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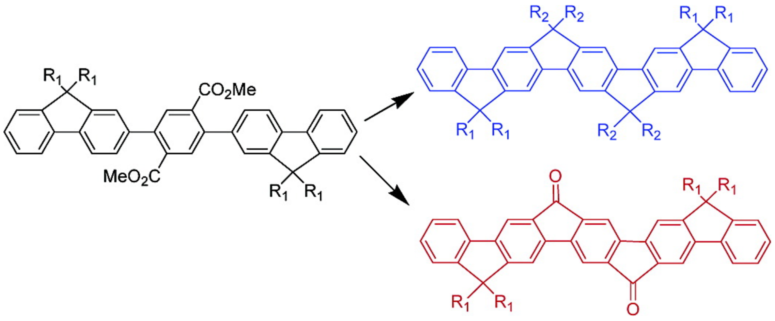
*J. Am. Chem. Soc.*, **2004**, 126 (22), 6987-6995 • DOI: 10.1021/ja0398823



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# Ladder-Type Pentaphenylenes and Their Polymers: Efficient Blue-Light Emitters and Electron-Accepting Materials via a Common Intermediate

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***Abstract:*** A new route to ladder-type pentaphenylenes has been developed in which both good hole-accepting p-type and electron-accepting n-type materials can be prepared from a common intermediate. This key intermediate is a pentaphenylene diester **5** obtained in high yield by Suzuki coupling of 2 equiv of fluorene boronates with 2,5-dibromoterephthalate. Addition of aryllithium followed by ring closure with boron trifluoride produced a blue-emitting ladder-type pentaphenylene. Bromination followed by reductive polymerization with nickel(0) gave new high molecular mass polymers, which show efficient blue emission with a very small Stokes shift. These polymers bridge the gap in emission between polyfluorenes and fully ladder-type polyphenylenes. An alternative ring closure of the dibromopentaphenylene diester **14** with acid made a diketone that is a good electron-accepting material, as it displays a reversible two-electron reduction. The reduction onset potential of $-0.875$ V against Ag/Ag$^+$ corresponds to a lowest unoccupied molecular orbital (LUMO) energy level of 3.53 eV, comparable to the work function of magnesium, suggesting that this unit could be used to greatly increase the injection of electrons into polymers containing it in a light-emitting diode (LED) or solar cell. A red-emitting material was prepared by Suzuki coupling of the dibromopentaphenylene **10b** with a perylene dye, thus offering the prospect of tuning the emission from pentaphenylene materials over the whole visible range by attachment of suitable dyes. Unoptimized single-layer organic LEDs that used **11b** showed stable pure-blue emission with brightnesses of over 200 cd/m$^2$ at 7 V, with moderate efficiencies.

## Introduction

Conjugated organic oligomers and polymers are the subject of considerable current interest as potential active materials in electronic applications such as organic light-emitting diodes (OLEDs),[1,2] plastic lasers,[3] photovoltaic devices (solar cells),[4] and field-effect transistors.[5] Two of the most important goals of research on organic materials for electronic applications are the obtaining of stable blue emission,[6] which is particularly required for full-color displays, and the preparation of good electron-accepting and -transporting (n-type) materials. Most organic materials are p-type materials, which accept and transport holes better than electrons, but n-type materials are urgently needed for use in n-type transistors, as the electron-accepting components in photovoltaic devices, and to increase the efficiency of LEDs by improving electron injection and transport.

Phenylene-based polymers are one of the most important classes of conjugated materials for electronic applications. In particular they are of great interest as potential blue-emitting materials in applications such as LEDs and polymer lasers. Three classes of polyphenylenes that have been of particular interest are polyfluorenes (PF, **1**),[7] polyindenofluorenes (PIF, **2**),[8,9] and ladder-type poly-*p*-phenylenes (LPPP, **3**)[10] (Figure 1). These materials all show efficient blue or blue-green emission in solution with the emission color red-shifting as the chain rigidity increases from 420 nm for **1**, through 430 nm for **2**, to 450 nm for **3**. However, the blue emission in the solid state is unstable, due to the rapid appearance of long-wavelength emission bands.[7,9,10] These were initially assigned to aggregation of the polymer chains,[7,9,11] but more recently it has been shown that

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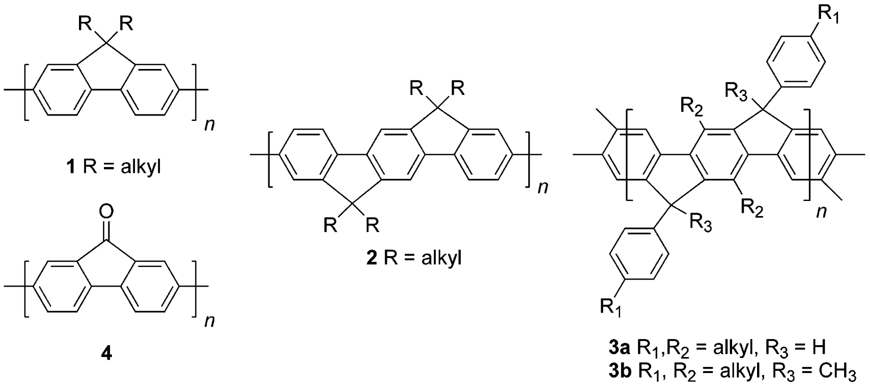

***Figure 1.*** Polyphenylene-based conjugated polymers.

the emission from PFs arises from emissive fluorenone defects formed by oxidation at the methine bridge.[12] There is also evidence suggesting that similar ketone defects may be responsible for the long-wavelength emission from PIF[13] and LPPP.[14]

Substitution of the bridgehead hydrogens in LPPP (**3a**) with methyl groups to give Me-LPPP (**3b**)[10] leads to suppression of the long-wavelength emission seen for **3a** but unfortunately also red-shifts the emission, so that **3b** is a blue-green emitter with an emission maximum at 470 nm. We have shown that attachment of aryl substituents to the bridgehead positions of PFs[15,16] and PIFs[17] suppresses the long-wavelength emission, due to both a lower susceptibility of the materials to oxidation and a reduction of exciton migration to any defect sites that might be formed. However, the emission maxima for these materials are around 425−435 nm, where the eye is not particularly sensitive, and an emission maximum around 440−450 nm is more desirable for maximum apparent brightness, i.e., better conversion of charge carriers to light observable by the human eye. A structure intermediate between PIF and Me-LPPP would show an emission maximum in this region. A suitable polymer is thus one in which the repeating unit is a bridged pentaphenylene. Such units have been prepared by Scherf and Grimme[18] and by Xia and Advincula[19] and reported to show photoluminescence (PL) emission maxima close to 430 nm, suggesting an emission maximum for the corresponding polymer of around 440 nm.

A second problem with phenylene-based polymers is that of charge injection due to the large differences between the energy levels for the polymer orbitals and the work functions of typical electrode materials. It has been previously shown that the hole injection into PFs can be improved by incorporation of triarylamine units within the chain[20] as end-capping units[21] or as side chains.[16] However, the problem of improving the electron-accepting properties remains. We have previously demonstrated that poly(9-fluorenone) (**4**) is a good electron-accepting material,[22] but this polymer is insoluble and has to be prepared by acid treatment of a polyketal precursor, which leads to problems in device fabrication as the material must be dedoped lest residual acid damage the electrodes. A soluble analogue of **4** would thus be a potential electron-transporting/emissive material. We anticipated that a ladder-type pentaphenyl with one or two ketone groups at the bridges would show good electron-accepting properties and that the polymer should be soluble.

We chose the pentaphenylene diester **5** (Figure 2) as the key intermediate in our new synthesis of ladder-type pentaphenylenes. We foresaw that this could be readily converted into a blue-emitting p-type compound **6**, intended as a monomer for a blue-emitting polymer, and into a diketone **7**, which we expected to be a good electron-accepting (n-type) material. In this way one could facilely prepare p- or n-type materials from a common intermediate.

We now report the short, efficient synthesis of the desired ladder-type pentaphenylenes, a blue-emitting polymer based on **6**, and an electron-accepting copolymer containing the diketone **7**.

## Results and Discussion

The synthesis of the blue-emitting monomer is shown in Scheme 1. Suzuki coupling of the fluorene-2-boronate ester **8** with the dibromoterephthalate **9** generated the key intermediate, the pentaphenylenediester **5**, in 92% yield. Addition of an excess of 4-alkylphenyllithium produced a diol that was facilely ring-closed by use of $BF_3$ etherate to generate the ladder-type pentaphenylenes **6a** (73%) and **6b** (95%). Bromination of **6** by $CuBr_2$ on alumina[23] gave the monomers **10a** (56%) and **10b** (91%). The polymers **11** were synthesized by a nickel(0)-mediated Yamamoto-type polymerization. Polymer **11a** had only limited solubility in tetrahydrofuran (THF), toluene, and dichlo-

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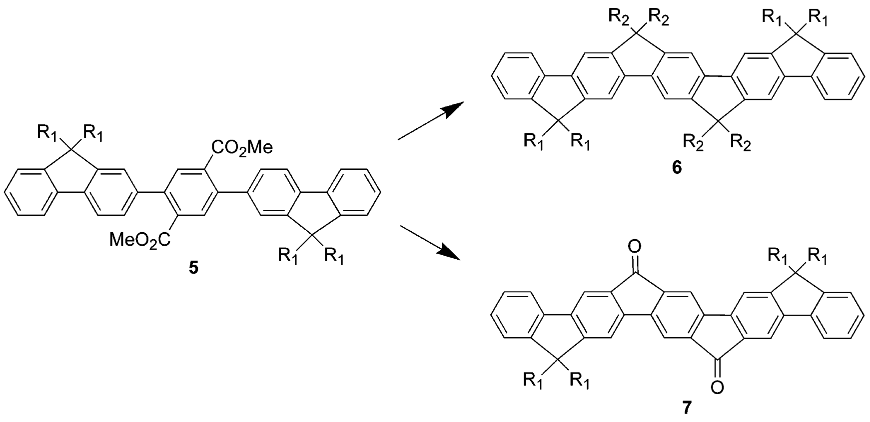
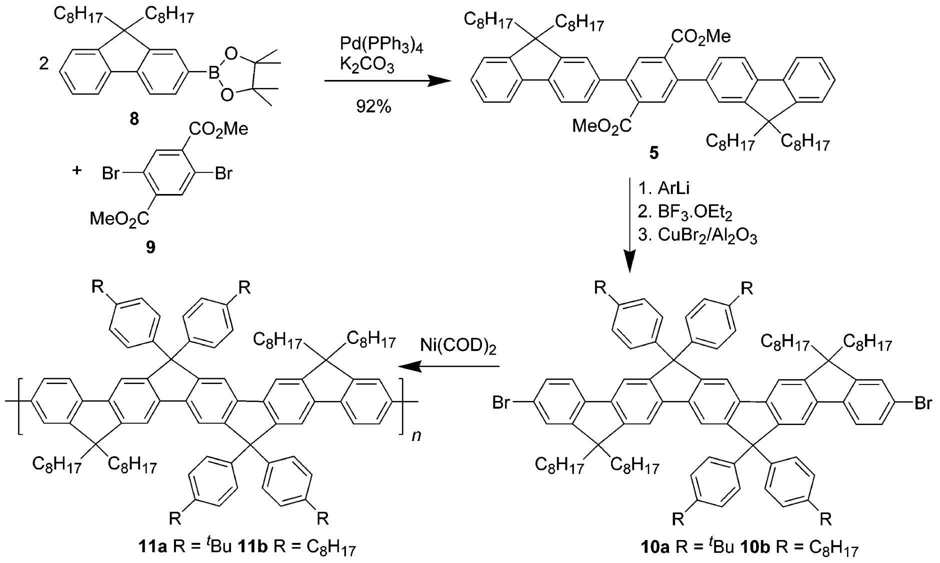


***Figure 2.*** Pentaphenylene monomers and the key intermediate in their synthesis.

***Scheme 1.*** Synthesis of Poly(pentaphenylene)s **11**



romethane, but **11b** was readily soluble in all these solvents. Gel-permeation chromatography (GPC) analysis with PPP (poly-*p*-phenylene) standards showed number-averaged molecular masses ($M_n$) of 4.38 × $10^4$ and 1.36 × $10^5$ for **11a** and **11b**, respectively, corresponding to degrees of polymerization of about 31 and 83, with polydispersities of 3.27 and 2.19.

The presence of bridgehead hydrogens due to incomplete alkylation has been shown to promote the formation of ketone defects in polyfluorenes,[12a] and so we tested the starting fluorene derivative and the pentaphenylenes **6** for their presence. We have found that upon addition of butyllithium to incompletely alkylated fluorenes in dry THF the appearance of the distinct red color of a fluorenyl anion can be clearly seen, even when the bridgehead hydrogens are not detectable by NMR, thus providing a simple but effective qualitative test for incomplete alkylation of fluorenes. No such color change was seen during the preparation of the boronate **8**, which we take as good evidence that there are no residual bridgehead hydrogens present in **8**. We also observed no color change upon testing solutions of the pentaphenylenes **6** with butyllithium, from which we conclude that they contain no detectable bridgehead hydrogens. Furthermore, no evidence of ketones was seen in the Fourier transform infrared (FTIR) spectra of the polymers **11**.

As expected, the optical properties of the polymers **11** were intermediate between those of PIF and LPPP. The solution absorption and emission spectra of **11b** are given in Figure 3. The polymers displayed blue photoluminescence (PL) in solution and both polymers **11a** and **11b** had an absorption maximum at 434 nm and an emission maximum at 445 nm. The optical properties are very similar to those of LPPP, with a very small Stokes shift between the absorption (434 nm) and emission (445 nm) maxima, indicative of the high degree of rigidity of the

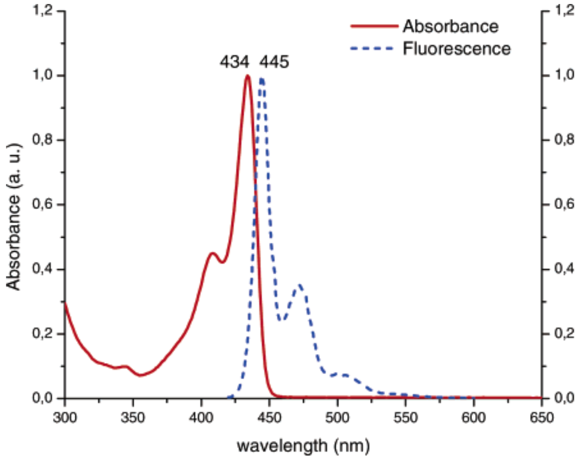
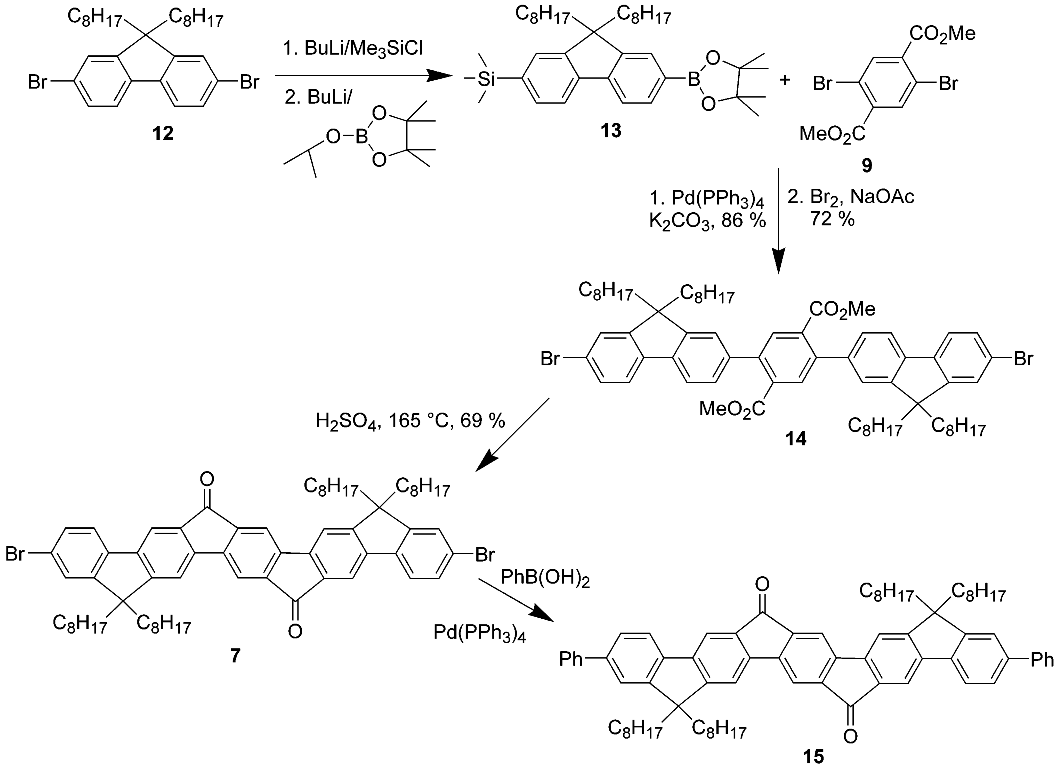


***Figure 3.*** Absorption and emission spectra of polymer **11b** in solution (THF).

*Scheme 2.* Synthesis of Pentaphenylenedione **15**



structure. A secondary emission peak is seen around 470 nm with a slight tail into the yellow region of the spectrum. The position of the emission maximum lies about midway between those of PIF (434 nm) and LPPP (450 nm), so that with these polymers the gap between unbridged and ladder-type polyphenylenes has been closed.

When the absorption and emission spectra of polymer **11b** in film (Figure 4) and solution (Figure 3) are compared, very similar spectra with no bathochromic shift are observed. This, together with the observation of a small Stokes shift, is not unexpected due to the ladder-type structure of the polymer backbone. The photoinduced absorption (PA) spectrum displays remarkable similarities to those of polymers **1** and **3b**,[24] with distinct features at 900, 700, and 620 nm. Given the similarity in the chemical structures of polymers **3b** and **11b**, the feature at 900 nm is assigned to a triplet−triplet absorption, whereas the features at 700 and 620 nm are assigned to the absorption of a polaron and its vibronic progression.

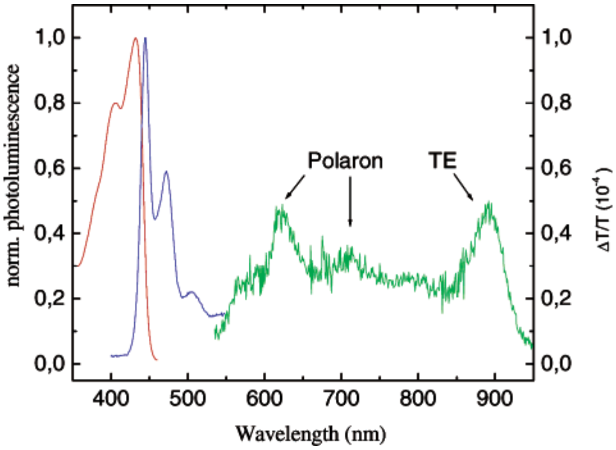


*Figure 4.* Photoluminescence excitation (red), emission (blue), and photoinduced absorption (green) spectra of polymer **11b** film.

Moreover, when the relative intensities of the PA signals are analyzed as compared to films of polymer **3b** recorded under comparable conditions (excitation density, film thickness, temperature),[25] it has to be noted that polymer **11b** does show a dramatically lower polaron as well as triplet exciton steady-state density under similar conditions. This is attributed to the fact that polymer **11b** does possess a low energetic disorder in the bulk material, which is also reflected in the steep onset of PL in the films. Since a high steady-state polaron as well as triplet exciton density represents a serious drawback in OLED and solid-state laser applications due to nonradiative quenching of singlet excitons at trapped polarons and triplet excitons,[25,26] polymer **11b** is thus a promising candidate for such applications.

As the bromination of the pentaphenylene **6b** requires careful monitoring to avoid overbromination, we investigated the possibility of using a trimethylsilyl group as a synthon to permit controlled introduction of the bromines (Scheme 2). 2,7-Dibromo-9,9-dioctylfluorene (**12**) was converted via the monosilyl compound to the boronate **13**. Again no evidence of residual bridgehead hydrogens was seen during the addition of butyllithium to **12**.

Suzuki coupling of this with the terephthalate **9** gave a crude disilylpentaphenylene in 86% yield. We found that it was not possible to satisfactorily purify this compound, and so the crude product was converted to the dibromide **14** with sodium acetate and bromine (72%). Because the bromodesilylation occurs far

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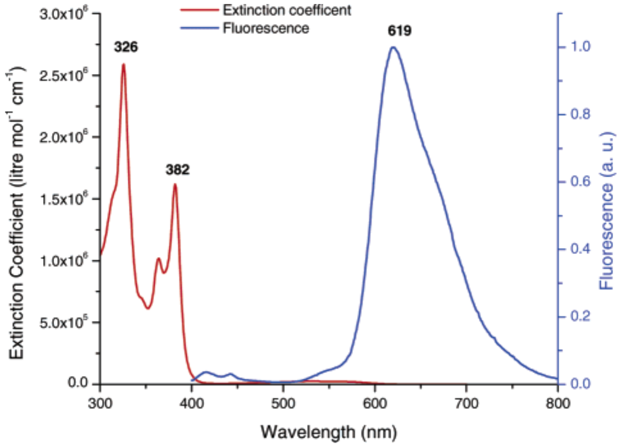

***Figure 5.*** Absorption and emission spectra of **7** in THF.

more quickly than the uncatalyzed bromination of the pentaphenylene, by stopping the reaction immediately after the bromodesilylation was complete we avoided any overbromination of **14**. The monomers **10** could then be obtained by addition of aryllithium and ring closure, but in view of the longer synthesis and lower overall yield, this route is inferior to that previously described. Treatment of **14** with concentrated sulfuric acid at 165 °C was found to induce a double intramolecular Friedel−Crafts acylation to produce the desired diketone **7** in 69% yield. By contrast, treatment of the unbrominated diester **5** under the same condition gave incomplete ring closure. Figure 5 shows the optical properties of **7** in solution. The unusually large gap between the absorption and emission maxima we interpret as arising from the presence of two chromophore units—the pentaphenylene backbone and the aryldiketone system. The absorption spectrum closely matches that for **6**, indicating that the absorption is from the former, but the expected emission around 400 nm is very weak, and instead the major emission occurs at 619 nm from the diketone system, with a corresponding weak absorption band at 550 nm, due to internal energy transfer between the two systems. More detailed studies including polarized absorption and emission measurements are underway to confirm this hypothesis.

To investigate the redox properties of this system, we treated **7** with an excess of benzeneboronic acid under Suzuki coupling conditions to obtain the model compound **15**. Cyclic voltammetry was performed on **15** against Ag/AgCl with a ferrocene/ferrocenium internal standard[27] (Figure 6). The diketone showed fully reversible p- and n-doping, with two reduction peaks at $-1.0$ and $-1.35$ V, which we assign to the reduction of the diketone to a quinonoidal dianion, and an oxidation peak at 1.46 V. The onsets for reduction and oxidation occurred at $-0.875$ and 1.31 V, from which we estimate the lowest unoccupied and highest occupied molecular orbital (LUMO and HOMO) energy levels to be 3.53 and 5.71 eV, respectively, given an energy level of 4.4 eV for Ag/AgCl.[7] This corresponds to an electrochemical band gap of 2.18 eV. The estimated LUMO energy means that there should be small barriers to injection of electrons into materials containing this unit from relatively air-stable metals such as magnesium (work function 3.7 eV) or aluminum (4.2 eV), thus obviating the need to use unstable low work function metals such as calcium as cathodes. Polymerization of **7** with nickel(0) gave an insoluble material, but copolymerization of **7** (20 mol %) with **6** produced a soluble polymer with good electron-accepting properties that is currently being evaluated as an electron-accepting component in photovoltaic devices. The results of those investigations will be published separately.

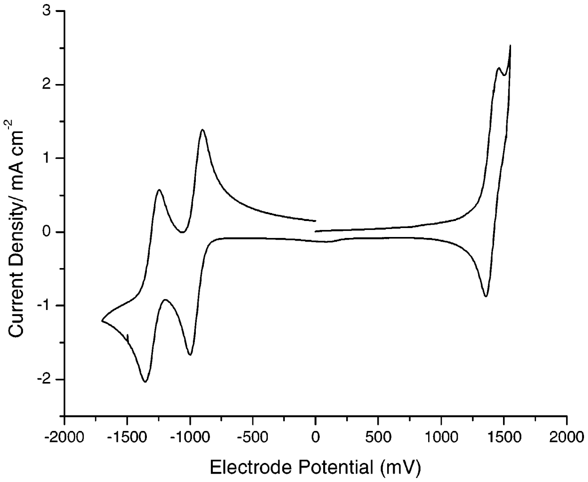

***Figure 6.*** CV of diketone **15**.

The pentaphenylenes **10** are blue emitters with PL maxima at 424 nm in solution. We have previously shown that efficient tuning of EL emission from polyfluorenes across the visible spectrum can be accomplished by introduction of perylene dyes into the polymer chain.[28] Since the emission maxima of **10** are close to those of polyfluorenes (425 nm), we anticipated that equally efficient energy transfer would occur if they were to be substituted with such dyes. Accordingly, we treated **10b** with a slight excess of the perylene boronate **16** in a Suzuki-type coupling (Scheme 3). The chromatographically purified product was confirmed by NMR and matrix-assisted laser desorption ionization time-of-flight spectroscopy (MALDI-TOF) to be the diadduct **17**. Figure 7 shows the optical properties of **17** measured in THF. The absorption from the pentaphenylene backbone is characterized by the maximum at 397 nm, and the absorption from the dye, by the maximum at 520 nm. As evidenced from Figure 7, there is some energy transfer in solution from the pentaphenylene core to the dye as the relative intensity of the emission maxima for the dye at 620 nm is greater than the relative intensity of the dye's absorption maximum. This is in contrast to the behavior of the fluorene−perylene copolymers mentioned above, where no energy transfer was seen in solution,[28] but this is explicable by the much lower amounts of dye (only 1−5 mol %) present in those materials. As in the aforementioned polymers, the solid-state PL shows that nearly complete energy transfer occurs so that the emission is almost exclusively from the dye. In addition to being a potential red-emitting material for LEDs or polymer lasers, this material is a suitable substrate for single-molecule spectroscopy experiments to probe the energy transfer processes between the chromophores.[29] Such studies are now underway and will be reported separately. By attaching different dyes to **10b**, it should be

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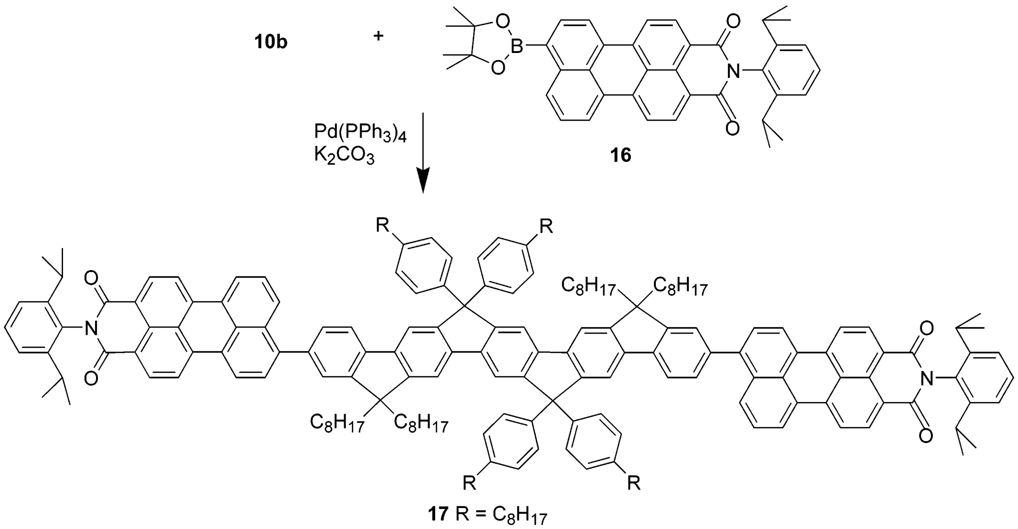
***Scheme 3.*** Synthesis of Dye-Substituted Pentaphenylene



possible to tune the emission color from blue to red or even into the near-infrared, and this is currently under investigation.

**Electroluminescence Measurements on Polymer 11b.** LEDs were prepared with configuration indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS)/**11b**/Ca/Al. As seen in Figure 8, the best devices showed blue emission (CIE[30] coordinates 0.17, 0.09) with a luminance of over 200 cd/m$^2$ that was stable during several minutes of operation at 6−7 V ($j$ = 78 mA) in a glovebox environment. As compared to devices fabricated from polymers **1** or **2** under identical conditions, no oxidative degradation of the polymer, i.e., the formation of keto-type defects and a corresponding emission band around 530 nm, could be observed. Best results were obtained from devices with rather thin emissive layers of ca. 50 nm. Thicker emissive layers not only produced devices with lower efficiencies but also caused rather strong self-absorption, resulting in less pure blue emission. However, these unoptimized single-layer devices show high leaking currents in reverse bias and only moderate efficiencies (0.25−0.5 cd/A), indicating that electron-transporting layers are required to obtain maximum efficiency. Investigations into device optimization are underway and will be reported separately.

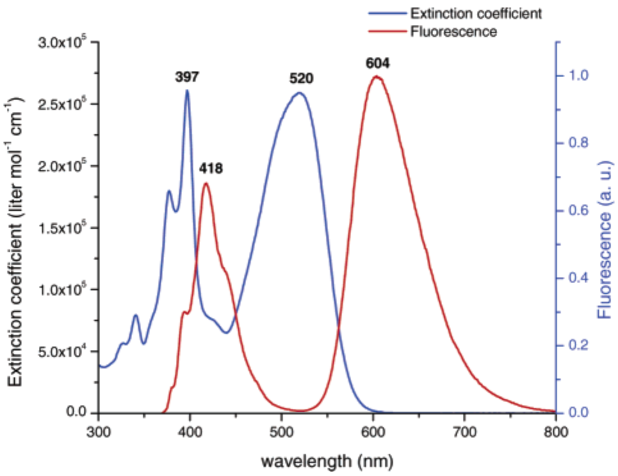


***Figure 7.*** Absorption and emission spectra of **17** in solution (THF).

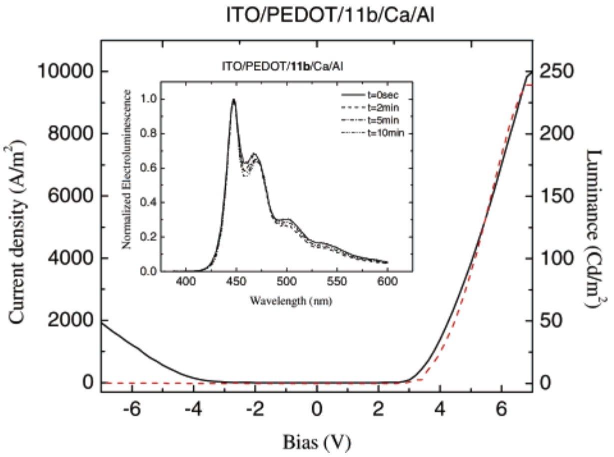


***Figure 8.*** Luminance (dashed line) and current density (solid line) from ITO/PEDOT:PSS/**11b**/Ca/Al. (Inset) Electroluminescence spectra from the same OLED.

**Electroluminescence Optimized to the Sensitivity of the Human Eye.** Figure 9 shows a comparison of the typical electroluminescence spectra obtained for polymers **1**, **2**, **3b**, and **11b** and a plot of the eye-sensitivity curve. As one can see, the EL spectrum of **1** hardly overlaps at all with the region where the eye is sensitive to light, meaning that for this polymer one is generating light in OLEDs that the eye cannot see (such polymers will thus show intrinsically low yields in terms of

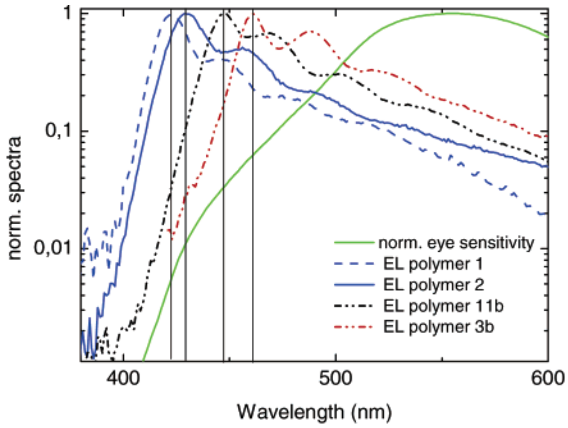


***Figure 9.*** Comparison of the typical electroluminescence spectra obtained for polymers **1**, **2**, **3b**, and **11b** and a plot of the eye-sensitivity curve.

candelas per ampere). Compared to polymer **1**, polymer **2** is already better suited for the human eye. An analysis of the sensitivity curve shows almost twice as high a sensitivity as for the peak emission of polymer **1**. The fact that both polymers give rise to a very similar color impression to the human eye is also well documented in the typical CIE color coordinates,[30] where for polymer **1** one typically finds $x = 0.17$ and $y = 0.14$, compared with $x = 0.18$ and $y = 0.13$ for polymer **2**. On the other hand, the EL spectrum of polymer **3b** which has proven to be rather stable against oxidative degradation, gives rise to a blue-green emission that corresponds to CIE coordinates of $x = 0.20$ and $y = 0.27$, which is already too much in the green spectral region to be utilized in a red−green−blue (RGB) display.

As can be seen from Figure 9, polymer **11b**, which has a chemical structure intermediate between those of polymers **2** and **3b**, has its maximum at a region where the human eye is 3 times as sensitive as for polymer **2** and 6 times as sensitive as for polymer **1**, while producing an emission with CIE coordinates of $x = 0.18$ and $y = 0.17$ that are very close to those of polymers **1** and **2**. Thus polymer **11b** not only has the advantage of being chemically more stable against oxidative degradation in the device but also of generating a sufficiently pure blue emission spectrum optimized to the human eye.

## Conclusions

Ladder-type pentaphenylenes have been prepared by short efficient syntheses via a pentaphenylene intermediate. Addition of aryllithiums followed by ring closure produced monomers for polymers that show bright blue emission with a very small Stokes shift. Coupling of the monomer with a perylene dye offers an efficient method to tune the emission color across the visible spectrum. Treatment of the intermediate with acid gave a diketone that shows good electron-accepting properties. In this way both p- and n-type materials can be readily obtained from a common intermediate. Single-layer OLEDs with **11b** showed stable pure-blue emission with brightnesses of over 200 cd/m$^2$ at 7 V, with efficiencies that leave room for device optimization. These initial results, however, clearly demonstrate that polymer **11b** has considerable potential as an emissive material for stable pure-blue emitting devices due to its having intrinsic advantages over other blue-emitting polymers in terms of its emission matching to the sensitivity of the human eye, being chemically more stable toward oxidative degradation and having a low intrinsic structural defect concentration.

## Experimental Section

All solvents were purified and freshly distilled prior to use according to literature procedures. 9,9-Dioctylfluorene-2-boronate ester **8**, dimethyl 2,5-dibromoterephthalate **9**, and 2,7-dibromo-9,9-dioctylfluorene were synthesized according to literature procedures. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DRX 250 (250 and 62.5 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[31] and polystyrene standards with narrow weight distributions. Cyclic voltammetry was performed on an EG&G Princeton Applied Research potentiostat, model 270, on 2 $\mu$m thick films deposited by solution coating onto precleaned ITO as a working electrode with an area of 0.2 cm$^2$. After being coated, the films were dried in a vacuum oven for 10 min. The measurements were carried out in acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte, with Ag/AgCl as reference electrode and a platinum wire as counterelectrode, respectively, and an internal ferrocene/ferrocenium standard.

The UV absorption measurements were performed on a Perkin-Elmer Lambda 15 spectrophotometer and the PL measurements in solution on a SPEX Fluorolog 2 type 212 steady-state fluorometer. Photoluminescence and excitation spectra of the polymer films were recorded on a Shimadzu RF5301 spectrofluorometer. For the photoinduced absorption measurements, the samples were mounted in a cryostat and cooled to 80 K. A standard halogen lamp operated at 160 W was used as a transmission source and an Ar$^+$ laser operated in multilane UV mode (3.53 eV, 3.41 eV) was used as excitation source.

The ITO/PEDOT-PSS/**11b**/Ca/Al OLEDs were fabricated by spin-casting the filtered PEDOT-PSS suspension onto cleaned ITO substrates and drying the PEDOT-PSS for 1 h in an argon atmosphere at 70 °C and for 2 h in a vacuum at 120 °C, followed by spin-casting of the toluene solutions (4 g/L) of polymer **11b**. After the devices were dried in a vacuum at 110 °C, the top electrodes were deposited by evaporation at a base pressure of $2 \times 10^{-6}$ mbar. Current−voltage characteristics were recorded on a Keithley 236 SMU. The luminance was measured by a Si photodiode in an integrating sphere, and the measured voltage was scaled to the absolute luminance measured with a Minolta LS-100 luminance meter at a single point in the upper part of the represented characteristics. The EL spectra were recorded on an Oriel Multispec CCD spectrometer and have been corrected accordingly.

**Synthesis of the Diester 5.** The boronate ester **8** (4.65 g, 9.0 mmol), diester **9** (1.52 g, 4.39 mmol), and $K_2CO_3$ (1.21 g, 8.8 mmol) were dissolved in THF (40 mL) and water (20 mL) in a 100 mL Schlenk flask. The solution was purged with argon for 20 min, and then tetrakis(triphenylphosphine)palladium (152 mg, 0.03 equiv) was added and the reaction was heated with stirring at 85 °C. The reaction was followed by TLC and after 16 h was worked up. The cooled mixture was extracted with diethyl ether, and the extract was washed with saturated salt and then dried over $MgSO_4$. The crude product so obtained was purified by chromatography on silica with 0−5% ethyl acetate in hexane as eluent. The product **5** was isolated as a thick viscous oil (3.94 g, 92%). $^1$H NMR: ($CD_2Cl_2$) $\delta$ 7.88 (s, 2H), 7.78 (m, 4H), 7.40−7.33 (m, 10H), 3.65 (s, 6H), 2.00 (t, 8H, $J = 8.5$ Hz), 1.21−1.07 (m, 40H), 0.62−0.83 (m, 20H). $^{13}$C NMR: $\delta$ 169.26, 151.74, 151.62, 141.89, 141.56, 141.43, 139.54, 134.37, 132.44, 128.02, 127.82, 127.59, 123.84, 123.73, 120.55, 120.29, 55.96, 52.78, 41.16, 32.54, 30.81, 30.05, 29.99, 24.56, 23.35, 14.58. FDMS: *m*/*z* 971.3 Elemental analysis: calcd C 84.07, H 9.34; found C 84.12, H 9.32.

**Synthesis of the Pentamers 6.** (a) A solution of 4-octylbromobenzene (3.05 mL, 3.4 g, 12.6 mmol) in dry THF (40 mL) in a 250 mL Schlenk flask, was cooled to −78 °C in an acetone/dry ice bath. *n*-Butyllithium in hexane (8.0 mL, 1.6 M, 12.8 mmol) was then added and the mixture was stirred for 20 min. Then a solution of the diester **5** (2.05 g, 2.1 mmol) in dry THF (40 mL) was added dropwise with stirring and the solution was slowly allowed to warm to room temperature. The mixture was stirred overnight and then quenched with brine. The mixture was extracted with diethyl ether, and the extract was washed with salt and dried over $MgSO_4$. The crude product was chromatographed on silica with 0−5% ethyl acetate in hexane as eluent to give the diol as a thick viscous oil. (3.39 g, 96%). $^1$H NMR: $\delta$ 7.61 (m, 2H), 7.45 (d, 2H, $J = 7.6$ Hz), 7.29 (m, 6H), 7.12 (m, 16H), 6.76 (m, 4H), 6.69 (s, 2H), 3.11 (s, 2H), 2.61 (t, 8H, $J = 7.6$ Hz), 1.77−0.45 (m, 128H). $^{13}$C NMR: $\delta$ 151.63, 151.23, 146.41, 144.19, 142.74, 141.71, 141.21, 141.05, 139.29, 136.29, 129.29, 128.76, 128.58, 127.93, 127.48, 124.32, 123.63, 120.35, 120.22, 83.91, 55.75, 40.55, 36.30, 32.72, 32.60, 32.45, 30.73, 30.30, 30.12, 30.09, 30.07, 30.04, 24.56, 23.46, 23.39, 14.65, 14.61. FDMS: *m*/*z* 1668.3.

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(30) CIE Standard Color Matching Functions 1931 2° observer.

(31) Vanhee, S.; Rulkens, R.; Lehmann, U.; Rosenauer, C.; Schulze, M.; Köhler, W.; Wegner, G. *Macromolecules* **1996**, *29*, 5136.

With R′ = *t*-Bu, the corresponding diol is isolated as a colorless solid in 54% yield. $^1$H NMR: $\delta$ 7.64 (m, 2H), 7.47 (d, 2H, $J$ = 7.9 Hz), 7.37−7.13 (m, 20H), 6.79 (d, 4H, $J$ = 7.9 Hz), 6.74 (s, 2H), 3.15 (s, 2H), 1.73−0.84 (m, 96H), 0.45 (m, 8H). $^{13}$C NMR: $\delta$ 151.58, 151.12, 150.90, 146.30, 144.07, 141.81, 141.23, 141.06, 139.05, 136.56, 129.49, 128.64, 127.92, 127.48, 125.48, 124.00, 123.64, 120.45, 120.35, 83.87, 55.72, 40.42, 35.17, 32.59, 31.95, 30.66, 30.01, 24.47, 23.44, 23.39, 14.63. FDMS: $m/z$ = 1442.4.

(b) Ring closure: The diol (3.30 g, 1.98 mmol) was dissolved in dichloromethane (30 mL, used as purchased), and $BF_3$ etherate (0.20 mL) was added with stirring at room temperature. The colorless solution turned deep brown immediately upon addition and became light yellow within minutes. After 10 min, methanol (50 mL) was added to the solution, whereupon the pentamer **6** started to precipitate as a colorless solid. The mixture was stirred for 12 h and then the solid was collected by filtration, washed with methanol, and dried. The product was redissolved in dichloromethane and precipitated again by addition of methanol. Isolated yield of **6b** = 3.06 g (95%). $^1$H NMR: $\delta$ 7.83 (s, 2H), 7.63 (m, 6H), 7.33−7.11 (m, 22H), 2.58 (t, 8H, $J$ = 7.6 Hz), 2.02 (t, 3H, $J$ = 7.9 Hz), 1.63−0.62 (m, 120H). $^{13}$C NMR: $\delta$ 152.80, 152.05, 151.88, 151.55, 144.35, 142.29, 141.83, 140.91, 140.87, 140.25, 129.11, 128.97, 127.63, 127.37, 123.65, 120.34, 118.16, 117.82, 115.35, 65.15, 55.61, 41.39, 36.28, 32.65, 32.55, 32.30, 30.82, 30.30, 30.22, 30.03, 30.01, 29.98, 24.67, 23.43, 23.34, 14.64, 14.60. FDMS: $m/z$ 1633.2. Elemental analysis: calcd C 89.75, H 10.25; found C 89.77, H 10.19.

For R′ = *t*-Bu, yield of **6a** = 73% as a colorless solid. $^1$H NMR: $\delta$ 7.84 (s, 2H), 7.69 (d, 4H, $J$ = 8.4 Hz), 7.61 (m, 2H), 7.34−7.26 (m, 22H), 2.01 (t, 8H, $J$ = 8.2 Hz), 1.29−0.61 (m, 96H). FDMS: $m/z$ 1407.3.

**Synthesis of Monomers 10.** The pentaphenylene **6b** (0.80 g, 0.49 mmol) was added to carbon tetrachloride (30 mL) in a 100 mL round-bottomed flask, followed by $CuBr_2$ on alumina (2.0 g).[23] The reaction was heated under reflux with stirring and monitored by FDMS, which showed nearly quantitative formation of the dibromide after 14 h. The reaction mixture was concentrated, and the residue was loaded on silica and chromatographed on silica with hexane as eluent. The product **10b** was isolated as a light yellow solid (0.80 g, 91%). $^1$H NMR: $\delta$ 7.82 (s, 2H), 7.66 (d, 4H, $J$ = 9.1 Hz), 7.42 (m, 6H), 7.24 (d, 8H, $J$ = 8.2 Hz), 7.12 (d, 8H, $J$ = 8.2 Hz), 2.58 (t, 8H, $J$ = 7.3 Hz), 2.00 (t, 8H, $J$ = 7.6 Hz), 1.59 (m, 8H), 1.31−0.78 (m, 112H). $^{13}$C NMR: $\delta$ 154.19, 152.90, 152.30, 151.23, 144.17, 142.38, 140.97, 140.85, 140.76, 140.69, 130.52, 129.14, 128.95, 126.92, 121.79, 121.51, 118.29, 117.97, 115.44, 65.17, 55.99, 41.28, 36.26, 32.65, 32.53, 32.29, 30.73, 30.69, 30.29, 30.22, 30.00, 29.97, 24.62, 23.43, 23.35, 14.64, 14.60. FDMS: $m/z$ 1780.50. Elemental analysis: calcd C 81.84, H 9.23; found C 81.99, H 9.24.

For R′ = *t*-Bu, isolated yield of **10a** = 56% as a light yellow solid. $^1$H NMR: $\delta$ 7.85 (s, 2H), 7.68 (d, 4H, $J$ = 11 Hz), 7.51−7.25 (m, 22H), 2.01 (t, 8H, $J$ = 6.6 Hz), 1.30−1.07 (m, 76H), 0.82−0.64 (m, 20H). $^{13}$C NMR: $\delta$ 154.21, 152.91, 152.30, 151.26, 150.36, 143.88, 140.94, 140.84, 140.77, 140.69, 130.53, 128.72, 126.92, 126.13, 121.83, 121.56, 118.35, 118.01, 115.54, 64.99, 56.02, 41.28, 35.08, 32.52, 31.86, 30.71, 29.95, 24.61, 24.55, 23.34, 14.59. FDMS: $m/z$ 1565.90. Elemental analysis: calcd C 81.30, H 8.50; found C 81.13, H 8.55.

**Synthesis of Poly(pentaphenylene)s 11.** Bis(cyclooctadiene)nickel (215.0 mg, 2.4 equiv), cyclooctadiene (96 $\mu$L, 2.4 equiv), and 2,2′-bipyridine (122.3 mg, 2.4 equiv) were dissolved in dry toluene (4 mL) and dry *N*,*N*-dimethylformamide (4 mL) in a Schlenk flask within a glovebox. The mixture was heated at 60 °C with stirring under argon for 20 min to generate the catalyst, and then a solution of the dibromide **6b** (584 mg, 0.33 mmol) in dry toluene (8 mL) was added. The reaction was heated at 75 °C for 2 days, whereupon the solution became so viscous that it ceased to stir. Then a mixture of toluene (4 mL) and bromobenzene (0.10 mL) was added and the mixture was heated at 75 °C for an additional 12 h. The mixture was then poured into a mixture of methanol and concentrated hydrochloric acid (1:1, 300 mL) and stirred for 4 h. The precipitated yellow solid was redissolved in THF (40 mL) and added dropwise to methanol (200 mL). The resulting solid was filtered off and subjected to Soxhlet extraction for 2 days in acetone. The residue was then redissolved in THF and precipitated again from methanol, filtered, washed with methanol, and dried. Isolated yield of **11b** = 508 mg (96%). Elemental analysis: calcd C 89.86, H 10.14; found C 89.27, H 10.15. GPC analysis: $M_n = 1.36 \times 10^5$, $M_w = 2.98 \times 10^5$, and $D = 2.19$ (against PPP standard); $M_n = 2.64 \times 10^5$, $M_w = 7.37 \times 10^5$, and $D = 2.79$ (against PS standard).

For R′ = *t*-Bu, starting with 300 mg of the monomer **10a**, the polymer **11a** was isolated in 96% yield. Elemental analysis: calcd C 90.54, H 9.46; found C 89.95, H 9.41. GPC analysis: $M_n = 4.38 \times 10^4$, $M_w = 1.43 \times 10^5$, and $D = 3.27$ (against PPP standard); $M_n = 7.05 \times 10^4$, $M_w = 3.28 \times 10^5$, and $D = 4.65$ (against PS standard).

**Synthesis of 7-Trimethylsilyl-9,9-di-*n*-octylfluorene-2-boronate (13).** *n*-Butyllithium in hexane (6.0 mL, 1.6 M, 9.6 mmol) was added to a solution of 2,7-dibromo-9,9-di-*n*-octylfluorene (**12**) (5.00 g, 9.13 mmol) in dry THF (50 mL) in a Schlenk flask at −78 °C, and the mixture was stirred for 20 min. Then chlorotrimethylsilane (1.5 mL, 1.29 g, 1.3 equiv) was added and the reaction was allowed to slowly warm to room temperature. The mixture was stirred overnight and the reaction was quenched with saturated brine. The product was extracted into diethyl ether, and the extract was washed with brine and dried over $MgSO_4$. The crude product was chromatographed on silica with hexane as eluent to give 2-bromo-7-trimethylsilyl-9,9-di-*n*-octylfluorene as a colorless oil (3.50 g, 71%).

*n*-Butyllithium in hexane (4.4 mL, 1.6 M, mmol) was added to a solution of 2-bromo-7-trimethylsilyl-9,9-di-*n*-octylfluorene (3.47 g, 6.41 mmol) in dry THF (75 mL) in a Schlenk flask at −78 °C, and the mixture was stirred for 20 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.44 mL, 1.31 g, 7.04 mmol) was added and the reaction was stirred for 24 h after warming to room temperature. The reaction was then quenched with brine, and the product was extracted into diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The crude product was chromatographed on silica with 0−3% ethyl acetate in hexane as eluent to give **13** as a colorless solid (2.67 g, 71%). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.73 (m, 4H), 7.51 (m, 2H), 1.99 (t, 4H, $J$ = 8.2 Hz), 1.36−0.54 (m, 42H), 0.31 (s, 9H). $^{13}$C NMR: $\delta$ 151.60, 151.34, 149.76, 145.29, 142.69, 141.07, 134.71, 133.01, 130.08, 129.03, 120.50, 120.25, 84.93, 56.22, 41.26, 33.01, 32.84, 31.11, 30.37, 25.98, 24.95, 23.85, 15.08, 0.01. FDMS: $m/z$ 588.90.

**Synthesis of Dibromopentaphenylene 14.** The boronate ester **13** (2.45 g, 4.16 mmol), the diester **9** (697 mg, 1.98 mmol), and $K_2CO_3$ (821 mg) were dissolved in a mixture of THF (20 mL) and $H_2O$ (10 mL) in a Schlenk flask, and the mixture was purged with argon for 20 min. To this was added tetrakis(triphenylphosphine)palladium (114 mg, 0.05 equiv), and the mixture was heated at 85 °C for 20 h. The cooled mixture was extracted with diethyl ether, and the extract was washed with brine and dried over $MgSO_4$. The residue was chromatographed on silica with 0−3% ethyl acetate in hexane to give the crude disilylpentaphenylene (1.89 g, 86%).

In a Schlenk flask, the diester (1.89 g, 1.69 mmol) was added to dry THF (34 mL) along with anhydrous sodium acetate (278 mg, 2 equiv) and cooled to 0 °C. Bromine (0.37 mL, 1.15 g, 4.2 equiv) was added and the mixture was stirred for 20 min. The reaction was quenched by addition of triethylamine (1.89 mL, 8 equiv), followed by an excess of aqueous $Na_2SO_3$. The product was extracted into diethyl ether, and the extract was washed with sodium sulfite solution and dried over $MgSO_4$. The residue was recrystallized from hot hexane to give the dibromide **14** as shiny colorless crystals (1.37 g, 72%). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.87 (s, 2H), 7.77 (d, 2H, $J$ = 7.9 Hz), 7.64 (d, 2H, $J$ = 7.9 Hz), 7.53−7.31 (m, 8H), 3.64 (s, 6H), 1.99 (t, 8H, $J$ = 8.8 Hz), 1.27−0.62 (m, 60H). $^{13}$C NMR: $\delta$ 169.06, 154.06, 151.27, 141.89, 140.58, 140.49, 140.05, 134.32, 132.51, 130.76, 128.06, 127.04, 123.87, 122.01, 121.96, 120.46, 56.36, 52.82, 41.08, 32.54, 30.74, 30.03, 29.99, 24.52, 23.36, 14.59. FDMS: *m*/*z* 1129.30. Elemental analysis: calcd C 72.33, H 7.85; found C 72.75, H 7.91.

**Synthesis of Dibromopentaphenylenedione 7.** The dibromide **14** (1.37 g) was added to 40 mL of 80% $H_2SO_4$ (made from 4 mL of $H_2O$ and 36 mL of concentrated $H_2SO_4$) and the mixture was heated with stirring at 165 °C for 3 h, during which time the white solid turned brown. The acid was decanted off and the product was extracted into dichloromethane, and the extract was washed with sodium hydrogen carbonate solution and dried over $MgSO_4$. The crude product was purified by chromatography on silica with 0−3% ethyl acetate in hexane as eluent to give the diketone **7** as a gray solid (0.88 g, 69%). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.97 (s, 2H), 7.86 (s, 2H), 7.65−7.49 (m, 8H), 2.03 (t, 8H, $J$ = 8.5 Hz), 1.25−0.62 (m, 60H). $^{13}$C NMR: $\delta$ 192.91, 159.79, 153.77, 146.79, 144.19, 142.53, 140.81, 139.69, 134.70, 131.11, 127.10, 122.66, 122.21, 116.50, 116.38, 116.27, 56.96, 40.88, 32.53, 30.66, 29.97, 29.95, 24.60, 23.37, 14.60. Elemental analysis: calcd C 74.42, H 7.57; found C 74.63, H 7.60.

**Synthesis of 15.** The diketone **7** (127.0 mg, 0.12 mmol), phenylboronic acid (36.5 mg, 0.30 mmol), $K_2CO_3$ (33 mg, 0.24 mmol), tetrahydrofuran (6.0 mL), and water (3.0 mL) were mixed in a Schlenk flask which was purged with argon for 15 min. Tetrakis(triphenylphosphine)palladium (5.5 mg, 5.0 $\mu$mmol) was added and the mixture was heated with stirring for 14 h at 85 °C. The product was extracted into ether, and the extract was washed with saturated brine and dried over $MgSO_4$. The residue was chromatographed on silica with 0−4% ethyl acetate in hexane as eluent to recover **15** as a gray solid (91.0 mg, 72%). $^1$H NMR: $\delta$ 8.02 (s, 2H), 7.86 (s, 2H), 7.83 (d, 2H, $J$ = 7.9 Hz), 7.71−7.62 (m, 10H), 7.49 (t, 4H, $J$ = 6.9 Hz), 7.37 (t, 2H, $J$ = 7.2 Hz), 2.11 (t, 8H, $J$ = 8.4 Hz), 1.18−1.07 (m, 40H), 0.80−0.71 (m, 20H). FDMS: *m*/*z* 1059.0.

**Synthesis of Dye End-Capped Pentaphenylene 17.** The dibromide **10b** (143 mg, 0.08 mmol), peryleneboronate ester **16** (100 mg, 0.16 mmol), $K_2CO_3$ (22 mg, 0.16 mmol), tetrahydrofuran (6 mL), and water (3 mL) were mixed together in a Schlenk flask which was purged with argon for 15 min. Tetrakis(triphenylphosphine)palladium (2.8 mg, 0.002 mmol) was added and the mixture was heated at 80 °C for 16 h. The product was extracted into dichloromethane, and the extract was washed with brine and dried over $MgSO_4$. The crude product was chromatographed on silica with 0−12% ethyl acetate in hexane as eluent to give the diadduct **17** as a red solid (36 mg, 17%). $^1$H NMR: 8.67−8.52 (m, 12H), 8.10 (d, 2H, $J$ = 8.5 Hz), 7.89−7.50 (m, 18H), 7.49−7.15 (m, 20H), 2.78 (septet, 4H, $J$ = 6.6 Hz), 2.61 (t, 8H, $J$ = 7.9 Hz), 2.11 (t, 8H, $J$ = 7.3 Hz), 1.63 (m, 8H), 1.40−1.14 (m, 104H), 0.90−0.78 (m, 32H). $^{13}$C NMR: 164.86, 152.98, 152.37, 152.27, 152.02, 146.93, 144.91, 144.30, 142.40, 141.87, 141.34, 140.95, 140.70, 139.10, 138.62, 138.48, 133.54, 132.67, 132.62, 132.45, 131.41, 130.09, 130.04, 129.55, 129.23, 129.18, 129.11, 129.02, 127.73, 127.70, 125.57, 124.89, 124.77, 124.55, 121.69, 121.53, 121.18, 120.90, 120.55, 118.34, 118.26, 118.18, 115.55, 115.49, 65.24, 55.88, 53.54, 41.36, 36.30, 32.66, 32.57, 32.31, 30.83, 30.30, 30.23, 30.08, 30.00, 29.86, 24.87, 24.49, 23.44, 23.37, 14.64, 14.62. MALDI-TOF: *m*/*z* 2594.0.

**Acknowledgment.** This work was supported by the Bundesministerium für Bildung und Forschung (Projects 13N8165 OLAS and 13N8215 OLED) and by DuPont Displays. J.J. acknowledges the Alexander von Humboldt Stiftung for the grant of a research fellowship. The CDL-AFM is a key member of the long-term AT&S research activities.

JA0398823