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Blue-Emitting Carbon- and Nitrogen-Bridged Poly(ladder-type tetraphenylene)s

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An efficient synthesis has been developed toward two new poly(ladder-type tetraphenylene)s, either with one nitrogen at the bridge-head position or all carbon-bridged, both of which were blue emitters. The two polymers exhibited very narrow emission centered around 445 nm, where the human eye is most sensitive. Polymer light-emitting diodes prepared under inert atmosphere in the standard configuration (indium tin oxide/poly(3,4-ethylenedioxythiophene):polystyrenesulfonic acid/polymer/Ca/Al) demonstrated very high luminance values, typically over 600−900 cd/m^2 at a bias of 10−15 V for the two polymers. The nitrogen-bridged poly(ladder-type tetraphenylene) demonstrated a lower electroluminescence onset voltage and was found to be more stable toward oxidative degradation compared to the all-carbon-bridged analogue, which undergoes oxidative degradation as evidenced by the appearance of a new emission maximum around 575 nm.

Introduction

Conjugated polymers and oligomers are attractive materials for a large range of electronic applications such as organic light-emitting diodes (OLEDs),[1,2] organic field effect transistors (OFETs),[3] polymer lasers,[4] and organic solar cells.[5,6] Phenylene based polymers such as poly(fluorene),[7] poly(indenofluorene),[8] poly(ladder-type pentaphenylene),[9] and ladder-type poly(*p*-phenylene)s[10] (Figure 1) are some of the most important classes of conjugated polymers for blue-emitting polymer light-emitting diodes (PLEDs). However, these polymers suffer from problems of (i) poor charge injection and transport and (ii) a tendency to oxidize at the bridge-head positions. This generates a ketone functionality, which leads to the appearance of a long wavelength emission band and the deterioration of device performance.[11] Recently, our group has shown that the fully arylated poly(indenofluorene)[12] and fully arylated ladder-type poly(pentaphenylene)[13] exhibited good stability compared to their alkyl counterparts. Poly(2,7-carbazole)s constitute an important class of blue-emitting materials in that the nitrogen at the bridge-head is stable toward oxidation, it is a good hole transporter, and the compound is readily available.[14−17] However, they suffer from the following disadvantages: (i) the emission maximum at 417 nm, where the eye is not particularly sensitive (emission maximum around 440−450

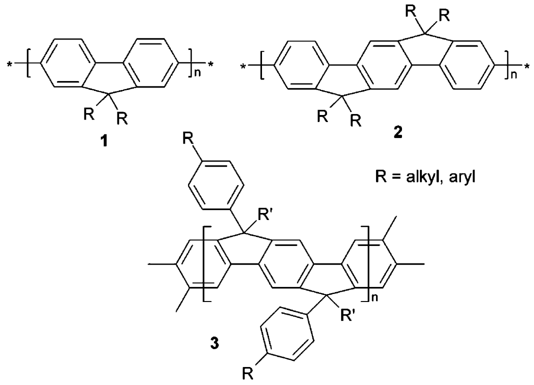

Figure 1. Polyphenylene based conjugated polymers.

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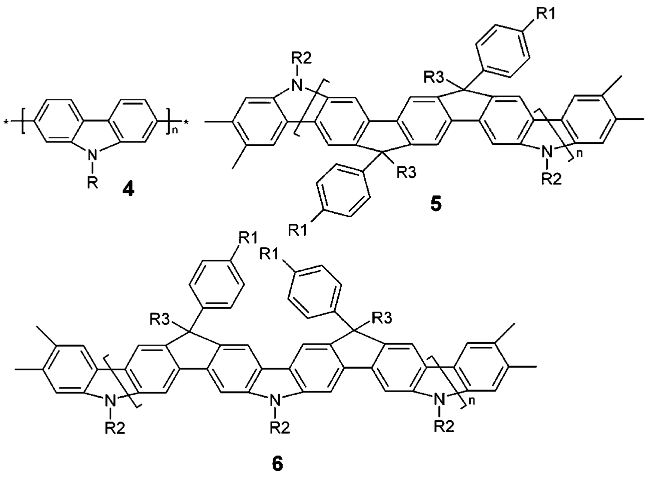

Figure 2. Carbazole based conjugated polymers.

nm is more desirable for maximum apparent brightness);[9] (ii) the 3,6-positions of carbazole being vulnerable to further reaction; and (iii) poor solubility, as only one alkyl chain can be attached to the nitrogen. Several ladder-type poly(*p*-phenylene) based materials containing carbazole have been synthesized (Figure 2), where the 3,6 positions were blocked.[18,19] These materials were stable to unwanted further reaction, but the emission maximum was bathochromically shifted to 480 nm; in addition, these materials were blue-green emitters. Qiu et al. have reported a semi-ladder poly(phenylene) containing carbazole and fluorene moieties which showed stable blue emission at 447 nm; however, the alkylated fluorene moieties were still susceptible to oxidation.[20] To address these problems, we report here the synthesis of a novel carbazole based ladder-type poly(tetraphenylene). This material is anticipated to retain the desired properties of the previously mentioned polymers, such as stability toward oxidation and emission maximum in the correct part of the visible spectrum, while overcoming the disadvantages. For comparison, a ladder-type poly(tetraphenylene) (with all carbon bridges) was also synthesized.

Experimental Section

All solvents were purified and freshly distilled prior to use 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 Lamda 9, and the photoluminescence (PL) measurements were recorded in solution on a SPEX Fluorolog 2 type 212 steady-state fluorometer. 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 distributions.

The indium tin oxide (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. Poly(3,4-ethylenedioxythiophene) (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-casted from solution and dried at 80 °C overnight in a vacuum. Metal electrodes were thermally deposited in a vacuum coating mounted in a glovebox at a base pressure below 2×10^{-6} mbar.

Electroluminescence (EL) spectra were recorded using an ORIEL spectrometer with an attached charge-coupled device camera. The current−luminance-voltage ($I-L-V$) 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).

2,7-Dibromo-*N*-(2-ethylhexyl)-3,6-bis(4-octylbenzoyl)carbazole (8). 2,7-Dibromo-*N*-(2-ethylhexyl)carbazole (1.0 g, 2.28 mmol) and $AlCl_3$ (0.73 g, 5.5 mmol) were dissolved in 1,2-dichloroethane (5 mL), and then 4-octylbenzoyl chloride (1.27 g, 4.8 mmol) was added slowly at room temperature. The mixture was stirred for 4 h at 50 °C and then quenched with ice. The inorganic precipitate was dissolved in 2 M HCl, and the product was extracted with dichloromethane. The organic fractions were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The product was purified by chromatography on silica gel with 0−10% ethyl acetate in hexane as the eluent to give compound **8** as a light yellow solid (1.8 g, 91%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 8.01 (s, 2H), 7.74 (m, 6H), 7.28 (d, 4H, $J = 8.2$ Hz), 4.22 (d, 2H, $J = 7.7$ Hz), 2.67 (t, 4H, $J = 7.7$ Hz), 2.13 (m, 1H), 1.70−1.15 (br m, 32H), 1.10−0.80 (br m, 12H).^{13}C NMR (62.5 MHz, CD_2Cl_2): δ 196.09, 150.30, 143.51, 135.56, 132.94, 131.13, 129.38, 122.53, 121.77, 118.53, 115.15, 48.88, 40.02, 36.78, 32.61, 31.87, 31.49, 30.15, 30.05, 29.97, 29.33, 25.11, 23.80, 23.41, 14.61, 14.53, 11.42. FDMS: *m*/*z* 870.0. Elem anal. Calcd: C, 69.04; H, 7.30; N, 1.61. Found: C, 69.02; H, 7.28; N, 1.55.

Synthesis of the Tetraphenylene Diketone 9. 4-Chlorophenylboronic acid (0.96 g, 6.18 mmol), diketone **8** (2.44 g, 2.81 mmol), and K_2CO_3 (775 mg, 5.62 mmol) were dissolved in tetrahydrofuran (THF; 20 mL) and water (5 mL) in a 50 mL Schlenk flask. The solution was purged with argon for 20 min, and then $Pd(PPh_3)_4$ (98 mg, 0.03 equiv) was added and the reaction was heated with stirring at 85 °C. The reaction was followed by TLC and was worked up after 24 h. The cooled mixture was extracted with dichloromethane, and the extract was washed with brine and then dried over $MgSO_4$. The crude product so obtained was purified by chromatography on silica gel with 0−20% ethyl acetate in hexane as the eluent. The product **9** was isolated as a colorless solid (2.15 g, 82%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 8.24 (s, 2H), 7.64 (d, 4H, $J = 8.1$ Hz), 7.49 (s, 2H), 7.29 (m, 8H), 7.16 (d, 4H, $J = 8.1$ Hz), 4.33 (d, 2H, $J = 7.3$ Hz), 2.62 (t, 4H, $J = 7.6$ Hz), 2.17 (m, 1H), 1.68−1.20 (m, 32 H), 1.0−0.80 (m, 12H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ 197.84, 149.01, 143.19, 140.58, 139.81, 136.38, 133.49, 131.70, 131.01, 130.58, 128.67, 122.98, 121.46, 111.56, 48.21, 39.79, 36.31, 32.28, 31.54, 31.20, 29.80, 29.62, 29.02, 24.77, 23.44, 23.07, 14.27, 14.15, 11.08. FDMS: *m*/*z* 931.1. Elem anal. Calcd: C, 79.80; H, 7.67; N, 1.50. Found: C, 79.72; H, 7.71; N, 1.46.

Synthesis of Dichlorotetraphenylene 10. (a) A solution of 4-octylbromobenzene (1.52 mL, 6.4 mmol) in dry THF (40 mL) in a 100 mL Schlenk flask was cooled to −78 °C in an acetone/dry ice bath. *n*-Butyllithium in hexane (4.21 mL, 1.6 M, 6.74 mmol) was then added, and the mixture was stirred for 20 min. Then a solution of the diketone **9** (2.0 g, 2.14 mmol) in dry THF (10 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 product was extracted

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into diethyl ether, and the extract was washed with brine and dried over $MgSO_4$. The crude product was chromatographed on silica gel with 0−5% ethyl acetate in hexane as the eluent to give the diol as a thick viscous oil (2.53 g, 90%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.35 (s, 2H), 7.04 (m, 22H), 6.78 (d, 4H, J = 8.4 Hz), 4.07 (d, 2H, J = 7.4 Hz), 2.74 (s, 2H), 2.62 (t, 8H, J = 7.4 Hz), 2.02 (m, 1H), 1.72−1.54 (m, 8H), 1.44−1.10 (m, 48H), 0.95−0.70 (m, 18H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ 145.61, 145.57, 142.38, 142.18, 140.41, 138.83, 137.30, 132.95, 131.77, 128.23, 127.94, 127.72, 121.61, 121.09, 83.42, 39.50, 35.90, 32.29, 32.02, 29.89, 29.81, 29.72, 28.57, 24.47, 23.36, 23.06, 15.75, 14.25, 14.12, 14.04, 11.86, 10.91. FDMS: *m*/*z* 1315.5. Elem anal. Calcd: C, 82.28; H, 8.82; N, 1.07. Found: C, 82.39; H, 8.82; N, 1.03.

(b) The diol (1.2 g, 0.91 mmol) was dissolved in 1,2-dichloroethane (10 mL), and BF_3·etherate (0.2 mL) was added with stirring at room temperature. The colorless solution turned deep blue immediately upon addition. The mixture was refluxed for 48 h, cooled, and then quenched by adding 20 mL of methanol upon which the monomer **10** started precipitating as a light yellow solid. The mixture was further stirred for 2 h, and 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 monomer **10** = 1.10 g (95%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.88 (s, 2H), 7.80 (d, 2H, J = 8.7 Hz), 7.70 (s, 2H), 7.37 (m, 4H), 7.06 (m, 16H), 4.30 (d, 2H, J = 7.4 Hz), 2.52 (t, 8H, J = 7.7 Hz), 2.21 (m, 1H), 1.64−1.15 (m, 56H), 1.04−0.78 (m, 18H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ 154.64, 143.69, 143.45, 142.34, 141.96, 139.62, 137.63, 133.21, 128.68, 128.27, 128.07, 126.74, 123.81, 121.30, 117.91, 100.66, 64.77, 48.19, 39.76, 35.82, 32.26, 31.84, 31.34, 29.85, 29.81, 29.60, 29.19, 24.95, 24.90, 23.48, 23.04, 14.24, 11.20. FDMS: *m*/*z* 1275.8. Elem anal. Calcd: C, 84.60; H, 8.76; N, 1.10. Found: C, 84.67; H, 8.73; N, 1.01.

Synthesis of Nitrogen-Bridged Poly(tetraphenylene) 11. Bis(1,5-cyclooctadiene)nickel (152 mg, 2.4 equiv), cyclooctadiene (0.068 mL, 2.4 equiv), and 2,2′-bipyridine (88 mg, 2.4 equiv) were dissolved in dry toluene (2 mL) and dry *N*,*N*-dimethylformamide (2 mL) in a Schlenk tube 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 monomer **10** (0.3 g, 0.23 mmol) in dry toluene (10 mL) was added. The reaction was heated at 80 °C for 2 days, where upon the solution became so viscous that it ceased to stir. Then a mixture of toluene (4 mL) and bromobenzene (0.1 mL) was added, and the mixture was heated at 80 °C for an additional 12 h. The mixture was then poured into a mixture of methanol and concentrated hydrochloric acid (1:1, 200 mL) and stirred for 4 h. The precipitated yellow solid was redissolved in THF (10 mL) and added dropwise to methanol (100 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 from a mixture of methanol and ammonia (4:1, 200 mL), filtered, washed with methanol, and dried. The isolated yield of polymer **11** was 214 mg (77%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.83 (br m, 10H), 7.17 (d, 8H, J = 7.2 Hz), 7.04 (d, 8H, J = 7.5 Hz), 4.96 (br m, 2H), 2.52(m, 8H) 2.24 (s, 1H), 1.70−1.10 (br m, 56H), 1.10−0.80 (br m, 18H). GPC analysis: $M_n = 4.6 \times 10^4$ g mol^{-1} and $D = 2.8$ (against PPP standard). Elem anal. Calcd: C, 89.57; H, 9.27; N, 1.16. Found: C, 89.38; H, 9.35; N, 1.05.

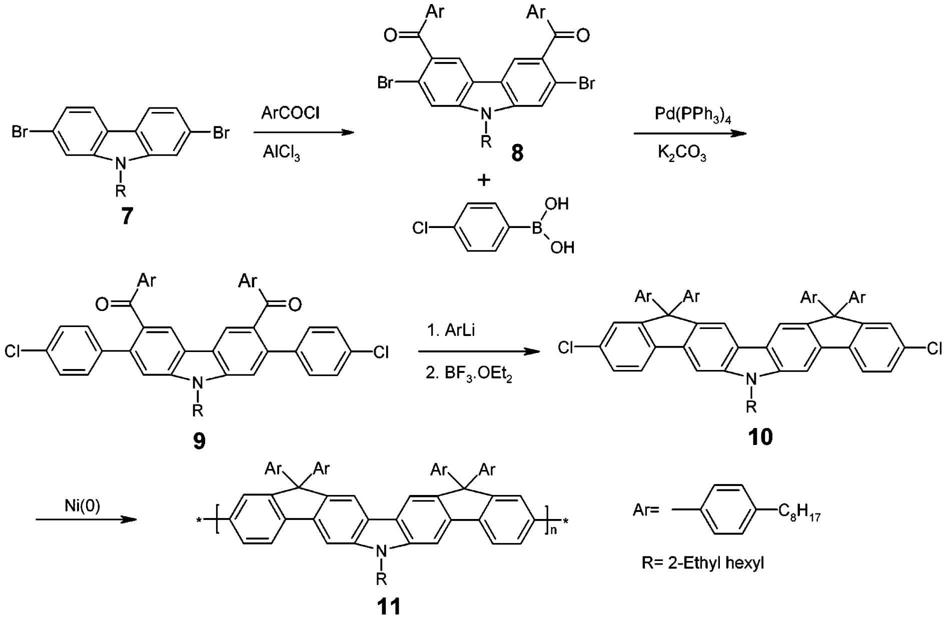
Synthesis of the Diester 12. The methyl 2-bromobenzoate (0.64 mL, 4.60 mmol), 9,9′-dioctyl-2,7-fluorenediboronic acid (1.00 g, 2.09 mmol), and K_2CO_3 (634 mg, 4.60 mmol) were dissolved in THF (8 mL) and water (4 mL) in a 50 mL Schlenk flask. The solution was purged with argon for 20 min, then $Pd(PPh_3)_4$ (80 mg, 0.03 equiv) was added, and the reaction was heated with stirring at 80 °C. The reaction was followed by TLC and was worked up after 24 h. The cooled mixture was extracted with dichloromethane, and the extract was washed with brine and then dried over $MgSO_4$. The crude product so obtained was purified by chromatography on silica gel with 0−30% ethyl acetate in hexane as the eluent. The diester **12** was isolated as a white solid (0.98 g, 71%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.80 (t, 4H, J = 6.7 Hz), 7.59 (m, 2H), 7.46 (m, 4H), 7.32 (m, 4H), 3.62 (s, 6H), 1.99 (m, 4H), 1.30−1.00 (m, 20H), 0.85−0.65 (m, 10H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ 169.52, 151.28, 143.07, 140.71, 140.37, 131.79, 131.45, 131.12, 129.95, 127.52, 127.41, 123.50, 119.80, 55.62, 52.09, 40.87, 32.17, 30.46, 29.70, 29.63, 24.17, 22.97, 14.20. FDMS: *m*/*z* 660.0. Elem anal. Calcd: C, 82.03; H, 8.26. Found: C, 82.01; H, 8.25.

Synthesis of the Tetraphenylene 13. (a) A solution of 4-octylbromobenzene (0.96 mL, 4.06 mmol) in dry THF (40 mL) in a 100 mL Schlenk flask was cooled to −78 °C in an acetone/dry ice bath. *n*-Butyllithium in hexane (2.67 mL, 1.6 M, 4.27 mmol) was then added, and the mixture was stirred for 20 min. Then a solution of the diester **12** (0.9 g, 1.36 mmol) in dry THF (10 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 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 gel with 0−5% ethyl acetate in hexane as the eluent to give the diol as a thick viscous oil (1.73 g, 94%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.49 (d, 2H, J = 7.8 Hz), 7.29 (d, 2H, J = 7.3 Hz), 7.24−7.92 (m, 20H), 6.83 (m, 6H), 3.02 (s, 2H), 2.62 (t, 8H, J = 7.6 Hz), 1.72−0.96 (m, 72H), 0.88 (t, 12H, J = 6.4 Hz), 0.79 (t, 6H, J = 6.6 Hz), 0.42 (s, 4H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ 150.93, 146.00, 145.57, 142.27, 141.87, 141.52, 140.12, 133.25, 130.70, 129.02, 128.35, 128.15, 127.07, 126.55, 124.02, 119.77, 83.68, 55.51, 35.88, 32.31, 32.22, 31.99, 30.21, 29.89, 29.76, 29.70, 24.15, 23.08, 23.01, 14.26, 14.22. FDMS: *m*/*z* 1356.3.

(b) The diol (1.5 g, 1.10 mmol) was dissolved in dichloromethane (10 mL), and BF_3·etherate (0.5 mL) was added with stirring at room temperature. The colorless solution turned deep blue immediately upon addition. The mixture was stirred overnight at room temperature and then quenched by adding 30 mL of methanol. No precipitation of the product was observed. Then, the mixture was extracted with diethyl ether, and the extract was washed with brine and dried over $MgSO_4$. The crude product was chromatographed on silica gel with 0−2% ethyl acetate in hexane as the eluent to give the tetraphenylene **13** as a thick viscous oil (1.27 g, 88%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.81 (d, 2H, J = 7.4 Hz), 7.75 (s, 2H), 7.58 (s, 2H), 7.30 (m, 6H), 7.06 (m, 16H), 2.54 (t, 8H, J = 7.4 Hz), 2.12 (m, 4H), 1.65−1.00 (m, 72H), 0.86 (t, 12H, J = 5.8 Hz), 0.77 (t, 6H, J = 6.6 Hz). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ 152.50, 151.63, 151.12, 143.75, 141.79, 141.63, 140.64, 139.77, 128.60, 128.36, 127.69, 126.43, 120.87, 120.24, 117.45, 114.92, 65.02, 54.86, 41.15, 35.81, 32.25, 32.17, 31.96, 31.83, 30.45, 29.85, 29.81, 29.59, 23.03, 22.94, 14.24, 14.18. FDMS: *m*/*z* 1319.7.

Synthesis of the Dibromotetraphenylene 14. The tetraphenylene **13** (1.0 g, 0.75 mmol) was added to carbon tetrachloride (20 mL) in a 100 mL round-bottom flask, followed by $CuBr_2$ on alumina (3.18 g). The reaction was heated under reflux with stirring and monitored by FDMS, which showed nearly quantitative formation of the dibromide after 16 h. The reaction mixture was concentrated, and the crude product so obtained was purified by chromatography on silica gel with hexane as the eluent. The monomer **14** was isolated as a light yellow solid (0.95 g, 86%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.72 (s, 2H), 7.69 (d, 2H, J = 8.0 Hz), 7.55 (s, 2H), 7.49 (m, 4H), 7.06 (m, 16H), 2.53 (t, 8H, J =

Scheme 1. Synthesis of Nitrogen-Bridged Poly(ladder-type tetraphenylene)



7.4 Hz), 2.08 (m, 4H), 1.64−1.00 (m, 72H), 0.87 (t, 12H, $J = 6.5$ Hz), 0.77 (t, 6H, $J = 6.6$ Hz). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ 154.64, 151.89, 151.08, 142.97, 142.12, 141.90, 139.76, 138.80, 130.91, 129.55, 128.79, 128.34, 121.73, 121.17, 117.59, 115.09, 65.16, 54.96, 41.10, 35.85, 32.29, 32.19, 31.83, 30.43, 29.87, 29.84, 29.63, 29.59, 24.33, 23.07, 22.98, 14.28, 14.22. FDMS: *m*/*z* 1477.2. Elem anal. Calcd: C, 80.46; H, 8.73. Found: C, 80.36; H, 8.75.

Synthesis of the Poly(tetraphenylene) 15. Bis(1,5-cyclooctadiene)nickel (225 mg, 2.4 equiv), cyclooctadiene (0.163 mL, 2.4 equiv), and 2,2′-bipyridine (130 mg, 2.4 equiv) were dissolved in dry toluene (2 mL) and dry *N*,*N*-dimethylformamide (2 mL) in a Schlenk tube 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 monomer **14** (0.50 g, 0.34 mmol) in dry toluene (12 mL) was added. The reaction was heated at 80 °C for 2 days, whereby the solution became so viscous that it ceased to stir. Then a mixture of toluene (5 mL) and bromobenzene (0.1 mL) was added and the mixture was heated at 80 °C for an additional 12 h. The mixture was then poured into a mixture of methanol and concentrated hydrochloric acid (1:1, 200 mL) and stirred for 4 h. The precipitated yellow solid was redissolved in THF (10 mL) and added dropwise to methanol (100 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 then precipitated from methanol (100 mL), filtered, and dried. The isolated yield of polymer **15** was 313 mg (70%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.80−7.45 (m, 10H), 7.30−6.90 (m, 16H), 2.70−1.95 (m, 12H), 1.65−0.95 (m, 72H), 0.86 (t, 12H, $J = 6.6$ Hz), 0.77 (t, 6H, $J = 6.7$ Hz). GPC analysis: $M_n = 3.5 \times 10^4$ g mol^{-1} and $D = 2.3$ (against PPP standard). Elem anal. Calcd: C, 90.21; H, 9.79. Found: C, 90.22; H, 9.69.

Results and Discussion

The synthetic approach toward carbazole based ladder-type poly(tetraphenylene) is shown in Scheme 1. 2,7-Dibromo-*N*-(2-ethylhexyl)carbazole (**7**) was synthesized according to the literature.[21] Friedel−Crafts acylation gave the 3,6-disubstituted carbazole **8**, which was coupled with 2 equiv of 4-chlorophenylboronic acid in the presence of Pd(PPh_3)$_4$ as the catalyst to generate the diketone **9** in 82% yield. Treatment with a slight excess of 4-octylphenyllithium produced the corresponding diol, which upon ring closure with BF_3•etherate gave the monomer **10** in 86% overall yield. The polymer **11** was synthesized using nickel(0) mediated Yamamoto-type polymerization of monomer **10** in 77% yield. GPC analysis against the PPP standard showed a M_n value of 4.6×10^4 g mol^{-1}, with a polydispersity index of 2.8. This corresponds to a degree of polymerization of about 38, and the resulting polymer had very good solubility in common organic solvents such as dichloromethane and THF.

For comparison, a ladder-type poly(tetraphenylene) with all carbon bridges was also synthesized. The synthetic scheme is outlined in Scheme 2. The diester **12** was synthesized in 71% yield by standard Suzuki coupling of commercially available 9,9′-dioctyl-2,7-fluorenediboronic acid and methyl 2-bromobenzoate. Addition of 4 equiv of 4-octylphenyllithium generated the corresponding diol which was ring closed by BF_3•etherate to give the ladder-type tetraphenylene **13** in 82% overall yield. In this case, the ring closure was obtained in quantitative yield by stirring the reaction mixture at room temperature. Although bromination using bromine led to overbromination, use of $CuBr_2$ on alumina gave the desired monomer **14** in nearly quantitative yield. This was polymerized by Yamamoto-type polycondensation to generate polymer **15** in 70% yield. GPC analysis using the PPP standard showed a M_n value of 3.54×10^4 g mol^{-1} with a polydispersity index of 2.3. This corresponds to a degree of polymerization of about 27, and the material had good solubility in common organic solvents.

Polymer **11** exhibited an absorbance maximum at 434 nm and a fluorescence maximum at 445 nm in THF solution (Figure 3), which were intermediate between that of polycarbazole (417 nm) and that of a fully ladderized polymer **6** (480 nm). The PL spectrum was characterized by a steep onset and by well-resolved vibrationally split maxima at 473 and 508 nm, which are homologous to the absorption

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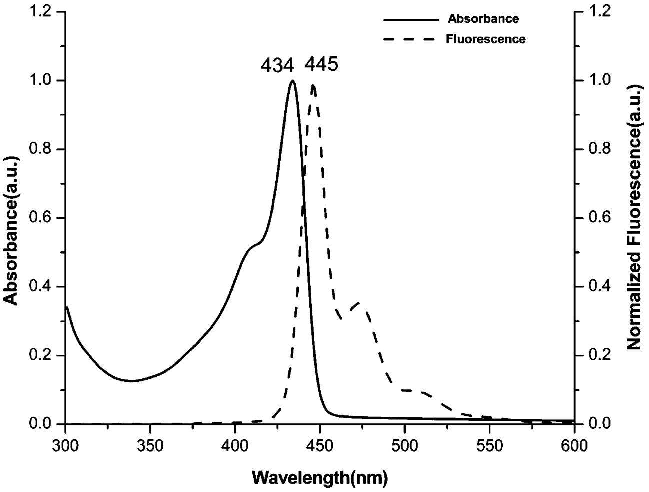


Figure 3. Optical properties of polymer **11**.

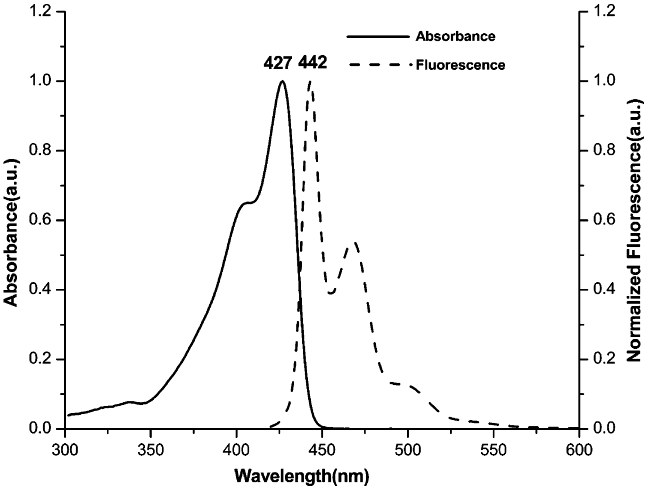


Figure 4. Optical properties of polymer **15**.

spectrum. The dominant PL maximum was only very slightly Stokes shifted by ∼70 meV, which is due to the ladder-type structure of the polymer hindering geometrical relaxations.

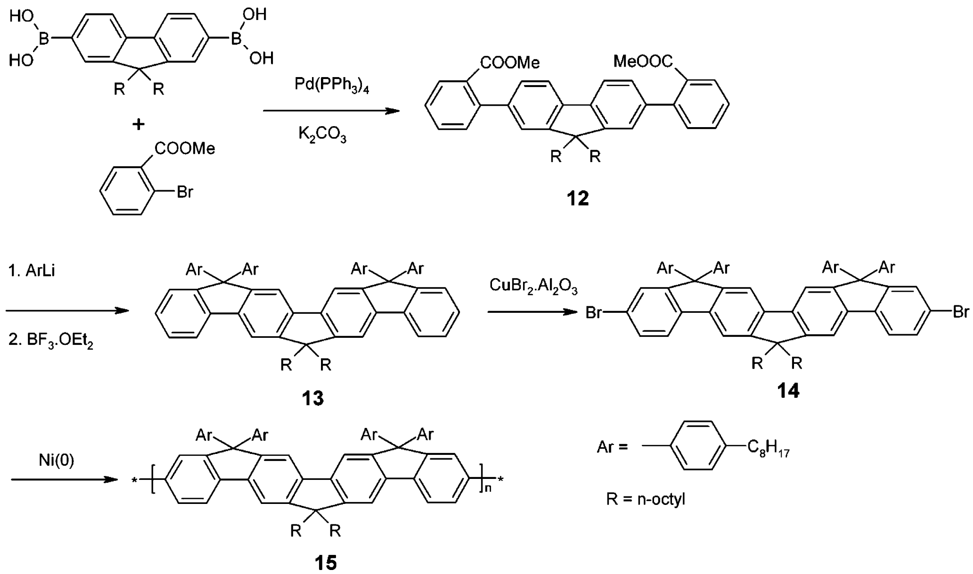
The UV−vis and fluorescence properties of the fully carbon-bridged polymer **15** in solution are depicted in Figure 4. The absorption spectrum exhibited the typical structure of a ladder-type polymer with a $\pi-\pi^*$ transition at 427 nm and a shoulder at 400 nm. The PL emission demonstrated a first maximum at 442 nm and vibronic fine structures at 468 and 500 nm. A low Stokes shift of ∼100 meV was found. As expected, the emission maximum for this polymer was between that of poly(indenofluorene) (430 nm)[8] and that of ladder-type poly(pentaphenylene) (445 nm).[9] Polymer **15** showed a weak hypsochromic shift of ∼20 meV in both the absorbance and the emission maximum as compared to the analogous nitrogen-bridged polymer **11**.

To investigate the redox properties, cyclic voltammograms were recorded for polymers **11** and **15** against Ag/AgCl with a ferrocene/ferrocenium internal standard. Both polymers showed only p-doping (anodic) peaks. However, polymer **15** exhibited a reversible anodic peak in contrast to polymer **11** which underwent irreversible oxidation. The band gap, calculated from the absorption onset, was estimated to be 2.72 eV for polymer **11** and 2.75 eV for polymer **15**. The onset of oxidation occurred at 1.20 and 1.23 V for polymers **11** and **15**, respectively, from which the highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) energy levels can be estimated.[22] These were calculated to be 5.53 and 2.81 eV for polymer **11** and 5.62 and 2.87 eV for polymer **15**, given that the energy level of Ag/AgCl is 4.4 eV. The lone pairs on nitrogen pushed up the HOMO by 0.09 eV and the LUMO by 0.06 eV in polymer **11** in comparison with the carbon-bridged polymer **15**.

Solid-State and EL Properties. Before discussing the EL properties, a brief comparison of the solid-state properties and the effects of thermal degradation of the two different polymers **11** and **15** are presented.

The film spectra of polymer **11** (Figure 5) exhibited no distinct difference compared to the solution spectra, apart from a small bathochromic shift of about 20 meV and a solid-state related broadening of the spectrum. On heating the

Scheme 2. Synthesis of Poly(ladder-type tetraphenylene)



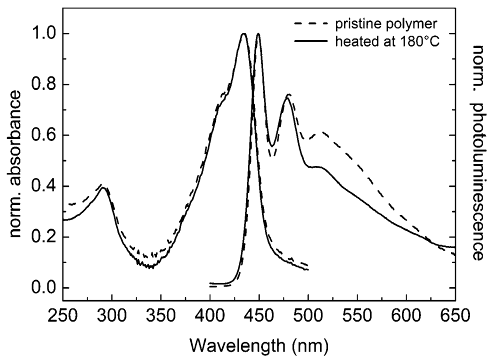


Figure 5. Absorption and PL spectra of polymer **11** for pristine and annealed film in air at 180 °C.

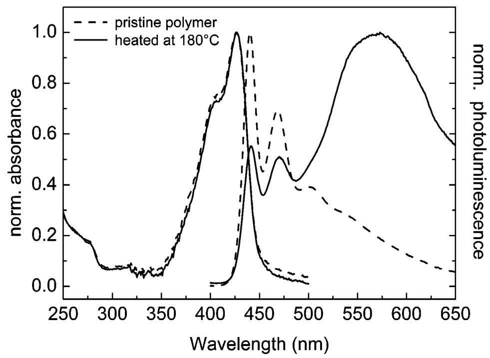


Figure 6. Absorption and PL spectra of polymer **15** for pristine and annealed film in air at 180 °C.

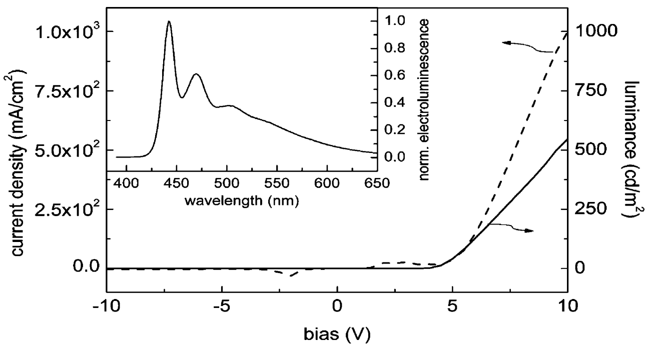


Figure 7. Bias/current and bias/EL characteristics and normalized EL of an ITO/PEDOT/polymer **11**/Ca/Al device.

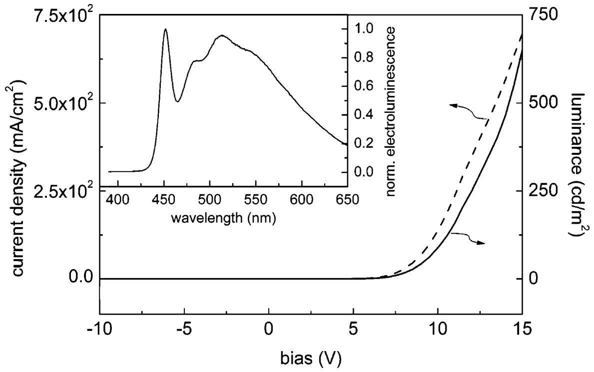


Figure 8. Bias/current and bias/EL characteristics and normalized EL of an ITO/PEDOT/polymer **15**/Ca/Al device.

polymer in air at 180 °C for 30 min, the polymer emission spectrum was almost unaltered and no oxidative degradation effects were observed. Note that the oxidative degradation at the 9-position of the carbon-bridged positions was hindered by the aryl substitution as previously reported[13] so that upon heating only the nitrogen bridge position could be affected, which was not observed.

In the case of polymer **15** (Figure 6), a comparison of the film and solution spectra exhibited no differences aside from a bathochromic shift of 20 meV. In contrast to polymer **11**, polymer **15** showed a strong alteration of the PL upon thermal stress in air. Heating the polymer for 30 min under ambient conditions led to the well-known formation of oxidative products in the form of ketonic defects with an emission centered at 575 nm, which increased with further degradation. The position of the ketonic defect emission was bathochromically shifted compared to polyfluorene, generally at 530 nm, due to the more extended conjugation of the tetraphenylene unit as compared to the fluorene unit. For comparison under inert conditions, that is, a dynamic vacuum of 10^{-6} mbar, no degradation of the polymer could be detected. From a previous study, it is known that the degradation is taking place at the dialkyl bridge-head in polymer **15**, which are susceptible toward oxidation.[13] Thus polymer **11** showed a clear advantage over the ladder-type poly(tetraphenylene) with all carbon bridges, in terms of oxidative degradation under an ambient atmosphere.

To test the polymers for their electroluminescent properties, PLEDs were prepared under an inert atmosphere in the standard configuration (ITO/PEDOT:PSS/polymer **11** or **15**/ Ca/Al).

As depicted in Figure 7, PLEDs prepared from polymer **11** demonstrated a deep blue EL emission spectrum with high luminance values of typically 700−900 cd/m² at a bias of 10 V, which was stable during several tens of minutes of operation under glovebox conditions. The color coordinates of the emission were $x = 0.19$, $y = 0.19$ according to the CIE standard 1931. The devices displayed the EL onset at about 4 V in the forward bias direction and exhibited moderate efficiencies of 0.1 cd/A.

In comparison, PLEDs (Figure 8) prepared from polymer **15** showed a green-blue EL emission spectrum with typical luminance values of 600 cd/m² at a bias of 15 V. The emission is composed of the blue emission of the polymer at 450 nm and an additional band at 510 nm with a shoulder at 540 nm.

The color coordinates of this emission are $x = 0.29$, $y = 0.41$ according to the CIE standard 1931. The devices showed the EL onset at about 5.5 V in the forward direction and exhibited only moderate efficiencies of less than 0.1 cd/A. The observation of the additional broad EL peak at 510 nm was unexpected. A comparison of the results from the degradation experiments obtained for the two polymers demonstrated that the peak at 510 nm, which was only observed in polymer **15**, cannot be related to an emission that has its origin in a product from an oxidative degradation. In such a case, the additional low energy band in EL should be located at about 570 nm as it was found for polymer **15** in PL upon degradation. To explain this observation one must focus on not only bulk polymer defects but also the observation of additional distinct spectral features in EL of

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PLEDs emerging from the interaction of the polymer with the (Ca)/Al electrode or the PEDOT/PSS interface. Such emission bands in the spectral region of 480−510 nm and their relation to the interface have been clearly identified for polyphenylene-type polymers in the literature as distinct features.[23−25] Such features only emerge upon coverage of the polymer with metals such as Al or Ca, and they are attributed to the formation of chemical defects in the polymer in a chemical degradation reaction caused by the low work function metal electrodes. Further studies on the exact nature of this defect emission are currently underway.

Conclusions

In conclusion, we have synthesized two new ladder-type tetraphenylene based polymers, both of which were blue emitters. Both polymers showed deep blue emission in solution with an emission maximum centered around 445 nm. The introduction of the carbazole unit in the ladder-type poly(tetraphenylene) led to a slight bathochromic shift of the emission and absorption spectra. Both polymers exhibited good EL properties in initial PLED tests with very high luminance values typically over 700−900 cd/m^2 at a bias of 10 V for polymer **11**. The polymer **15** displayed a rather strong low energy emission band at 510 nm, which can be attributed to an interaction of the polymer with the deposited metal electrode.

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