Macromolecules **2008**, *41*, 7287−7295

Articles

Highly Luminescent Polymers Containing the 2,3,5,6-Tetraarylated Pyrrolo[3,4-*c*]pyrrole-1,4-dione (*N*-Aryl DPP) Chromophore in the Main Chain

Kai Zhang and Bernd Tieke*

Institut für Physikalische Chemie, Universität zu Köln, Luxemburger Str. 116, D-50939 Köln, Germany

Received June 19, 2008; Revised Manuscript Received August 13, 2008

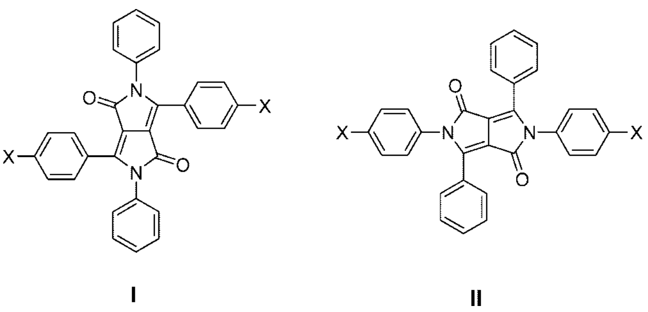
ABSTRACT: Synthesis and characteristic properties of polymers P-1−P-3 are described containing the 2,3,5,6-tetraarylated pyrrolo[3,4-*c*]pyrrole-1,4-dione unit in the main chain. P-1 is prepared from 2,5-bis(4-*t*-butylphenyl)-3,6-bis(4′-bromophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP1) and 9,9-di-*n*-hexylfluorene-2,7′-bispinacolatoboronester **3**, P-2 from 2,5-bis(4′-bromo-phenyl)-3,6-bis(4-*t*-butylphenyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP2) and **3**, and P-3 from DPP1, **3**, and 2,5-bis(*n*-hexyloxybenzene)-1,4-bispinacolatoboronester **4** via Pd-catalyzed Suzuki coupling. Molecular weights of the polymers are about 8000−10 000 Da. All polymers are soluble in common organic solvents such as toluene, chloroform, dichloromethane, tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO) and exhibit a strong fluorescence with Stokes shift up to 56 nm (P-3) and quantum yield up to 81% (P-1). Although P-1 and P-2 are isomers, their optical and electrochemical properties are very different. P-1 with a polyconjugated carbon backbone exhibits absorption and fluorescence maxima of 516 and 569 nm, respectively, which are bathochromically shifted by 15−25 nm with regard to monomer DPP1. In P-2, the π-conjugation of the backbone is interrupted by the lactam N-atoms, so that absorption and fluorescence are similar to those of monomer DPP2 (498 and 531 nm, respectively). Properties of polyconjugated copolymer P-3 are similar to those of P-1. Band gaps of P-1 and P-2 are 2 and 2.3 eV, respectively. Cyclovoltammetric studies indicate irreversible oxidation and reduction cycles.

1. Introduction

1,4-Diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) and its derivatives represent a class of brilliant red high performance pigments.[1−3] Recently, several attempts have been made to use DPP-based compounds as active materials in electronic devices. One of these attempts is based on the preparation of DPP-containing polymers, which can be processed into thin films from solution.[4−10] The preparation of highly soluble DPP-polymers is based on the use of soluble monomers, which requires substitution of the lactam NH groups of the DPP units by alkyl or other groups avoiding the strong hydrogen bonding pattern between the lactam groups.[4−7,11] Most DPP polymers reported so far either carry *n*-hexyl,[4−9] 3,5-bis-*t*-butylbenzyl,[7] *n*-octyl,[9] or ethylhexyl[8,10] substituent groups in order to increase the solubility. N-Arylation of the lactam groups might be an alternative approach to avoid the hydrogen bonding of lactam units and to render the DPP compounds soluble.

Up to the present, N-arylated DPP derivatives have not been used as monomers for the preparation of DPP-based polymers. Though the synthesis of N-arylated DPP derivatives has already been reported,[12] there is no publication yet describing the use of the compounds as monomers for polymerization. Polymerization of the N-arylated DPP derivatives may proceed either via the functionalized phenyl groups in the 3- and 6-position (type I) or via functionalized N-aryl groups in the 2- and 5-position of the pyrrolopyrrole-1,4-dione chromophore. The two possible monomer structures I and II are represented in Scheme 1.

Scheme 1. Isomeric DPP Monomers (X = Polymerizable Unit, e.g., Br)



The purpose of the present work is (a) to describe the synthesis and characteristic properties of new conjugated polymers with *N*-aryl-DPP units in the main chain and (b) to characterize the different optical and electrochemical properties of polymers containing the isomeric monomers I and II. The polymers will be characterized using spectroscopic methods (NMR, UV/vis, fluorescence spectroscopy) and cyclic voltammetry.

2. Experimental Section

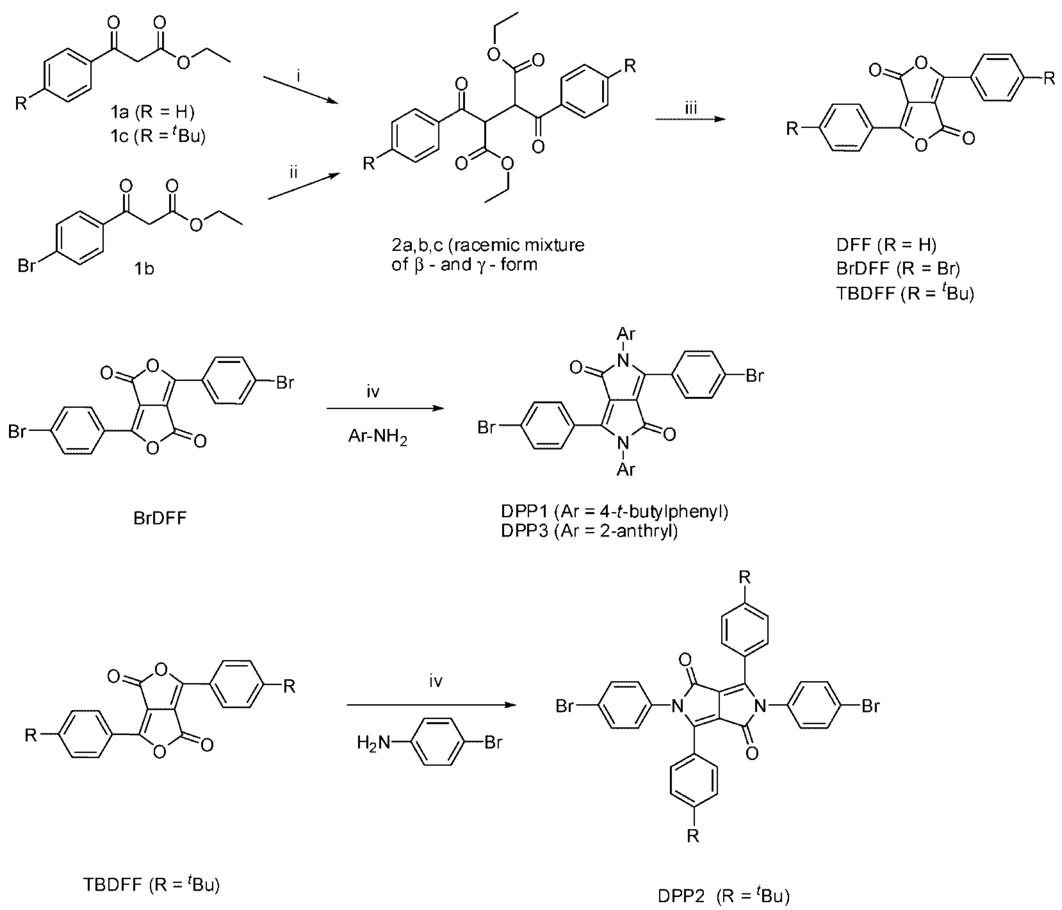
Materials. Ethyl 3-oxo-3-phenylpropionate **1a** was obtained from Fluka. Ethyl 3-oxo-3-(4′-bromophenyl)propionate **1b** was prepared from 1-(4′-bromophenyl)ethanone, diethylcarbonate, and sodium hydride in toluene.[13] Ethyl 3-oxo-3-(4′-*t*-butylphenyl)propionate **1c** was prepared from ethyl 3-oxobutyrate, 4-*t*-butylbenzoyl chloride, and sodium ethylate in dry ethanol.[14] 9,9-Di-*n*-hexylfluorene-2,7′-bispinakolato-boronester **3** was synthesized from fluorene according to a literature method.[15] 2,5-Di-*n*-hexyloxybenzene-1,4-bis(pinakolato-boronester) **4** was prepared from 1,4-dibromo-2,5-di-*n*-hexyloxybenzene[16] as described below. 2-Aminoanthracene, 4-bro-

---

* To whom correspondence should be addressed. E-mail: tieke@uni-koeln.de.

10.1021/ma801376r CCC: $40.75

Scheme 2. Monomer Synthesis: (i) (1) Na, Ether, (2) I_2, $Na_2S_2O_3$; (ii) (1) Br_2, Dichloromethane, (2) NaH, Dichloromethane, (3) Reflux, Dichloromethane, 3 h; (iii) 290°C; (iv) DCC, CF_3COOH, Chloroform



moaniline, 1-bromo-*n*-hexane, 1-(4-bromophenyl)ethanone, *n*-butyllithium (2.5 M solution in hexane), dicyclohexylcarbodiimide, diethylcarbonate, ethyl 3-oxobutyrate, iodine, potassium carbonate, sodium, sodium hydride (60 wt% in mineral oil), sodium hydrogen carbonate, sodium thiosulfate, 4-*t*-butylbenzoyl chloride, tetrakis(triphenylphosphine)palladium(0), and trifluoracetic acid were purchased from Acros, Fluka, Merck, and Sigma-Aldrich and used without further purification. Tetrahydrofuran (THF) was distilled over sodium hydride under nitrogen. Other solvents (ethanol, toluene, chloroform) were purified and dried as usual.

Instrumentation. ^{1}H 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 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 a SEC column combination (Latek/Styragel 50/1000) nm pore size). All measurements were carried out in tetrahydrofuran at 45 °C. The columns were calibrated versus commercially available polystyrene standards. Cyclic voltammograms were recorded using a potentiostat PG390 from Heka Company. A thin film of the polymer was cast on an indium tin oxide (ITO) electrode and cycled in CH_3CN containing 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate as electrolyte salt. Counter and reference electrodes were platinum.

Monomer Synthesis. *Diethyl 2,3-Dibenzoylsuccinate (**2a**).* A solution of ethyl 3-oxo-3-phenylpropionate (8.25 g, 43 mmol) in 120 mL of dry ether was added to a suspension of sodium metal (1 g, 44 mmol) in ether (50 mL), and the mixture was stirred overnight under nitrogen. A solution of iodine (5.54 g, 21.5 mmol) in ether (30 mL) was added in small portions with vigorous stirring. The mixture was stirred for 2 h, and a saturated solution of sodium thiosulfate (30 mL) was added. The organic phase was separated, dried ($MgSO_4$), and evaporated. The crude oily product crystallized from cold ethanol. Yield: 1.39 g (21%). Melting point: 123 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.19 (d, 4H), 7.65 (t, 4H), 7.55 (t, 2H), 5.63 (s, 2H), 3.98 (q, 4H), 0.99 (t, 6H).

*Diethyl 2,3-Bis(4-bromobenzoyl)succinate (**2b**).* (i) Half of ethyl 3-oxo-3-(4′-bromophenyl)propionate (5.108 g, 19 mmol) was dissolved in dichloromethane (30 mL), and a solution of bromine (3 g, 19 mmol) in dichloromethane (15 mL) was added dropwise with stirring. The mixture was then stirred for 30 min and washed with saturated aqueous sodium hydrogen carbonate and water. The dichloromethane solution was dried ($MgSO_4$) and evaporated. (ii) Sodium hydride (0,76 g, 60 wt % in mineral oil, 19 mmol) was washed with hexane and then suspended in dry dichloromethane (20 mL). To this was added the other half of ethyl 3-oxo-3-(4′-bromophenyl)propionate (5.108 g, 19 mmol) in dichloromethane (10 mL). The mixture was refluxed for 15 min, and then the crude product of (i) in dry dichloromethane (15 mL) was added. The mixture was refluxed with stirring for 3 h. The suspension was cooled, washed with water (3 × 20 mL), and dried ($MgSO_4$). Evaporation gave a yellow oil which crystallized from cold ethanol. Yield: 2.522 g (25%). Melting point: 146 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.05 (d, 4H), 7.68 (d, 4H), 5.57 (s, 2H), 4.01 (q, 4H), 1.00 (t, 6H).

*Diethyl 2,3-Bis(4′-t-butylbenzoyl)succinate (**2c**).* A solution of ethyl 3-oxo-3-(4′-*t*-butylphenyl)propionate (8.987 g, 36 mmol) in 150 mL of dry ether was added to a suspension of sodium metal (0.833 g, 36 mmol) in ether (50 mL), and the mixture was stirred overnight under nitrogen. A solution of iodine (4.568 g, 18 mmol) in ether (40 mL) was added in small portions with vigorous stirring. The mixture was stirred for 2 h, and a saturated solution of sodium thiosulfate (50 mL) was added. The organic phase was separated, dried ($MgSO_4$), and evaporated. The residue was purified by flash

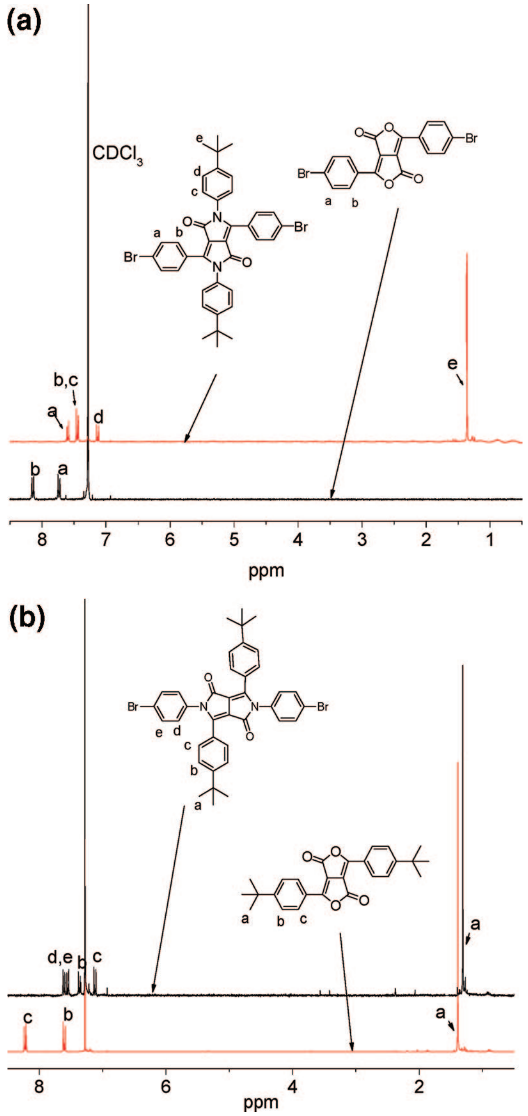


Figure 1. ^{1}H NMR spectra (300 MHz) of monomers BrDFF and DPP1 (a) and monomers TBDFF and DPP2 (b).

column chromatography over silica gel with a mixture of dichloromethane and toluene (4:1, $R_f = 0.7$). Yield: 1.866 g (21%). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.19 (d, 4H), 7.65 (t, 4H), 5.63 (s, 2H), 3.98 (q, 4H), 1.31 (s, 18H), 0.99 (t, 6H).

3,6-Diphenylfuro[3,4-c]furane-1,4-dione (DFF). Diethyl 2,3-dibenzoylsuccinate (**2a**) (2.78 g, 7.51 mmol) was slowly heated in vacuo (290−300 °C), cooled down (220−230 °C), and heated up again. After a further cooling−heating cycle, the brown material was refluxed with methanol (30 mL) and filtered. The residue was recrystallized from toluene (100 mL) and further purified by silica gel flash column chromatography (chloroform, $R_f = 0.76$). The fluorescent fraction was collected and recrystallized from methanol to furnish 1.02 g (47%) of orange needles. Melting point: 288 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.30 (d, 4H), 7.52−7.67 (m, 6H). UV ($CHCl_3$): 455, 425, 402 nm; ε (455) = 4.4×10^4 cm^2 mol^{-1}.

3,6-Bis(4′-bromophenyl)furo[3,4-c]furane-1,4-dione (BrDFF). Diethyl 2,3-bis(4-bromobenzoyl)succinate (**2b**) (6.335 g, 11.73 mmol) was slowly heated in vacuo (290−300 °C), cooled down (220−230 °C), and heated up again. After a further cooling−heating cycle, the brown material was refluxed with methanol (50 mL) and filtered. The residue was recrystallized from toluene (100 mL) and further purified by silica gel flash column chromatography (chloroform, $R_f = 0.82$). The fluorescent fraction was collected and recrystallized from methanol to furnish 1.50 g (53%) of orange needles. Melting point: >300 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.13 (d, 4H), 7.75 (d, 4H). UV ($CHCl_3$): 470, 438, 421 nm; ε (470) = 4.9×10^4 cm^2 mol^{-1}; PL ($CHCl_3$): 481, 514, 560 nm.

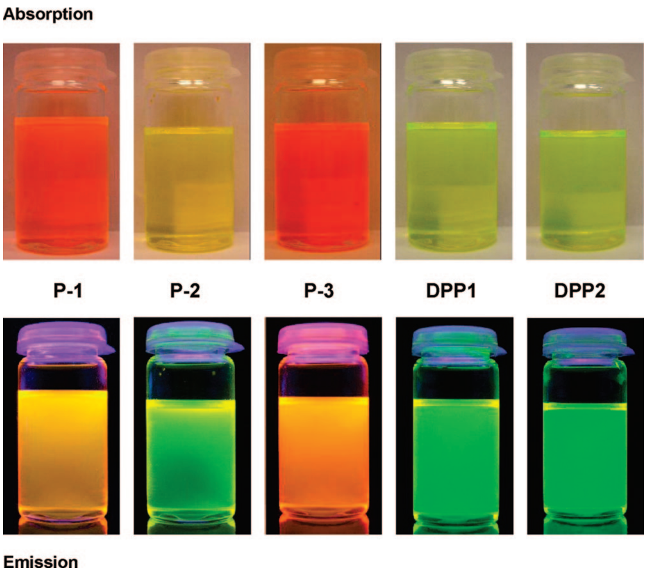


Figure 2. Images of polymer solutions P-1, P-2, and P-3 and monomer solutions DPP1 and DPP2 (from left to right). The upper row shows the absorption colors, and the lower row shows the emission colors.

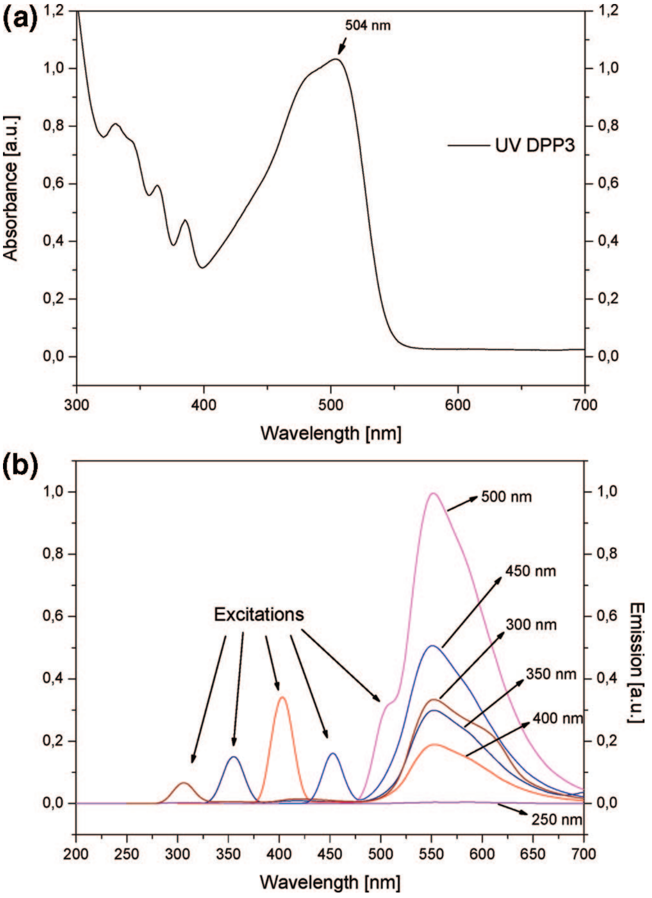
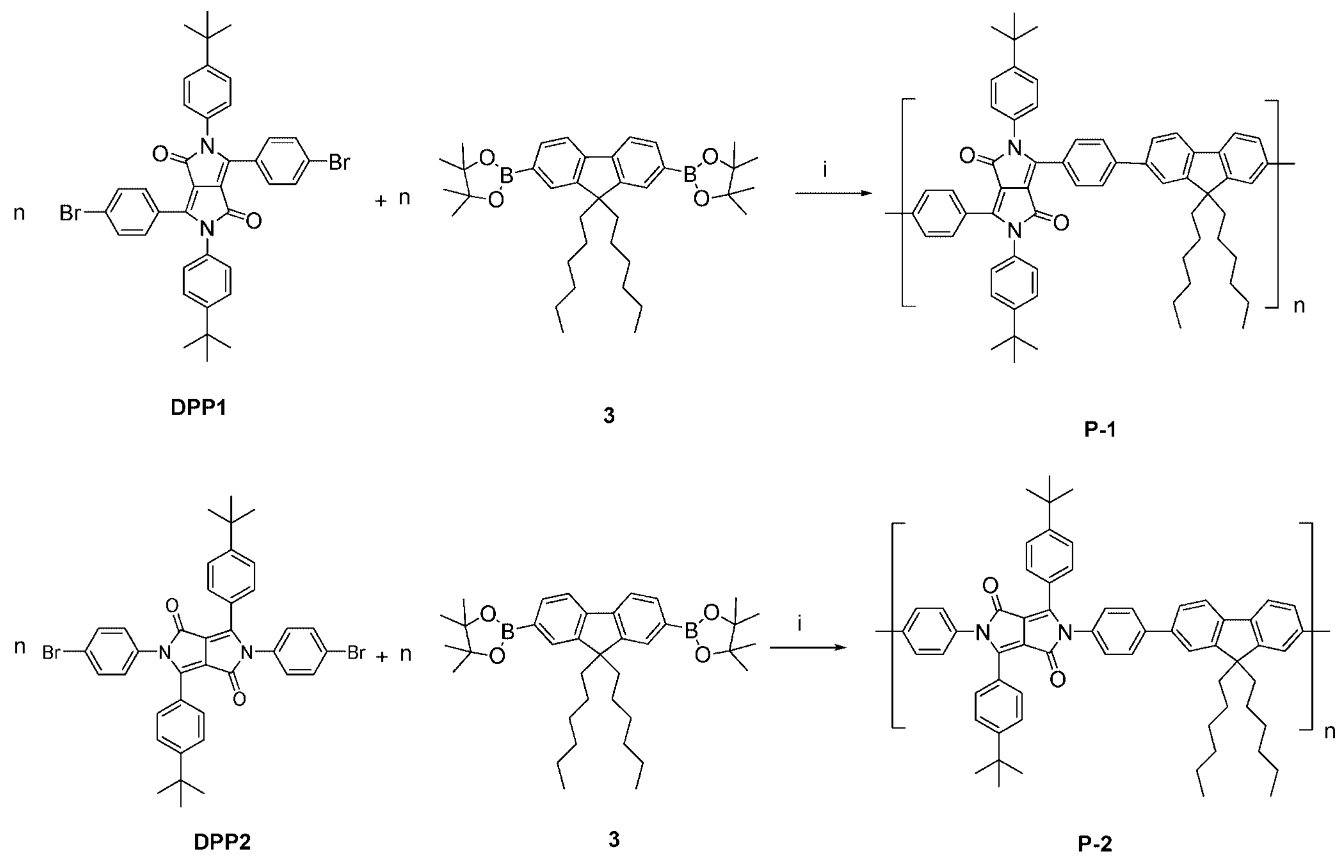


Figure 3. UV/vis absorption (a) and fluorescence spectra (b) of DPP3. In (b), the influence of the excitation wavelength on the fluorescence spectra is shown.

3,6-Bis(4′-t-butylphenyl)furo[3,4-c]furane-1,4-dione (TBDFF). Diethyl 2,3-bis(4′-*t*-butylbenzoyl)succinate (**2c**) (2.28 g, 4.62 mmol) was slowly heated in vacuo (290−300 °C), cooled down

Scheme 3. Polymer Synthesis: (i) Pd(0), K_2CO_3, Toluene/Water, 2 Days



(220−230 °C), and heated up again. After a further cooling−heating cycle, the brown material was refluxed with methanol (50 mL) and filtered. The residue was recrystallized from toluene (100 mL) and further purified by silica gel flash column chromatography (chloroform, $R_f = 0.76$). The fluorescent fraction was collected and recrystallized from methanol to furnish 0.80 g (43%) of orange needles. Melting point: >300 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.23 (d, 4H), 7.60 (d, 4H), 1.38 (s, 18H). UV ($CHCl_3$): 467, 436, 411 nm; ε (467) = 4.5 × 10^4 cm^2 mol^{-1}; PL ($CHCl_3$): 480, 510 nm.

2,5-Dihydro-2,5-bis(4-t-butylphenyl)-3,6-bis(4′-bromophenyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP1). 3,6-Bis(4′-bromophenyl)-furo[3,4-*c*]furane-1,4-dione (BrDFF) (1.00 g, 2.20 mmol), 4-*t*-butylaniline (0.98 g, 6.60 mmol), dicyclohexylcarbodiimide, (1.37 g, 6.67 mmol), and trifluoroacetic acid (10 μL, 0.10 mmol) in chloroform (150 mL) were stirred at room temperature for 3 days. A total of 20 mL of ethanol was added to dissolve the crystallized *N,N′*-dicyclohexylurea, and the mixture was filtered. The filtrate was purified by silica gel column chromatography (toluene). The dye was precipitated from the toluene solution by the addition of methanol as red crystals with a red solid-state fluorescence. Yield: 0.76 g (49%). Melting point: >300 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.11−7.63 (16 aromatic C−H), 1.38 (s, 18H). UV ($CHCl_3$): 502, 477, 337 nm.

2,5-Dihydro-2,5-bis(4′-bromophenyl)-3,6-bis(4-t-butylphenyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP2). 3,6-Bis(4′-*t*-butylphenyl)-furo[3,4-*c*]furane-1,4-dione (TBDFF) (0.4 g, 1 mmol), *p*-bromoaniline (0.872 g, 5 mmol), dicyclohexylcarbodiimide, (0.618 g, 3 mmol), and trifluoroacetic acid (3 μL, 0.04 mmol) in chloroform (80 mL) were stirred at room temperature for 3 days. The crystallized *N,N′*-dicyclohexylurea was removed by filtration, and the filtrate was purified by silica gel column chromatography (toluene). The dye was precipitated from the toluene solution by the addition of methanol as orange crystals with a red solid-state fluorescence. Yield: 0.315 g (44%). Melting point: >300 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.52−7.63 (m, 8H), 7.38 (d, 4H), 7.11 (d, 4H), 1.32 (s, 18H). UV ($CHCl_3$): 492, 468, 334 nm; ε (492) = 2.9 × 10^4 cm^2 mol^{-1}.

2,5-Dihydro-2,5-bis(4-anthryl)-3,6-bis(4′-bromophenyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP3). 3,6-Bis(4′-bromophenyl)furo[3,4-*c*]furane-1,4-dione (BrDFF) (0.2 g, 0.45 mmol), 2-aminoanthracene (0.286 g, 1.48 mmol), dicyclohexylcarbodiimide, (0.278 g, 1.35 mmol), and trifluoroacetic acid (1.7 μL, 0.02 mmol) in chloroform (100 mL) were stirred at room temperature for 3 days. The crystallized *N,N′*-dicyclohexylurea was removed by filtration, and the filtrate was purified by silica gel column chromatography (toluene). The dye was precipitated from the toluene solution by the addition of methanol as dark red crystals with a red solid-state fluorescence. Yield: 0.16 g (45%). Melting point: >300 °C. UV ($CHCl_3$): 504, 385, 360, 345, 330 nm.

*2,5-Di-n-hexyloxybenzene-1,4-bis(pinacolato-boronester) (**4**).* A total of 1 g (2.29 mmol) of 1,4-dibromo-2,5-di-*n*-hexyloxybenzene,[16] 1.347 mg (13.74 mmol) of potassium acetate, 1.165 g (4.59 mmol) of bispinacolatodiboron, and 25 mg (0.11 mmol) of palladium acetate were dissolved in 20 mL of dimethylformamide (DMF). The mixture was purged with nitrogen for 30 min, heated to 80 °C, and stirred for 5 h. After cooling to room temperature, the mixture was poured into 100 mL of water. A gray precipitate was obtained, which was filtered and recrystallized from chloroform/ethanol. Yield: 0.71 g (58%) of white crystalline solid. Melting point: 76 °C. ^{1}H NMR ($CDCl_3$) (δ in ppm): 7.12 (aromatic H), 3.96 (α-CH_2), 1.80 (β-CH_2), 1.31−1.58 (CH_2), 1.33 (ester CH_3), 0.92 (alkyl CH_3).

Polymer Synthesis. *Synthesis of P-1.* Under nitrogen, a 20 mL Schlenk tube was charged with 0.063 g (0.11 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-*n*-hexylfluorene (**3**) and 0.076 g (0.11 mmol) of 2,5-dihydro-2,5-bis(4-*t*-butylphenyl)-3,6-bis(4′-bromophenyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP1) dissolved in 5 mL of toluene. Subsequently, 3.8 mg (0.003 mmol) of tetrakis-(triphenylphosphino)palladium(0) and 0.2 mL of 2 M aqueous sodium carbonate solution were added. The

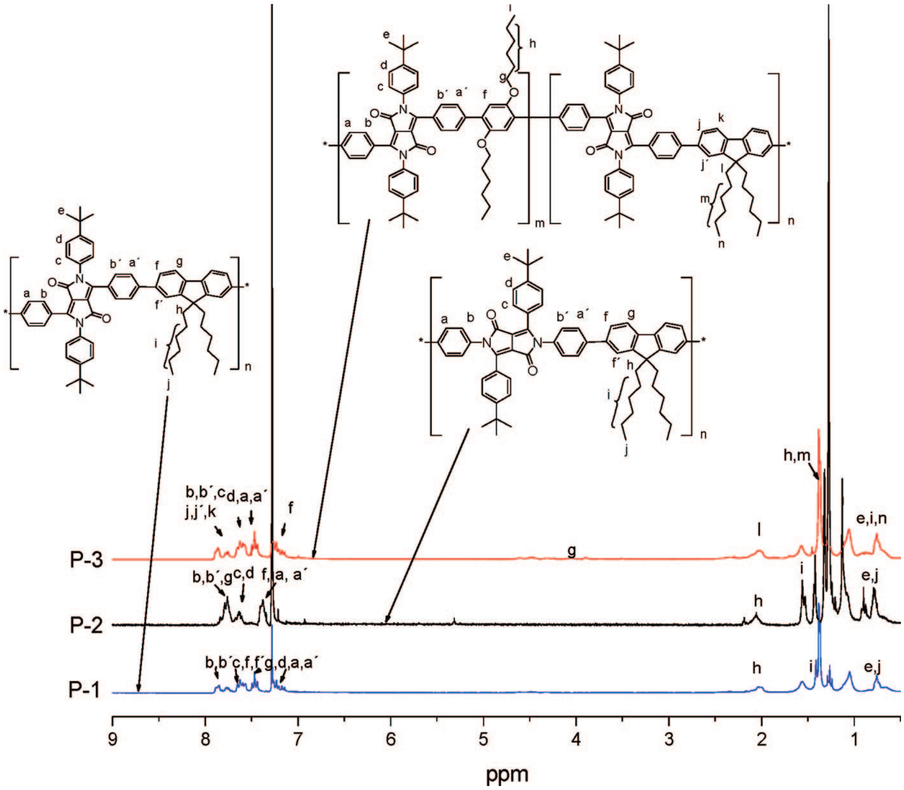
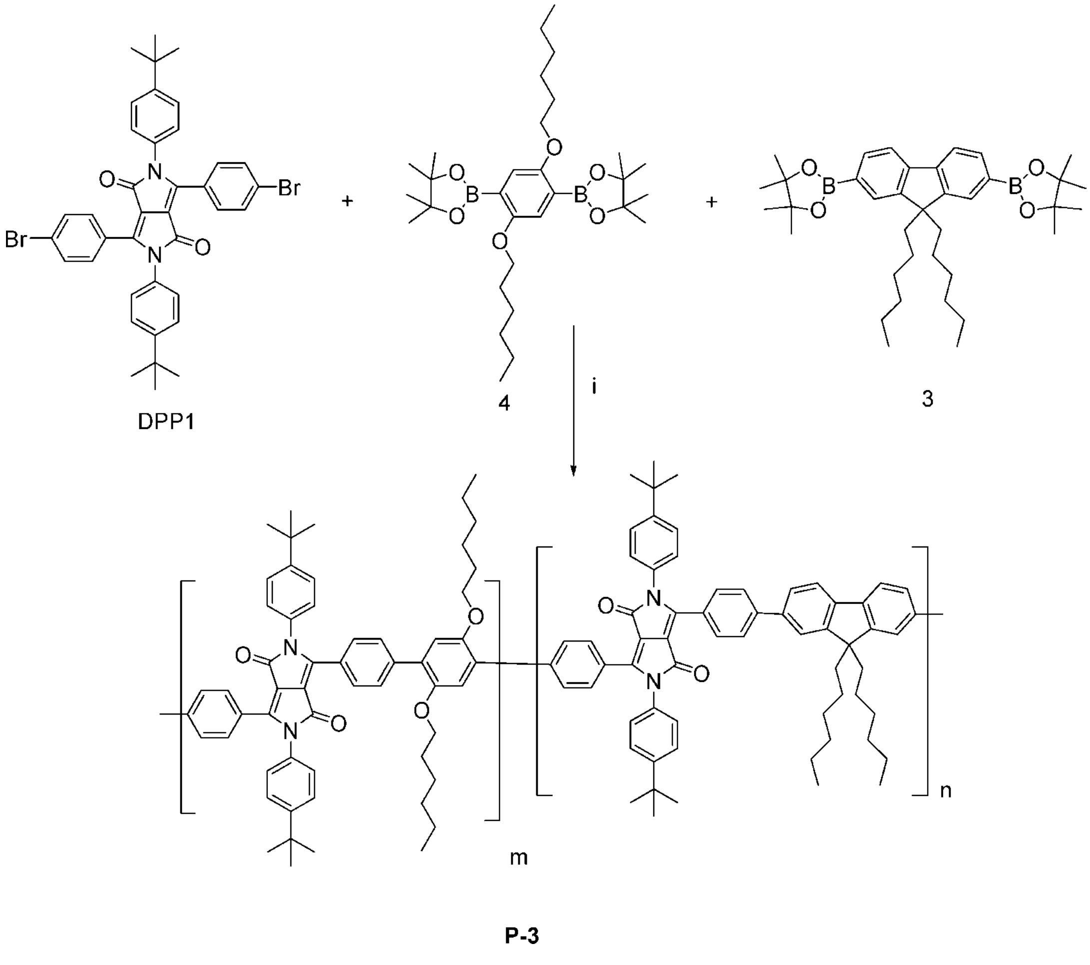


Figure 4. ^{1}H NMR spectra (300 MHz) of polymers P-1, P-2, and P-3.

Scheme 4. Copolymer Synthesis: (i) Pd(0), K_2CO_3, Toluene/Water, 2 Days



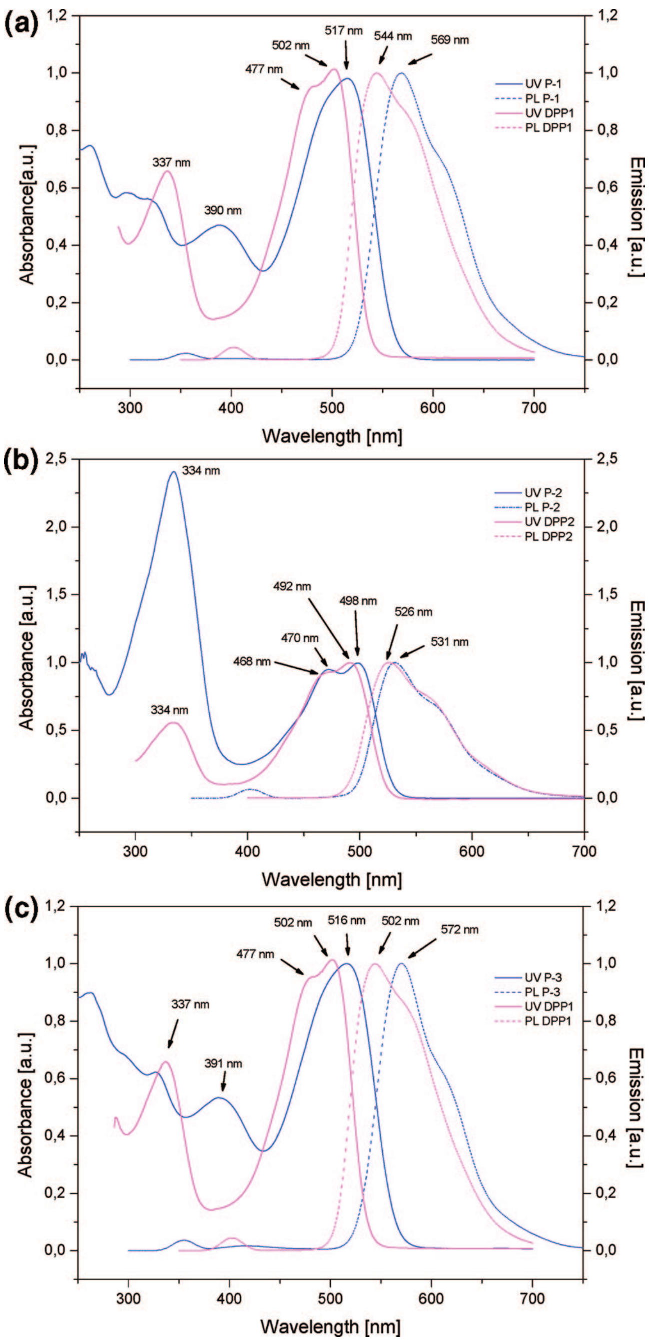


Figure 5. UV/vis absorption and fluorescence spectra of DPP1 and P-1 (a), DPP2 and P-2 (b), and DPP1 and P-3 (c).

Table 1. Molecular Weights and Optical Properties of the Polymers

	M_w	polydispersity	λ_{max} (nm)[a]	λ_{em} (nm)[a]	Stokes shift (nm)	Φ_f (%)
P-1	7500	1.3	517	569	52	81
P-2	9400	1.7	498	531	33	73
P-3	7700	1.6	516	572	56	77

[a] In chloroform.

reaction mixture was then stirred under nitrogen at 100 °C for 36 h. After this period, the reaction mixture was diluted with 20 mL of toluene and washed with water twice. The organic phase was separated, dried ($MgSO_4$), and concentrated in vacuo. The polymer was then precipitated upon addition of methanol, filtered off, and washed with methanol. After drying in a stream of nitrogen, 61 mg (63%) of a red solid was obtained. Molecular weight: 7500 Da. Polydispersity: 1.3. ^1H NMR ($CDCl_3$): δ (ppm) 7.21−7.80 (m, aromatic CH), 1.92−2.06 (m, α-CH_2 of fluorene), 0.70−1.61 (m, alkyl). UV ($CHCl_3$): 517, 390 nm; ε (517) = 1.0 × 10^4 cm^2 mol^{-1}; IR (cm^{-1}): 2963.5 (m), 1636.7 (s), 1516.2 (w), 1409.9 (w), 1359.4 (w), 1260.3 (s), 1091.2 (s), 1017.7 (s), 862.9 (w), 799.1 (s).

Synthesis of P-2. Under nitrogen, 0.1 g (0.14 mmol) of 2,5-dihydro-2,5-bis(4′-bromophenyl)-3,6-bis(4-*t*-butylphenyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP3), 0.083 g (0.14 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-*n*-hexylfluorene (**3**), and 5 mg (0.004 mmol) of tetrakis-(triphenylphosphino)palladium(0) were dissolved in 10 mL toluene. After stirring for 30 min, 0.2 mL of 2 M aqueous sodium carbonate solution was added. The reaction mixture was then stirred under nitrogen at 105 °C for 36 h. After this period, the reaction mixture was diluted with 30 mL of toluene and washed with water twice. The organic phase was separated, dried ($MgSO_4$), and concentrated in vacuo. The polymer was then precipitated upon addition of methanol, filtered off, and washed with methanol. After drying in a stream of nitrogen, 32 mg (25%) of a red solid was obtained. Molecular weight: 9400 Da. Polydispersity: 1.6. ^1H NMR ($CDCl_3$): δ (ppm) 7.13−7.87 (m, aromatic CH), 2.06 (m, α-CH_2 of fluorene), 0.80−1.57 (m, alkyl). UV ($CHCl_3$): 498, 470, 334 nm; ε (498) = 2.4 × 10^4 cm^2 mol^{-1}; IR (cm^{-1}): 2962.2 (m), 1690.0 (w), 1633.7 (s), 1496.6 (sh), 1455.6 (sh), 1363.8 (s), 1315.0 (sh), 1260.6 (s), 1145.1 (w), 1093.9 (m), 1072.8 (m), 1018.8 (s), 863.9 (sh), 798.3 (s).

Synthesis of Copolymer P-3. Under nitrogen, a 20 mL Schlenk tube was charged with 0.06 g (0.08 mmol) of 2,5-dihydro-2,5-bis(4-*t*-butylphenyl)-3,6-bis(4′-bromophenyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP1), 0.024 g (0.04 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-*n*-hexylfluorene (**3**), 0.022 (0.04 mmol) of 2,2′-(2,5-bis(*n*-hexyloxy)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane), and 0.003 g (0.04 mmol) of tetrakis-(triphenylphosphino)palladium(0) dissolved in 5 mL of toluene. After stirring for 30 min, 0.2 mL of 2 M aqueous sodium carbonate solution was added. The reaction mixture was then stirred under nitrogen at 105 °C for 36 h. After this period, the reaction mixture was diluted with 20 mL of toluene and washed with water twice. The organic phase was separated, dried ($MgSO_4$), and concentrated in vacuo. The polymer was then precipitated upon addition of methanol, filtered off, and washed with methanol. After drying in a stream of nitrogen, 0.096 g (70%) of a red solid was obtained. Molecular weight: 7700 Da. Polydispersity: 1.6. ^1H NMR ($CDCl_3$): δ (ppm) 7.10−7.92 (m, aromatic CH), 1.90−2.11 (m, α-CH_2 of fluorene), 0.60−1.62 (m, alkyl). UV ($CHCl_3$): 516, 391 nm; ε (516) = 1.1 × 10^4 cm^2 mol^{-1}; IR (cm^{-1}): 2962.6 (s), 1719.6 (w), 1685.8 (m), 1600.9 (m), 1515.1 (m), 1466 (m), 1408.7 (m), 1363.8 (m), 1261.3 (s), 1092.0 (s), 1016.9 (s), 863.7 (w), 798.1 (s).

3. Results and Discussion

Synthesis of the Monomers. The synthetic pathway to the N-arylated monomers DPP1−DPP3 is outlined in Scheme 2. Starting from the benzoyl acetic acid esters **1a**−**c**, the corresponding dimers **2a**−**c** were prepared via oxidative dimerization with iodine.[12,17] Dimers were heated to 280 °C to form the diketofurofuran (DFF) derivatives listed in Scheme 1.[12,18] Besides the unsubstituted DFF (see Supporting Information), the (4,4′-dibromophenyl)-DFF (BrDFF) and the (4,4′-di-*t*-butylphenyl)-DFF (TBDFF) were synthesized.

The N-arylated monomers DPP1−DPP3 were prepared from the dilactons by condensation with primary arylamine derivatives in presence of DCC as outlined in Scheme 2. The method of lactam formation was adapted from Langhals et al.[12] DPP1 and DPP2 were readily soluble in common organic solvents and could be used as monomers in the subsequent polymerization reaction, whereas the *N*-anthracenyl-DPP-derivative (DPP3) was minimally soluble and could not be readily polymerized.

Characteristic Properties of DFF Derivatives and DPP Monomers. The proton NMR spectra of BrDFF and monomer DPP1 prepared are shown in Figure 1a. While BrDFF only shows the proton signals of the two phenyl groups at 7.75 and

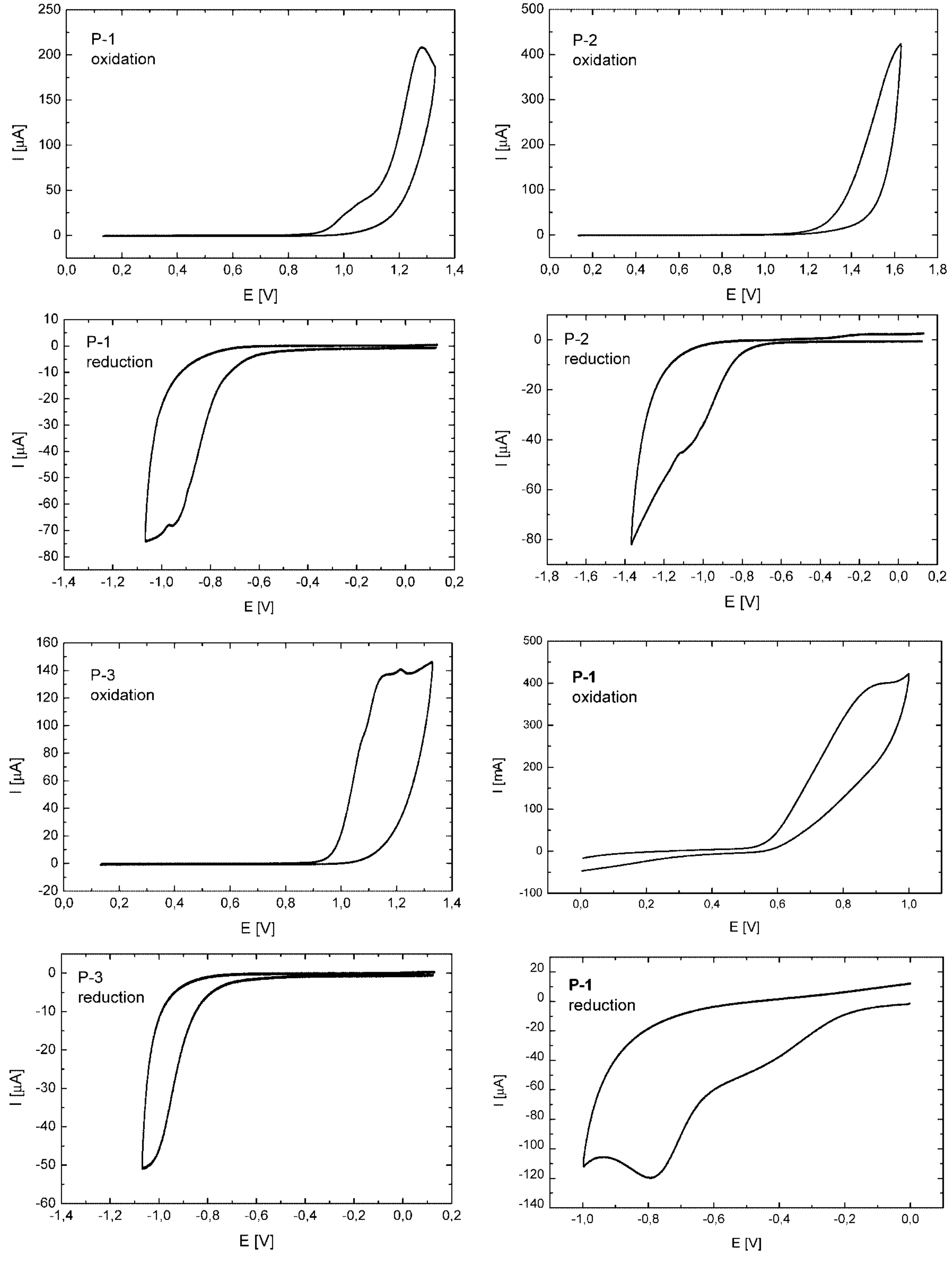


Figure 6. Cyclic voltammograms of P-1, P-2, and P-3. Scan rate: 25 mV s^{-1}. $T = 20$ °C. Electrolyte solution: 0.1 M $(TBA)PF_6$ in acetonitrile.

8.13 ppm, the corresponding DPP1 exhibits additional signals from the *t*-butyl group attached to the N-aryl unit at 1.32 ppm. The proton signals from the four phenyl groups occur between 7.11 and 7.63 ppm. TBDFF exhibits signals of the methyl protons of the *t*-butyl group at 1.38 ppm and signals of the phenyl protons between 7.60 and 8.23 ppm (Figure 1b). After reaction with 4-bromoaniline to yield DPP2, signals of the methyl protons shifted to 1.32 ppm and the phenyl protons occurred between 7.52 and 7.63 ppm. The new proton signals from the 4-bromophenyl groups appear at 7.11 and 7.38 ppm (Figure 1b).

The DFF derivatives are orange crystalline powders, which are readily soluble in common organic solvents. Yellow solutions with blue (DFF, TBDFF) or green fluorescence (BrDFF) are formed. Extinction coefficients of the absorption maxima are ε (455) = 4.4×10^4 cm^2 mol^{-1} for DFF, ε (467) = 4.5×10^4 cm^2 mol^{-1} for TBDFF, and ε (470) = 4.9×10^4 cm^2 mol^{-1} for BrDFF. For optical absorption and emission spectra of DFF, see the Supporting Information.

The corresponding dibromodiketopyrrolopyrrole monomer DPP1 is obtained as deep red flakes, and monomer DPP2 as orange flakes. Both compounds are readily soluble in common

Table 2. Band Gap Data of P-1 to P-3[a]

polymer	abs λ_{onset} (nm) on film	opt/electrochem band gap (eV)	oxidation onset (V) {HOMO (eV)}	reduction onset (V) {LUMO (eV)}
P-1	581	2.13/0.78	0.42 {−4.82}	−0.36 {−4.04}
P-2	541	2.29/0.98	0.70 {−5.10}	−0.28 {−4.12}
P-3	579	2.14/0.99	0.43 {−4.83}	−0.56 {−3.84}

[a] Band gap (E_{opt}) measured at the onset of electronic absorption of the polymer film ($E_{\mathrm{opt}} = 1240/E_{\mathrm{onset}}$ eV). HOMO−LUMO gap according to the equations:[20] $-E_{\mathrm{LUMO}} = E_{\mathrm{onset(red)}} + 4.4$ eV and $-E_{\mathrm{HOMO}} = E_{\mathrm{onset(ox)}} + 4.4$ eV, where $E_{\mathrm{onset(ox)}}$ and $E_{\mathrm{onset(red)}}$ are the onset potentials for the oxidation and reduction processes, respectively, of polymer thin films versus SCE.

solvents, with the solutions exhibiting a yellow color with greenish fluorescence (Figure 2). The absorption maximum of DPP1 is at 502 nm, that is, 10 nm bathochromically shifted with regard to DPP2, while the emission maximum is even more shifted to longer wavelengths (see Figure 5). The reason could be that the bromophenyl groups of DPP1 are in π-conjugation with the heterocyclic DPP chromophore, while in DPP2 the bromophenyl groups are attached to the lactam N-atoms, which are not π-conjugated with the core chromophore.

Since DPP3 is only minimally soluble in common solvents, it could only incompletely be analyzed using solution spectroscopic methods. While the solubility was too low to measure well-resolved NMR spectra, it was possible to monitor optical absorption and emission spectra in chloroform. The UV/vis absorption spectrum in Figure 3a shows the broad absorption band of the DPP unit with a maximum at 502 nm and additional bands at 330, 345, 360, and 385 nm, which can be ascribed to the anthracene absorption. In the fluorescence spectrum (Figure 3b), the additional bands from the anthracene do not occur. Only a broad emission band with maximum at 553 nm occurs, which varies in intensity with the excitation wavelength. The lack of the anthracene bands can be interpreted by an energy transfer from the anthracenyl groups to the DPP unit. The strongly absorbing anthracenyl groups act as antennae for blue light, which is subsequently transferred to the central heterocyclic DPP chromophore.

Synthesis of the Polymers. The polymers P-1 to P-3 were synthesized using the Pd-catalyzed Suzuki polycondensation reaction outlined in Scheme 3. For polymerization, the dibrominated isomeric monomers DPP1 and DPP2 were converted with di-*n*-hexylfluorene bispinacolatoboronester **3** to yield the polymers P-1 and P-2, respectively, carrying isomeric DPP units in the main chain. In addition, monomer DPP1 was also reacted with a 1:1 molar mixture of monomers **3** and **4** (**4**: 2,5-di-*n*-hexyloxyphenylene-1,4-bispinacolatoboronester) to yield polymer P-3 (Scheme 4). Compound **4** was used as the comonomer because of its excellent ability to improve the solubility of the polymer.

Characteristic Properties of DPP-Based Polymers. Polymers P-1 to P-3 were soluble in common organic solvents such as dichloromethane, chloroform, toluene, or dimethyl sulfoxide but insoluble in methanol. This allowed us to analyze the molecular structure of the polymers using ^{1}H NMR spectroscopy. In Figure 4, the spectra of the three polymers are compared. All polymers show the typical signals of the protons of the alkyl groups attached to the fluorene unit at 0.7−1.6 ppm and the protons of the fluorene frame at 7.6−7.8 ppm. In addition, all polymers exhibit the intense signal of the protons from the *t*-butyl group of N-arylated DPP at 1.33 ppm. Additional signals in the aromatic region between 7.2 and 7.8 ppm can be ascribed to protons from the phenyl groups of DPP. For the copolymer P-3, additional signals of the α-CH_2 group of the alkoxy side chains of comonomer **4** occur at about 4 ppm. The origin of a splitting of these signals into four peaks is not yet clear.

P-1 was obtained in 63% yield as a dark red powder, which was strongly fluorescent in the solid state. The molecular weight of the polymer was 7500 Da (see Table 1). Polymer solutions in chloroform or toluene are orange with a bright orange to red luminescence. As indicated in Figure 5, the UV/vis absorption of the polymer has its maximum at 517 nm; that is, the maximum is bathochromically shifted by 15 nm with regard to monomer DPP1. The reason is the formation of a polyconjugated molecule with a lower band gap than that of the original monomer. Similarly, the luminescence is shifted to a longer wavelength by 25 nm. The polymer exhibits a Stokes shift of 52 nm, and its quantum yield of fluorescence is 81%, a very high value.

P-2 was obtained in 73% yield as a dark red powder with strong fluorescence in the solid state. The molecular weight was 9400 Da. Different from the case of P-1, P-2 forms yellow solutions with greenish yellow fluorescence, very similar to that of the corresponding monomer DPP2. In chloroform, the absorption maximum of the monomer is at 492 nm, while the polymer has its maximum at 498 nm (Figure 5b). The same holds for the luminescence: The fluorescence maximum of the monomer is at 526 nm, and for the polymer at 531 nm. The small difference is due to the fact that the polycondensation reaction does not lead to a polyconjugated backbone. Instead, the π-conjugation of the backbone is interrupted at the lactam N-atoms. Due to the coupling of the fluorene unit of monomer **3** with the two *N*-phenyl groups of DPP2, a quaterphenylene-type oligomer is formed between the N-atoms of the lactam units. The strong absorption of P-2 at 334 nm can be ascribed to the presence of these oligomer units in the backbone.[19] The lack of any fluorescence from these units indicates an efficient energy transfer to the DPP units. This might explain the high quantum yield of fluorescence of 76% for P-2.

The copolymer P-3 was obtained in 70% yield from DPP1 and monomers **3** and **4**. The dark red powder is strongly fluorescent in the solid state. The molecular weight was 7700 Da. Solutions of the polymer in chloroform are intensely orange with absorption and fluorescence maxima at 516 and 572 nm, respectively (Figure 5c). While the fluorescence of the monomer is greenish yellow, it is shifted to orange for the polymer. In general, the optical properties are quite similar to those of P-1. The partial replacement of dialkylfluorene by dialkoxyphenylene units only has a minor effect on the absorption and emission properties (compare the data in Table 1)

The electrochemical properties were studied using cyclic voltammetry (CV). Oxidative and reductive cycles of thin polymer films cast onto ITO-coated glass electrodes are shown in Figure 6. It can be seen that the oxidation of P-1 and P-3 sets in at a potential $E_{\mathrm{onset,ox}}$ of about 1 V (vs SCE), and the reduction at −0.6 to −0.7 V. Either process is irreversible. Compared with P-1 (or P-3), the onset potentials for oxidation and reduction of P-2 are shifted to more positive and negative values, respectively (see also Table 2). The reason is the lack of π-conjugation in the backbone of this polymer. Consequently, P-2 exhibits a larger band gap of 2.4 eV compared with that of P-1 or P-3 (about 2 eV; see Table 2)

4. Summary and Conclusions

Our study shows that dibrominated tetraaryl-DPP compounds can be polymerized in Pd-catalyzed Suzuki coupling reactions. Depending on whether the functional bromine atoms are attached to the aryl groups in the 3- and 6-position or in the 2- and 5-position of the central DPP chromophore (type I or II monomers, respectively), two isomeric polymers are obtained, which are very different in their optical and electrochemical properties. A type I monomer leads to a polymer forming an orange solution with bright red luminescence. Optical absorption and fluorescence are bathochromically shifted by 20 nm with regard to the monomer due to the formation of a π-conjugated backbone. A type II monomer leads to a polymer forming a yellow solution with greenish yellow luminescence. Optical absorption and fluorescence resemble those of the monomer because the π-conjugation is interrupted at the lactam N-atoms, which are part of the polymer backbone. Due to the different electronic structure of the backbones, the band gap values are different, that is, about 2 eV for the polyconjugated polymer and 2.3 eV for the other one containing the N-atoms in the backbone.

In the polyconjugated N-arylated polymer, the electronic structure of the backbone is the same as that in the previously reported polyconjugated N-alkylated DPP-polymers,[10] which were also synthesized via Suzuki coupling. The only difference is the solubility of the polymer, which is much lower for the N-arylated one. Therefore, in order to improve the solubility, alkyl groups had to be attached to the aryl groups, for example, the *t*-butyl groups in P-1 to P-3.

Our study demonstrates that N-arylation of the DFF-based compounds allows one to prepare a variety of interesting DPP monomers, in which the N-aryl units can act as UV-absorbing groups transferring the energy to the DPP core chromophore. Due to the energy transfer, monomers and polymers with high fluorescence quantum yields become accessible.

It may also be pointed out that N-arylation of DFF compounds can be used for polymerization, if DFF is reacted with difunctional arylamines such as 4,4′-diaminodiphenylmethane. Using this method, DPP polymers become accessible in a one-step one-pot reaction from DFF.

Acknowledgment. Dr Mathias Düggeli from Ciba Specialty Chemicals, Basel, Switzerland, is kindly thanked for helpful discussions. Dr. Yu Zhu is thanked for helpful comments and technical support.

Supporting Information Available: ^{1}H NMR-spectra of DFF, **1b**, **1c**, **2a−c**, and **4**; UV/vis absorption and fluorescence spectra of DFF. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hao, Z.; Iqbal, A. *Chem. Soc. Rev.* **1997**, *26*, 203.
(2) Iqbal, A.; Jost, M.; Kirchmayr, R.; Pfenniger, J.; Rochat, A.; Wallquist, O. *Bull. Soc. Chim. Belg.* **1988**, *97*, 615.
(3) Iqbal, A.; Cassar, L.; Rochat, A. C.; Pfenniger, J.; Wallquist, O. *J. Coat. Technol.* **1988**, *60*, 37.
(4) Chan, W. K.; Chen, Y.; Peng, Z.; Yu, L. *J. Am. Chem. Soc.* **1993**, *115*, 11735.
(5) Beyerlein, T.; Tieke, B. *Macromol. Rapid Commun.* **2000**, *21*, 182.
(6) Beyerlein, T.; Tieke, B.; Foreno-Lenger, S.; Brütting, W. *Synth. Met.* **2002**, *130*, 115.
(7) Smet, M.; Mellen, B.; Dehaen, W. *Tetrahedron Lett.* **2001**, *42*, 6527.
(8) Rabindranath, A. R.; Zhu, Y.; Heim, I.; Tieke, B. *Macromolecules* **2006**, *39*, 8250.
(9) Cao, D.; Liu, Q.; Zeng, W.; Han, S.; Peng, J.; Liu, S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2395.
(10) Zhu, Y.; Rabindranath, A. R.; Beyerlein, T.; Tieke, B. *Macromolecules* **2007**, *40*, 6981.
(11) Potrawa, T.; Langhals, H. *Chem. Ber.* **1987**, *120*, 1075.
(12) Langhals, H.; Grundei, T.; Potrawa, T.; Polborn, K. *Liebigs Ann.* **1996**, 679.
(13) Holub, J. M.; O'Toole-Colin, K.; Getzel, A.; Argenti, A.; Evans, M. A.; Smith, D. C.; Dalglish, G. A.; Rifut, S.; Wilson, D. L.; Taylor, B. M.; Miott, U. *Molecules* **2004**, *9*, 135.
(14) Burton, I. *J. Chem. Soc.* **1928**, 915.
(15) (a) Beyerlein, T. Dissertation, Universität zu Köln, **2001**. (b) Jo, J.; Chi, C.; Höger, S.; Wegner, G.; Yoon, D. Y. *Chem.−Eur. J.* **2004**, *10*, 2681.
(16) Vahlenkamp, T.; Wegner, G. *Macromol. Chem. Phys.* **1994**, *195*, 1933.
(17) Paal, C.; Schulze, H. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 3799; **1902**, *35*, 175.
(18) Knorr, L.; Scheidt, M. *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 1167.
(19) Gillam, A. E.; Hey, D. H. *J. Chem. Soc.* **1939**, 1170; **1941**, 364.
(20) Bredas, J. L.; Silbey, R.; Boudreux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555.

MA801376R