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A Fully Aryl-Substituted Poly(ladder-type pentaphenylene): A Remarkably Stable Blue-Light-Emitting Polymer

Josemon Jacob,[†] Stefan Sax,[‡] Martin Gaal,[‡] Emil J. W. List,[‡] Andrew C. Grimsdale,[†,§] and Klaus Müllen*,[†]

Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany, and Christian Doppler Laboratory "Advanced Functional Materials", Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria, and Institute of Nanostructured Materials and Photonics, Joanneum Research, Franz-Pichler-Strasse 30, A-8160 Weiz, Austria

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ABSTRACT: A new poly(ladder-type pentaphenylene) bearing aryl groups at all bridgehead positions has been prepared. In comparison to previously reported bridged poly(*p*-phenylene)-type polymers such as polyfluorene and polyindenofluorene, this polymer is optimized for maximum overlap of the blue emission with the sensitivity of the human eye. Furthermore, the introduction of aryl substituents at all the bridgeheads produces a material which shows remarkably stable blue emission in light-emitting diodes and is not subject to oxidative degradation-induced defect formation. In particular, a comparison of the novel fully aryl-substituted polymer with a partially aryl-substituted polymer reveals that the oxidative degradation-induced defect formation can be almost completely eliminated upon aryl substitution.

Introduction

Conjugated polymers are of considerable academic and industrial importance as the active materials in the emerging new technologies of organic light-emitting diodes (OLEDs)[1,2] and polymer lasers.[3] The full realization of these technologies will require the development of materials that produce efficient, stable blue emission.[4] Much research into blue-emitting polymers has centered on *p*-phenylene-based materials such as poly(dialkylfluorene)s (PFs, **1**),[5,6] poly(tetraalkylindenofluorene)s (PIFs, **2**),[7,8] and ladder-type polyphenylenes (LPPPs, **3**) (Figure 1).[9] All these materials suffer from problems with color purity and color stability. The emission from PFs and PIFs is blue-violet in color (emission maxima $\lambda_{\max} = 420-430$ nm), while LPPPs ($\lambda_{\max} = 450-470$ nm) produce blue-green emission, and so recently we introduced a new type of blue-emitting polymer, poly(ladder-type pentaphenylene) (**4**),[10] which displays a purer blue emission ($\lambda_{\max}$ 443 nm) with a very small Stokes shift and well-resolved vibrational bands. Devices were constructed which produced blue emission with moderate efficiencies.

The second problem of color stability in polymers **1**−**3** manifests itself by the rapid appearance of long-wavelength emission bands during operation of LEDs,[5,8,9] which were initially attributed to aggregation of the polymer chains.[5,8,11] More recently, it has been shown that the emission from PFs arises from the formation of fluorenone defects,[6,12] and similar ketone defects have been proposed as the origins for the long-wavelength band from PIFs[13] and LPPPs.[14] We have previously shown that replacement of the bridgehead alkyl substituents with aryl groups in PFs[15,16] and PIFs[17] suppresses the long-wavelength emission due both to a lower susceptibility toward oxidation of the arylated bridgeheads and to hindrance of exciton migration to any defect sites that may arise. Although LEDs using polymer **4** showed stable blue emission when operated for several minutes at 6−7 V in a glovebox,[10] further testing revealed that the emission was not stable over longer periods or upon operation outside a glovebox. This we attribute to the susceptibility of the dialkyl bridgeheads toward oxidation leading to the formation of keto defects at the bridgeheads although extreme care was taken in the synthesis to ensure complete alkylation.[10] It has been previously reported that chemical defects arising from partial alkylation at the bridgeheads in ladder-type poly(phenylenes) can lead to keto defects either during synthesis or device operation.[6] It soon became apparent that the synthesis of a fully arylated polymer as in **5** can help eliminate or minimize the possibility of partially substituted bridgeheads and thereby improve stability of such materials. Toward this, we now report on the synthesis of a fully arylated poly(ladder-type pentaphenylene) **5** and the results of device testing confirming that it produces much more stable blue emission than **4**.

Results and Discussion

Synthesis and Characterization. The synthetic approach to the desired polymer **5** is outlined in Scheme 1. To prepare a fully arylated pentaphenylene, it was necessary to first synthesize a 9,9-diarylfluorene-2-boronate. Starting from commercially available reagents, 4′-trimethylsilylbiphenyl-2-carboxylic acid methyl ester (**6**) was synthesized by a standard Suzuki-type coupling reaction in 97% yield. Addition of 2 equiv of aryllithium produced the corresponding alcohol, and then exchange of the trimethylsilyl group with a bromine atom followed by ring closure using BF_3·etherate generated the diaryl-substituted monobromofluorene **7** (73%). The monobromide **7** was first converted to the corresponding boronate ester **8** (78%), and then Suzuki coupling with 2,5-dibromodimethyl terephthalate (**9**) gave the pentaphenylene diester **10** in 91% yield. The ladder-type pentaphenylene **11** was then synthesized in

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[†] Max-Planck-Institute for Polymer Research.

[‡] Graz University of Technology and Institute of Nanostructured Materials and Photonics.

[§] Current address: Bio21 Institute, University of Melbourne, 30 Flemington Road, Parkville 3010, Victoria, Australia.

* Corresponding author. E-mail: muellen@mpip-mainz.mpg.de.

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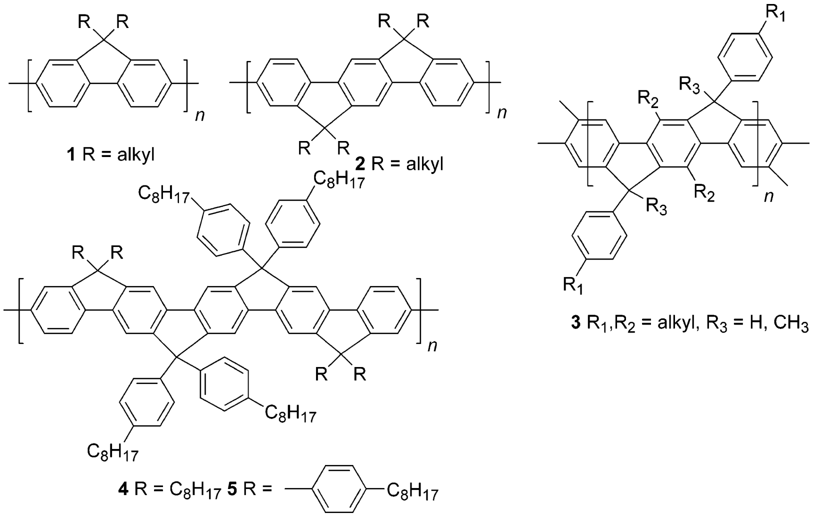
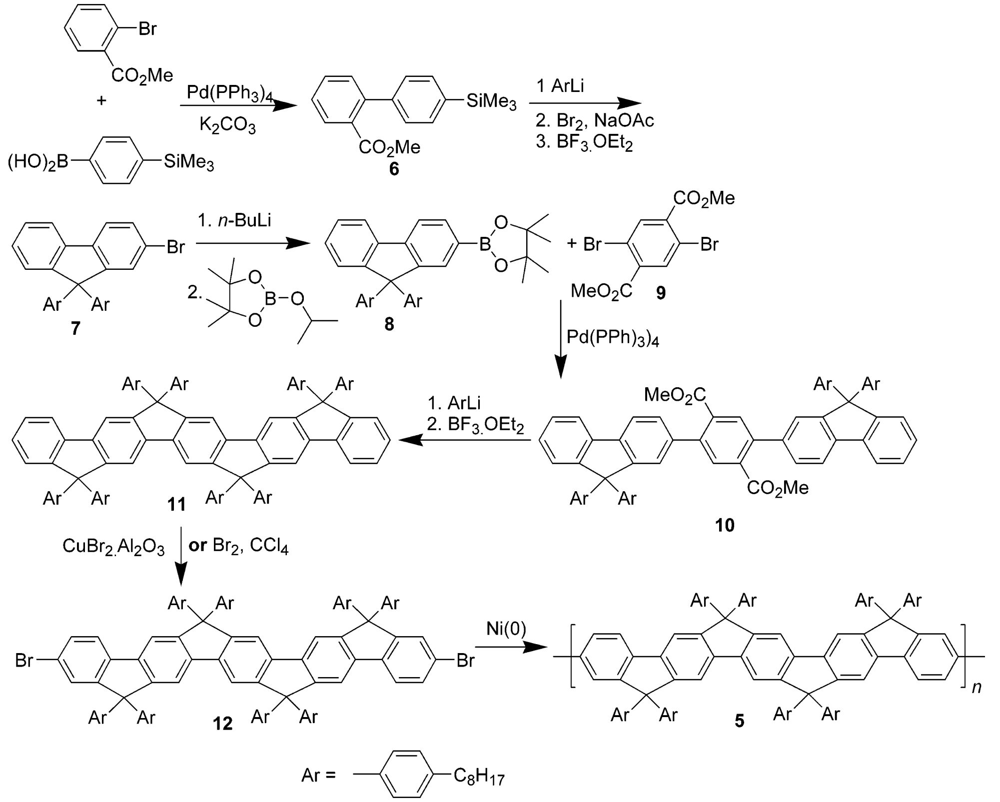


Figure 1. Polyphenylene-based conjugated polymers.

Scheme 1. Synthesis of Polymer 5



92% yield by addition of 4 equiv of aryllithium to the diester followed by ring closure using BF_3·etherate. From this, the monomer **12** was obtained in nearly quantitative yield by bromination using $CuBr_2$ on alumina or Br_2 in CCl_4. The polymer **5** was then obtained (86%) by standard Yamamoto-type polycondensation using stoichiometric nickel(0) reagent.

GPC analysis using PPP standard showed a M_n value of 2.80×10^4 with a polydispersity of 2.65. This corresponds to a degree of polymerization of around 16, and the all-aryl polymer **5** possesses excellent solubility in solvents such as dichloromethane, chloroform, and toluene and good film-forming abilities. Thermogravimetric analysis (TGA) showed the material to be stable up to 350 °C, and DSC analysis showed no phase transition in the temperature range from −50 to 300 °C (see Supporting Information for details).

Polymer **5** shows blue fluorescence in solution with an emission maximum at 441 nm (Figure 2), which is essentially identical to that of the aryl−alkyl polymer **4**. In the film, the fluorescence shows a maximum at $\lambda_{max} = 444$ nm. The absorption is also in the blue spectral region with its maximum at 434 nm, resulting in a very small Stokes shift of 7 nm, which is due to the rigidity of polymer **5**. A comparison of the film and solution spectra reveals a small bathochromic shift of the film spectra of ca. 6 nm as well as a moderate broadening of the spectra in absorption and emission. The broadening as well as the bathochromic shift is typical for such polymers and can be attributed to the formation of additional, more planar conformations of the polymer in the solid state.[6]

To determine their overall stability against the formation of oxidative keto-type defects yielding the un-

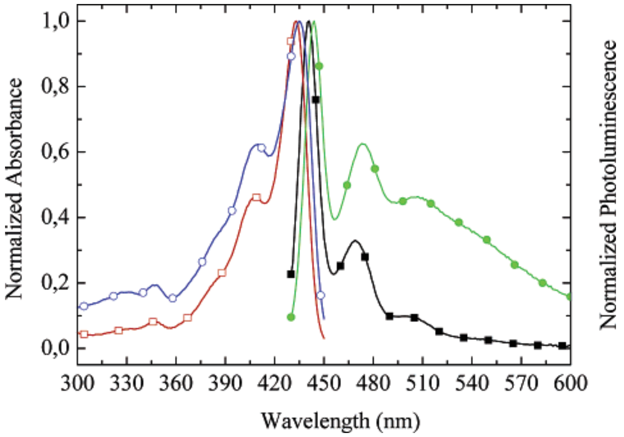


Figure 2. Absorption (left) and photoluminescence (right) of polymer **5** in film (circles) and solution (squares).

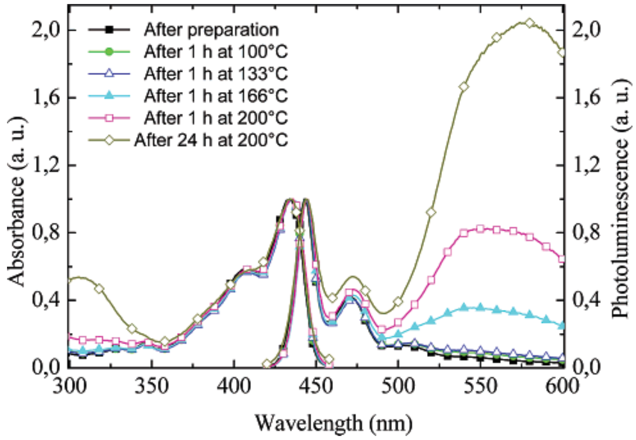


Figure 3. Normalized photoluminescence and absorption spectra of a spin-coated polymer **4** film before and after annealing in air. The film was measured directly after preparation (filled squares), stored in the dark under ambient atmosphere, and heated stepwise. Filled circles: after 1 h at 100 °C; open triangles: 1 h at 133 °C; filled triangles: 1 h at 166 °C; open squares: 1 h at 200 °C; open diamonds: 24 h at 200 °C.

wanted low-energy emission band at ca. 530 nm, spin-coated films on glass substrates of both polymers **4** and **5** were exposed to oxygen under thermal stress conditions in an accelerated lifetime test. The evolution upon thermal stress in air of the photoluminescence for polymer **4** is shown in Figure 3. Successive heating at increasing temperatures (100, 133, 166, and 200 °C) on a hot plate, each for 1 h under the influence of regular atmosphere, leads to the well-known formation of oxidative products in the form of ketonic defects with an emission centered at 540 nm, which increases with ongoing degradation. Note that simultaneous IR measurements (not depicted) made on silicon wafers only showed a very weak trace of a carbonyl stretching mode emerging at 1721 cm^{-1}. This is not surprising as the absolute amount of ketonic defects formed this polymer **4** is already very low (<0.5%), due to the clean synthesis and stable chemical structure of this polymer. Note that under inert conditions, i.e., a dynamic vacuum of 10^{-6} mbar, no degradation of the polymer was detected.

By comparison, Figure 4 shows the identical thermal degradation series under ambient conditions as shown above now for the fully aryl-substituted polymer **5.** As can be clearly seen polymer **5** shows no sign of an ongoing formation of a ketonic defect even after 24 h at 200 °C. From the absorption spectra, both polymers **4** and **5** show an increasing absorbance on annealing at 200 °C for 24 h. This can be attributed to the fact the conjugated polymer was degraded at this temperature on long heating, whereas the phenyl rings are not and hence the relative increase in ring absorbance. A more careful analysis of the photoluminescence data, however, reveals the emergence of a band below 560 nm which together with the observation of a general decrease of the overall relative quantum yield by ca. 65% in the polymer upon degradation is attributed to a partial decomposition of the polymer (due to the formation of nonemissive defects). The control experiment under inert conditions did not show any alterations in the spectra and no decrease of the overall quantum yield.

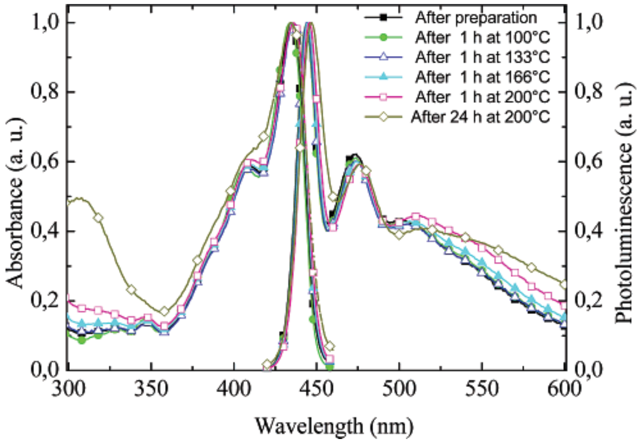


Figure 4. Normalized photoluminescence spectra of a spin-coated polymer **5** film before and after annealing. Again, the film was measured directly after preparation (filled squares), stored in darkened atmosphere, and heated stepwise. Filled cycles: after 1 h at 100 °C; open triangles: 1 h at 133 °C; filled triangles: 1 h at 166 °C; open squares: 1 h at 200 °C; open diamond: 24 h at 200 °C.

This comparison of the two polymers under extreme thermal stress conditions clearly reveals the drastic improvement of polymer **5** over polymer **4**. It becomes clearly evident that the dialkyl bridgeheads in polymer **4** are susceptible toward oxidation, which can be solved by making a fully aryl-substituted poly(ladder-type pentaphenylene) **5** to yield a blue-light-emitting polymer highly stable against oxidative degradation.

To test this hypothesis, polymer **5** was also tested under device conditions. OLEDs were prepared with configuration ITO/PEDOT:PSS/polymer **5**/Ca/Al. The devices show an onset of the emission at ca. 4 V and a blue emission (CIE coordinates 0.17, 0.09) with a luminance typically above 200 cd/m^2, which is stable during several tens of minutes of operation at and up to 14 V and a current density of up to ca. $j = 10^4$ A/m^2 under glovebox conditions. However, these unoptimized single-layer devices show only moderate efficiencies (0.1−0.5 cd/A), indicating that electron-transporting layers are required to obtain maximum efficiency in the device. Investigations into device optimization are underway and will be reported separately. As can be seen in Figure 5, biasing the device at rather high voltages and current densities does not lead to any alteration in the emission spectrum. Comparing these results to polymer **4**, where a minor degree of degradation has been observed upon driving the device at high voltages and current densities, these results clearly demonstrate that the chemical structure of polymer **5** offers a

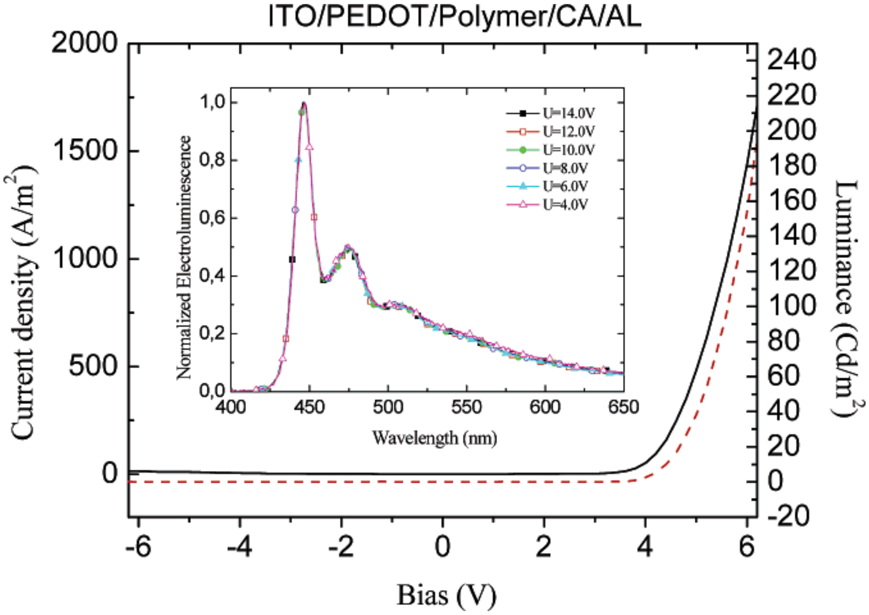


Figure 5. *I*/*V* characteristics and normalized electroluminescence of an ITO/PEDOT/polymer **5**/Ca/Al device operated at different bias.

considerable improvement and considerable potential as an emissive material for fully stable pure blue-emitting devices.

Conclusion

An efficient synthesis of a new poly(ladder-type pentaphenylene) **5** in which all the bridgeheads are fully substituted with aryl groups has been developed. Single-layer OLEDs with **5** showed stable blue emission with a luminance typically over 200 cd/m^2 which is stable during several tens of minutes of operation at or below 14V. Accelerated stability test studies show remarkable resistance to oxidation at the bridgeheads in oxidative degradation experiments under thermal stress conditions as well as during LED operation at high current densities. These results confirm that arylation of the bridgeheads in ladder-type polyphenylenes is a key element in designing stable blue materials.

Experimental Section

All solvents were purified and freshly distilled prior to use according to literature procedures. Dimethyl 2,5-dibromoterephthalate (**9**) was synthesized according to a literature procedure. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 250 (250 and MHz, respectively). UV–vis data were recorded on a Perkin-Elmer Lambda 9. Gel permeation chromatography (GPC) analysis was performed with PL gel columns (10^3 and 10^4 Å pore widths) connected to a UV–vis detector against poly-*p*-phenylene and polystyrene standards with narrow weight distribution.

UV–vis transmission spectra were measured using a Perkin-Elmer Lambda 9 spectrophotometer. PL emission and excitation spectra were recorded using a Shimadzu RF5301 spectrofluorometer or a SPEX Fluorolog 2 Type 212 spectrometer.

The ITO-covered glass substrates for the PLEDs were thoroughly cleaned in a variety of organic solvents and exposed to an oxygen plasma dry cleaning step. PEDOT:PSS (Baytron P from Bayer Inc.) layers were spin-coated under ambient conditions and dried according to specifications by Bayer Inc. under an inert atmosphere. The emissive polymer films were spin-cast from solution and dried at 80 °C overnight in vacuo. Metal electrodes were thermally deposited in a custom made Balzers MED010 vacuum coating unit at base pressures of below 2×10^{-6} mbar.

EL spectra were recorded using an ORIEL spectrometer with an attached CCD camera. The current/luminance/voltage (ILV) characteristics were recorded in a customized setup using a Keithley 236 source measure unit for recording the current/voltage characteristics while recording the luminance using a calibrated photodiode attached to an integrating sphere (Ulbrich).

4′-Trimethylsilylbiphenyl-2-carboxylic Acid Methyl Ester (6). 2-Bromomethylbenzoate (2.78 mL, 19.80 mmol) 4-trimethylsilylphenylboronic acid (5.00 g, 25.75 mmol), and K_2CO_3 (3.56 g, 25.75 mmol) were mixed with 30 mL of H_2O and 60 mL of THF in a 250 mL Schlenk flask. The solution was purged with argon for 10 min, and then $Pd(PPh_3)_4$ (458 mg, 0.40 mmol) was added and the reaction heated for 16 h at 80 °C. Removal of solvent followed by chromatography on silica using 0–4% ethyl acetate in hexane as eluent gave the ester **6** as a colorless solid (5.48 g, 97%). ^{1}H NMR: δ 7.72 (dd, J = 7.3 Hz, 1.0 Hz, 1H) 7.48 (m, 3H) 7.38–7.29 (m, 2H) 7.23 (m, 2H) 3.59 (s, 3H) 0.24 ppm (s, 9H). ^{13}C NMR: δ 170.21, 143.71, 143.03, 140.61, 134.49 (2 peaks), 132.63, 132.40, 132.18, 131.05, 129.11 (2 peaks), 128.58, 53.22, 0.01 ppm. Elemental analysis: Calcd: C, 71.79; H, 7.09. Found: C, 71.59; H, 7.13

Synthesis of 2-Bromo-9,9-bis(4-octylphenyl)-9*H*-fluorene (7). (**a**) 4-Octylbromobenzene (7.10 g, 26.37 mmol) was dissolved in 50 mL of dry THF and cooled to −78 °C in an acetone/dry ice bath. Then *n*-butyllithium (17.0 mL of 1.6 M solution in hexanes, 27.25 mmol) was added dropwise, and the mixture was stirred for 20 min. To this, a solution of **6** (2.50 g, 8.79 mmol) in 20 mL of dry THF was added dropwise, and the reaction was stirred overnight. The reaction was then quenched with brine and extracted into ether, and the extract was washed with brine and dried over $MgSO_4$. The crude product was chromatographed on silica using 0–3% ethyl acetate in hexane as eluent, to give the adduct (bis(4-octylphenyl)-(4′-trimethylsilylbiphenyl-2-yl)methanol) as a colorless viscous oil (5.39 g, 95%). FDMS: m/z = 632.10 (M + H_2O). ^{1}H NMR: δ 7.32–7.15 (m, 4H) 7.11–7.00 (m, 9H) 6.80 (m, 3H) 2.86 (s, 1H) 2.61 (t, J = 7.6 Hz, 4H) 1.62 (pentet, J = 7.3 Hz, 4H) 1.32 (m, 20H) 0.88 (t, J = 6.6 Hz, 6H) 0.25 ppm (s, 9H). ^{13}C NMR: δ 147.08, 146.56, 144.22, 143.37, 142.58, 140.73, 134.31, 133.80, 131.41, 130.16, 129.33, 129.21, 128.23, 127.74, 84.60, 36.97, 33.43, 33.11, 33.06, 31.02, 30.82, 24.19, 15.39, −0.01 ppm.

(**b**) To bis(4-octylphenyl)-(4′-trimethylsilylbiphenyl-2-yl)-methanol (5.30 g, 8.19 mmol) in 165 mL of THF, sodium acetate (672 mg, 8.19 mmol) was added, and the mixture was cooled to 0 °C. Then Br_2 (2.74 g, 16.38 mmol) was added, and the mixture was stirred for 20 min. Then triethylamine (3.34 g, 32.80 mmol) was added followed by 1.0 M sodium sulfite solution. The product was extracted into ether, and the extract was washed with brine and dried over $MgSO_4$. Since mass spectrometry indicated there was partial ring closure of the product to form the fluorene derivative, the crude product was used in the next step. The crude bromide was dissolved in 20 mL of dichloromethane and 0.20 mL of BF_3·etherate was added. The reaction was stirred overnight and then quenched with methanol. After removal of solvent, the crude product was chromatographed on silica using hexane as eluent to give **7** (3.65 g, 72% for 2 steps). FDMS: *m/z* 622.10. ^{1}H NMR: δ 7.75 (d, $J = 8.2$ Hz, 1H) 7.66 (dd, $J = 7.9$ Hz, 0.6 Hz) 7.50 (m, 2H) 7.35 (m, 3H) 7.05 (m, 8H) 2.55 (t, $J = 7.6$ Hz, 4H) 1.56 (m, 4H) 1.36−1.26 (m, 20H) 0.87 ppm (t, $J = 6.9$ Hz, 6H).

2-[9,9-Bis(4-octylphenyl)-9*H*-fluorene-2-yl]-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (8). A solution of the bromide **7** (2.00 g, 3.21 mmol) in 60 mL of dry THF was cooled to −78 °C. Then, 2.21 mL of 1.6 M *n*-butyllithium was added, and the mixture was stirred for 20 min. To this, 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (0.84 g, 4.49 mmol) was added, and the reaction was stirred overnight. After 16 h, the reaction was quenched with saturated salt, the product was extracted into ether, and the extract was washed with brine and dried over $MgSO_4$. After removal of solvent, the residue was chromatographed on silica using 0−2% ethyl acetate in hexane as eluent to isolate the boronate **8** as a colorless solid (1.68 g, 78%). FDMS: *m/z* 669.10 ^{1}H NMR: δ 7.85 (m, 4H) 7.46−7.31 (m, 3H) 7.14 (m, 8H) 2.61 (t, $J = 7.6$ Hz, 4H) 1.63 (pentet, $J = 7.3$ Hz, 4H) 1.37 (m, 32H) 0.95 ppm (t, $J = 6.9$ Hz, 6H). ^{13}C NMR: δ 153.15, 151.77, 143.80, 142.33, 140.59, 134.94, 132.68, 129.02, 128.76, 128.25, 126.95, 121.42, 120.37, 84.60, 65.75, 36.30, 32.74, 32.34, 30.31, 30.09, 25.55, 25.48, 23.52, 14.74 ppm.

Synthesis of the Pentaphenylene Diester 10. Dimethyl 2,5-dibromoterephthalate (**9**) (346 mg, 0.98 mmol), the boronate **8** (1.58 g, 2.36 mmol), and K_2CO_3 (327 mg, 2.36 mmol) were dissolved in 30 mL of THF and 10 mL of H_2O in a Schlenk flask. The reaction was purged with argon for 15 min, and then tetrakis(triphenylphosphine)palladium (45 mg, 0.04 equiv) was added and the reaction was heated at 85 °C for 14 h. Removal of solvent followed by chromatography on silica using 0−4% ethyl acetate in hexane as eluent gave the pentaphenylene diester **10** as a white solid (1.14 g, 91%). FDMS: *m/z* 1276.40. ^{1}H NMR: δ 7.87 (d, $J = 7.9$ Hz, 2H) 7.83 (d, $J = 7.9$ Hz, 2H) 7.78 (s, 2H) 7.45−7.31 (m, 10H) 7.07 (m, 16H) 3.4 (s, 6H) 2.54 (t, $J = 7.6$ Hz, 8H) 1.56 (pentet, $J = 7.0$ Hz, 8H) 1.28 (m, 40H) 0.88 ppm (t, $J = 6.3$ Hz, 12H). ^{13}C NMR: δ 168.83, 152.69, 152.32, 143.77, 142.36, 141.57, 140.51, 140.33, 140.02, 134.21, 132.54, 129.02, 128.70, 128.64, 128.39, 128.29, 127.15, 126.88, 121.14, 120.9865.76, 52.73, 36.21, 32.66, 32.30, 30.22 (2 peaks), 30.02, 23.44, 14.64 ppm. Elemental Analysis: Calcd: C, 86.61; H, 8.37. Found: C, 86.63; H, 8.41.

Synthesis of the Pentaphenylene 11. A solution of 4-octylbromobenzene (1.35 g, 5.01 mmol) in 50 mL of dry THF was cooled to −78 °C. Then 3.20 mL of 1.6 M *n*-butyllithium was added and stirred for 20 min. To this, the diester **10** (1.07 g, 0.84 mmol) was added dropwise, and the mixture was stirred overnight. FDMS analysis of the reaction showed formation of the desired diol at *m/z* 1971.80 together with small amounts of ring closed products. Hence, the crude product after workup was used as such in the next step. This crude product was dissolved in 30 mL of dichloromethane, and 0.20 mL of BF_3·etherate was added. The colorless solution turned dark brown instantaneously and then became light yellow after 10 min. The reaction was quenched with methanol, and the product was recovered by chromatography on silica using 0−2% ethyl acetate in hexane to isolate **11** as a white solid (1.43 g, 92% for 2 steps). FDMS: *m/z* 1937.20. ^{1}H NMR: δ 7.71−7.64 (m, 8H), 7.34−6.97 (m, 38H), 2.54 (m, 16H), 1.57 (m, 16H), 1.40−1.15 (m, 80H), 0.88 ppm (t, 24H, $J = 6.30$ Hz). Elemental Analysis: Calcd: C, 90.53; H, 9.47. Found: C, 90.61; H, 9.45

Synthesis of the Monomer 12. Pentaphenylene **11** (1.10 g, 0.57 mmol) was dissolved in 30 mL of carbon tetrachloride and cooled in an ice bath. Then Br_2 liquid (0.22 g, 1.36 mmol) was added and stirred for 14 h. FDMS analysis showed the formation of the dibromide quantitatively at *m/z* 2095.00. The reaction was quenched with sodium sulfite solution and worked up to obtain a crude product which was recrystallized from THF and ethanol (product was first dissolved in 50 mL of THF and then 100 mL of ethanol was added). The dibromide **12** was isolated as light yellow needles (1.16 g, 98%). ^{1}H NMR: 7.70 (s, 2H) 7.65 (s, 2H) 7.64 (s, 2H) 7.54 (d, $J = 7.9$ Hz, 2H) 7.44 (m, 4H) 7.21−7.04 (m, 32H) 2.56 (t, $J = 7.6$ Hz) 1.58 (m, 16H) 1.42−1.19 (m, 80H) 0.89 ppm (t, $J = 6.0$ Hz, 24H). Elemental Analysis: Calcd: C, 83.71; H, 8.66. Found: C, 83.75; H, 8.71

The bromination was also carried out using $CuBr_2$ on alumina although this reaction was slow compared to that using of Br_2.

Synthesis of the Pentaphenylene Polymer 5. A mixture of bis(1,5-cyclooctadiene)nickel(0) (221 mg, 0.80 mmol), cyclooctadiene (0.10 mL, 0.80 mmol), 2,2′-bipyridine (125 mg, 0.80 mmol), DMF (5 mL), and toluene (3 mL) in a Schlenk flask was heated at 60 °C for 20 min. Then the monomer (0.70 g, 0.33 mmol) dissolved in 12 mL of toluene was added dropwise, and the reaction was heated at 75 °C for 48 h. Bromobenzene (0.10 mL) was then added, and the reaction mixture was heated for an additional 6 h. The reaction mixture was poured dropwise into 250 mL of methanol whereupon the polymer precipitated out as pellets. The polymer was filtered off and then suspended in 300 mL of 1:1 methanol and concentrated HCl for 6 h. The dried polymer was then subjected to Soxhlet extraction with acetone for 24 h and then redissolved in 30 mL of THF. This was then added dropwise to a mixture of 150 mL of methanol and 150 mL of 25% aqueous ammonia. The precipitated polymer **5** was filtered off, washed with methanol, and dried to give a yellow solid (555 mg, 86%). GPC analysis: $M_n = 2.83 \times 10^4$; $D = 2.65$ (PPP standard), and $M_n = 4.45 \times 10^4$; $D = 3.53$ (PS standard). TGA analysis: stable up to 350 °C.

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Supporting Information Available: TGA and DSC thermograms for polymer **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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