Highly Luminescent 1,4-Diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole- (DPP-) Based Conjugated Polymers Prepared Upon Suzuki Coupling

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ABSTRACT: Five new soluble conjugated polymers are described, which were prepared upon Suzuki polycondensation reactions. They alternately consist of dialkylated 1,4-diketo-3,6-diphenyl-pyrrolo[3,4-*c*]pyrrole (**DPP**) units and carbazole, triphenylamine, benzo[2,1,3]thiadiazole, anthracene, and fluorene units. The polymers were prepared from 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**1a**), 1,4-diketo-2,5-di-(2-ethylhexyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**1b**), or 1,4-diketo-2,5-dihexyl-3,6-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolo[3,4-*c*]pyrrole (**1c**), and 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-ethylhexylcarbazole (**2**), 4,4′-dibromotriphenylamine (**3**), 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylamine (**4**), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**5**), 9,10-anthracenebispinacolatoboron ester (**6**), and 4,7-dibromo-2,1,3-benzothiadiazole (**7**). The polymers exhibit brilliant red colors. They are soluble in common organic solvents and form orange to red solutions with absorption maxima between 479 and 515 nm. Polymer solutions are highly fluorescent with photoemission maxima between 552 and 600 nm. Photoluminescence quantum yields up to 86% could be determined. The polymers exhibit molecular weights up to 20 000 Da. Cyclic voltammetric studies indicate quasi-reversible oxidative cycles, while reductive cycles are irreversible. Exemplary studies on the electroluminescence of the DPP−fluorene copolymer indicate a maximum emission at 600 nm, the turn-on voltage being 3.5 V. Maximum efficiencies up to 0.5% and a brightness of 50 cd m^{-2} could be reached.

1. Introduction

1,4-Diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole and its derivatives, so-called DPPs, are high performance pigments used in paints, color inks, and plastics.[1,2] Their colors range from yellowish orange to bluish red. However, DPPs are insoluble in water or common organic solvents due to $\pi-\pi$-stacking and a strong hydrogen-bonded structure in the solid state.[3] In order to use the DPP chromophore in electronic devices, it is necessary to prepare soluble and film forming DPP compounds. Previous studies have shown that soluble DPP derivatives with deep color and strong luminescence can be prepared upon alkylation of the lactam units.[4,5] If properly functionalized, alkylated DPP monomers can be used for preparation of oligomers,[6] dendrimers[7,8] and polymers.[9−20] These materials show intense red colors, strong red photoluminescence, and electroluminescence,[15,17] which renders them attractive as active materials in a variety of electronic devices.

DPP-containing polymers have been prepared upon radical polymerization,[10,11] polycondensation,[12] polyaddition,[12,16] polymer modification[13] and Pd-catalyzed cross-coupling reactions.[14−20] In previous work,[6,9,14−20] Suzuki-,[21] Stille-,[22] and Heck-coupling[23] reactions were used to prepare a number of new, red-emitting DPP-containing conjugated polymers. Among the Pd-catalyzed coupling reactions, Suzuki-coupling turned out to be the most suitable method for preparation of DPP-containing conjugated polymers, because high molecular weight polymers with high fluorescence quantum yield can be obtained. However, up to now, only a limited number of conjugated DPP polymers consisting of DPP and alkyl-[14] or alkoxy[15]-substituted phenylene or fluorene units,[17,24] or merely consisting of DPP units[18] ("poly-DPP"), could be prepared using Suzuki-type arene−arene coupling reactions.[21]

The purpose of our present article is therefore to report on new DPP-containing conjugated polymers prepared upon the Pd-catalyzed Suzuki cross-coupling reaction. Our study indicates the broad applicability of Suzuki coupling for the preparation of highly luminescent DPP-containing π-conjugated polymers. Starting from the dihexylated dibromo−DPP derivative **1a** and the diboronic ester derivatives of 9-(2-ethyl)hexylcarbazole (**2**), triphenylamine (**4**), and 9,9-dihexylfluorene (**5**), the polymers **P−DPP−CBZ**, **P−DPP−TPA1**, and **P−DPP−FLR** were prepared. **P−DPP−ANT** was synthesized from the bis(2-ethyl)-hexyl-substituted dibromo−DPP derivative **1b** and the 9,10-anthracene bis(pinacolato)boron ester **6** (Scheme 1). Polymers **P−DPP−TPA2** and **P−DPP−BTZ** were prepared from the dialkylated DPP diboronic ester derivative **1c** and 4,4-dibromotriphenylamine (**3**) or 4,7-dibromo-2,1,3-benzothiadiazole (**7**), respectively (Scheme 2).

Our contribution is aimed at describing the synthesis and the characteristic properties of the new polymers. Molecular weight distribution and optical and electrochemical properties were investigated using gel permeation chromatography, UV, IR, NMR, and fluorescence spectroscopy and cyclic voltammetry. From **P−DPP−FLR**, a larger quantity was prepared and electroluminescent properties were investigated after fabrication of corresponding devices. New intensely colored, red emitting polymers with good solubility in common organic solvents are presented, which might be useful for electronic applications.

2. Experimental Section

Materials. 1-Bromohexane, 1-bromo-2-ethylhexane, carbazole, triphenylamine, fluorene, 2,1,3-benzothiadiazole, 9,10-dibromoanthracene, *N*-bromosuccinimide (NBS), 2-isopropoxy-4,4,5,5-tet-

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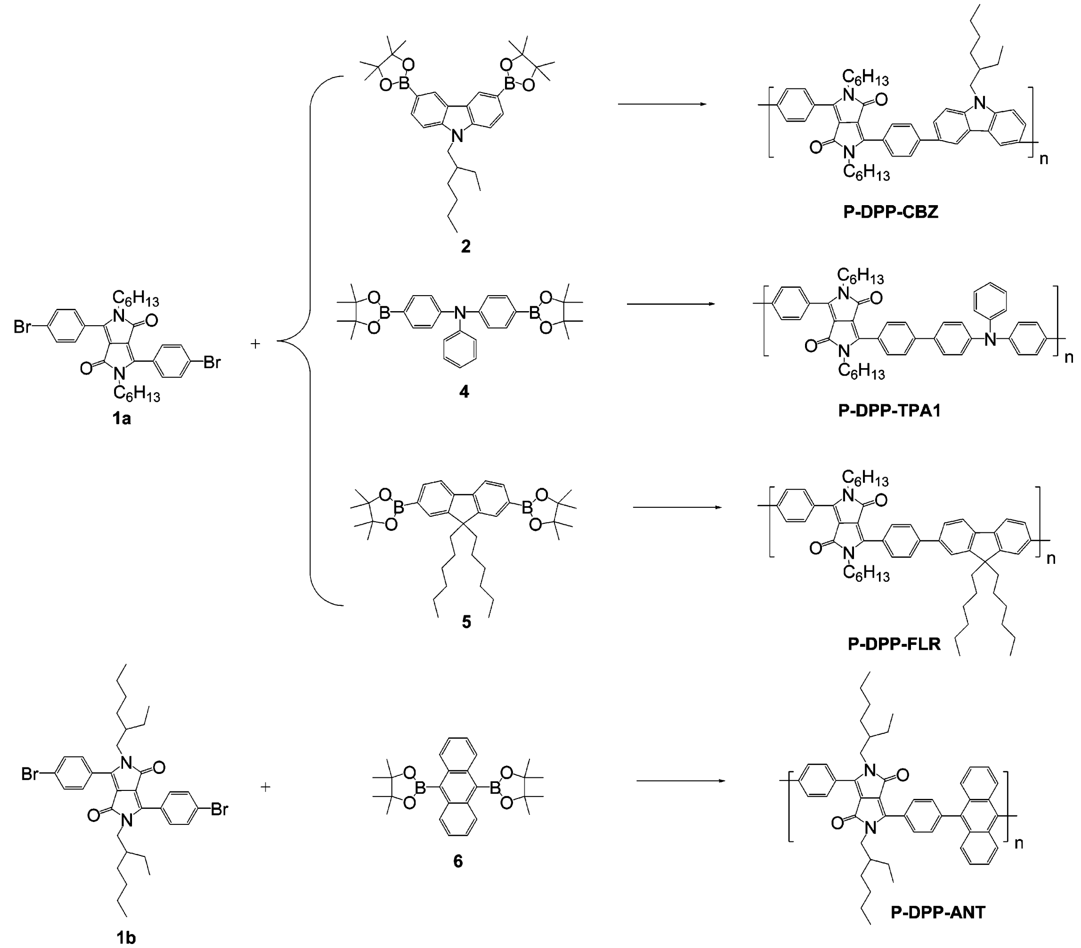
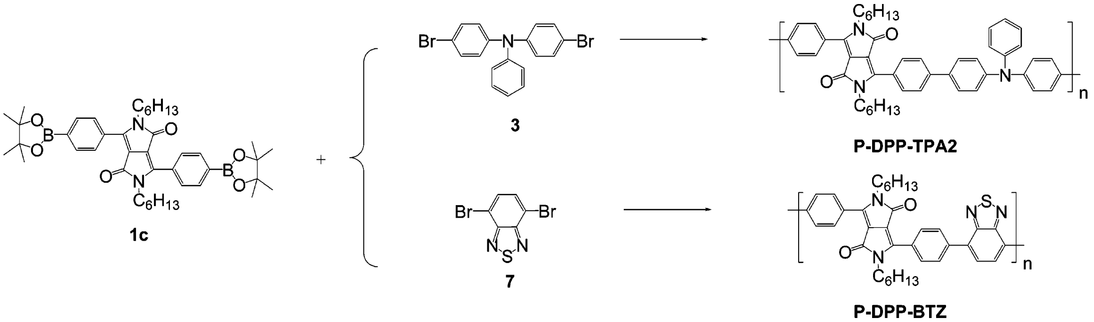
Scheme 1. Suzuki Cross-Coupling Polycondensation of P−DPP−CBZ, P−DPP−TPA1, and P−DPP−FLR



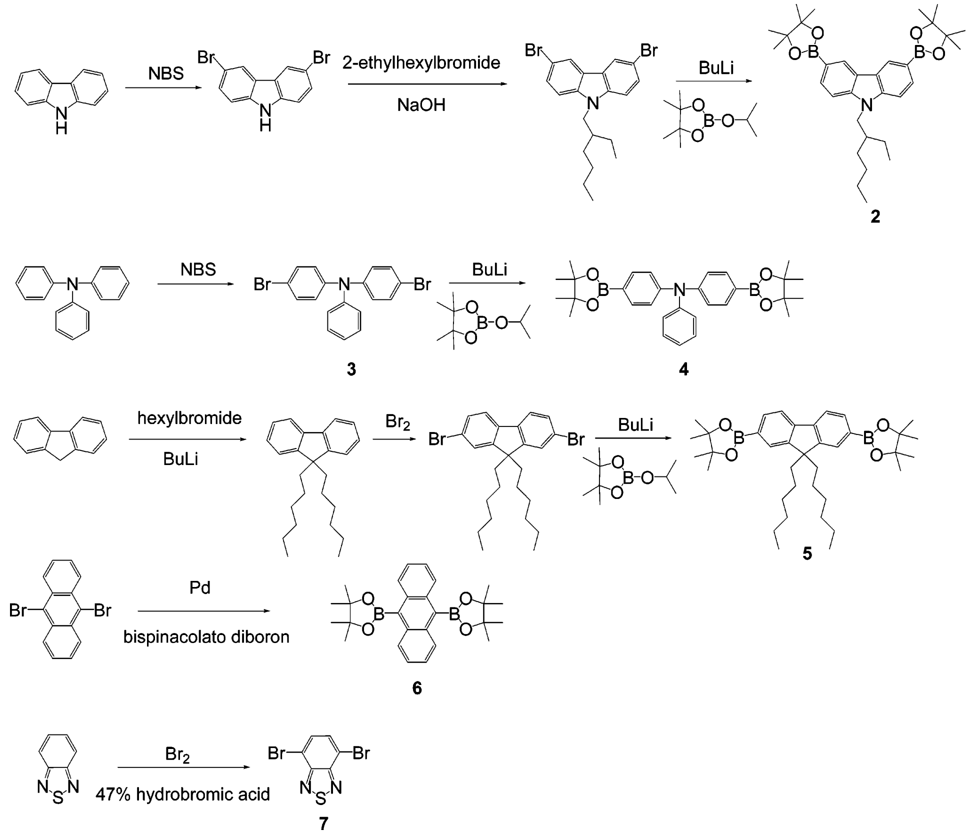
Scheme 2. Suzuki Cross-Coupling Polycondensation of P−DPP−TPA2 and P−DPP−BTZ



ramethyl-1,3,2-dioxaborolane, *n*-butyllithium (2.5 M solution in hexane), palladium(II) acetate ($Pd(OAc)_2$), tris(*o*-tolyl)phosphine, tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), acetonitrile (HPLC grade), tetrabutylammonium bromide, and tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$) were obtained from Acros or Aldrich and used without further purification. Bis(pinacolato)diboron was purchased from Combi-Blocks Inc. Tetrahydrofuran (THF) was distilled over sodium hydride under nitrogen. *N*-Methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF) were distilled over CaH_2, acetone was distilled over P_2O_5. Other organic solvents were purified and dried as usual. Chromatographic separations were carried out using Acros silica gel 60 (0.060 − 0.200 mm). 1,4-Diketo-3,6-bis(4-bromophenyl)-pyrrolo[3,4-*c*]pyrrole was supplied by Dr. M. Dueggeli and Dr. R. Lenz from Ciba Specialty Chemicals, Basle (Switzerland). DPP monomers **1a**, **1b**, and **1c** were prepared by using the previously published method.[18] 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-*n*-hexylfluorene (**5**) was synthesized from fluorene according to a literature method[24] (see also Scheme 3).

Instrumentation. ^1H NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300 MHz. UV/vis absorption spectra were recorded on a Perkin-Elmer Lambda 14 spectrometer. Photoluminescence spectra were recorded on a Perkin-Elmer LS50B spectrometer. Photoluminescence quantum yields of the polymers were measured in chloroform or toluene solutions with an excitation wavelength of 400 nm, the values were calculated by comparing with Rhodamine 6G in ethanol ($\Phi_f = 0.95$). Molecular weights were determined upon size exclusion chromatography (SEC) using a Waters/Millipore UV detector 481 and an SEC column combination (Latek/Styragel 50/1000) nm pore size). All measurements were carried out in tetrahydrofuran at 45 °C. The columns were calibrated vs commercially available polystyrene standards. Thermal properties were investigated using a Perkin-Elmer DSC-7 apparatus. The heating rate was 30° min^{-1}. Cyclic voltammograms were recorded using a potentiostat PG390 from Heka Company. A thin film of the polymer was cast on an ITO electrode and cycled in CH_3CN containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte salt. Counter and reference electrodes were platinum.

Scheme 3. Preparation of Various Monomers Used in the Study



The voltage data were calculated for the standard calomel electrode (SCE). Scan rate: 25 mV s^{-1}; T: 20 °C. EL spectra were determined with an Ocean Optics S2000 Fiberoptic spectrometer with CCD array and 600 lines/mm grating. Voltage and light intensities were measured simultaneously using a Keithley 236 source measure unit and a Si-photodiode connected to a Keithley 485 picoamperemeter. To collect all emitted light the sample was thereby put into an integrated sphere. To obtain absolute values of the emitted light intensity (mW cm^{-2}) the whole system of the integrated sphere and the photodiode were calibrated. Luminance measurements (cd m^{-2}) were performed at selected voltages using a Minolta CS-100 spot-photometer. The film thickness was measured with a Dectac Surface Profiler. Thin films were prepared from chloroform solution (15 mg/mL) using a commercially available Hamatech spincoater (10 s at 1200 rpm, 20 s at 1700 rpm, 30 s at 1000 rpm).

Monomer Synthesis. 3,6-Dibromocarbazole. A modified version of a previously reported method[25] was used. Carbazole (35.65 g, 213 mmol) was dissolved in DMF (300 mL) at 0 °C with stirring. To this was dropped a solution of NBS (75.89 g, 426 mmol) in 200 mL DMF. After being stirred at room temperature for 2 h, the solution was poured into 2000 mL of water, filtered, and washed with 2000 mL water. The white residue was recrystallized in ethanol and gave 3,6-dibromocarbazole as colorless crystals (58.9 g, 85%). ^{1}H NMR (CDCl$_3$): δ (ppm) 7.32 (d, 2H), 7.54 (d, 2H), 8. 1(s, 1H), 8.15 (s, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 139.1, 129.1, 123.71, 123.65, 113.5, 111.3. Melting point: 215−216 °C.

3,6-Dibromo-9-(2-ethylhexyl)carbazole. A modified version of a previously reported method[26] was used. 3,6-Dibromocarbazole (6.5 g, 20 mmol) was dissolved in 50 mL of acetone. The phase-transfer reagent [(C$_4$H$_9$)$_4$N]HSO$_4$ (0.41 g, 1.21 mmol), 2-ethylhexyl bromide (5.79 g, 30 mmol), and NaOH (1.6 g, 40 mmol) were added. The reaction mixture was stirred and refluxed for 4 h. The solvent was removed, and 300 mL of toluene was added. Then the mixture was washed with brine (3 × 200 mL) and dried over anhydrous magnesium sulfate. The solvent was concentrated using a rotary evaporator. Column chromatography of the residue over silica gel with petrol ether as eluent gave the product as a colorless liquid (7.1 g, 81%). ^{1}H NMR (CDCl$_3$): δ (ppm) 0.92 (t, 6H), 1.31 (m, 8H), 2.01 (m, 1H), 4.12 (d, 2H), 7.24 (d, 2H), 7. 56(d, 2H), 8.15 (s, 2H). ^{13}C NMR (CDCl$_3$, 300 MHz): δ (ppm) 129.0, 123.4, 123.2, 113.0, 111.0, 47.7, 39.4, 31.1, 28.9, 24.5, 23.1, 13.1, 10.9.

3,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(2-ethylhexyl)carbazole (2). The reaction was carried out similar to a method briefly described in the literature.[27] Using a syringe, 8.63 mL of 2.5 M *n*-BuLi (20.2 mmol) in hexane was added to a solution of 3,6-dibromo-9-ethylhexylcarbazole (2.73 g, 6.23 mmol) in THF (160 mL) at −78 °C with stirring. After the reaction mixture was stirred for 1 h at this temperature, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.2 mL, 20.4 mmol) was added. The reaction mixture was stirred at −78 °C for additional 1 h and then was gradually warmed to room temperature and stirred overnight. After the reaction, 100 of mL water and 100 mL of ether were added to the solution. Then the mixture was washed with brine (3 × 40 mL) and the organic layer was dried over MgSO$_4$. The solvent was evaporated using a rotary evaporator. Column chromatography of the residue over silica gel with a mixture of hexane and ethyl acetate (10:1; $R_f \approx 0.6$) as eluent gave **2** as a white solid (0.98 g, 30%). ^{1}H NMR (CDCl$_3$): δ (ppm) 0.90 (t, 6H), 1.30 (m, 8H), 1.41 (m, 24H) 2.01 (m, 1H), 4.19 (d, 2H), 7.39 (d, 2H), 7. 91 (d, 2H), 8.68 (s, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 143.5, 132.3, 128.4, 123.2, 108.8, 83.9, 47.8, 39.6, 31.3, 29.1, 25.4, 24.7, 23.4, 14.5, 11.3.

4,4′-Dibromotriphenylamine (3). The method[25] for bromination of carbazole was adapted. Triphenylamine (3.65 g, 15 mmol) was dissolved in DMF (75 mL) with stirring. To this mixture was added solid NBS (5.34 g, 30 mmol) in small portions. The color of the solution gradually changed from colorless to clear green and then back to light yellow. After stirring at room temperature for 24 h, 160 mL of dichloromethane was added to the solution. Then the reaction mixture was washed with water (1 × 80 mL, 4 × 40 mL), and the organic layer was dried over MgSO$_4$. The solvent was evaporated below 40 °C using a rotary evaporator. Column chromatography of the residue over silica gel with a mixture of hexane and dichloromethane (5:1; $R_f \approx 0.7$) as eluent gave **3** as a colorless oil, which solidified below room temperature (0.98 g, 30%). ^{1}H NMR (CDCl$_3$): δ (ppm) 6.95 (d, 4H), 7.08 (d, 2H), 7.10 (m, 1H), 7.29 (m, 2H), 7.36 (d, 4H).

4,4′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylamine (4). The same method[27] as described for the carbazole diboronester was used (see also the method in ref 28). Using a syringe, 8.3 mL of 2.5 M *n*-BuLi (19.35 mmol) in hexane was added to a solution of 4,4′-dibromotriphenylamine (2.6 g, 6.45 mmol) in THF (50 mL) at −78 °C with stirring. First the color of the solution turned to red-purple and then gradually changed to light yellow. The mixture was stirred at −78 °C for 1 h. Then the temperature was allowed to increase to room temperature. After that, the mixture was cooled to −78 °C again, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.94 mL, 19.35 mmol) was added using a syringe. The reaction mixture was stirred at −78 °C for additional 2 h and then was gradually warmed to room temperature and stirred overnight. The clear solution was diluted with ether (100 mL) and washed with water (3 × 50 mL). The organic layer was dried over MgSO$_4$, and the solvents were concentrated below 40 °C using a rotary evaporator. Flash column chromatography of the residue over silica gel with a mixture of hexane and ethyl acetate mixture (100:5; $R_f \approx 0.3$) as eluent gave **4** as a white solid (0.48 g, 15%). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.35 (s, 24H), 7.02 (d, 4H), 7.08 (d, 2H), 7.10 (m, 1H), 7.26 (m, 2H), 7.66 (d, 4H).

9,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene (6). In a nitrogen atmosphere, 0.540 g (1.61 mmol) of 9,10-dibromoanthracene and 0.898 g (3.54 mmol) of bis(pinacolato)diboron were dissolved in 50 mL of DMF followed by the addition of 11 mg (3 mol %) of palladium acetate and 0.473 g (4.82 mmol) of potassium acetate. The reaction mixture was then stirred at 80 °C while the progress of the reaction was monitored by TLC on silica with toluene as eluent. After 7 h an almost complete consumption of starting material and monoborylated product was indicated. Therefore, the hot reaction mixture was poured into 100 mL of water leading to precipitation of a microcrystalline gray-greenish product, which was filtered off and dried in the air. The residue was treated with dichloromethane and insoluble material was filtered off. Recrystallization from ethanol afforded the product as a slightly greenish microcrystalline powder. Yield: 0.16 g (23%). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.61 (s, 24H; CH$_3$), 7.45 (m, 4H), 8.65 (m, 4H). ^{13}C NMR (CDCl$_3$, 300 MHz): δ (ppm) 135.0, 129.0, 126.0, 84.7, 25.5. Melting point: >290 °C.

4,7-Dibromo-2,1,3-benzothiadiazole (7). A modified version of a previously reported method[27] was used. 2,1,3-Benzothiadiazole (2.72 g, 20 mmol) and 15 mL of 47% aqueous HBr were mixed and heated under reflux with stirring, while bromine (9.6 g, 60 mmol) was slowly dropped into the mixture within 1 h. To facilitate stirring, another 10 mL of 47% aqueous HBr was added and the mixture was heated under reflux for 2 h after completion of the bromine addition. Then the mixture was filtered while hot, cooled, filtered again, washed well with water, and recrystallized with 40 mL of ethanol to give **7** as white needles (4.15 g, 71%). ^{1}H NMR (CDCl$_3$): δ (ppm) 7.72 (s, 2H). ^{13}C NMR (CDCl$_3$, 300 MHz): δ (ppm) 153.0, 132.3, 114.0. Melting point: 188−189 °C.

Polymer Syntheses. Synthesis of P—DPP—CBZ. Under nitrogen, 0.2 g (0.326 mmol) of 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**1a**), 0.173 g (0.326 mmol) of 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(2-ethylhexyl)carbazole (**2**), 5 mg (3 mol %) of palladium(II) acetate, and 35 mg of tris(*o*-tolyl)phosphine were dissolved in 5 mL of toluene and stirred at room temperature for 30 min. Subsequently 0.226 g of potassium carbonate (1.63 mmol) and 10 mg of tetrabutylammonium bromide were dissolved in 2 mL of water and added to the reaction mixture under nitrogen atmosphere. Then the reaction mixture was heated and kept under reflux in nitrogen atmosphere for 24 h. After cooling, 50 mL of chloroform was added, and the mixture was filtered through Celite to remove residual palladium. Then the filtrate was concentrated, the residue was redissolved in a minimum amount of chloroform and precipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. Molecular weight: 15 500 Da. Polydispersity: 2.1. Yield: 61%. ^{1}H NMR (CDCl$_3$): δ (ppm) 0.7−1.8 (C−CH$_2$,CH$_3$), 2.1(CH), 3.90 (DPP α-CH$_2$), 4.25 (carbazole α-CH$_2$), 7.52, 7.79 (DPP aromatic CH), 7.92, 8.02, 8.48 (carbazole aromatic CH).

Synthesis of P—DPP—TPA. Method 1: Under nitrogen, 0.217 g (0.355 mmol) of 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)-pyrrolo[3,4-*c*]pyrrole (**1a**), 0.177 g (0.355 mmol) of 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylamine (**4**), 5 mg (3 mol %) of palladium(II) acetate, and 35 mg of tris(*o*-tolyl)phosphine were dissolved in 5 mL toluene and stirred at room temperature for 30 min. Subsequently 0.294 g of potassium carbonate (2.13 mmol) and 10 mg of tetrabutylammonium bromide were dissolved in 2 mL of water and added to the reaction mixture in a nitrogen atmosphere. Then the reaction mixture was heated and refluxed in nitrogen atmosphere for 24 h. After cooling, 50 mL of chloroform was added, and the mixture was filtered through Celite to remove residual palladium. Then the filtrate was concentrated, and the residue was redissolved in a minimum amount of chloroform and precipitated in ethanol. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. Molecular weight: 3700 Da. Polydispersity: 1.5. Yield: 40%.

Method 2: Under nitrogen, 0.084 g (0.119 mmol) 1,4-diketo-2,5-dihexyl-3,6-bis-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)pyrrolo[3,4-*c*]pyrrole (**1c**), 0.048 g (0.119 mmol) of 4,4′-dibromotriphenylamine (**3**) and 4.1 mg (3 mol %) of tetrakis-(triphenylphosphino)palladium(0) were dissolved in 5 mL of toluene and stirred at room temperature for 30 min. Subsequently 0.098 g of potassium carbonate (0.72 mmol) and 10 mg of tetrabutylammonium bromide were dissolved in 2 mL of water and added to the reaction mixture in nitrogen atmosphere. Then the reaction mixture was heated and kept under reflux in a nitrogen atmosphere for 24 h. After cooling, 50 mL of chloroform was added, and the mixture was filtered through Celite to remove residual palladium. Then the filtrate was concentrated, and the residue was redissolved in a minimum amount of chloroform and precipitated in ethanol. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. Molecular weight: 7400 Da. Polydispersity: 1.9. Yield: 30%. ^{1}H NMR (CDCl$_3$): δ (ppm) 0.7−1.8 (C−CH$_2$,CH$_3$), 3.85 (α-CH$_2$), 7.0−7.4(TPA, CH) 7.59 (TPA, CH), 7.77, 7.93 (DPP aromatic CH).

Synthesis of P—DPP—FLR. Under nitrogen, 1.23 g (2 mmol) of 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**1a**), 1.17 g (2 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-*n*-hexylfluorene (**5**), and 60 mg (3 mol %) of tetrakis(triphenylphosphino)palladium(0) were dissolved in 20 mL of toluene and stirred at room temperature for 30 min. Subsequently 0.141 g of potassium carbonate (1.02 mmol) and 10 mg of tetrabutylammonium bromide were dissolved in 2 mL of water and added to the reaction mixture in a nitrogen atmosphere. Then the reaction mixture was heated and refluxed under nitrogen for 72 h. After cooling, 100 mL of acetone was added. The precipitate was filtered and washed with acetone, 2 N hydrochloride acid, and acetone, successively. The polymer was collected as an orange powder and dried under vacuum for 24 h. Molecular weight: 20 000 Da. Polydispersity: 2.1. Yield: 61%. ^{1}H NMR (CDCl$_3$): δ (ppm) 0.7−1.8 (C−CH$_2$,CH$_3$), 2.05 (α-CH$_2$, fluorene), 3.84 (α-CH$_2$, DPP), 7.7−7.5 (aromatic CH, fluorene), 7.84 (aromatic CH, DPP), 7.96 (aromatic CH, DPP).

Synthesis of P—DPP—ANT. Under nitrogen, a 20 mL Schlenk tube was charged with 0.043 g (0.10 mmol) of 9,10-anthracenebis-(pinacolato)boron ester (**6**) and 0.058 g (0.09 mmol) of 1,4-diketo-2,5-di(2-ethylhexyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**1b**) dissolved in 5 mL of toluene. Subsequently, 5.7 mg of tetrakis-(triphenylphosphino)palladium(0) and 0.33 mL of 2 M aqueous sodium carbonate solution were added. Then the reaction mixture was stirred under nitrogen at 90 °C for 36 h. After this period, the reaction mixture was diluted with 5 mL of toluene and washed with water twice. The organic phase was separated and concentrated in vacuo. The polymer was then precipitated upon addition of ethanol, filtered off and washed with ethanol. After drying in a

Table 1. Molecular Weights and Optical Properties of Different Polymers[a]

	M_w	polydispersity	λ_{max}(nm) solution/film	λ_{em} (nm) solution/film	Stokes shift	Φ_f (%)
P−DPP−CBZ	16 500	2.2	506/527	585/638	79/111	46
P−DPP−TPA1	3700	1.5	497/...	595/...	98/...	
P−DPP−TPA2	7400	1.9	511/526	587/621	76/95	85
P−DPP−BTZ	7000	1.7	515/528	600/665	85/137	19
P−DPP−ANT	6000	1.3	479/482	552/580	73/98	86
P−DPP−FLR	20 000	2.1	500/512	574/599	74/87	70

[a] UV and photoluminescence were measured in chloroform (**P−DPP−CBZ, P−DPP−BTZ, P−DPP−ANT** and **P−DPP−FLR**) or toluene (**P−DPP−TPA1/2**). The excitation wavelength for photoluminescence spectra is 350 nm. Quantum yields of the polymers were measured in chloroform (**P−DPP−CBZ, P−DPP−BTZ, P−DPP−ANT**, and **P−DPP−FLR**) or toluene (**P−DPP−TPA2**) solution with an excitation wavelength of 400 nm, the values were calculated by comparing with Rhodamine 6G in ethanol ($\Phi_f = 0.95$)

stream of nitrogen, 20 mg of a red solid were obtained. Molecular weight: 6000 Da. Polydispersity: 1.3. Yield: 40%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.65−1.80 (alkyl), 3.88 (α-CH_2), 7.42 (anthracene aromatic CH), 7.78 (DPP aromatic CH), 8.11 (anthracene aromatic CH).

Synthesis of P—DPP—BTZ. Under nitrogen, 0.120 g (0.170 mmol) of 1,4-diketo-2,5-dihexyl-3,6-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolo[3,4-*c*]- pyrrole (**1c**), 0.050 g (0.170 mmol) of 4,7-dibromo-2,1,3-benzothiadiazole (**7**), 2.2 mg (3 mol %) of palladium(II) acetate and 6.1 mg of tris(*o*-tolyl)-phosphine were dissolved in 5 mL of toluene and stirred at room temperature for 30 min. Subsequently, 0.141 g of K_2CO_3 (1.02 mmol) and 10 mg of tetrabutylammonium bromide were dissolved in 2 mL of water and added to the reaction mixture in nitrogen atmosphere. Then the reaction mixture was heated and kept under reflux in nitrogen atmosphere for 24 h. After cooling, 50 mL of chloroform was added, and the mixture was filtered through Celite to remove residual palladium. Then the filtrate was concentrated, and the residue was redissolved in a minimum amount of chloroform and precipitated in acetone. The whole procedure was carried out twice. The polymer was collected and dried under vacuum for 24 h. Molecular weight: 7000 Da. Polydispersity: 1.7. Yield: 70%. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.7−1.8 (C−CH_2,CH_3), 3.87 (α-CH_2), 7.82 (aromatic CH).

3. Results and Discussion

3.1. Synthesis of the Monomers. The synthesis of the monomers is shown in Scheme 3. The 1,4-diketo-2,5-dialkyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrroles with alkyl being *n*-hexyl (**1a**) and 2-ethylhexyl (**1b**) as well as the corresponding diboronic ester derivative 1,4-diketo-2,5-dihexyl-3,6-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)- pyrrolo-[3,4-*c*]pyrrole (**1c**) were prepared according to previously reported methods.[18] The diboronic esters of carbazole and triphenylamine were prepared from the corresponding brominated derivatives and successive treatment with *n*-butyllithium and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, respectively. In order to increase the solubility of the monomer, the active proton of the carbazole NH group was alkylated with 2-ethylhexyl bromide before the lithiation was carried out. In the case of the 4,7-dibromo-2,1,3-benzothiadiazole, the lithiation was not applied, because 2,1,3-benzothiadiazole is not stable enough to bear such a strong base as *n*-butyllithium. Instead the DPP diboronic ester **1c** was coupled with 4,7-dibromo-2,1,3-benzothiadiazole (**7**). The 9,10-anthracenebis(pinacolato)boron ester **6** was prepared via a Pd-catalyzed reaction with bis-(pinacolato)diboron.

3.2. Suzuki Coupling Polycondensation. The polymers were synthesized upon Suzuki coupling polycondensation. The preparation route is shown in Schemes 1 and 2. For the coupling, toluene was chosen as the solvent in order to reach a high reaction temperature. At first we used tetrakis(triphenylphosphine)palladium(0) as catalyst. However, the combination of palladium(II) acetate and tris(*o*-tolyl)phosphine was found to be more efficient in obtaining high molecular weights. This is probably due to the ligand tris(*o*-tolyl)phosphine, which is usually applied to prevent the incorporation of phosphorus in the polymer main chain. In some reactions, tetrabutylammonium bromide was used as a phase-transfer catalyst. Furthermore, this salt also worked as a source for bromine.[29,30] After the reaction, the diluted reaction mixture was passed through a Celite column to remove the residual catalyst. Then the polymers were precipitated in acetone or ethanol forming red powders after drying. For some of the polymers, removal of catalyst and the dissolution/reprecipitation procedure had an inevitable, negative effect on the polymer yield. For the preparation of **P−DPP−TPA**, two different strategies were applied: first, dibromo DPP **1a** and the diboronic ester of triphenylamine **4** were polymerized, but the molecular weight of the resulting polymer (**P−DPP−TPA1**) was only 3.7 kDa. Alternatively the diboronic ester of DPP **1c** and dibromotriphenylamine **3** were polymerized. With this approach, a polymer (**P−DPP−TPA2**) with a molecular weight of 7.4 kDa could be obtained. The higher molecular weight of **P−DPP−TPA2** also caused a small bathochromic shift of the UV absorption maximum compared with **P−DPP−TPA1**. The difference in the molecular weight may be due to the poor crystallization of the diboronic ester derivative of triphenylamine **4**, which renders the purification of this compound very difficult. In the case of the preparation of **P−DPP−ANT**, the dialkylated DPP monomer **1b** was used to increase the solubility of the polymer. The preparation of **P−DPP−FLR** was carried out in a larger scale so that it could be used for fabrication of electroluminescent devices.

The polymers are very soluble in chloroform and toluene. Except for **P−DPP−BTZ**, all polymers are also very soluble in THF. **P−DPP−BTZ** could only be dissolved in THF after ultrasonic treatment of the polymer dispersion. The weight-average molecular weight and the polydispersity of the polymers are listed in Table 1. Among the polymers, **P−DPP−FLR** exhibits the highest molecular weight of 20 kDa, which can partly be ascribed to the presence of the additional two hexyl substituent groups in the fluorene units enhancing the solubility.

The proton NMR spectra of monomer **1a** and the various polymers are shown in Figure 1. All spectra show signals of the DPP phenylene protons at about 7.6 ppm, and signals of the *n*-hexyl- (or 2-ethylhexyl-) substituted lactam groups of DPP in the region from 0.7 to 1.8 ppm. The signal of the methylene group adjacent to the lactam N atom of the DPP unit appears around 3.8 ppm. For the carbazole-containing polymer **P−DPP−CBZ**, the signal of the methylene group adjacent to the carbazole N atom appears at 4.25 ppm, the signal of the methylidyne group occurs at 2.1 ppm. Regarding the triphenylamine-based polymer **P−DPP−TPA2**, the characteristic signals of the phenylic protons adjacent to the N atom are between 6.9 and 7.2 ppm. **P−DPP−ANT** was prepared from **1c** and **6**, the characteristic

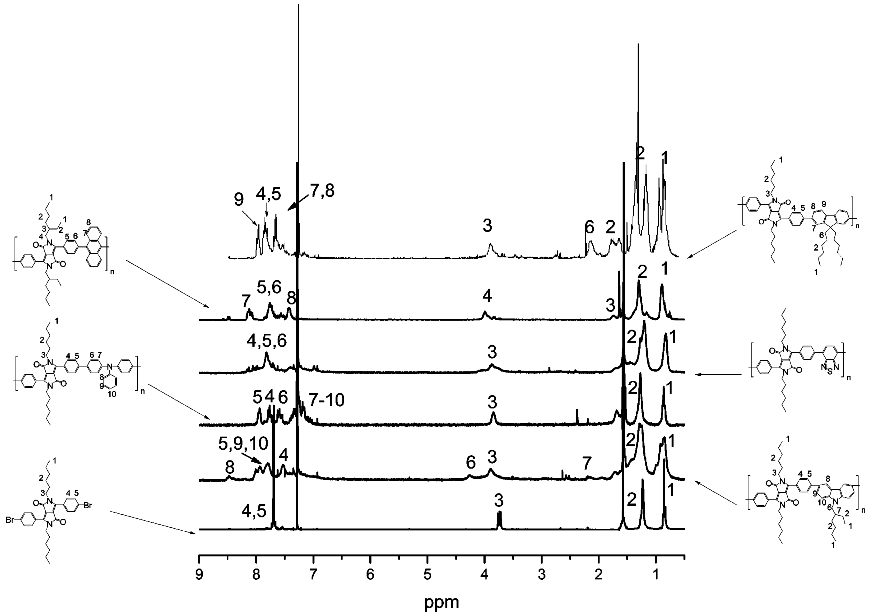


Figure 1. 300 MHz-^{1}H NMR spectra of monomer **1a** and polymers **P−DPP−CBZ**, **P−DPP−TPA2**, **P−DPP−BTZ**, **P−DPP−ANT**, and **P−DPP−FLR**.

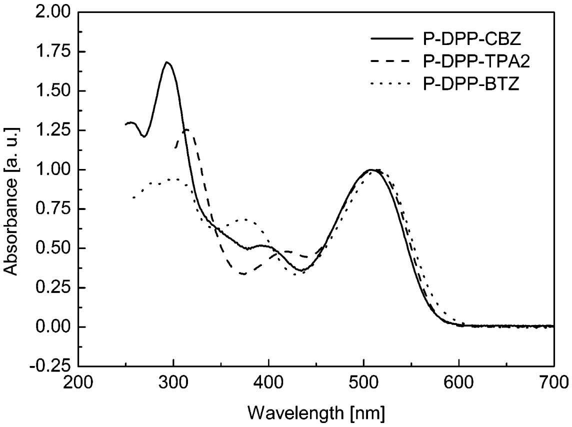


Figure 2. UV/vis absorption spectra of **P−DPP−CBZ**, **P−DPP−TPA2** in toluene and **P−DPP−BTZ** in chloroform.

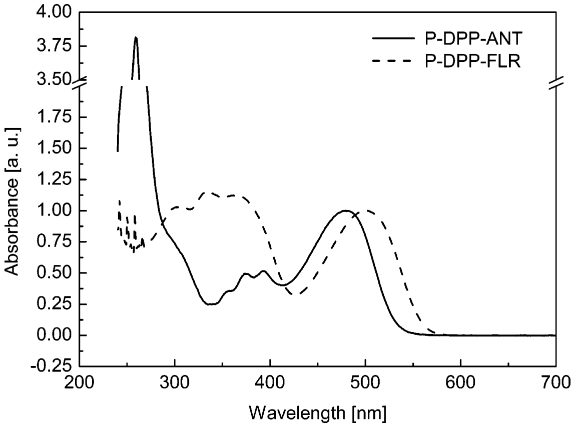


Figure 3. UV/vis absorption spectra of **P−DPP−ANT** and **P−DPP−FLR** in chloroform.

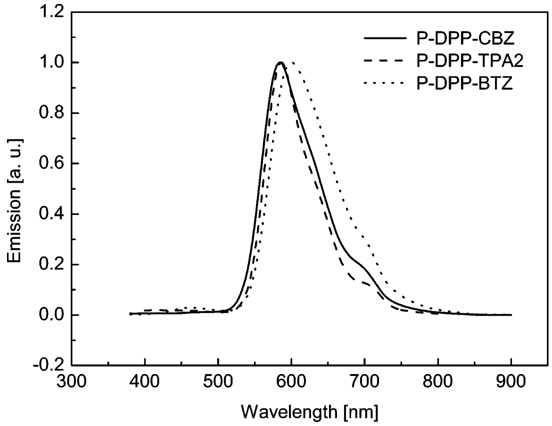


Figure 4. Photoluminescence spectra of **P−DPP−CBZ** and **P−DPP−TPA2** in toluene and **P−DPP−BTZ** in chloroform.

signals of the 2-ethylhexyl group occurring at 1.8 ppm (from the methylidyne group) and at 3.88 ppm (from the α-CH$_2$ group). The signals of the anthracene group occur at 7.42 and 8.11 ppm, respectively. For **P−DPP−FLR**, the signal of the α methylene group occurs at 2.05 ppm.

3.3. Thermal Properties. The thermal properties of the new polymers were investigated. Up to 300 °C, no melting of the polymers could be detected. At temperatures above 250 °C, the originally red polymers turned gradually dark, indicating the onset of decomposition. Differential scanning calorimetry indicated a step-like transition for all polymers investigated, which occurred between 120 and 155 °C depending on the polymer structure and can be ascribed to a glass transition (T_g). The T_g values of **P−DPP−TPA2**, **P−DPP−ANT**, **P−DPP−BTZ**, and **P−DPP−CBZ** are at 120, 145, 145, and 155 °C, respectively. Any endothermic transitions, which can be ascribed to a melting of the alkyl substituent groups, are missing. Thus, it is unlikely that the alkyl groups of the hairy-rod-like polymers are present in a crystalline state.

3.4. Optical and Photoluminescent Properties of the Polymers. The UV/visible absorption and fluorescence spectra of the polymers are shown in Figures 2−5, and the absorption and fluorescence maxima of the solutions are compiled in Table 1. While monomers **1a**, **1b**, and **1c** form yellow solutions in chloroform with absorption maxima at 476, 476, and 479 nm, respectively, most of the polymers form bright red solutions. Except for **P−DPP−ANT**, the maximum absorption in the visible is found in the wavelength region between 500 and 515 nm (Figures 2 and 3). For **P−DPP−ANT**, the maximum

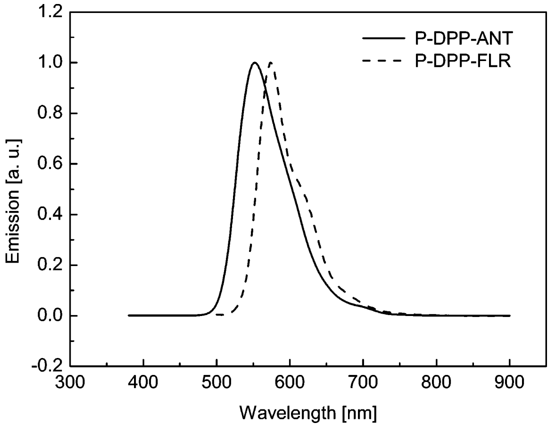


Figure 5. Photoluminescence spectra of **P−DPP−ANT** and **P−DPP−FLR** in chloroform.

absorption is at 479 nm, which is red-shifted by only 3 nm compared with the corresponding monomer **1b** and at much shorter wavelengths than for the other DPP-based conjugated polymers. Possibly there is only weak π-conjugation between the DPP and anthracene units caused by a large tilt angle between the π-planes of these units along the polymer backbone, as known from 9,10-diphenylanthracene[31]. The large tilt angle might be a consequence of the bulky size of the anthracene unit. Compared with monomer **1a**, the absorption maxima of polymers **P−DPP−CBZ**, **P−DPP−TPA2**, **P−DPP−BTZ**, and **P−DPP−FLR** exhibit a bathochromic shift of 24 to 39 nm due to the extension of the π-conjugated system. The bathochromic shifts are smaller than for the previously reported poly-DPP−thienylenes[19] containing electron-accepting DPP and electron-donating thienylene units (or ethylenedioxythiophene or bithiophene units) in an alternating sequence. In the new polymers, the charge transfer between DPP and comonomer unit is less pronounced, and therefore, the bathochromic shift is smaller. However, for the poly-DPP−thienylenes the photoluminescence quantum yield Φ_f was only up to 36%, while the Φ_f values of the new polymers are much higher, which can be ascribed to a more efficient energy transfer from the comonomer to the DPP unit. For most of the new polymers, high quantum yields between 46 and 86% could be determined, if they were excited at a wavelength of 400 nm (see Table 1). The fluorescence quantum yield of 86% of **P−DPP−ANT** in toluene is the highest value reported for a DPP-containing conjugated polymer so far. The new polymers exhibit a maximum emission between 552 and 600 nm, as indicated in Figures 4 and 5. The UV absorption spectra of solid films of the polymers were also measured, the absorption maxima occur between 512 and 528 nm (not shown). Compared with the solution spectra, the absorption maxima of the films are shifted by 13 to 25 nm toward longer wavelengths. The emission maxima of **P−DPP−CBZ**, **P−DPP−TPA2**, **P−DPP−BTZ**, and **P−DPP−FLR** as solid films occur at 638, 621, 665, and 599 nm, respectively (Table 1).

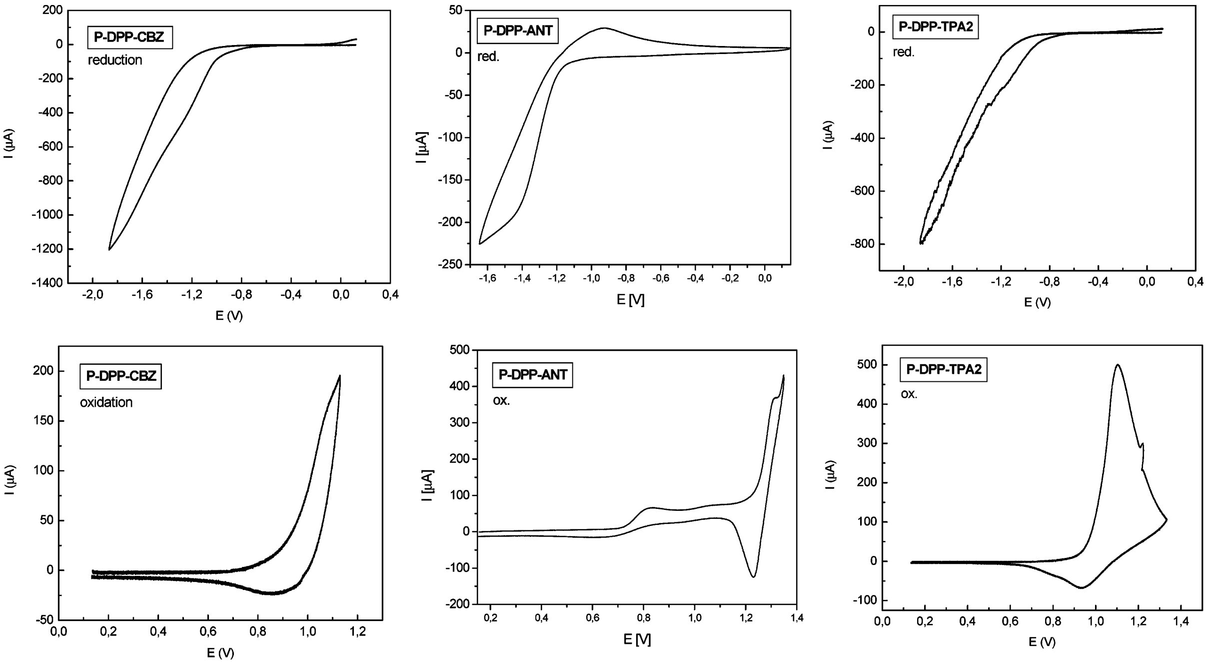


Figure 6. Cyclic voltammograms of polymers **P−DPP−CBZ**, **P−DPP−ANT**, and **P−DPP−TPA2**. Scan rate: 25 mV s^{-1}. $T = 20$ °C. Electrolyte solution: 0.1 M (TBA)PF$_6$ in acetonitrile.

Table 2. Band Gap Data of Different Polymers[a]

polymer	abs λ_{onset} (nm) on film	opt/electrochem band gap (eV)	oxidation onset (V) {HOMO (eV)}	reduction onset (V) {LUMO (eV)}
P−DPP−CBZ	615	2.02/1.90	0.93 {−5.33}	−0.97 {−3.43}
P−DPP−TPA2	596	2.08/1.82	0.97 {−5.37}	−0.85 {−3.55}
P−DPP−BTZ	617	2.01/1.77	0.94 {−5.34}	−0.83 {−3.57}
P−DPP−ANT	528	2.40/2.40	1.20 {−5.60}	−1.20 {−3.20}
P−DPP−FLR	588	2.11/1.76	0.81 {−5.21}	−0.95 {−3.45}

[a] Band gap (E_{opt}) measured at the onset of electronic absorption of the polymer film ($E_{\text{opt}} = 1240/\lambda_{\text{onset}}$ eV). HOMO−LUMO gap according to the equation: $-E_{\text{LUMO}} = E_{\text{onset(red)}} + 4.4$ eV and $-E_{\text{HOMO}} = E_{\text{onset(ox)}} + 4.4$ eV, where $E_{\text{onset(ox)}}$ and $E_{\text{onset(red)}}$ are the onset potentials for the oxidation and reduction processes of polymer thin films vs SCE.

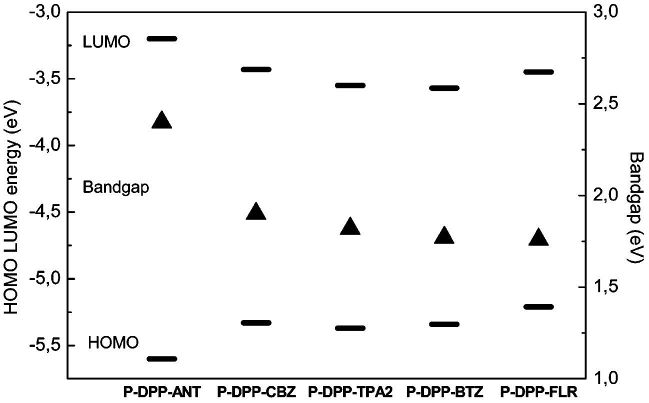


Figure 7. HOMO and LUMO levels of the polymers.

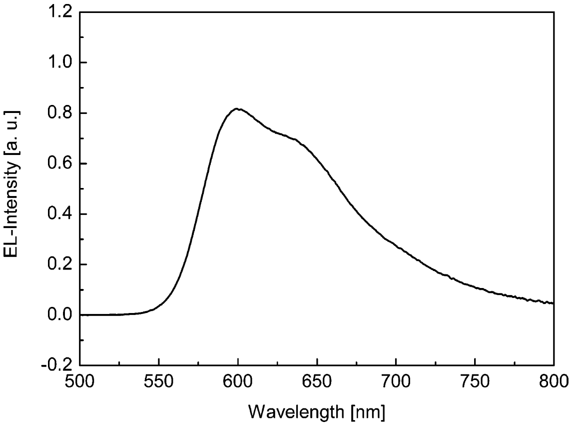


Figure 8. Electroluminescence spectrum of **P−DPP−FLR** from ITO/**P−DPP−FLR**/Al device.

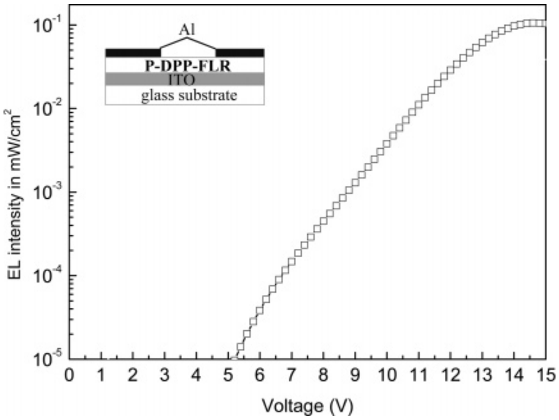


Figure 9. Plot of light intensity vs voltage of ITO/**P−DPP−FLR**/Al device.

3.5. Electrochemical Properties. The electrochemical properties of the polymers were studied using cyclic voltammetry (CV). Oxidative and reductive cycles of some of the polymers are shown in Figure 6, and CV data are compiled in Table 2. All polymers exhibit quasi-reversible oxidative cycles with onset potential $E_{\text{onset(ox)}}$ between 0.81 and 1.20 V (vs SCE), while the reductive cycles are always irreversible. The HOMO and LUMO levels were calculated using the equations[32]

$$-E_{\text{HOMO}} = E_{\text{onset(ox)}} + 4.4 \text{ eV}$$

and

$$-E_{\text{LUMO}} = E_{\text{onset(red)}} + 4.4 \text{ eV}$$

In Table 2 and Figure 7, the HOMO and LUMO levels are listed. On the basis of the HOMO/LUMO calculation, the band gap can be determined. Alternatively, the band gaps can also be calculated from the onset of the optical absorption using the equation

$$E_{\text{opt}} = 1240/\lambda_{\text{onset}} \text{ eV}$$

As shown in Table 2, the band gap values from the optical measurements and the electrochemical experiment match well except for **P−DPP−FLR**, which exhibits the lowest electrochemical band gap of all polymers investigated.

3.6. Electroluminescent Properties of P—DPP—FLR. **P−DPP−FLR** was chosen as an example to study the electroluminescent properties of the new polymers mainly because of the high molecular weight of 20 000 Da, which enabled spin-casting of the polymer into thin films easily. Electroluminescent properties of the other polymers will be reported in a subsequent publication. First the electroluminescence performance was examined in the device configuration of ITO/**P−DPP−FLR**/Al, the thickness of the polymer layer being 75 nm. In Figure 8, the electroluminescence spectrum is shown. Between 12 and 25 V, the spectral shape was constant and the emission maximum appeared at 600 nm, the same wavelength as found in the photoluminescence spectrum. Figure 8 also indicates a low turn-on voltage of only 4.5 V for the ITO/**P−DPP−FLR**/Al device. At a voltage of 15 V and a current density of 0.2 A cm^{-2}, the light intensity was 0.1 mW cm^{-2} (Figure 9). The maximum brightness of the device was 15 cd m^{-2}, the corresponding external quantum efficiency was 0.1%. In order to increase the efficiency of the device, additional hole- and electron-transporting layers of poly(ethylenedioxythiophene) (PEDOT) and 1,3-bis(5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD7), respectively, were applied. The new multilayered device consisted of ITO/PEDOT/**P−DPP−FLR**/OXD7/Ca/Mg:Al, the thickness of the polymer layer was 100 nm. For this device, the turn-on voltage was lowered to 3.5 V. The external efficiency of the device was 0.5%, while the brightness at 20 V was approximately 50 cd m^{-2}. If only PEDOT or OXD7 were used as additional layer, the efficiency was only slightly improved with respect to the single layer device, the value was about 0.2%.

4. Summary and Conclusions

Our study shows that a variety of DPP-containing conjugated polymers can be prepared by using the Suzuki cross-coupling polycondensation. The polymers exhibit moderate to high molecular weights and are readily soluble in common organic solvents. Except for **P−DPP−ANT**, the polymers exhibit bright red colors and a strong red luminescence. Compared with the DPP monomers **1a** and **1b**, the absorption of the polymers is bathochromically shifted by 24−39 nm. The color shift is smaller than for the previously reported poly-DPP-thienylenes, probably because of weaker charge transfer interactions between the DPP and the comonomer units. Instead the fluorescence quantum yields are much higher, which can be ascribed to an efficient energy transfer from the comonomer to the DPP units along the backbone. The small shift of **P−DPP−ANT** might be caused by a large tilt angle between the π-planes of the DPP and anthracene chromophore, which strongly reduces the conjugation length. In particular, **P−DPP−TPA**, **P−DPP−ANT**, and **P−DPP−FLR** are interesting because of their high photoluminescence quantum yields of 70−86%. The polymer **P−DPP−CBZ** is also very promising for its high molecular weight, excellent solubility, relatively high photoluminescence quantum yield (46%) and quasi-reversible oxidation behavior. As exemplarily demonstrated for **P−DPP−FLR**, electroluminescent devices can be made exhibiting an efficiency of 0.5% and a brightness of 50 cd m^{-2} without much optimization. This confirms previous studies of our group[15] and others.[17,20] The study also indicates that the DPP unit can be looked at as a suitable building block introducing bright red color and intense red photo- and electroluminescence in a variety of conjugated polymers. The resulting polymers are therefore candidates as active materials in polymer light-emitting devices.

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