

Red Emitting N-Functionalized Poly(1,4-diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole) (Poly-DPP): A Deeply Colored Polymer with Unusually Large Stokes Shift

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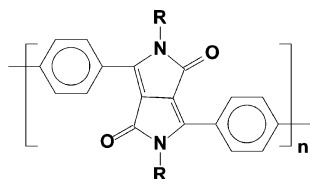
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ABSTRACT: New π -conjugated polymers are described, which entirely consist of aryl–aryl-coupled 1,4-diketo-2,5-dialkyl-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) units. The alkyl groups are *n*-hexyl (**4a**) or 2-ethylhexyl (**4b**) groups. The polymers are synthesized using nickel-promoted and palladium-catalyzed one-pot coupling reactions starting from 1,4-diketo-2,5-dialkyl-3,6-di(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (dibromo-DPP) as monomer, or conventional palladium-catalyzed coupling of dibromo-DPP and the 3,6-bis(pinacolato)boronester derivative of DPP. Polymers exhibit molecular weights up to 33 000 and are excellently soluble in chloroform and toluene. Deep red solutions (λ_{max} of **4b**: 525 nm) with intense red photoemission (λ_{max} of **4b**: 632 nm) and unusually large Stokes shift up to 107 nm are obtained. Cyclic voltammetry indicates quasi-reversible oxidation and reduction behavior, the onset potentials of **4b** are +1.03 and –0.74 V vs SCE, respectively. From these potentials, HOMO/LUMO levels of –5.47 and –3.70 eV, respectively, can be calculated. Good solubility and processability into thin films render the compounds suitable for electronic applications.

1. Introduction

In our contribution, new red emitting polymers based on the *N*-alkylated 1,4-diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) unit are reported, the common structure of the polymer being



The alkyl substituents groups R are either *n*-hexyl or 2-ethylhexyl.

DPP and some of its derivatives are commercialized as high performance pigments with exceptional light, weather and heat stability.^{1,2} Recent studies have shown that the incorporation of DPP units into polymers,^{3–9} dendrimers,¹⁰ polymer–surfactant complexes,¹¹ and oligomers¹² results in deeply colored, highly photoluminescent^{4–12} and electroluminescent^{8,9} materials. In all DPP-containing polymers reported so far, the DPP units were copolymerized with other monomer units, either in polyester polycondensation,⁶ polyaddition,⁶ or palladium-catalyzed Stille³ and Suzuki^{7–9,12} polycondensation reactions. In the present article we report on new DPP-based homopolymers, which only contain the *N*-alkylated DPP-chromophore as para-linked repeating unit (the so-called “poly-DPP”). The polymer is deep red and shows an intense bordeaux-red photoemission. Several preparation routes are described. They always start from the dialkylated 1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole⁷ and lead to the polymer in either one or two reaction steps. The first route follows the well-established Ni-promoted coupling of dihaloarenes.¹³ The other

routes basically follow the Pd-catalyzed arene coupling described by Suzuki and Miyaura.¹⁴ The coupling reactions are either carried out as one-pot, two-step reaction using bis(pinacolato)diboron and the corresponding dibromo-DPP derivative,^{15,16} or they follow the conventional palladium-catalyzed polycondensation of the 1:1 molar mixture of the dibromo-DPP and the diboronester of DPP.¹⁷ In our contribution, the polymers are characterized with regard to molecular structure, molecular weight and weight distribution, optical and electrochemical properties using size exclusion chromatography (SEC), ¹H NMR, UV/vis absorption, and fluorescence spectroscopy, and cyclic voltammetry.

2. Experimental Section

Materials. 1-Bromohexane, 1-bromo-2-ethylhexane, tetrakis(triphenylphosphine)palladium(0), potassium *tert*-butoxide, 2,2-bipyridine, bis(1,5-cyclooctadiene)nickel, 1,5-cyclooctadiene (cod), palladium(II) acetate, diphenylphosphinoferrocene (dppf), palladium(II) chloride, and acetonitrile (HPLC grade) were obtained from Acros, Fluka, and Aldrich and used without further purification. Bis(pinacolato)diboron (bpdB) 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 CaH₂. 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 kindly supplied by Dr. M. Dueggeli and Dr. R. Lenz from Ciba Specialty Chemicals, Basle, Switzerland.

Instrumentation. ¹H NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300 MHz for ¹H experiments. UV/vis absorption spectra were recorded on a Perkin-Elmer Lambda 14 spectrometer. Photoluminescence spectra were recorded on a Perkin-Elmer LS50B spectrometer. 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. Cyclic voltammograms were recorded using a potentiostat PG390 from Heka

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electronic, Lambrecht, Germany. For data acquisition and potentiostat control, the POTPULSE software (Heka), version 8.4 was used. A thin film of the polymer was cast on a Pt electrode and cycled in CH₃CN containing 0.1 M tetrabutylammoniumhexafluorophosphate. Counter electrode: Au. Reference: Pt. Voltage data were calculated for standard calomel electrode (SCE). Scan rate: 40 mV s⁻¹. *T*: 20 °C.

Monomer Synthesis. 1,4-Diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (2a). First, 8.92 g (20 mmol) of 1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**1**), 4.94 g (44 mmol) of potassium *tert*-butoxide, and 150 mL of dry NMP were heated to 60 °C. 16.9 mL (120 mmol) 1-bromohexane was slowly added and the mixture was stirred at 60 °C for 18 h. After cooling to room temperature, 250 mL of toluene was added and the reaction mixture was washed with water to remove the NMP. The organic solution was concentrated using a rotary evaporator. The raw material was purified by column chromatography on silica using dichloromethane as the solvent. 5.1 g (42%) of an orange, polycrystalline powder were obtained. The melting point was 183 °C. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.70–1.0 (m, 6H, methyl), 1.00–1.25 (m, 12H, methylene), 1.58 (m, 4H, β -CH₂), 3.70 (t, 4H, N-CH₂), 7.65 (d, 4H), 7.66 (d, 4H). UV(CHCl₃): 476 nm; photoluminescence (PL): 533 nm.

1,4-Diketo-2,5-di(2-ethylhexyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (2b). First, 8 g (18 mmol) of 1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**1**) and 4.0255 g (36 mmol) of potassium *tert*-butoxide were suspended in dry NMP and vigorously stirred at 60 °C for 30 min, and then 20.8 g (108 mmol) of 1-bromo-2-ethylhexane was added dropwise over a period of 90 min. After 20 h, the reaction mixture was diluted with 100 mL of toluene and washed with water and brine several times. The organic phase was dried over magnesium sulfate and concentrated using a rotary evaporator. The crude product was purified by column chromatography on silica using toluene as the solvent. Thus, 2.7 g (23%) of bright orange needles were obtained. The melting point was 128 °C. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 0.67–1.00 (m, 12H, methyl), 1.00–1.25 (m, 16H, methylene), 1.55 (m, 2H, β -CH), 3.69 (d, 4H, N-CH₂), 7.63 (s, 8H).

1,4-Diketo-2,5-dihexylpyrrolo[3,4-*c*]pyrrole-3,6-diphenyl-4-pinacolato Boron Ester (3a). First, 1 g (1.63 mmol) of 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**2a**) and 0.91 g (3.59 mmol) of bis(pinacolato)diboron were dissolved in 60 mL of degassed DMF followed by the addition of 0.022 g (6 mol %) of palladium(II) acetate and 0.9593 g of (9.80 mmol) potassium acetate. The reaction mixture was vigorously stirred under nitrogen at 80 °C for 2 h. During this period, the progress of the reaction was monitored by thin-layer chromatography (TLC) (silica, dichloromethane/MeOH, 10:1). After completion, the reaction mixture was poured in distilled water to induce the precipitation of the crude product. A red solid formed, which was filtered off, rinsed with water, and dried under ambient conditions. The crude product was dissolved in a minimum amount of dichloromethane and poured into ethanol to precipitate polymeric side products. After filtration, the mother liquor was concentrated using a rotary evaporator. Upon cooling, 0.7 g (61%) of the pure product were obtained as bright red flakes. The melting point was 235 °C. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.70–1.0 (m, 6H, methyl), 1.00–1.25 (m, 12H, methylene), 1.41 (s, 24H, B-O-C-CH₃), 1.58 (m, 4H, β -CH₂), 3.75 (t, 4H, N-CH₂), 7.80 (d, 4H), 7.95 (d, 4H).

1,4-Diketo-2,5-di(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-3,6-diphenyl-4-pinacolato Boron Ester (3b). In a 100 mL round-bottom flask, 0.5 g (0.75 mmol) of 1,4-diketo-2,5-di(2-ethylhexyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**2b**) and 0.417 g (1.64 mmol) of bis(pinacolato)diboron were dissolved in 30 mL of degassed DMF followed by the addition of 5 mg (3 mol %) of palladium(II) acetate and 0.22 g (2.24 mmol) of potassium acetate. The reaction mixture was stirred under nitrogen at 80 °C. The progress of the reaction was monitored by TLC on silica using dichloromethane as solvent. After 150 min, the starting material was almost quantitatively converted and the reaction mixture was poured into distilled water to induce precipitation of the crude product. The

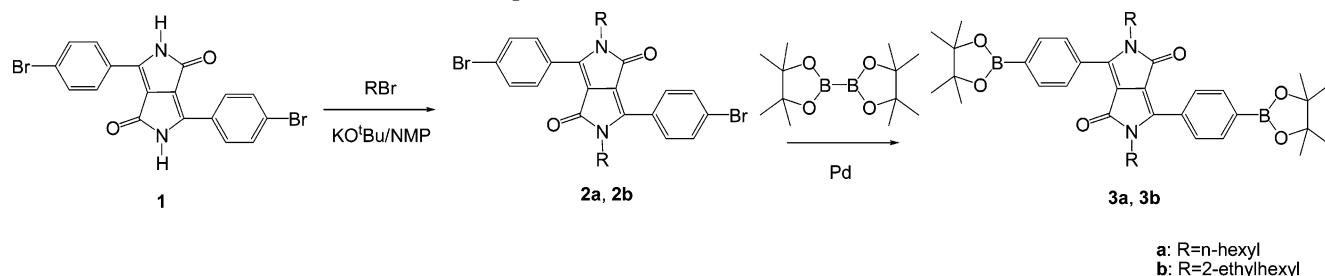
orange solid was filtered off, rinsed with water, and dried under ambient conditions. The pure product was obtained as orange powder. Upon heating, the solid product decomposed at 204 °C. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 0.64–1.00 (m, 12H, methyl), 1.00–1.25 (m, 16H, methylene), 1.36 (s, 24H, B-O-C-CH₃), 1.56 (m, 2H, β -CH), 3.72 (d, 4H, N-CH₂), 7.74 (d, 4H), 7.94 (d, 4H).

Polymer Synthesis. Synthesis of P-4a-1. A 2.0 g (7.27 mmol) sample of bis(1,5-cyclooctadiene)nickel(0), 1.136 g (7.27 mmol) of 2,2-bipyridine, and 0.7 mL (6.06 mmol) of 1,5-cyclooctadiene were dissolved in 65 mL of DMF under nitrogen. To this mixture, 3.722 g (6.06 mmol) of solid 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**2a**) were added in small portions within 90 min. Then the mixture was heated to 60 °C and stirred for 48 h. After cooling to room temperature, it was poured into 500 mL of methanol acidified with aqueous HCl. Then the precipitate was filtered and washed with another 500 mL of the acidified methanol. Finally the precipitate was collected, successively washed with 500 mL of methanol, 250 mL of EDTA solution (pH = 3.8), 250 mL of EDTA solution (pH = 9) and 300 mL of water, and dried in a vacuum. A 2.714 g (99%) yield of a dark red powder were obtained. The solid polymer decomposed at a temperature of approximately 295 °C. Molecular weight: 3100. Polydispersity: 1.6. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.74–1.20 (alkyl-H); 3.63 (N-CH₂); 7.29 (aromatic CH); 7.67 (aromatic CH).

Synthesis of P-4a-2. Under nitrogen atmosphere, 0.1224 g (0.2 mmol) of 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**2a**), 0.122 g (0.48 mmol) of bis(pinacolato)diboron, 0.180 g (0.6 mmol) of potassium acetate, 1.5 mg (3 mol %) of palladium(II) chloride and 9 mg of dppf were dissolved in 30 mL of DMF. The mixture was heated to 80 °C for 100 min until no starting material (**2a**) could be detected anymore. After that, 5 mg (2 mol %) of tetrakis(triphenylphosphine)palladium, 0.1224 g (0.2 mmol) of **2a** and 0.089 g (0.6 mmol) of potassium carbonate in aqueous solution were added to the mixture. Simultaneously 30 mL of toluene was added to dissolve all solids. The reaction mixture was heated to 95 °C for 12 h. After the mixture was cooled, 200 mL of toluene was added, and the mixture was extracted with water to remove DMF and salts. The organic solution was dried in a vacuum, redissolved in a minimum amount of chloroform, and precipitated in ethanol. The whole procedure was carried out twice. The polymer was collected and dried in a vacuum to give 0.147 g (82%) of a black powder. The polymer did not melt or decompose up to 295 °C. Molecular weight: 8700. Polydispersity: 1.6. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.70–1.80 (alkyl-H); 3.73 (N-CH₂); 7.38 (aromatic CH); 7.76 (aromatic CH).

Synthesis of P-4a-3. In a 20 mL Schlenk tube, 0.061 g (0.1 mmol) of **2a** and 0.070 g (0.1 mmol) of **3a** were dissolved in degassed toluene at room temperature. After addition of 5.7 mg (5 mol %) of tetrakis(triphenylphosphine)palladium(0) and finally 0.3 mL of 2 M aqueous sodium carbonate solution, the reaction mixture was stirred under nitrogen at 90 °C for 24 h. The mixture was then diluted with an appropriate amount of toluene, cooled to room temperature, and washed with water and brine several times. The aqueous phase was separated and extracted with chloroform. The combined organic phases were dried over magnesium sulfate and concentrated in a vacuum. An excess of methanol was used to precipitate the polymer which was filtered off, washed with methanol, and dried under ambient conditions. Finally 0.060 g (66%) of a dark red solid were obtained. The polymer did not melt or decompose up to 295 °C. Molecular weight: 6500. Polydispersity: 1.6. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.74–1.70 (alkyl-H); 3.85 (N-CH₂); 7.35 (aromatic CH); 7.75 (aromatic CH).

Synthesis of P-4b-4. In a 100 mL round-bottom flask, 0.5 g (0.75 mmol) of 1,4-diketo-2,5-di(2-ethylhexyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole (**2b**) and 0.417 g (1.64 mmol) of bis(pinacolato)diboron were dissolved in 30 mL of degassed DMF followed by the addition of 5 mg (3 mol %) of palladium(II) acetate and 0.22 g (2.24 mmol) potassium acetate. The reaction mixture was stirred under nitrogen at 80 °C. The progress of the reaction was monitored by TLC on silica with dichloromethane as the

Scheme 1. Preparation Route to Monomers **2a**, **2b** and **3a**, **3b**

solvent. After 140 min, it was indicated that the starting material had been completely reacted. Then the reaction was turned to Suzuki conditions by adding 20 mL of toluene, another 0.5 g (0.75 mmol) of **2b**, 0.043 g (5 mol %) of tetrakis(triphenylphosphine)palladium(0), and 2.5 mL of 2 M aqueous potassium carbonate solution. The temperature was raised to 90 °C, and the reaction mixture was stirred for 12 h under nitrogen. Then it was diluted with ca. 20 mL of toluene, cooled to room temperature, and washed with water several times. The organic phase was dried over magnesium sulfate and concentrated using a rotary evaporator. The polymer was precipitated in a large excess of ethanol, filtered off, and washed with ethanol. After drying, 0.69 g (90%) of a brilliant red powder was obtained. The polymer did not melt or decompose up to 295 °C. Molecular weight: 33 000. Polydispersity: 3.1. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.74–1.70 (alkyl-H); 3.85 (N-CH₂); 7.35 (aromatic CH); 7.75 (aromatic CH).

3. Results and Discussion

3.1. Synthesis of Monomers **2a and **2b**.** The starting compound for the synthesis of the polymer is the dibrominated DPP derivative **1**. Because of the hydrogen-bonding of the lactam units, **1** is poorly soluble in common organic solvents and cannot directly be used as monomer. To increase the solubility, the lactam groups were either alkylated upon reaction with 1-bromohexane or with 1-bromo-2-ethylhexane (Scheme 1). The resulting alkylated DPP derivatives **2a** and **2b** were purified using column chromatography. After purification, bright red polycrystalline materials with melting points of 183 and 128 °C, respectively, and high solubility in common organic solvents was obtained. The UV spectrum of **2a** indicates two peaks at 476 and 305 nm (Figure 1). The corresponding spectrum of **2b** is similar: a long wavelength peak occurs at 476 nm and a shoulder at 300 nm (Figure 4). The two monomers **2a** and **2b** are highly fluorescent with maximum emission at 533 and 525 nm, respectively.

3.2. Synthetic Routes to Polymer **4a.** One of the classical methods for preparation of polyarylenes is the dehalogenating

coupling of dihaloarenes, which is promoted by Ni(0) complexes such as Ni(cod)₂.¹⁸ In a first approach to prepare poly-DPP we have chosen this well-known method. The reaction was carried out using Ni(cod)₂, cod and 2,2'-bpy as coupling reagents. The resulting polymer is denoted as **4a-1** ("a" for the hexyl substituent groups, and "1" for the first approach).

The Ni(0) coupling has some disadvantages, which favored the search for more suitable methods of dehalogenative coupling: (i) Ni(cod)₂ is highly sensitive to moisture so that the reaction has to be carried out under completely dry conditions, (ii) large amounts of nickel are needed (1.0–1.2 equiv to the monomers), so that (iii) the workup procedure is tedious because large nickel residues have to be removed. As an alternative, we used a recently reported one-pot variant¹⁶ of the well-known Suzuki-Miyaura cross-coupling. According to this route, **2a** is converted into **3a** upon addition of bis(pinacolato)diboron as condensation reagent and PdCl₂(dppf) as catalyst. **3a** is not worked up, but immediately polymerized upon further addition of **2a**, potassium carbonate and tetrakis(triphenylphosphine)palladium as the catalyst. The polymer obtained from this procedure is denoted as **4a-2**. The two one-pot polycondensation routes to poly-DPP are outlined in Scheme 2.

Besides the one-pot routes we also applied the classical Pd-catalyzed Suzuki polycondensation starting from equimolar amounts of **2a** and **3a** outlined in Scheme 3. This method is generally applicable for the coupling of DPP derivatives with a variety of aromatic units. First, the DPP bis(pinacolato)diboronester **3a** has to be prepared from **2a** (Scheme 1). After purification of **3a**, a 1:1 molar mixture of **2a** and **3a** is polymerized as described in the experimental part. The polymer obtained upon the Suzuki coupling is denoted as polymer **4a-3** (Scheme 3).

3.3. Characteristic Properties of Polymer **4a-1** to **4a-3**.

Molecular Weight. In this chapter, the characteristic properties of dihexylated poly-DPP obtained upon the three different preparation methods are compared. The polymer is obtained as a dark red (in a single case almost black) powder, and is well soluble in organic solvents such as chloroform and toluene, but less soluble in THF. In polymer **4a-1**, most of the nickel could be removed after careful cleaning, the residual nickel content was 14 mg/kg. In Table 1, the weight-average molecular weight, the polydispersity, and the optical properties are listed. Size exclusion chromatography indicated that the Ni-mediated polymerization only leads to oligomers with molecular weight of 3100, which corresponds to an average degree of polymerization of about 7. Different from this, the Pd-catalyzed one-pot coupling route leads to a polymer with molecular weight of 8700 corresponding to a degree of polymerization of about 20. The molecular weight obtained upon the classical Suzuki route is somewhat lower. For all polymers, the polydispersity is 1.6. Our study clearly indicates that the Pd-catalyzed one-pot reaction is superior to the Ni-promoted reaction. It proceeds more rapidly, and the yield and molecular weight of the polymer are higher.

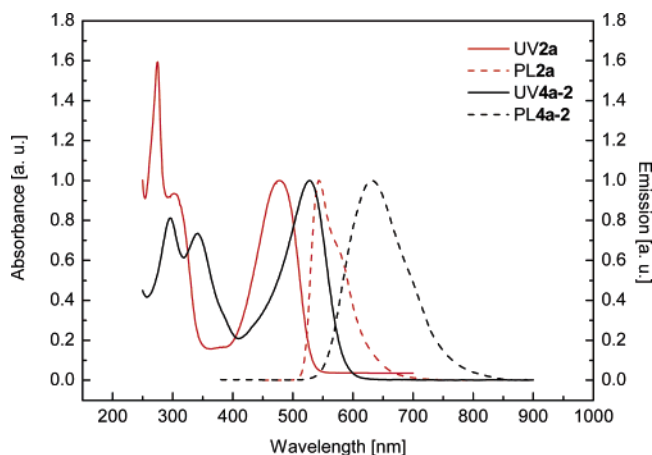


Figure 1. UV/visible and photoluminescence spectra of monomer **2a** and polymer **4a-2** in chloroform.

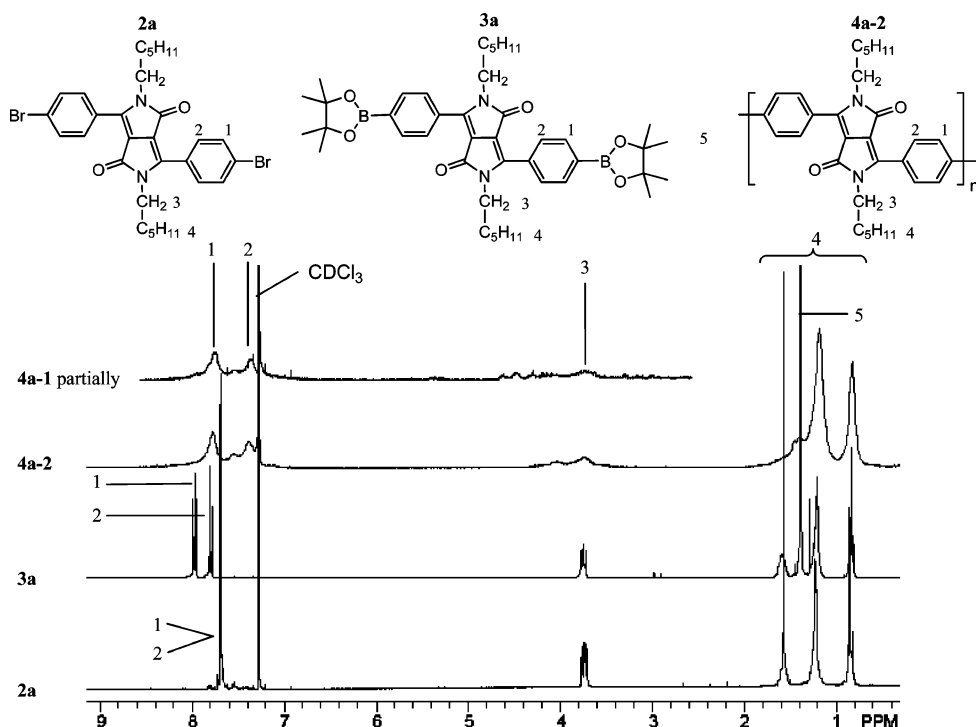


Figure 2. ^1H NMR spectra of monomers **2a**, **3a**, and polymers **4a-2** and **4a-1** (partial).

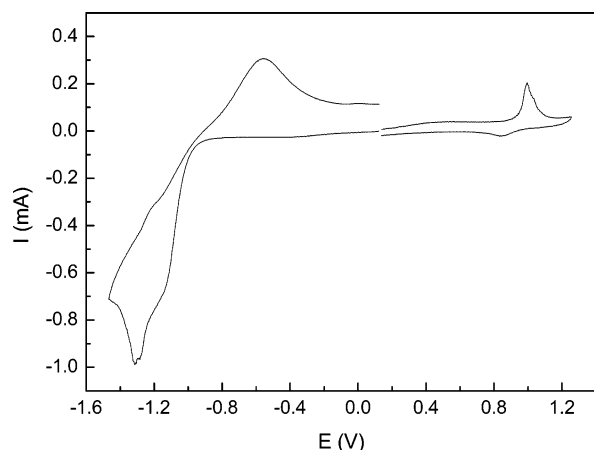


Figure 3. Cyclic voltammogram of polymer **4a-2** as thin film on Pt electrode (reference SCE). The CV was carried out in 0.1 M (TBA)-PF₆ in acetonitrile, scan rate: 40 mV/s, $T = 20^\circ\text{C}$.

UV Absorption and Fluorescence Spectra. The optical properties of the dihexylated poly-DPPs **4a-1** to **4a-3** are very similar. As the UV absorption spectrum of **4a-2** in chloroform indicates, the polymer exhibits three maxima at 528, 340, and 296 nm (Figure 1). The absorption coefficient (ϵ value) of the 528 nm peak is $1.36 \times 10^4 \text{ L monomol}^{-1} \text{ cm}^{-1}$. The polymerization is accompanied by a large bathochromic shift from 476 to 528 nm, which originates from the extension of the π -conjugated system. Although **4a-1** is only an oligomer, its spectrum is quite similar to **4a-2** or **4a-3** (not shown). The reason is that the individual polymer chains of **4a-1** contain about 14 phenylene and 7 pyrrolopyrrol units on average, which is obviously enough to cause that the influence of the chain length on λ_{max} becomes negligible.

The fluorescence spectra of the three polymers are also very similar. The spectrum of polymer **4a-2** is shown in Figure 1. The polymer exhibits a bordeaux-red emission color, the fluorescence maximum appears at 631 nm (which is red-shifted by 87 nm compared with the monomer **2a**). For polymer **4a-2**,

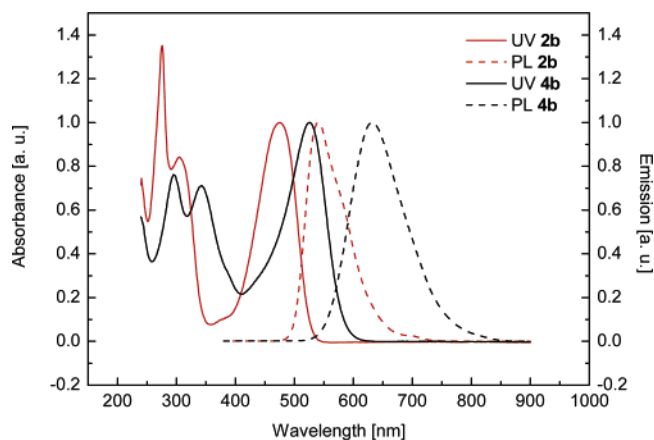
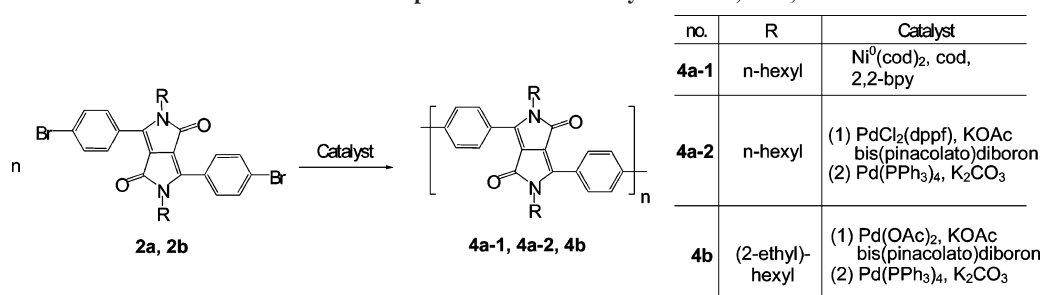


Figure 4. UV/visible and photoluminescence spectra of monomer **2b** and polymer **4b** in chloroform.

the quantum yield of fluorescence was determined to be 13%. This value was much lower than for the corresponding monomer **2a** (95%). The difference might be due to the partial O-alkylation during polymerization, and to traces of phosphor and palladium in the polymer, which still might be present after applying standard cleaning procedures as described in the experimental part. From the fluorescence behavior a Stokes shift of 103 nm can be derived, the largest value ever reported for a DPP-containing polymer. UV and fluorescence spectra of polymer films cast from chloroform solution are very similar to the solution spectra with the exception that the absorption and emission maxima are red-shifted by 7 to 8 nm (not shown; for data, see Table 1).

Proton NMR Spectroscopy. The ^1H NMR spectrum of polymer **4a-2** is shown in Figure 2. The spectrum indicates strong signals in the δ -region from 0.7 to 1.8 ppm originating from the alkyl protons. The signal of the α -methylene unit directly attached to the N atom of the lactam unit appears at 3.72 ppm. The origin of the small signal at 4.03 ppm is unclear. It might be due to α -methylene units attached to the O atom of the lactam carbonyl group. Since this signal is absent in the

Scheme 2. One Pot Preparation Route to Polymers 4a-1, 4a-2, and 4b



Scheme 3. Preparation of Polymer 4a-3 upon Polycondensation of 2a and 3a

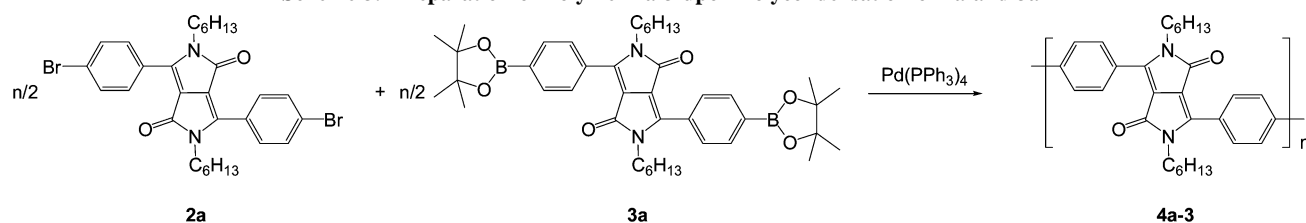
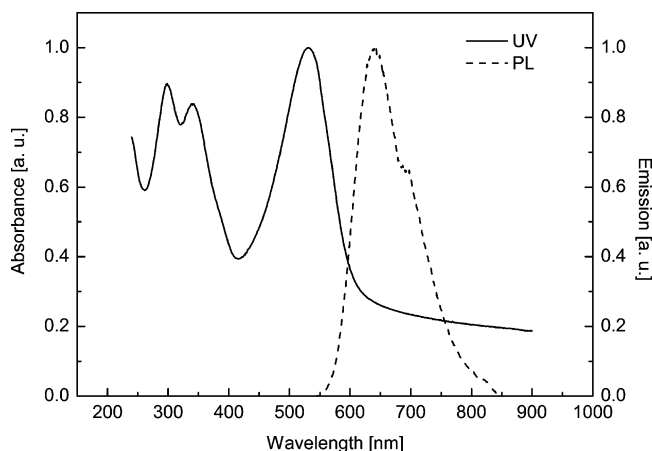


Table 1. Molecular Weights and Optical Properties of Different Polymers

	M_w	polydispersity	UV (nm) solution/film	PL (nm) solution/film	Stokes shift solution/film
4a-1	3070	1.6	530/—	633/—	103/—
4a-2	8700	1.6	528/535	631/640	103/105
4b	33 000	3.1	525/531	632/640	107/109
4a-3	6500	1.6	523/533	627/643	104/110

monomer **2a**, the change from N-alkylation to O-alkylation must have taken place during the polymerization, perhaps under the influence of the aqueous basic environment present during the coupling reaction. The small size of the peak indicates that less than 10 percent of the hexyl groups have changed their position. The signals of the phenylene protons occur between 7.29 and 7.67 ppm (the strong peak at 7.27 ppm originates from protons in the solvent CDCl₃). The spectrum of polymer **4a-3** is almost identical with **4a-2** (not shown), whereas polymer **4a-1** exhibits additional small signals in the region from 3.5 to 5.5 ppm. The signals can be ascribed to side products or end groups due to the low molecular weight. A section of the proton NMR spectrum of **4a-1** ranging from 2.5 to 8.5 ppm is shown in Figure 5. In addition, the spectrum of monomer **3a** is indicated. It is a very well resolved spectrum, showing the signals of the protons of the hexyl group and the methyl groups of the bis(pinacolato)-boronester at 0.7 to 1.7 ppm. The triplet at about 3.75 ppm originates from the α -methylene unit bound to the N atom of

Figure 5. UV/visible and photoluminescence spectra of polymer **4b** as solid film.Table 2. Band Gap Data of Different Polymers^a

polymer	absorption λ_{onset} (nm) in solution	opt/electrochem band gap (eV)	oxidation onset (V) {HOMO {eV}}	reduction onset (V) {LUMO {eV}}
4a-1	592	2.09/—	— {—}	— {—}
4a-2	587	2.11/1.93	0.95 {−5.39}	−0.98 {−3.46}
4b	586	2.12/1.77	1.03 {−5.47}	−0.74 {−3.70}
4a-3	581	2.13/—	— {—}	— {—}

^a Band gap (E_{opt}) measured at the onset of electronic absorption of the polymer solution ($E_{\text{opt}} = 1240/\lambda_{\text{onset}}$ eV). HOMO–LUMO gap according to the equation: $-E_{\text{LUMO}} = E_{\text{onset}(\text{red})} + 4.44$ eV and $-E_{\text{HOMO}} = E_{\text{onset}(\text{ox})} + 4.44$ eV, where $E_{\text{onset}(\text{ox})}$ and $E_{\text{onset}(\text{red})}$ are the onset potentials for the oxidation and reduction processes of polymer thin films vs SCE.

the lactam unit. The four symmetric signals at 7.8 and 7.98 originate from the phenylene groups of DPP.

Electrochemistry. Cyclic voltammetric (CV) data for the polymers **4a-1** to **4a-3** are given in Table 2, and a representative cyclic voltammogram of polymer **4a-2** is shown in Figure 3. Thin polymer films cast from chloroform solution onto a Pt electrode were investigated. As depicted in the Figure, the polymer shows quasi-reversible oxidation processes, the onset potential for oxidation ($E_{\text{ox}}^{\text{on}}$) was observed at 0.95 V (vs SCE), from which a HOMO energy level of -5.39 eV was calculated using the equation $-E_{\text{HOMO}} = E_{\text{ox}}^{\text{on}} + 4.44$ eV.¹⁹ The onset potential for reduction ($E_{\text{red}}^{\text{on}}$) was found at -0.98 eV. From, this value, a LUMO level of -3.76 eV was calculated. On the basis of $E_{\text{ox}}^{\text{on}}$ and $E_{\text{red}}^{\text{on}}$, the electrochemical band gap of **4a-2** is 1.93 eV. Taking into account an onset of the optical absorption at $\lambda_{\text{onset}} = 587$ nm, the optical band gap $E_{\text{opt}} = 1240/\lambda_{\text{onset}}$ [eV] can be determined to be 2.11 eV (see also Table 2).

Synthesis and Characteristic Properties of Polymer 4b. Polymer **4b** was synthesized from **2a** in a one-pot, two-step route similar to polymer **4a-2** (Scheme 2). Instead of using the PdCl₂(dppf) catalyst, we used palladium(II) acetate, free of ligand, as suggested by Zhang et al.²⁰ The molecular weight of

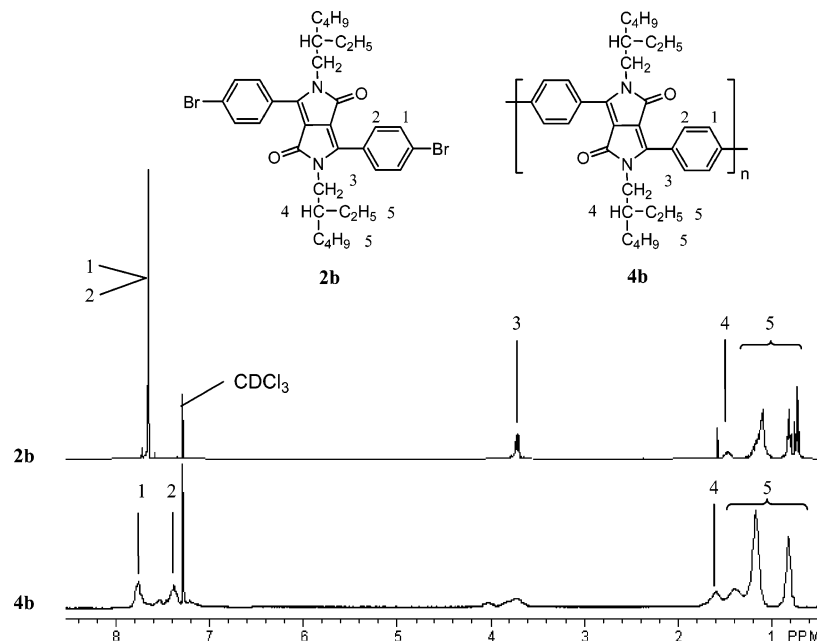


Figure 6. ^1H NMR spectra of monomer **2b** and polymer **4b**.

the polymer was 33 000, by far the highest one obtained upon the various polymerization routes. The polymer is excellently soluble in common organic solvents such as chloroform, toluene and THF. The optical spectra of **4b** are similar to **4a-2** with absorption maxima at 525, 342, and 295 nm and a fluorescence maximum at 632 nm (Figure 4). The quantum yield of fluorescence of polymer **4b** was 20%. Compared with the monomer **2b**, the absorption is bathochromically shifted by about 50 nm due to the extension of the π -conjugated chromophore. Solid films of **4b** cast from chloroform solution exhibit an absorption maximum at 531 nm and a fluorescence maximum at 640 nm, the Stokes shift is 107 nm (Figure 5).

^1H NMR spectra of monomer **2b** and polymer **4b** are shown in Figure 6. The monomer exhibits strong signals in the region from 0.67 to 1.55 ppm originating from the (2-ethyl)hexyl unit. The doublet at 3.69 ppm can be ascribed to the α -methylene unit of the alkyl group directly attached to the N atom of the lactam group. The strong signal at 7.63 ppm originates from the protons of the phenyl group of **2b**. The polymer peaks are generally broader. The main difference is the occurrence of a new peak at about 4.02 ppm, which also occurred for polymer **4a-2** (Figure 2), and might indicate a side reaction during the coupling process, in which the N-alkylation is partially changed into O-alkylation catalyzed upon the presence of aqueous potassium carbonate. In the region of the aromatic protons, two signals occur at 7.35 and 7.75 ppm. The signals indicate the presence of two nonequivalent protons at the phenyl groups, which is the result of the arene coupling reaction.

CV data of **4b** are given in Table 2, a representative cyclic voltammogram is shown in Figure 7. It is very similar to the CV diagram of **4a-2** in Figure 3 and shows quasi-reversible oxidation and reduction processes. The onset potential for oxidation, $E_{\text{ox}}^{\text{on}}$, occurs at 1.03 eV, from which a HOMO energy level of -5.47 eV could be calculated. The onset potential for reduction, $E_{\text{red}}^{\text{on}}$, is found at 0.74 eV. From this value a LUMO level of -3.70 eV could be calculated (Table 2). On the basis of these measurements, the electrochemical band gap could be determined to be 1.77 eV. Taking into account a λ_{onset} value of 586 nm, the optical band gap could be calculated to be 2.12 eV, which is quite similar to **4a-2**.

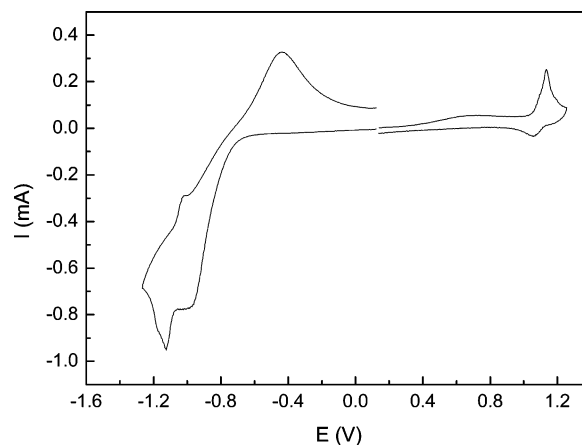


Figure 7. Cyclic voltammogram of polymer **4b** as thin film on Pt electrode (reference SCE). The CV was carried out in 0.1 M (TBA)-PF₆ in acetonitrile, scan rate: 40 mV/s. $T = 20$ °C.

4. Summary and Conclusions

In our contribution, it is demonstrated that dialkylated poly-DPPs can be prepared from dihalo-DPP derivatives using Ni-promoted and Pd-catalyzed arene coupling reactions. Best results concerning molecular weight and structural unity are obtained, if a modified version of the Miyaura arylboronate synthesis is applied, in which the PdCl₂(dppf) catalyst is substituted against palladium(II) acetate, free of any ligands. For the first time, this reaction step was successfully integrated in the one-pot synthesis of a fully conjugated polyarylene. The resulting poly-DPP exhibits interesting optical and electrochemical properties: Deep red color, intense red fluorescence with unusually large Stokes shift of more than a hundred nanometer, and quasi-reversible oxidation and reduction behavior render the polymers attractive for electronic applications.

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