Phenol-functionalized bifluorene 1b (*n* = 0) was prepared using the same procedure described for the preparation of **1a** from phenol borate, **6b**, and bromophenol **5b**: MS (FAB$^+$) *m/e* 778 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 7.8−6.7 (m, 30, ArH), 4.7 (s(br), 2, OH), 1.25 ppm (s, 18, *tert*-butyl).

Phenol-Capped Terfluorene 1a (*n* = 1). A mixture of phenol bromide **5a** (3.288 g, 6 mmol), 2,7-bis(trimethyleneboronato)-9,9-dihexylfluorene (1.266 g, 3 mmol), hexaethylguanidinium chloride (HEG) (80 μL, 0.15 mmol), 150 mL of toluene, and 2 M K$_2$CO$_3$ (25 mL) was degassed with argon for 20 min then tetrakis(triphenylphosphine)palladium(0) (75 mg) was added and the mixture was immersed in a 110 °C bath. The mixture was stirred under a positive nitrogen pressure for 4.5 h then was allowed to cool to room temperature, at which point only one spot was evident via TLC. 3-(Diethylenetriamino)propyl-functionalized silica gel (SiliCycle) (75 mg, 200−400 mesh) was added and the mixture allowed to stir for half an hour. The mixture was then filtered through Celite. The filtrate was washed successively with equal volumes of 10% HCl (1×), water (2×), and brine (1×). Evaporation of solvent afforded a residue that was dissolved in ethyl acetate and passed through a short silica gel column to afford a white solid (10−25% ethyl acetate−hexane): MS (FAB$^+$) *m/e* 1271 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 7.95−7.2 (m, 26, ArH), 7.1 and 6.8 (AB doublets, 8, phenol ArH), 4.96 (s, 2, OH), 2.05 (m, 4, 9-α-CH$_2$) and 1.03 and 0.7 ppm (m, 22, hexyl-H's) yield, 85%.

Phenol-Capped Terfluorene 1b (*n* = 1). A mixture of phenol bromide **5b** (7.74 g, 16.5 mmol), 2,7-bis-trimethyleneboronato-9,9-dihexylfluorene (4.07 g, 8.1 mmol), hexaethylguanidinium chloride (40 mg, 0.15 mmol), and 2 M K$_2$CO$_3$ (50 mL) was degassed with argon for 20 min and then tetrakis(triphenylphosphine)palladium(0) (0.26 g, 0.225 mmol) was added and the mixture was immersed in a 110 °C bath. The mixture was stirred under a positive nitrogen pressure for 23 h and then filtered through Celite. The filtrate was washed successively with equal volumes of 10% HCl (1×), water (2×), and brine (1×). The solution was then passed through a fritted filter containing a 5−10 mm layer of 3-(diethylenetriamino)propyl-functionalized silica gel (SiliCycle) (200−400 mesh). Evaporation of solvent afforded a residue that was dissolved in ethyl acetate and passed through a short silica gel column to afford 8 g of an orange solid. A 3.0 g sample of this material was chromatographed on 120 g of silica gel (10−25% ethyl acetate−hexane) to yield 1.96 g of the desired product: MS (FAB$^+$) *m/e* 1110 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 7.9−7.2 (m, 32, ArH), 6.75 (d, 4, ArH o-phenol), 4.9 (s(br), 2, OH), 2.05 (br-s, 4, 9-α-CH$_2$), 1.3 (s, 18, *tert*-butyl), 1.1 and 0.7 ppm (s(br), 22, aliphatics).

Phenol Bromide Dimer 7. A mixture of 2.22 g (3.72 mmol) of phenol borate **5a** and 2,7-dibromo-9,9-dihexylfluorene (9.8 g, 20 mmol, 5.4 equiv), tetraethylammonium hydroxide (5.5 mL of a 20% aqueous solution), and 100 mL of toluene was degassed with argon for 20 min and then tetrakis(triphenylphosphine)palladium(0) was added and the mixture was stirred under a positive nitrogen pressure and immersed in a 75 °C bath for 3 h. The cooled mixture was diluted with 50 mL of 1 N HCl, stirred for 10 min, and then filtered through Celite. The aqueous phase was discarded and the organic phase was washed successively with equal volumes of water (3×) and brine (1×). The solution was then passed through a fritted filter containing a 5−10 mm layer of 3-(diethylenetriamino)propyl-functionalized silica gel (SiliCycle) (200−400 mesh) and anhydrous CaSO$_4$ and stripped to afford 12.6 g of a residue that was chromatographed on 120 g of silica gel. Elution with hexane afforded 7.9 g of recovered 2,7-dibromo-9,9-dihexylfluorene (100%). Elution with 5−10% ethyl acetate/hexane afforded 2.4 g (73%) of **7** as a white foam. MS (FAB$^+$) *m/e* 882 and 880 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 7.9−6.7 (m, 20, ArH), 4.9 (s, 1, OH), 2.0 (m(br), 4, 9-αCH$_2$'s), 1.2−0.6 ppm (m(br), 22, aliphatic H's).

Pentamer via Coupling of 7 with 2,7-Bis(trimethyleneboronato)-9,9-dihexylfluorene, 1a (*n* = 3). Bromophenol **7** (0.651 g, 0.739 mmol) and 2,7-bis(trimethyleneboronato)-9,9-dihexylfluorene (0.178 g, 0.355 mmol) were dissolved in 50 mL of toluene and 15 mL of 2 M K$_2$CO$_3$ solution. The solution was degassed with argon for 20 min and then hexaethylguanidinium chloride (40 μL, 0.075 mmol) was added along with tetrakis(triphenylphosphine)palladium(0) (0.008 g, 0.70 mmol). Reaction was heated at 110 °C under nitrogen for 24 h. The cooled mixture was diluted with 20 mL of 1 N HCl, stirred for 10 min, and then filtered through Celite. The aqueous phase was discarded and the organic phase was washed successively with equal volumes of water (3×) and brine (1×). The solution was then passed through a fritted filter containing a 5−10 mm layer of 3-(diethylenetriamino)propyl-functionalized silica gel (SiliCycle) (200−400 mesh) and anhydrous CaSO$_4$ and stripped to afford a residue that was chromatographed on silica gel (10−25% EtOAc/Hexanes) to afford 0.45 g of **1a** (*n* = 3): MS (FAB$^+$) *m/e* 1936 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 8.0−7.25 (m, 38, ArH), 7.1 and 6.8 (AB doublets, 8, phenol-ArH), 4.80 (s, 2, OH), 2.1 (m, 12, 9-α-CH$_2$), 1.1 and 0.8 ppm (m, 66, hexyl-H's)

2-Bromo-7-(trimethylsilyl)-9,9-dihexylfluorene, 8. 2,7-Dibromo-9,9-dihexylfluorene (50 g, 101.63 mmol) was dissolved in dry THF (150 mL) at ambient temperature. The mixture was cooled to −78 °C, at which point *n*-butyllithium (78.5 mL of a freshly titrated 1.3 M solution, 102.05 mmol) was added dropwise. The metalation reaction was monitored by quenching aliquots with saturated ammonium chloride followed by LC analysis. After 30 min at −78 °C, 15 mL of trimethylsilyl chloride (15% excess, *d* = 7.88 mmol/mL) was added. The reaction mixture was allowed to warm to room temperature, diluted with 100 mL of ether, and washed successively with equal volumes of water (3×) and brine (1×). The organic phase was dried over MgSO$_4$ and stripped to afford **8** as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 7.7−7.37 (m, 6 (Ar−H), 2.0 (m, 4, 9-α-CH$_2$), 1.18, 0.82, and 0.70 (m, 22, hexyl-H's), 0.38 ppm (s, 9, Si−CH$_3$). The main impurity was found to be 2,7-bis(trimethylsilyl)-9,9-dihexylfluorene.

2-(Trimethylsilyl)-9,9-dihexylfluorene-7-pinacolatoborate, 9. A solution of bromide **8** (4.85 g, 10 mmol), bis-

(pinacolato)diboron (2.54 g, 10 mmol), potassium acetate (2.00 g, 20.0 mmol), and palladium(II) acetate (0.100 g, 0.45 mmol) in *N*,*N*-dimethylformamide (25 mL) was stirred and heated at 75 °C under a positive nitrogen pressure for 2 days. The cooled mixture was poured into 150 mL of water slightly acidified with HCl. The precipitated solids were collected by filtration and then stirred with ethyl acetate and filtered again through Celite. The ethyl acetate solution was washed with 1 N HCl (2×), water (3×), and brine (1×) and then passed through a cone of anhydrous $CaSO_4$. Removal of solvent afforded a residue that was chromatographed on silica gel eluted with hexane−5% EtOAc/hexane to afford a purified residue that was crystallized from methanol to afford pure **9**: MS (EI^+) *m/e* 532 (M^+); ^1H NMR ($CDCl_3$) δ 7.85−7.5 (m, 6, ArH), 2.0 (t, 4, 9-α-CH_2), 1.4 (s, 12, pinacol-CH_3), 1.1 (m, 12, hexyl-CH_2), 0.8 (t, 6, hexyl-CH_3), 0.61(m, 4, hexyl-CH_2), 0.35 ppm (s, 9, Si−CH_3).

α,ω-2,2′-Bis(trimethylsilyl)-9,9-dihexylfluorene Trimer 10. A mixture of bromide **8** (9.00 g, 15.96 mmol), 2,7-bis(trimethyleneboronato)-9,9-dihexylfluorene (3.78 g, 7.98 mmol), tetraethylammonium hydroxide (7.5 mL of a 40% aqueous solution), and toluene (150 mL) was degassed with argon for 20 min, and then tetrakis(triphenylphosphine)palladium(0) (0.075 g, 0.065 mmol) was added. The reaction mixture was heated at 75 °C under a positive nitrogen pressure for 24 h. The cooled mixture was diluted with 20 mL of 1 N HCl, stirred for 10 min, and then filtered through Celite. The aqueous phase was discarded and the organic phase was washed successively with equal volumes of water (3×) and brine (1×). The solution was then passed through a fritted filter containing a 5−10 mm layer of 3-(diethylenetriamino)propyl-functionalized silica gel (SiliCycle) (200−400 mesh) and anhydrous $CaSO_4$ and stripped to afford a residue that was chromatographed on silica gel (10−25% EtOAc/hexanes) to afford the crude product, which was again purified by column chromatography eluting with hexanes to afford pure **10**: MS (FAB^+) *m/e* 1144 (M^+); ^1H NMR ($CDCl_3$) δ 7.9−7.6 (m, 18, ArH), 2.0 (m(br), 12, 9-α-CH_2), 1.2 and 0.8 (m(br), 66, hexyl-H), 0.3 ppm (s, 18, Si−CH_3).

α,ω-2,2′-Diiodo-9,9-dihexylfluorene Trimer 11. Trimethylsilylated trimer **10** (6.54 g, 5.72 mmol) was dissolved in carbon tetrachloride (35 mL) at room temperature. The solution was cooled to 0 °C and iodine monochloride (11.73 mL of a 1 M solution in methylene chloride, 11.44 mmol) was added dropwise over 15 min. The reaction was stirred vigorously for another 35 min and then was allowed to warm to ambient temperature. A concentrated solution of sodium sulfite was added until the dark color of the solution disappeared. The organic phase was separated, washed (3×) with water and brine, and dried over $MgSO_4$, and solvent was removed under vacuum to afford a white solid residue of **11**: MS (FAB^+) *m/e* 1250 (M^+); ^1H NMR ($CDCl_3$) δ 7.9−7.5 (m, 18, ArH), 2.0 (m(br), 12, 9-α-CH_2), 1.18 and 0.8 ppm (m, 66, hexyl-H).

α,ω-2,2′-Bis(trimethylsilyl)-9,9-dihexylfluorene Pentamer 12. A mixture of diiodo compound **11** (2 g, 1.6 mmol), borate **9** (1.70 g, 3.2 mmol), toluene (50 mL), and 2 M K_2CO_3 (15 mL) was degassed with argon for 20 min and then hexaethylguanadinium chloride (40 μL, 0.075 mmol) and tetrakis(triphenylphosphine)palladium(0) (8 mg, 0.007 mmol) was added. The mixture was heated at 110 °C under a positive nitrogen pressure for 24 h. The cooled mixture was diluted with 20 mL of 1 N HCl, stirred for 10 min, and then filtered through Celite. The aqueous phase was discarded and the organic phase was washed successively with equal volumes of water (3×) and brine (1×). The solution was then passed through a fritted filter containing a 5−10 mm layer of 3-(diethylenetriamino)propyl-functionalized silica gel (SiliCycle) (200−400 mesh) and anhydrous $CaSO_4$ and stripped to afford a residue that was chromatagraphed on silica gel (10−25% EtOAc/hexanes) to afford pure **12** (1 g) as a white foamy solid with a green-blue tinge: MS (MALDI-TOF) *m/e* 1915 (M^+); ^1H NMR ($CDCl_3$) δ 8.0−7.5 (m, 30, ArH), 2.1 (m(br), 20, 9-α-CH_2), 1.2 and 0.8 (m, 110, hexyl-H), 0.4 ppm (s, 18, Si−CH_3).

α,ω-2,2′-Diiodo-9,9-dihexylfluorene Pentamer 13. Bis(trimethylsilyl) pentamer **12** (0.95 g, 0.525 mmol) was dissolved in 20 mL of carbon tetrachloride. The solution was cooled to 0 °C and iodine monochloride (1.08 mL of a 1 M solution in methylene chloride, 2.05 mmol) was added dropwise over 15 min. The reaction mixture was allowed to warm to ambient temperature over 30 min and was then quenched with saturated sodium sulfite solution. The mixture was transferred to a separatory funnel and the organic phase was washed with water (3×) and brine (1×) then dried over $MgSO_4$. Removal of solvent in vacuo afforded a light yellow solid (1.0 g, 99.5%): MS (MALDI-TOF) *m/e* 1915 (M^+); ^1H NMR ($CDCl_3$) δ 7.9−7.5 (m, 30, ArH), 2.1 (m(br), 20, 9-α-CH_2), 1.2 and 0.8 ppm (m, 110, hexyl-H); for quantitative ^{13}C NMR ($CDCl_3$), see the Supporting Information.

12 + 5a: Phenol-Functional Heptamer 1a (*n* = 5). Diiodo compound **13** (0.3635 g, 0.1898 mmol) and borate **6a** (0.25 g, 0.4176 mmol) was added to 25 mL of toluene, 1 mL of 40% tetraethylammonium hydroxide, and 1 mL of water. The mixture was degassed with argon for 20 min and then tetrakis(triphenylphosphine)palladium(0) (0.0225 g, 0.019 mmol) was added and the mixture was stirred under a positive nitrogen pressure at 75 °C for 24 h. The cooled mixture was diluted with 20 mL of 1 N HCl, stirred for 10 min, and then filtered through Celite. The aqueous phase was discarded and the organic phase was washed successively with equal volumes of water (3×) and brine (1×). The solution was then passed through a fritted filter containing a 5−10 mm layer of 3-(diethylenetriamino)propyl-functionalized silica gel (SiliCycle) (200−400 mesh) and anhydrous $CaSO_4$. Removal of solvent in vacuo afforded a residue that was chromatagraphed on silica gel (0−50% EtOAc/hexanes) to afford pure **1a** (*n* = 5) (0.300 g, 61%) as a gum: MS (MALDI-TOF) *m/e* 2600 (M^+); ^1H NMR ($CDCl_3$) δ 8.0−7.3 (m, 50, ArH), 7.2 and 6.8 (AB doublets, 8, phenol-ArH), 4.75 (s, 2, OH), 2.2 (m, 20, 9-α-CH_2), 1.2 and 0.8 ppm (m, 110, hexyl-H's).

Statistical Oligomer 14. A mixture of 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (0.301 g, 0.6 mmol), 2,7-dibromo-9,9-dihexylfluorene (0.197 g, 0.4 mmol), **5a** (0.220 g, 0.4 mmol), tetramethylammonium hydroxide (1.0 mL of a 20% aqueous solution), and 15 mL of toluene was degassed with argon for 20 min and then tetrakis(triphenylphosphine)palladium(0) (0.03 g, 0.026 mmol) was added. The mixture was stirred under a positive nitrogen pressure and immersed in a 75 °C bath for 3 h. The cooled mixture was diluted with 25 mL of 1 N HCl, stirred for 10 min, and then filtered through Celite. The aqueous phase was discarded and the organic phase was washed successively with equal volumes of water (3×) and brine (1×). The solution was then passed through a fritted filter containing a 5−10 mm layer of 3-(diethylenetriamino)propyl-functionalized silica gel (SiliCycle) (200−400 mesh) and anhydrous $CaSO_4$ and stripped to afford a tan solid that was dissolved in CH_2Cl_2 and precipitated into methanol. The collected solid was dried in a vacuum oven to afford ∼0.4 g of oligomer **14**: ^1H NMR ($CDCl_3$) δ 7.9−7.2 (m, 57, ArH), 7.1 and 6.8 (AB doublets, 8, phenol ArH), 4.8 (s, 2, OH), 2.1 (m(br), 25, 9-α-CH_2), 1.1 and 0.8 ppm (m(br), 167, hexyl-H); ^{31}P NMR endgroup quantitation; M_n (calcd = 3761, *n* = 8.50); MS (MALDI-TOF) (major signals) *m/e* (rel intensity), 1270 (**14**, *n* = 0) (32), 543 (phenyl cap, *n* = 0) (50), 1935 (**14**, *n* = 1) (100), 2208 (*n* = 1, phenyl cap) (40), 2600 (**14**, *n* = 2) (65), 2872 (*n* = 2, phenyl cap) (15), 3266 (**14**, *n* = 3) (30%), 3930 (**14**, *n* = 4) (11), 4596 (**14**, *n* = 5) (6), 5259 (**14**, *n* = 6) (3).

2-Bromo-7-(4-hydroxycumyl)-9,9-dihexylfluorene, 15. Butyllithium (6.25 mL of 1.6 M in hexane, 10.0 mmol) was added over 20 min to a solution of 2,7-dibromo-9,9-dihexylfluorene (5.0 g, 10.16 mmol) in dry THF at −78 °C. This solution was stirred at −78 °C for 1.5 h and then quenched with 5 mL (excess) of dry acetone. The mixture was stirred with saturated NH_4Cl and transferred to a separatory funnel. The organic phase was washed with water and brine and then solvent was removed on a rotary evaporator. The residue was dissolved in CH_2Cl_2, and phenol (1.9 g, 20 mmol) was added followed by 0.5 mL of methanesulfonic acid. After stirring for 2 h at room temperature, the mixture was transferred to a separatory funnel, washed with water (3×) and brine (1×), and then passed through a cone of anhydrous $CaSO_4$. Evaporation of solvent followed by chromatography on 150 g of silica gel afforded bromophenol **15** as an oil (4.45 g, 80%): MS (FAB^+) *m/e* 546, 548 (M^+); ^1H NMR ($CDCl_3$) δ 7.6−6.7 (m, 10, ArH), 5.2 (s, 1, OH), 1.9 (m, 4, 9-αCH_2's), 1.75 (s, 6, gem-CH_3), 1.2−0.5 (m, 22, aliphatics).

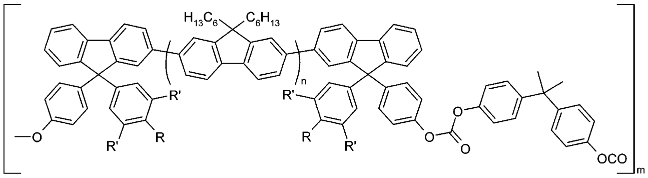
Cumylphenol-Functionalized Trimer 16. A mixture of bromophenol **14** (0.460 g, 0.84 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (0.200 g, 0.40 mmol), tetraethylammonium hydroxide (0.5 g of a 40% aqueous solution), water (1 mL), and toluene (10 mL) was degassed for 20 min with argon. Tetrakis(triphenylphosphine)palladium(0) (0.015 g, 0.014 mmol) was added, and the mixture was stirred under a positive nitrogen pressure and heated at 75 °C for 3 h. The cooled mixture was stirred with 10 mL of 1 N HCl for 15 min and then filtered through Celite. The organic phase was washed successively with water (2 × 25 mL) and brine (1 × 25 mL) and then passed through a 1 mm column of 3-(diethylenetriamino)propyl-functionalized silica gel (SiliCycle) (200−400 mesh). Evaporation of solvent afforded 0.7 g of a residue that was chromatographed on 25 g of silica gel eluted with hexane to 20% ethyl acetate/hexane to afford pure **15**: MS (FAB^+) *m/e* 1266 (M^+); ^1H NMR ($CDCl_3$ δ 7.9−7.3 (m, 18, fluorene-ArH), 7.2 and 6.8 (AB doublets, 8, phenol ArH's), 4.8 (s, 2, OH), 2.2 (m, 4, middle fluorene α-CH_2), 2.0 (m, 8, end fluorene α-CH_2), 1.75 (s, 12, cumyl-CH_3), 1.2 and 1.5 (m, 66, aliphatics).

Polymers. Alternating Polycarbonates from Fluorene Oligomer Bis-phenols and BPA−Bis-chloroformate. A typical procedure for the preparation of perfectly alternating oligomer−BPA copolycarbonates is as described for the preparation of the copolymer derived from BPABCF and phenol-functional heptafluorene **1a** ($n = 5$). A dry reaction vessel equipped with a magnetic stirring bar and a septum fitted with a syringe leading to a dry nitrogen bubbler was charged with the bis-phenol (MW = 2600) (178.2 mg, 0.0685 mmol), BPABCF (24.2 mg, 0.0685 mmol), and 1.5 mL of dry CH_2Cl_2. The resulting solution was immersed in an ice-salt bath for 15 min and then charged with 25 μL (0.179 mmol) of dry triethylamine. The mixture was maintained at 0−5 °C with stirring for 1 h, allowed to warm to room temperature, and stirred for an additional hour. Then the mixture was diluted with 1.0 mL of CH_2Cl_2, 1.0 mL of 10% $NaHCO_3$ was added, and the mixture was stirred for 10 min and then transferred to a separatory funnel. The aqueous phase was discarded and the organic phase was washed successively with equal volumes of 1 N HCl (1×) and water (2×). The solution was concentrated to about two-thirds of its original volume and then precipitated into 40 mL of methanol. The collected polymer was redissolved in CH_2Cl_2 and this solution was added slowly to 100 mL of boiling, deionized water. The solids were again collected, air-dried, redissolved in fresh CH_2Cl_2 and reprecipitated again into 50 mL of methanol. The resulting polymer was dried at 50 °C in a vacuum oven for 18 h. Gel permeation chromatography (relative to polystyrene) indicated M_w = 56.2K, M_n = 24.3K, M_w/M_n = 2.31.

Other polycarbonates were prepared similarly. Pertinent characterization data is presented in Table 1.

Device Fabrication and Measurement. For hole-only devices, indium−tin oxide (ITO) coated glass was cleaned, exposed to UV/ozone for 10 min, coated with about 60 nm of poly(3,4-ethylenedioxythiophene)−poly(styrenesulfonate) (PEDOT:PSS), baked in air at about 170 °C for at least 10 min, and then coated with the copolymer by spin-coating from a 20 mg/mL solution in *m*-xylene. A shadow mask with eight 0.03 cm^2 holes was used to vacuum-deposit top electrodes. For the hole-only samples, about a 60-nm-thick film of gold was evaporated at a rate of about 0.8 nm/s. For the electron-only samples, we used aluminum as the bottom electrode and a thin layer of sodium fluoride plus aluminum for the top electrode. Several samples with different spin speeds were made to allow interpolating for a target value of 50 nm. Electrical contact was made with a thin gold wire mounted to a microprobe. For the initial characterization we used a Textronix curve tracer and then recorded the I−Vs of the stable pixels with a standard source/measuring unit. The values reported are for the polarity corresponding to hole injection from the PEDOT contact and electron injection from the top contact.

Table 1. Polycarbonates Derived from Phenol-Capped Oligofluorenes and BPABCF



2a (R=H, R'=CF_3)

2b (R=tBu, R'=H)

polymer	M_w (10^3)	M_n (10^3)	M_w/M_n	UV_{max}, eV	E_g (UV), eV	HOMO (CV)	LUMO (CV)	E_g (CV), eV
2a ($n = 0$)	29.9	10.3	2.9	3.75	3.36	5.86	2.55	3.40
2a ($n = 1$)	50.8	15.3	3.31	3.49	3.14	5.71	2.47	3.24
2a ($n = 3$)	15.2	7.6	1.99	3.34	3.05	5.69	2.38	3.31
2a ($n = 5$)	56.1	24.3	2.31	3.29	3.02	5.69	2.34	3.35
2b ($n = 0$)	42.9	9.3	4.61	3.75	3.35	5.92	2.17	3.75
2b ($n = 1$)	18.9	9.2	2.05	3.49	3.10	5.61	2.18	3.43

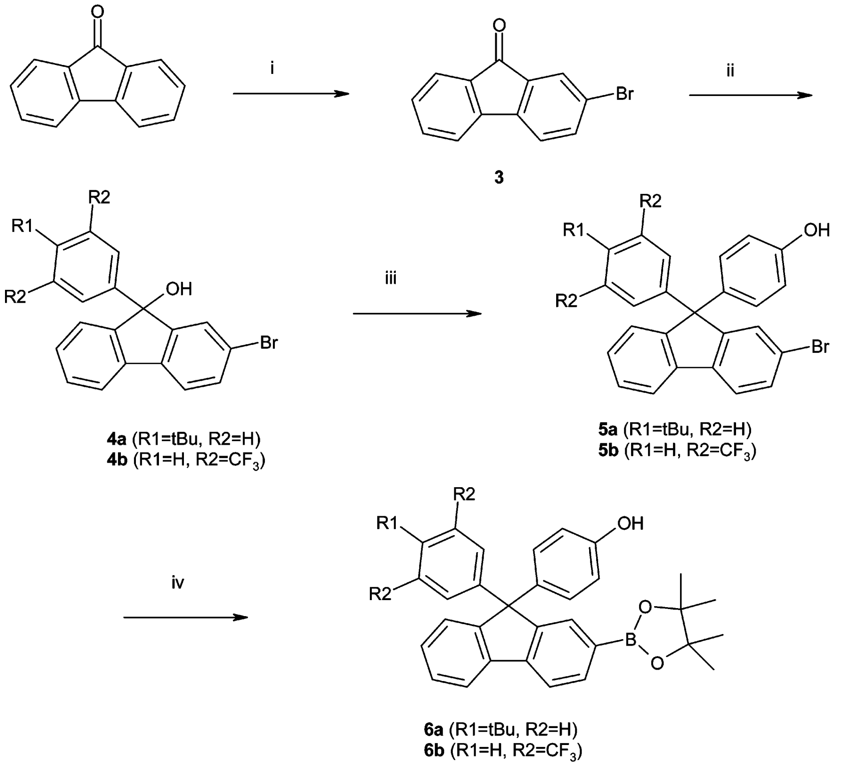
For the bipolar results the structure was glass/ITO/PEDOT:PSS followed by about a 65-nm-thick emissive polymer, a vacuum deposited cathode of 4 nm of sodium fluoride (NaF), and about 100-nm-thick aluminum.

Cyclic Voltammetry. The solution used for electrochemical measurements was prepared by dissolving 0.1 M dry tetrabutylammonium tetrafluoborate (98% min., GFS Chemicals) in acetonitrile (HPLC grade, J.T. Baker). Acetonitrile was distilled and freeze-dried before use. All cyclic voltammetric curves were obtained using a standard electrochemical setup consisting of a CH Instruments model 660A potentiostat and the three-electrode cell. The cell was placed in a glovebox (water below 1 ppm, oxygen below 2 ppm). A platinum disk (0.2 cm^2) was polished with 1 μm alumina before every experiment and used as a working electrode. The polymeric films were deposited by spin coating (about 3000 rpm, spin coater made in house) outside the glovebox. The reference electrode, Ag/Ag^+ [0.1 M $AgNO_3$ (99.9%, Alfa-Ventron) in acetonitrile], was calibrated vs a Fc/Fc^+ (98%, Aldrich) electrode (0.017 V vs Ag/Ag^+). Platinum mesh was used as a counter electrode. Voltammograms were recorded at 0.1 V/s always starting at the open circuit potential. The procedure to calculate HOMO and LUMO values from oxidation and reduction potentials respectively follows ref 32.

Results and Discussion

Synthesis of Phenol-Functionalized Oligofluorenes. The synthesis of discrete fluorene oligomers has been reported by several authors.[12−19] Most relevant to this study is the divergent/convergent approach used by Chen and co-workers to prepare a series of discrete 9,9-dialkylfluorene oligomers through a hexadecamer.[17] Although this approach suited our purposes as a general strategy for building up fluorene units, the need to link these oligomeric segments into high molecular weight polymers required a capping agent suitable for Suzuki coupling to the ends of the conjugated segments (an aryl halide or boronic acid derivative) that also bore functionality for linking the oligomeric segments in a subsequent polymerization reaction. Bromophenols **5a** and **5b**, readily obtained in three steps from fluorenone as outlined in Scheme 1, fulfilled this requirement. Bromophenols **5a,b** were also converted to the corresponding pinacol borates **6a,b**, either by a lithiation/borylation sequence or by palladium-catalyzed borylation with bis(pinacolato)diboron (Scheme 1).

Scheme 1. Synthesis of Phenol-Functionalized Bromides and Boronates



i. NBS, CH_3SO_3H
ii. ArMgBr, NH_4Cl
iii. Phenol/CH_2Cl_2/CH_3SO_3H
iv. Bis-pinacolatodiboron, $Pd(OAc)_2$,DMF, isopropoxypinacolatoboron

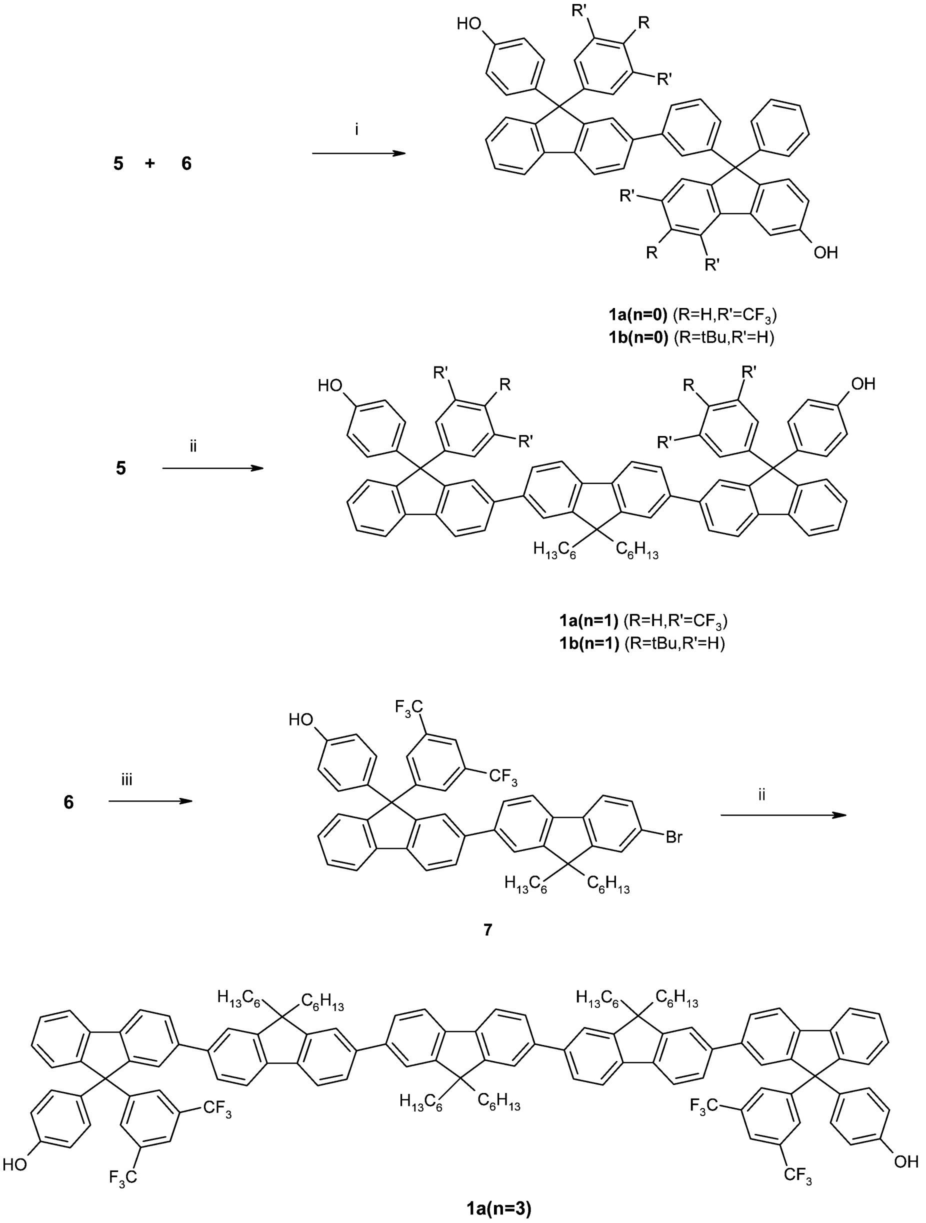
With these phenol-functionalized capping agents in hand, the synthesis of discrete phenol-capped oligomers **1a,b** (n = 0, 1) and **1a** (n = 3) (pentamer) was accomplished as depicted in Scheme 2. Heptamer **1a** (n = 3) was prepared as outlined in Scheme 3.

The oligomers were, in general, obtained as viscous gums, foams, or oils after purification by silica gel column chromatography. These materials tended to retain solvents rather tenaciously, particularly ethyl acetate from chromatographic purification. The purity of the oligomers was generally assessed by liquid chromatography, gel permeation chromatography, and ^{1}H NMR and mass spectroscopy. The aromatic protons on the end-group phenol substituents in the ^{1}H NMR spectrum appeared upfield from the rest of the aromatic protons. Integration of these protons relative to the hexyl protons α to the C9 fluorene position provided a good method of purity assessment. Gel permeation chromatographic (GPC) traces for discrete oligomers **1a** (n = 0, 1, 3, 5) and of a statistical oligomer **14** with an average length of nominally 10.5 fluorene units are presented in Figure 1. For the dimer two peaks corresponding to the D, L, and meso isomers are observed. The average of the two dimer peaks and the peaks of the trimer, pentamer, and heptamer follow a linear trend vs the reciprocal fluorene oligomer length, which can be used to calibrate the GPC time axis. For the statistical oligomer, only lengths of an odd number of fluorene units are expected according to the method of preparation. Even though some peaks are slightly shifted, the contribution of oligomers with three, five, seven, and nine fluorenes are clearly resolved, and the longer ones are visible in the initial tail.

After making adjustments for retained solvents, the oligomers were pure enough in most cases to afford high molecular weight polymers on reaction with difunctional linking agents.

In choosing a structural motif to introduce functionality into the oligofluorenes, a 4-*tert*-butyl phenyl group was initially selected as the “spectator” group residing at the 9-position that would also bear the phenol. It was noticed rather early, however, that oligomers bearing this “spectator” group were often contaminated with trace amounts yellow-colored impurities that proved to be fluorenone derivatives in which both the phenol and the aryl group were replaced with a carbonyl. These fluorenone contaminants were effective even in trace amounts at quenching the natural blue fluorescence of the oligomers and polymers derived from them, affording products that exhibited a red-shifted and less efficient photoluminescence. Treatment of the monomers or polymers with sodium borohydride restored efficient blue emission, but the long wavelength emission returned quickly when devices fabricated with these reduced materials were operated under ordinary conditions. This behavior is similar to what has been observed for polyfluorenes that have been exposed to typical photooxidation conditions and is thought to be due to fluorenone defects that develop when these polymers are oxidized.[33−35] Given the stability of 9-arylfluorenyl cations, anions, and radicals, loss of phenol, phenoxide, or a phenyl radical from the 9,9-diaryl end group of these oligomers should be facile under the influence of heat and acidic, basic, or transition metal reagents used in synthetic operations involving these substrates. Indeed, the FAB$^+$ mass spectra of oligomers bearing the 9-(4-hydroxyphenyl)-9-(4-*tert*-

Scheme 2. Synthesis of Phenol-Capped Dimers 1a (*n* = 0) and 1b (*n* = 0), Trimers 1a,b (*n* = 1), and Pentamer 1a (*n* = 3)



1a(n=0) (R=H,R'=CF_3)
1b(n=0) (R=tBu,R'=H)

1a(n=1) (R=H,R'=CF_3)
1b(n=1) (R=tBu,R'=H)

7

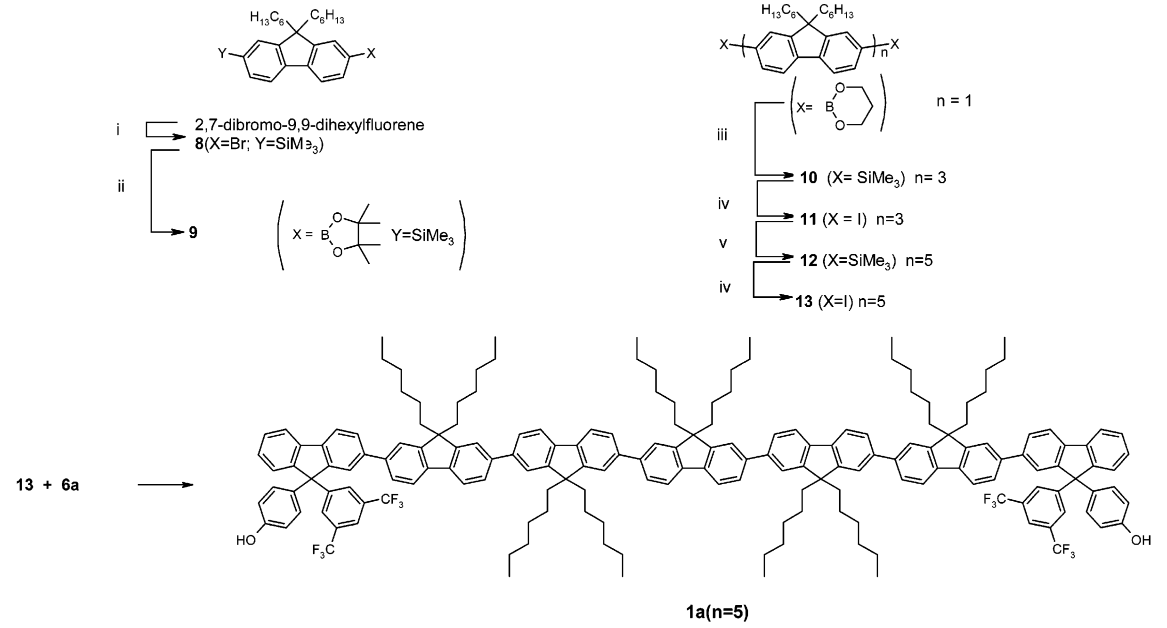
1a(n=3)

i. $(Ph_3P)_3Pd(0)$, Et_4NOH, toluene
ii. 2,7-bis-trimethyleneboronato-9,9-dihexylfluorene, $(Ph_3P)_3Pd(0)$, Et_4NOH, toluene
iii. 2,7-dibromo-9,9-dihexylfluorene (6 eq), $(Ph_3P)_3Pd(0)$, Et_4NOH, toluene

butylphenyl) end groups exhibited peaks at ($M^+ - 94$) and ($M^+ - 134$) resulting from loss of the 9-aryl substituents. In an effort to minimize or avoid this fragmentation, a more electron-deficient aryl "spectator" group, 3,5-bis(trifluoromethyl)phenyl was employed to lessen the tendency for loss of phenol from the 9-position by destabilizing the 9-arylfluorenyl cation. Phenol-capped oligomers prepared with this substituent at the 9-position were typically not contaminated with yellow fluorenone impurities. Moreover, the FAB^+ mass spectra of these oligomers did not exhibit the prominent $(M - aryl)^+$ signals noted before. Accordingly, this substituent was used to prepare the majority of oligomers used in this study. Changing the "spectator" group in the 9-position from *tert*-butylphenyl to bis(trifluoromethyl)-phenyl also had a surprisingly large effect on the LUMO values (vide infra) for the lower members of the oligomer series. This result is somewhat surprising, since the 9-position in the oligofluorenes is remote from the *p*-phenylene segments that make up the conjugated system.

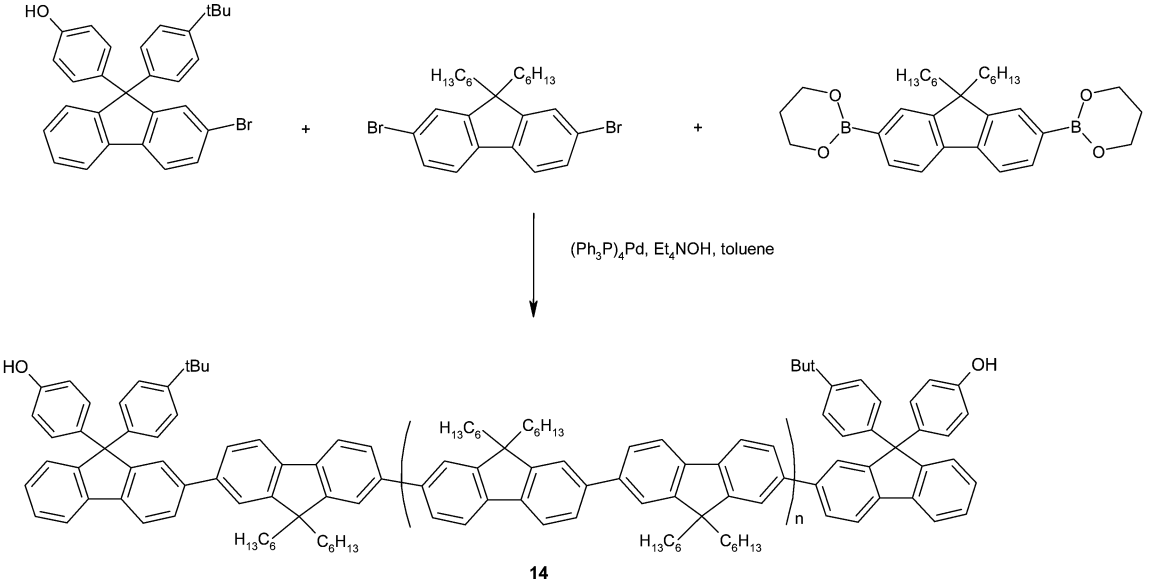
In addition to the series of discrete phenol-capped oligomers, statistical oligomers **14** were also prepared by condensing a stoichiometric imbalance of bis-boronate and dibromide monomers in the presence of bromophenol chain stopper **5a** under typical Suzuki polymerization conditions and varying the ratio of bis-boronate to dibromide to achieve the desired oligomer

Scheme 3. Synthesis of Phenol-Capped Heptamer 1a (n = 5)



i. BuLi (-78C), TMS-Cl
ii. bis-pinacolatodiboron/Pd(OAc)$_2$/DMF
iii. **8**/(Ph$_3$P)$_4$Pd, Et$_4$NOH,Toluene
iv. ICl,CCl$_4$
v. **9**/(Ph$_3$P)$_4$Pd, Et$_4$NOH,Toluene
vi. (Ph$_3$P)$_4$Pd,Et$_4$OH,Toluene

Scheme 4. Synthesis of Phenol-Capped Statistical Oligomers



14

length (Scheme 4). After some optimization this procedure produced oligomers that, for the most part, were phenol-capped at both ends.

The MALDI-TOF spectra of these oligomers (see Figure 2, Supporting Information), however, revealed that in addition to the expected phenol-capped oligomers, a series of oligomers having phenols at one end and phenyl caps at the other end were produced. The phenyl end caps are likely derived from the phosphine ligand,[36] since use of tritolylphosphine in place of triphenylphosphine, produced tolyl-capped rather than the phenyl-capped byproducts. With some optimization of the procedure, these monofunctional byproducts could be minimized but not completely avoided. Quantitative analysis of the phenolic-OH content of these oligomers by derivatization with 1,3-phenylene phosphorochloridite in the presence of a known amount of 2,4,6-trichlorophenol as an internal standard, followed by ^{31}P NMR analysis of the resulting mixture, enabled adjustment of the stoichiometry in polymerizations so that high molecular weight polymers could be obtained from these oligomers.[37] For comparative purposes, poly-9,9-dihexylfluorene was also prepared by Suzuki condensation of equimolar amounts of 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) and 2,7-dibromo-9,9-dihexylfluorene.

Polymer Synthesis. The purified phenol-functionalized oligomers could be converted to polymers using a variety of linking chemistries to obtain polycarbonates,

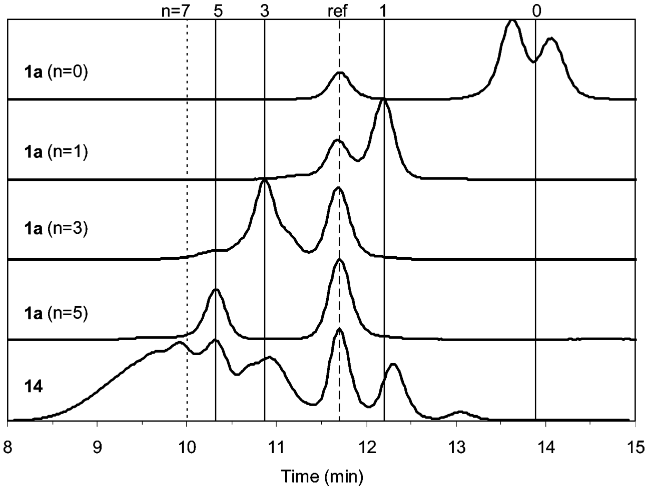


Figure 1. Gel permeation chromatograms of discrete oligomers **1a** (n = 0, 1, 3, 5) and statistical oligomer **14**.

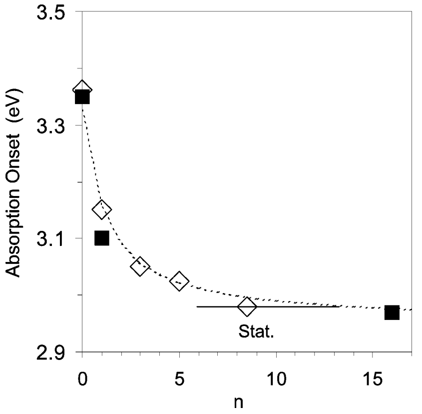


Figure 2. Optical absorption onset in methylene chloride vs the length of the fluorene blocks. The values for the *tert*-butyl-substituted dimer and trimer and for the hexylfluorene homopolymer are shown with closed symbols.

polyethers, polyformals, polysilyl ethers, and polyether siloxanes (see Supporting Information). This versatility was demonstrated for oligomer **1b** (n = 1) as depicted in Scheme 5.

To assess trends in electronic properties as a function of oligomer length, polycarbonates **2a** and **2b**, derived from reaction of the phenol-capped oligomers with BPA−bis-chloroformate (BPABCF), were prepared. Condensation of these monomers in methylene chloride at 0−5 °C in the presence of a slight excess of triethylamine afforded high molecular weight, colorless, transparent, and highly emissive polymers with excellent solubility and film-forming properties. As quantities of these polymers were limited and needed for device fabrication, thermal analysis generally was not carried out. For the few materials that were subjected to DSC analysis, no discernible transitions were noted in the range from about 50 to 350 °C. Molecular weight, optical properties, and CV data for all the polymers are presented in Table 1.

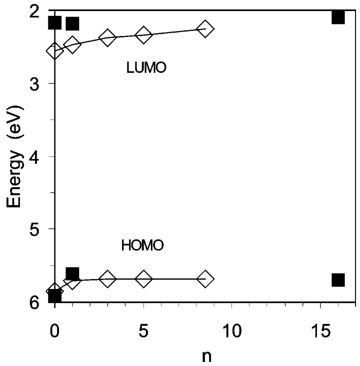
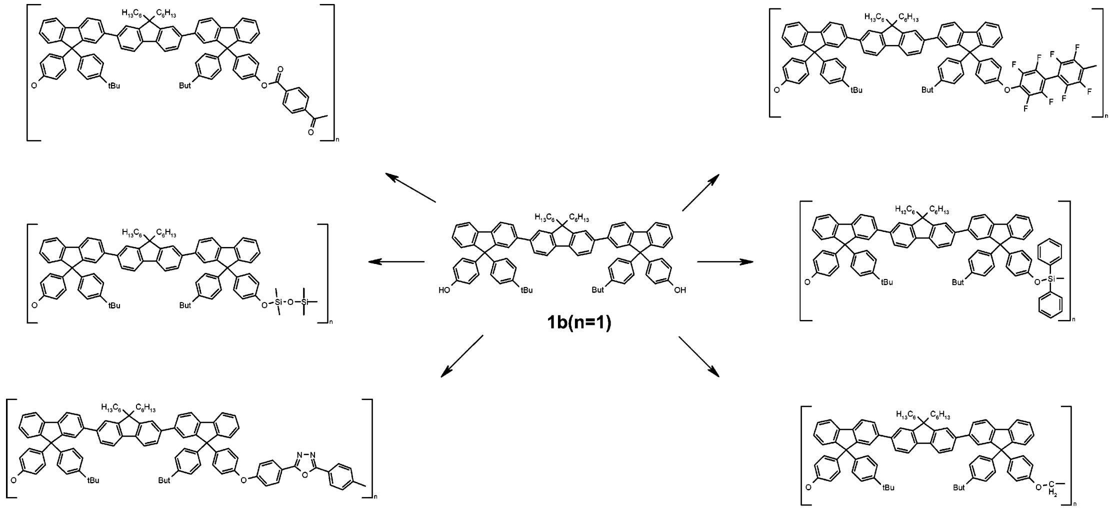


Figure 3. HOMO and LUMO values for polymers derived from **1a** (n = 0−5), **1b** (n = 0,1 closed squares), **14**, and poly-9,9-dihexylfluorene (closed square).

Optical absorption and cyclic voltammetry (CV) were measured for all polymers to gauge the energy levels of the excitons and charge carriers. The optical gap of polymers **2a** (n = 0, 1, 3, 5) decreases with chain length, as demonstrated in earlier works,[38] and quickly approaches the value for the polymer. In addition to the series for **2a**, the figure also shows values for polycarbonates derived from the dimer and trimer **2b**, showing only a minor shift of the absorption onset due to this change in substitution.

Figure 3 shows the LUMO and HOMO values as measured by CV of polymers derived from the **2a** series of oligomers with n = 2, 3, 5, 7, the statistical $n \approx 8.5$ oligomer, and those derived from oligomers **2b** with *tert*-butyl-substituted end groups (n = 0, 1) and of poly-9,9-dihexylfluorene made by Suzuki polymerization. In general, with increasing conjugation length, the HOMO levels typically decrease and the LUMO levels increase[39]

Scheme 5. Various Polymers Derived from Terfluorene 1b (n = 1)



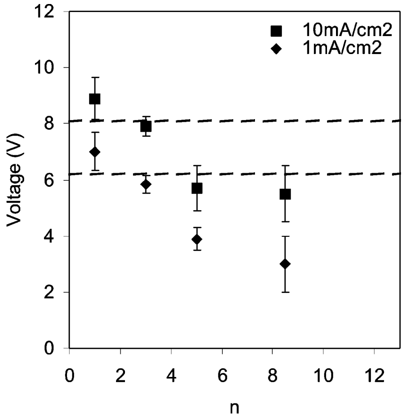


Figure 4. The voltage at a current density of 1 mA/cm^2 (diamonds) and 10 mA/cm^2 (squares) for hole-only devices for 50-nm-thick copolymer films derived from oligomers with n = 1, 3, 5 and statistical oligomer **14** (n ~ 8.5). The two dashed lines depict the voltages measured for a poly-9,9-dihexylfluorene homopolymer.

as the HOMO−LUMO difference is equal to the decreasing optical band gap minus the exciton binding energy. One can see that the behavior of the HOMO levels of the **2a** copolymer series follows this expectation for $n = 0$ and 1 and then flattens, approaching the value for the homopolymer within experimental uncertainty. However, the LUMO values for this series significantly decrease in magnitude, contrary to expectation. To understand whether this trend was due to substituent effects, we compare values for the dimer and trimer of structure **2b**. Note that due to the change in substitution, the LUMO of the dimer is shifted by almost 0.4 eV. This trend of the LUMO for series **2a** may be due to the large electron-withdrawing effect of the CF_3 substituents on the terminating fluorene units. As this substitution only affects the end groups of the fluorene oligomers, the LUMO gradually recovers with length and seems to approach that of the hexylfluorene homopolymer. This result also implies a significant reduction in exciton binding energy via CF_3 substitution, which can trivially be derived from the difference of HOMO, LUMO, and optical band gap.

A major motivation of this study was to understand the effect of the conjugation length on the charge transport properties. We suspected that for short conjugated segments, the sizable insulating linking groups might impede current flow. To separate the effects for holes and electrons, we used ITO/PEDOT bottom contacts with gold top contacts for hole-only devices, and aluminum bottom contacts with sodium fluoride/aluminum top contacts for electron-only devices. Figure 4 compares the saturated hole-only voltages for 1 and 10 mA/cm^2 (interpolated for a thickness of 50 nm) for the polycarbonates derived from oligomers **1a** and **14**, with the values for the poly-9,9-dihexylfluorene. The voltages drop significantly with length and starting with the pentamer are below the values for the homopolymer. As all the presented materials have similar hole-injection barriers vs PEDOT, we attribute the increase of hole currents with oligomer length to an increase in hole mobility. The comparison with an analogue homopolymer shows that the mobility of such copolymers can be superior above a certain oligomer length. Electron-only devices showed a less pronounced decrease of voltage with length with values of about 3.5 to 5 V at 1 mA/cm^2 for the copolymers and 7.5 V for the homopolymer.

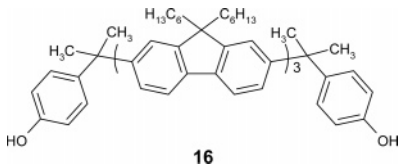
Table 2. Device Operating Characteristics (turn-on voltage, operating voltage, and device lifetime) for Polymers Made from Selected Phenol-Capped Oligomers

oligomer	turn-on voltage	V at 10 mA/cm^2	life (h) at ~4 mA/cm^2
1a (n = 1)	4.9	6.5	*a*
1b (n = 1)			*a*
15	5.1	6.4	0.1
1a (n = 3)	4.5	5.4	<0.1
1a (n = 5)	3.7	4.6	0.13
14 (n = 8.5)	3.9	4.2	1.7

[a] Less than 1 min.

The electroluminescence of bipolar devices was investigated for all mentioned materials using ITO/PEDOT:PSS as the anode, a vacuum-deposited cathode of 4 nm sodium fluoride (NaF), and about 100 nm aluminum. Similar to the behavior of hole-only devices, the bipolar voltage also drops with conjugation length, with the voltages about equal for the heptamer and homopolymer. The external quantum efficiency at a current density of 10 mA/cm^2 and a target thickness of 65 nm of the emissive layer ranged from 0.12% to 0.7% and was similar to that obtained with commercial[40] samples of poly-9,9-dihexylfluorene and poly-9,9-dioctylfluorene homopolymers. The CF_3-substituted copolymers with n = 3 and 7 exhibited the best efficiency, which might simply be due to their superior purity or to uncontrolled details of the electron hole charge balance. For the operational stability (Table 2), a drastic increase was observed with increasing conjugation length. The reason for this is not fully understood but might be due to instability of the phenolic and aryl substituent at the 9 position of the terminal fluorene groups.

Motivated by the suspicion that functionality at the 9-position of the oligomer termini might affect operational stability, terfluorene **16** was prepared (see Experimental Section) and converted to a polymer by reaction with BPABCF. The stability of a standard device made with this version of a linked terfluorene oligomer compares favorably with devices made from **1a** or **1b** with n = 1, indicating that the phenol in the 9-position may be detrimental to stability.



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Summary

A series of discrete (n = 2, 3, 5, and 7) and statistical phenol-capped fluorene oligomers have been synthesized. High molecular weight polycarbonate polymers derived from these oligomers were prepared using BPA−bis-chloroformate (BPABCF) as a linking group. Trends in the optical and electrical properties were determined. Device data for this family of emissive copolymers indicates that charge mobility increases with conjugation length and is better than that of an analogue homopolymer. We attribute this improvement to a number of features, including reduction of accidental chemical defects, a better-defined distribution of conjugation length, and possibly a better local alignment. A surprising shift in LUMO values due to CF_3 substitution at the ends of the oligomers was observed. This feature may reduce the barrier for electron injection from common cathodes for these materials. In the future we hope this flexible approach will lead to light-emitting devices with improved efficiency and will give greater flexibility in tuning physical properties required for multilayered devices.

Supporting Information Available: Preparative procedures and characterization data for polymers depicted in Scheme 5; Quantitative ^{13}C NMR spectrum of diiodopentafluorene **13** and MALDI-TOF spectrum of statistical oligomer **14**. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Phys.* **1987**, *51*, 913.
(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(3) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2002**, *12* 828.
(4) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 926.
(5) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965.
(6) Bernius, M.; Inbasekaran, M.; Woo, E.; Wu, W.; Wujkowski, L. *Thin Solid Films* **2000**, *363*, 55.
(7) Wu, W.; Inbasekaran, M.; Hudack, M.; Welsh, D.; Yu, W.; Cheng, Y.; Wang, C.; Kram, S.; Tacey, M.; Bernius, M.; Fletcher, R.; Kiszka, K.; Munger, S.; O'Brien, J. *Microelectron. J.* **2004**, *35*, 343.
(8) Chou, C.-H.; Shu, C.-F. *Macromolecules* **2002**, *35*, 9673.
(9) Tang, H.-Z.; Fujiki, M.; Zhang, Z.-B.; Torimitsu, K.; Motonaga, M. *Chem. Commun.* **2001**, 2426.
(10) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
(11) Menon, A.; Dong, H.; Niazimbetova, Z. I.; Rothberg, L. J.; Galvin, M. E. *Chem. Mater.* **2002**, *14*, 3668.
(12) Jo, J.; Chi, C.; Hoger, S.; Wegner, G.; Yoon, D. Y. *Chem. Eur. J.* **2004**, *10*, 2681.
(13) Chen, A. C. A.; Culligan, S. W.; Geng, Y.; Chen, S. H.; Klubek, K. P.; Vaeth, K. M.; Tang, C. W. *Adv. Mater.* **2004**, *16*, 783.
(14) Geng, Y.; Trajkovska, A.; Culligan, S. W.; Ou, J. J.; Chen, H. M. P.; Katsis, D.; Chen, S. H. *J. Am. Chem. Soc.* **2003**, *125*, 14032.
(15) Geng, Y.; Chen, A. C. A.; Ou, J. J.; Chen, S. H.; Klubek, K.; Vaeth, K. M.; Tang, C. W. *Chem. Mater*. **2003**, *15*, 4352.
(16) Geng, Y.; Culligan, S. W.; Trajkovska, A.; Wallace, J. U.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 542.
(17) Katsis, D.; Geng, Y. H.; Ou, J. J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H. Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 1332.
(18) Geng, Y.; Katsis, D.; Culligan, S. W.; Ou, J. J.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 463.
(19) Geng, Y.; Trajkovska, A.; Katsis, D.; Ou, J. J.; Culligan, S. W.; Chen, S. H. *J. Am. Chem. Soc.* **2002**, *124*, 8337.
(20) Tirapattur, S.; Belletête, M.; Drolet, N.; Leclerc, M.; Durocher, G. *Macromolecules* **2002**, *35*, 8889.
(21) Beaupré, S.; Ranger, M.; Leclerc, M. *Macromol. Rapid Commun.* **2000**, *21*, 1013.
(22) Belletête, M.; Ranger, M.; Beaupré, S.; Leclerc, M.; Durocher, G. *Chem. Phys. Lett.* **2000**, *316*, 101.
(23) Mastrorilli, P.; Nobile, C. F.; Grisorio, R.; Rizzuti, A.; Suranna, G. P.; Acierno, D.; Amendola, E.; Iannelli, P. *Macromolecules* **2004**, *37*, 4488.
(24) Wu, C.-C.; Lin, Y.-T.; Wong, K.-T.; Chen, R. -T.; Chien, Y.-Y. *Adv. Mater.* **2004**, *16*, 61.
(25) Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C. H.; Su, Y. O.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc. B* **2002**, *124*, 11576.
(26) Kim, Y.-H.; Shin. D.-C.; Kim, S.-H.; Ko, C.-H.; Yu, H.-S.; Chae, Y.-S.; Kwon, S.-K. *Adv. Mater.* **2001**, *13*, 1690.
(27) Wu, C.-C.; Liu, T.-L.; Lin, Y.-T.; Hung, W.-Y.; Ke, T.-H.; Wong, K.-T.; Chao, T.-C. *Appl. Phys. Lett.* **2004**, *85*, 1172.
(28) Wu, C.-C.; Liu, T.-L.; Hung, W.-Y.; Lin, Y.-T.; Wong, K.-T.; Chen, R.-T.; Chen, Y.-M.; Chien, Y.-Y. *J. Am. Chem.* Soc. **2003**, *125*, 3710.
(29) Coulson, D. R. *Inorg. Synth.* **1990**, *28*, 107−9.
(30) Suffert, J. *J. Org. Chem.* **1989**, *54*, 509.
(31) Hwang, S.; Chen, Y. *Polymer* **2000**, *41*, 6581.
(32) Janietz, S.; Bradley, D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.
(33) Gong, X.; Iyer, P. K.; Moses, D.; Bazan, G. C.; Heeger, A. J.; Xiao, S. S. *Adv. Mater.* **2003**, *13*, 325.
(34) Gaal, M.; List, E. J. W.; Scherf, U. *Macromolecules* **2003**, *36*, 4236.
(35) List, E. J. W.; Guentner, P. S. dF.; Scherf, U. *Adv. Mater.* **2002**, *14*, 374.
(36) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441.
(37) Williams, E. A.; Donahue, P. E.; Early, T. A. Unpublished results. Details of the procedure will be published separately.
(38) Cornil, J.; Beljonne, D.; Heller, C. M.; Campbell, I. H.; Laurich, B. K.; Smith, D. L.; Bradley, D. D. C.; Müllen, K.; Bredas, J. L. *Chem. Phys. Lett.* **1997**, *278*, 139.
(39) Gebhardt, V.; Bacher, A.; Thelakkat, M.; Stalmach, U.; Meier, H.; Schmidt, H.-W.; Haarer, D. *Adv. Mater.* **1999**, *11*, 119.
(40) Commercial polyfluorene samples used in this study were obtained from Cambridge Display Technologies (CDT), Cambridge, UK, or American Dye Source, Inc. (ADS), Baie D'urfe, Quebec, Canada.

MA0518353