Macromolecules

Deeply Colored Polymers Containing 1,3,4,6-Tetraarylpyrrolo[3,2b]pyrrole-2,5-dione (IsoDPP) Units in the Main Chain

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Supporting Information

ABSTRACT: Synthesis and characteristic properties of polymers **P1–P4** containing 1,3,4,6-tetraarylated pyrrolo[3,2-*b*]pyrrole-2,5-dione (isoDPP) units in the main chain are described. **P1** and **P2** were prepared upon palladium-catalyzed polycondensation of 3,6-bis(4-bromophenyl)-1,4-bis(4-*tert*-butylphenyl)pyrrolo[3,2-*b*]pyrrole-2,5-dione (**M1**) or 1,4-bis: (4-bromophenyl)-3,6-bis(4-*tert*-butylphenyl)pyrrolo[3,2-*b*]-pyrrole-2,5-dione (**M2**) and 2,2'-(9,9-dihexyl-9*H*-fluoren-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**M4**), while **P3** and **P4** were synthesized upon polycondensation of 3,6-



bis(5-bromothien-2-yl)-1,4-bis(4-dodecylphenyl)pyrrolo[3,2-b]pyrrole-2,5-dione (M3) and 2,5-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)thiophene (M5) or 9-(2-ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole (M6). Deeply colored polymers with molecular weights between 3.5 and 22 kDa were obtained. The polymers were soluble in common organic solvents such as dichloromethane, chloroform, and tetrahydrofuran. All polymers exhibit broad absorption bands with high extinction coefficients ($\epsilon > 2 \times 10^4$ L mol⁻¹ cm⁻¹) but weak fluorescence, the quantum yields being below 1%. Although P1 and P2 are isomers, their optical properties are rather different. P1 with polyconjugated backbone exhibits an absorption maximum at 409 nm, while P2 has a maximum at 360 nm due to interruption of π -conjugation at the lactam N atoms. The presence of thienyl-isoDPP units in the backbone causes a red-shift of the absorption to 489 nm (P3) and 435 nm (P4). All polymers exhibit nearly irreversible oxidation and reduction behavior. Bandgaps of the polymers with phenyl-substituted isoDPP units (P1 and P2) are at about 2 eV, while those of polymers with thienyl-substituted isoDPP (P3 and P4) are at about 1.5 eV.

1. INTRODUCTION

In recent years, the tailoring of specific π -conjugated polymer structures led to new materials with interesting optoelectronic properties.¹⁻⁴ A useful method to prepare such polymers is based on the incorporation of deeply colored and fluorescent organic dyes and colorants in conjugated polymers. Recent examples are related to conjugated polymers containing the diketopyrrolopyrrole (DPP),^{5,6} isoindigo,⁷ quinacridone,⁸ benzodifuranone,⁹ and benzodipyrrolidone chromophores.¹⁰ Especially the DPP-based polymers have proven useful for applications as active components in light-emitting¹¹ and photovoltaic devices.¹²

Previous studies on DPP-based polymers were always concerned with polymers containing the diketopyrrolo[3,4*c*]pyrrole (or pyrrolo[3,4-*c*]pyrrole-2,5-dione) unit, which is prepared upon either condensation of arylnitriles with succinic acid diesters¹³ or a reaction of diketofuro[3,4-*c*]furans with arylamines to yield the corresponding bislactams.¹⁴ Besides diketopyrrolo[3,4-*c*]pyrrole derivatives, the regioisomeric diketopyrrolo[3,2-*b*]pyrrole (or pyrrolo[3,2-*b*]pyrrole-2,5-dione, isoDPP) derivatives (Figure 1) also represent useful organic pigments. Previously, isoDPP derivatives were prepared in three steps starting from (*N*-phenylacetyl)acetic acid amino ester¹⁵ or in one step from pulvinic acid.¹⁶ A new and efficient synthesis was recently described by Langer et al.¹⁷ Having



Figure 1. Molecular structures of diketopyrrolo[3,4-*c*]pyrrole (DPP) and regioisomeric diketopyrrolo[3,2-*b*]pyrrole (isoDPP) derivatives.

studied conjugated polymers with the diketopyrrolo[3,4*c*]pyrrole chromophore, we recently turned to the isomer and prepared and characterized a number of related polymers containing the tetraarylated diketopyrrolo[3,2-*b*]pyrrole unit. Up to now, only very little has been reported on these polymers. Recently a patent was filed on polymers containing N,N'-dialkylated diaryl diketopyrrolo[3,2-*b*]pyrrole units.¹⁸

The purpose of the present article is to describe synthesis as well as optical and electrochemical properties of a collection of tetraaryl-isoDPP-containing conjugated polymers. Dibrominated tetraaryl-isoDPP monomers were prepared upon condensation of 2 equiv of ethyl arylacetates with 1 equiv of oxalic acid bis(arylimidoyl) dichlorides.¹⁷ The resulting isoDPP

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monomers were polymerized with aryl diboronester compounds using palladium-catalyzed Suzuki coupling reactions.¹⁹ The polymers were characterized using size exclusion chromatography, spectroscopic methods (NMR, UV, fluorescence), and cyclic voltammetry. Deeply colored polymers of moderate to high molecular weight and in some cases rather low bandgaps of 1.4 to 1.8 eV were obtained, which might be useful for electronic applications.

2. EXPERIMENTAL SECTION

2.1. Materials. *Reagents.* The monomers 2,2'-(9,9-dihexyl-9H-fluoren-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**M4**) and 9-(2-ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole (**M6**) were prepared according to literature methods.^{20,21} Monomer 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-thiophene (**M5**) was kindly provided by BASF Schweiz AG. Tetrakis(triphenylphosphine)palladium(0), 4-*tert*-butylaniline, 4-bromoaniline, 4-dodecylaniline, oxalyl chloride, ethyl 2-(4-bromophenyl)-acetate, ethyl 2-thienylacetate, sodium bis(trimethylsilyl)amide solution (1 M), N-bromosuccinimide (NBS), phosphorus pentachloride, and potassium carbonate were obtained from Aldrich, Acros, and Fluka and used without further purification. Methyl *tert*-butylphenylacetate was obtained from SAFC and converted into the ethyl ester.²² Solvents were of analytical grade and used without further purification.

Synthesis of N,N'-Bisaryloxalamides 1a–1c. N,N'-Bis(4-tertbutylphenyl)oxalamide, 1a. 3.79 mL (44.8 mmol) of oxalyl chloride was dropwisely added to a stirred solution of 4-*tert*-butylaniline (15.00 mL, 94.2 mmol) and triethylamine (14.70 mL, 112.1 mmol) in 360 mL of THF under N₂ at 0 °C. After addition, the reaction was allowed to warm up to room temperature while it was stirred for 2 h. Then the reaction mixture was concentrated in vacuum and diluted with 200 mL of water. The white precipitate was collected by filtration, washed with dilute 1 M HCl (200 mL) and water (2 × 200 mL), and dried in vacuum. 1a was isolated as a white solid (13.5 g, 85%); mp 218–220 °C. ¹H NMR (300 MHz, d_1 -CHCl₃) δ (ppm): 9.31 (<u>s</u>, h-2H), 7.61– 7.58 (<u>d</u>, 1-4H), 7.61–7.58 (<u>d</u>, 1-4H), 1.33 (<u>s</u>, a-18H). ¹³C NMR (300 MHz, d_1 -CHCl₃) δ (ppm): 157.54, 148.62, 133.69, 126.11, 119.63, 34.56, 31.36. HRMS (ESI): m/z [M + Na]⁺ 375.32.

N,N'-Bis(4-bromophenyl)oxalamide, **1b**. The synthesis was carried out in analogy to **1a** except that oxalyl chloride (3.45 mL, 40.0 mmol), 4-bromoaniline (14.9 g, 84.0 mmol), and triethylamine (6.97 mL, 100.0 mmol) were used. **1b** was isolated as a white solid (15.6 g, 98%); mp 305–308 °C. ¹H NMR (300 MHz, d_1 -CHCl₃) δ (ppm): 9.32 (s, c-2H), 7.63–7.55 (dd, a,b-8H), 7.61–7.58 (d, 1-4H). ¹³C NMR (500 MHz, d_1 -CHCl₃) δ (ppm): 130.0, 120.0. HRMS (ESI): m/z [M + H]⁺ 400.42.

N,N'-Bis(4-dodecylphenyl)oxalamide, 1c. The synthesis was carried out in analogy to 1a except that oxalyl chloride (0.73 mL, 8.6 mmol), 4-dodecylaniline (5.00 g, 19.1 mmol), and triethylamine (3.18 mL, 23.0 mmol) were used. 1c was isolated as a white solid (3.9 g, 35%); mp 165–167 °C. ¹H NMR (300 MHz, d_2 -CH₂Cl₂) δ (ppm): 9.33 (s, f-2H), 7.61–7.25 (dd, de-8H), 2.51 (m, c-4H), 1.69 (s, b-40H), 1.29 (s, a-6H). ¹³C NMR (500 MHz, d_1 -CHCl₃) δ (ppm): 142.9, 135.7, 128.6, 123.9, 119.5, 75.0, 36.0, 33.0, 30.2, 24.9, 14.9.

Synthesis of Oxalic Acid N,N'-Bisarylimidoyl Dichlorides **2a**–**2c**. Oxalic Acid N,N'-Bis(4-tert-butylphenyl)imidoyl Dichloride, **2a**. 10.57 g (30.0 mmol) of **1a** and 13.7 g (66.0 mmol) of PCl₅ were dissolved in 300 mL of toluene and refluxed for 24 h under N₂. Then the solution was filtered, and the solvent and POCl₃ formed upon the reaction were removed in vacuum. The residue was recrystallized from *n*-heptane to give yellow crystals. Yield 10.1 g (86%), mp 163–165 °C. ¹H NMR (300 MHz, d_1 -CHCl₃) δ (ppm): 7.47–7.4 (<u>d</u>, 1-4H), 7.13– 7.10 (<u>d</u>, k-4H), 1.35 (<u>s</u>, a-18H). ¹³C NMR (500 MHz, d_1 -CHCl₃) δ (ppm): 150.0, 142.8, 126.12, 125.8, 120.7, 119.5, 34.6, 31.6, 31.5, 30.1. HRMS (ESI): m/z [M + H]⁺ 389.31.

Oxalic Acid N,N'-Bis(4-bromophenyl)imidoyl Dichloride, **2b**. The synthesis was carried out in analogy to **2a** except that **1b** (5.97 g, 15.0 mmol) and 6.87 g (33.0 mmol) of PCl₅ were used. **2b** was isolated as a

yellow solid (4.5 g, 69%); mp 180–183 °C. ¹H NMR (300 MHz, DMSO) δ (ppm): 7.71–7.10 (<u>dd</u>, a,b-8H). ¹³C NMR (500 MHz, d_1 -CHCl₃) δ (ppm): 159.0, 137.4, 132.0, 126.11, 122.9, 117.0. HRMS (ESI): m/z [M + Na]⁺ 455.02.

Oxalic Acid N,N'-Bis(4-dodecylphenyl)imidoyl Dichloride, 2c. The synthesis was carried out in analogy to 2a except that 1c (3.90 g, 6.8 mmol) and 5.63 g (27.0 mmol) of PCl₅ were used. 2c was isolated as a yellow oil. Since the oil was not stable under ambient conditions it was used in the next reaction step without further purification.

Synthesis of M1-M3. 3,6-Bis(4-bromophenyl)-1,4-bis(4-tertbutylphenyl)pyrrolo[3,2-b]pyrrole-2,5-dione, M1. To a 200 mL THF solution of the ethyl 2-(4-bromophenyl)acetate 14.17 g, 40.0 mmol) was added a THF solution of sodium bis(trimethylsilyl)amide solution (1 M, 42.0 mL, 146.0 mmol). After stirring for 1 h the reaction mixture was cooled to -78 °C, and a solution of 2a (7.79 g, 20.0 mmol) in 120 mL of THF was slowly added under stirring (30 min). The temperature was allowed to rise to ambient, and the mixture was stirred for 2 h. Then the mixture was transferred to an aqueous solution of NH₄Cl (5 M, 1 L). Addition of a mixture of ether and THF (1:1) resulted in precipitation of the product, which was isolated upon filtration, washed with ether, dried in vacuum, and precipitated in methanol. Yield: 5.12 g (36%) of a yellow powder; mp >300 °C. ¹H NMR (300 MHz, d_1 -CHCl₃) δ (ppm): 7.32–7.20 (dd, d,e-8H), 7.05– 6.94 (dd, b,c-6H), 1.34 (s, a-18H). ¹³C NMR (500 MHz, d_1 -CHCl₃) δ (ppm): 148.3, 142.8, 142.7, 135.4, 133.6, 131.8, 125.6, 122.5, 120.5, 34.8, 31.6, 31.5. IR (KBr, cm⁻¹): 3131 (ν_{σ} C_{ar}H), 2957–2867 (ν_{r} CH₃), 1730 (v, C=O), 1689 (v, CN), 1511–1418 (v, C=C), 562 (v, CBr). UV (CHCl₃): 360 nm; PL (CHCl₃): 628 nm (excitation at 300 nm). HRMS (ESI): m/z [M + H]⁺ 711.26. Anal. Calcd for C₃₈H₃₄Br₂N₂O₂: C/H 13.32. Found: C/H 13.82.

1,4-Bis(4-bromophenyl)-3,6-bis(4-tert-butylphenyl)pyrrolo[3,2-b]pyrrole-2,5-dione, **M2**. The synthesis was carried out in analogy to **M1** except that ethyl 2-(4-tert-butylphenyl)acetate (52 g, 20.5 mmol), sodium bis(trimethylsilyl)amide in THF solution (21.00 mL, 1 M, 76.0 mmol), and **2b** (4.35 g, 10.0 mmol) were used. **M2** was isolated as a yellow solid (2.3 g, 32%); mp >300 °C. ¹H NMR (300 MHz, d₁-CHCl₃) δ (ppm): 7.36–7.21 (dd, a,b-8H), 7.03–7.01 (dd, c,d-8H), 1.33 (s, e-18H), 6.41–6.39 (d, g-2H), 2.68–2.63 (t, f-4H), 1.65–1.63 (m, e-4H), 1.26 (s, b,c,d-12H), 0.88 (t, a-6H). HRMS (ESI): m/z [M + Na]⁺ 733.02. Anal. Calcd for C₃₈H₃₄Br₂N₂O₂: C/H 13.32. Found: C/H 14.03. UV (CHCl₃): 330 nm; PL (CHCl₃): 613 nm (excitation at 300 nm).

1,4-Bis(4-dodecylphenyl)-3,6-bis(thiophen-2-yl)-pyrrolo[3,2-b]-pyrrole-2,5-dione, **3**. The synthesis was carried out in analogy to **M1** except that ethyl 2-thienylacetate (3.24 g, 19.1 mmol), sodium bis(trimethylsilyl)amide solution in THF solution (15.47 mL, 1 M, 76.0 mmol), and **2c** (9.82 g, 22.0 mmol) were used. 3 was isolated as a yellow solid (1.2 g, 23%); mp >300 °C. ¹H NMR (300 MHz, d_1 -CHCl₃) δ (ppm): 7.28–7.26 (d, d-4H), 7.23–7.20 (d, e,h-6H), 6.76–6.73 (t, f-2H), 6.41–6.39 (d, g-2H), 2.68–2.63 (t, f-4H), 1.65–1.63 (m, e-4H), 1.26 (s, b,c,d-12H), 0.88 (t, a-6H). UV (CH₂Cl₂): 421 nm; PL (CH₂Cl₂): 635 nm (excitation at 420 nm).

Synthesis of 3,6-Bis(5-bromothiophene-2-yl)-1,4-bis(4dodecylphenyl)pyrrolo[3,2-b]-pyrrole-2,5-dione, M3. Compound 3 (1.50 g, 2.7 mmol) was dissolved in 100 mL of anhydrous chloroform, covered with aluminum foil, and stirred at room temperature under N₂ for 15 min. Then N-bromsuccinimide (1.18 g, 6.6 mmol) was added, and the reaction mixture was kept at room temperature for 40 h. Subsequently the mixture was poured into 100 mL of methanol. The solid was collected by filtration, washed with several portions of hot methanol, and dried in vacuum. M3 was obtained as an orange solid (1.5 g, 79%), mp >300 °C. ¹H NMR (300 MHz, d_1 -CHCl₃) δ (ppm): 7.48–7.44 (d, l-4H), 7.24–7.21 (d, k-4H), 6.67–6.65 (d, i-2H), 6.09–6.07 (d, j-2H), 1.37 (s, a-18H). ¹³C NMR (500 MHz, d_1 -CHCl₃) δ (ppm): 159.9, 157.9, 143.9, 142.4, 141.9, 141.1, 129.8, 129.2, 127.1, 35.6, 31.9, 31.5, 29.7, 29.6, 29.5, 29.4, 29.1, 22.7, 14.1. Anal. Calcd for C₅₀H₆₂Br₂N₂O₂S₂ (946.98): C, 63.42; H, 6.60; N, 2.96. Found: C, 63.09; H, 6.52; N, 2.92. UV (CH₂Cl₂): 429 nm; PL (CH₂Cl₂): 639 nm (excitation at 400 nm); UV (film): 420 nm. *e* (DCM): 40 229 L mol⁻¹ cm^{-1} .

Scheme 1. Synthesis of isoDPP Monomers M1-M3^a



"Reagents and conditions: (i) THF, 0 °C; (ii) PCl₅, toluene, 110 °C; (iii) THF, -78 to 0 °C; (iv) NBS, chloroform, room temperature.

Synthesis of the isoDPP Polymers. Polymer P1. 50.0 mg (0.70 mmol) of M1, 41.0 mg (0.70 mmol) of M4, and 2.4 mg (0.002 mmol) tetrakis(triphenylphosphino)palladium(0) were dissolved in a mixture of toluene/dioxane (1.5 mL/0.75 mL) and purged with nitrogen for 10 min. Then the mixture was heated to 100 °C, a solution of 24 mg (0.70 mmol) of $K_2 \text{CO}_3$ in 0.75 mL of Milli- $Q_{\text{Plus}}\text{-water}$ was added, and the mixture was stirred under reflux for 24 h. After cooling to room temperature, the reaction mixture was diluted with 20 mL of toluene and successively extracted with 2 \times 30 mL of brine and 30 mL of water. The organic phase was dried over MgSO4. After concentration in vacuum the residue was poured in 20 mL of methanol to precipitate the polymer. The polymer was filtered off and dried in vacuum. 26 mg (42%) of an orange powder was obtained; mp >300 °C. Molecular weight (GPC, THF, 40 °C): $M_{\rm W}$ = 7.6 kDa, $M_{\rm N}$ = 5.9 kDa, PD = 1.3. ¹H NMR (300 MHz, d_1 -CHCl₃): $\delta = 7.75 - 7.45$ (m, f, g, h-H), 7.37-7.15 (m, b, c, d, e-H), 1.99 (m, i-H), 1.35 (s, a-H), 1.33-1.04 (m, j-H), 0.79 (t, k-H). Anal. Calcd for C₆₃H₆₆N₂O₂: C/H 11.04. Found: C/H 10.81. UV (CHCl₃): 328, 409 nm, PL (CHCl₃): 625 nm (excitation at 400 nm); PL quantum yield Φ : 0.7%.

Polymer P2. The synthesis was carried out as described for P1 except that M2 instead of M1 was used as monomer. An orange-yellow powder was obtained (165 mg, 52%); mp >300 °C. Molecular weight (GPC, THF, 40 °C): $M_W = 3.4$ kDa, $M_N = 2.5$ kDa, PD = 1.37. ¹H NMR (300 MHz, d_1 -CHCl₃): $\delta = 7.88-7.47$ (m, f, g, h-H), 7.37–7.20 (dd, b, c-H), 7.06–6.98 (dd, d, e-H), 2.05 (m, i-H), 1.32 (s, a-H), 1.43–1.07 (m, j-H), 0.79 (t, k-H). Anal. Calcd for C₆₃H₆₆N₂O₂: C/H 11.04. Found: C/H 11.67. UV (CHCl₃): 331, 360 nm (sh), PL (CHCl₃): 611 nm (excitation at 400 nm); PL quantum yield Φ : 0.2%.

Polymer **P3**. The synthesis was carried out as described for **P1** except that **M3** and **M5** were used as monomers. A purple powder was obtained (120 mg, 70%); mp >300 °C. Molecular weight (GPC, THF, 40 °C): $M_w = 21$ kDa, $M_N = 4$ kDa, PD = 5.6. ¹H NMR (300 MHz, d_2 -

CH₂Cl₂) δ (ppm): 7.24–6.92 (<u>m</u>, d,e,f,g,h,i –14H), 2.58 (<u>m</u>, c-4H), 1.73–0.90 (<u>m</u>, b-40H), 0.83 (<u>m</u>, a-6H). Anal. Calcd for C₅₄H₆₆N₂O₂S₂₃: C, 74.44; H, 7.63; N, 3.22. Found: C, 74.56; H, 8.09; N, 2.96. UV (CH₂Cl₂): 489 nm, PL (CH₂Cl₂): 610 (sh), 720 nm (excitation at 400 nm); PL quantum yield Φ : 0.2%.

Polymer P4. The synthesis was carried out as described for P1 except that M3 and M6 were used as monomers. A red powder was obtained (150 mg, 69%); mp >300 °C. Molecular weight (GPC, THF, 40 °C): M_w = 6.6 kDa, M_N = 4.1 kDa, PD = 1.6. ¹H NMR (300 MHz, d_2 -CH₂Cl₂) δ (ppm): 8.04−6.05 (<u>m</u>, j-p-18H), 4.17 (<u>m</u>, i-2H), 2.58−3.12 (<u>m</u>, h-4H), 1.23−1.06 (<u>m</u>, d₂e,f,g-45H), 0.85 (<u>m</u>, a,b,c-12H). Anal. Calcd for C₇₀H₈₇N₃O₂S₂: C, 78.83; H, 8.22; N, 3.94. Found: C, 77.02; H, 8.34; N, 3.76. UV (CH₂Cl₂): 345, 435 nm, PL (CH₂Cl₂): 643 nm (excitation at 480 nm).

2.2. Methods. Instrumentation. ¹H NMR spectra were recorded using a Bruker DPX 300 spectrometer, which operates at 300 MHz. UV/vis absorption spectra were recorded using a Perkin-Elmer Lambda 14 spectrometer. Photoluminescence spectra were recorded using a Perkin-Elmer LS50B spectrometer. Photoluminescence quantum yields were measured in chloroform (P1, P2) and dichloromethane solution (P3, P4). The excitation wavelength was 400 nm (P1-P3) and 480 nm (P4). The values were calculated by comparing with Rhodamine 6G in ethanol ($\Phi_f = 0.95$). For size exclusion chromatography (SEC) a Waters/Millipore UV detector 481 and an SEC column combination (Latek/Styragel 50/1000 nm pore size) were used. All measurements were carried out in tetrahydrofuran at 45 °C. The columns were calibrated using commercially available polystyrene standards. High resolution mass spectrometry (HRMS) was carried out on a Thermo LTQ Orbitap XL-linear ion trap analyzer using electrospray ionization (ESI); resolution: normal scan. Electrochemical experiments were performed using a PG390 potentiostat from Heka Co. (model PG 390, Heka Electronic, Lambrecht, Scheme 2. Synthesis of Polymers P1-P4^a



"Reagents and conditions: (i) Pd(PPh₃)₄, K₂CO₃, toluene/dioxane/water, reflux, 24 h; (ii) Pd(PPh₃)₄, K₂CO₃, toluene/water, reflux, 24 h.

polymer	$M_{\rm W}$ [Da]	PD	λ_{\max} [nm]	$\lambda_{\rm em}$ [nm]	Stokes shift	$\Phi_{ m F}$ [%]	extinct coeff ε (λ) [L mol ⁻¹ cm ⁻¹]		
P1	7600	1.3	328, 409 ^a	625	216	0.7	30947 (409 nm) ^a		
P2	3400	1.4	331, 360 ^a	611	251	0.4	27609 (360 nm) ^a		
Р3	21000	5.6	489 ^b	631, 720	231	0.5	21322 (489 nm) ^{b}		
P4	6500	1.6	345, 435 ^b	643	208	0.3	19960 (345 nm) ^b		
							10400 (435 nm) ^b		
^a In chloroform. ^b In dichloromethane.									

Germany). A thin film of the polymer was cast on an ITO electrode and cycled in acetonitrile (saturated with nitrogen) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as electrolyte salt. Reference and counter electrodes were platinum. The voltage data were calculated for the standard calomel electrode (SCE). Scan rate: 50 mV s⁻¹; temperature: 20 °C. Onset potentials were determined from the intersection of two tangents drawn at the rising and background currents of the cyclic voltammogram.

3. RESULTS AND DISCUSSION

We began our studies with the synthesis of dibromo-substituted isoDPP monomers **M1**, **M2**, and **M3**. The method described by Langer et al. was applied.¹⁷ According to this method, oxalic acid bis(arylimidoyl) dichlorides 2a-2c were reacted with ethyl arylacetates to yield monomers **M1** and **M2** and compound **3** (Scheme 1). The three-stage synthesis led to the tetraarylated isoDPP derivatives in good yield. In order to improve the solubility, derivatives containing 4-*n*-dodecylphenyl groups instead of 4-*tert*-butylphenyl groups were prepared. However, attempts to prepare N-alkylated derivatives via oxalic acid

bis(alkylimidoyl) dichlorides failed. In addition to the synthesis of the 1,3,4,6-tetraphenylated monomers **M1** and **M2** it was also possible to prepare a 1,4-diphenyl-3,6-dithienyl-substituted derivative 3, which was subsequently brominated with NBS to yield monomer **M3**. Because of the donor (D) character of the thiophene units and the acceptor (A) character of the diketopyrrolopyrrole units, it was hoped that D–A interactions are introduced in the molecule leading to a bathochromic shift of the absorption maximum, which in fact turned out to be the case.

M1 and M2 were synthesized first. M1 carries the polymerizable 4-bromophenyl units in the 3- and 6-position and M2 in the 1- and 4-position. From M1 the formation of π -conjugated polymers with the carbon–carbon chain passing through the isoDPP units can be expected, whereas M2 should lead to polymers with interruption of π -conjugation at the N atoms of the lactam units. Corresponding results were already obtained for polymerization of 1,3,4,6-tetraarylated pyrrolo[3,4-c]pyrrole-2,5-dione (DPP) monomers.^{5g}



Figure 2. ¹H NMR spectra of P1, P2 in deuterated chloroform and P3, P4 in deuterated dichloromethane.

M1 and M2 were obtained as orange solids of limited solubility in a variety of organic solvents. M1 was readily soluble in chlorinated solvents, whereas M2 was moderately soluble in dipolar aprotic solvents such as *N*-methylpyrrolidone and dimethylformamide at high temperature. The limited solubility of the compounds is a consequence of their highly unsaturated structure, and the lack of long alkyl chains, which could not be introduced directly at the lactam N atoms using our synthetic approach. The ¹H NMR spectrum of M1 displayed all the expected resonances with no discernible peaks corresponding to impurities (see Supporting Information). A proton NMR spectrum of M2 in chloroform was monitored at 40 °C. It shows the expected resonances (see Supporting Information).

Optical spectra of M1 (see Supporting Information) indicate a strong absorption maximum at 360 nm, the extinction coefficient being near 20 000 L mol⁻¹ cm⁻¹, and a tail at long wavelengths reaching to 520 nm. The fluorescence is only weak, and the maximum occurs at 635 nm. M2 exhibits an absorption maximum at 330 nm, a shoulder at about 360 nm, and a long wavelength tail reaching to 520 nm. The maximum fluorescence of M2 is at 613 nm. For both compounds, extremely large Stokes shifts of more than 260 nm were found, but the quantum yields of the fluorescence were below 1%.

Compound 3 was prepared upon reaction of oxalic acid N,N'bis(4-dodecylphenylimidoyl) dichloride (2c) with ethyl 2thienvlacetate. The subsequent bromination of 3 with NBS led to monomer M3 in good yield. It was also possible to prepare M3 from ethyl 5-bromo-2-thienyl acetate and 2c in a one-step reaction. However, the yield from this reaction was only a few percent. Proton NMR spectra of 3 and M3 are shown in the Supporting Information. The spectrum of 3 shows the expected signals of the thiophene protons at 6.50-6.70 ppm. For M3 the signals appear at 6.12–6.70 ppm due to the bromination. Optical spectra of M3 in dichloromethane (see Supporting Information) indicate an absorption maximum at 429 nm and a tail at long wavelengths up to 570 nm. The absorption coefficient at λ_{max} is 40 229 L mol⁻¹ cm⁻¹. The solution is weakly fluorescing with a maximum at 639 nm, the Stokes shift being 210 nm.



Figure 3. UV/vis absorption and emission spectra of P1, P2 in chloroform and P3, P4 in dichloromethane.

The polymers P1-P4 were prepared upon palladiumcatalyzed Suzuki cross-coupling reaction of M1-M3 with aromatic diboronic acid esters M4-M6 as indicated in Scheme 2.

The yields were between 42 and 70%. The molecular weights were between 3.4 and 21 kDa. Characteristic data are compiled in Table 1. The low molecular weight of P2 was due to the poor solubility of M2 in the reaction medium. P1 and P2 were obtained as deep red and orange red powders, respectively, while P3 and P4 were obtained as purple and red powders. P1 was only slightly soluble in common organic solvents such as THF, dichloromethane, and chloroform, whereas P2 was moderately soluble in various organic solvents. P3 and P4 were readily soluble in common organic solvents except alcohols. The molecular structure was analyzed using ¹H NMR spectroscopy. In Figure 2, the ¹H NMR spectra of the four polymers are shown. P1 and P2 exhibit typical proton signals from the alkyl groups between 0.7 and 1.5 ppm, the strong signal at 1.33 ppm originating from the tert-butyl groups. The signal at about 2 ppm originates from the α -CH₂ protons of 9,9'-dihexylfluorene. The signals of the aromatic protons occur at 6.9-7.9 ppm. P3 and P4 exhibit strong signals of the dodecyl protons of isoDPP at 0.7-2.4 ppm and signals of the aromatic protons at 6.5-8.0 ppm. Additional signals of the 2ethylhexyl protons appear at 2.5 and 4.2 ppm.

Optical Properties. Optical absorption and fluorescence spectra of the polymers are shown in Figure 3. All polymers are deeply colored, the extinction coefficients of the strongest bands being higher than 20 000 L cm⁻¹ mol⁻¹ (see also Table 1).

Scheme 3. Molecular Structures of Four Isomeric Polymers Containing isoDPP Units (Upper Row) and DPP Units (Lower Row) with Conjugated Main Chain (Left) and Nonconjugated Chain (Right)^a



^aThe conjugated chain is indicated in blue, and the nonconjugated parts are indicated in red and green. Data of DPP polymers are taken from ref Sg.



Figure 4. Colors of P1 (a), P2 (b), P3 (c), and P4 (d) in various solvents.

P1 and P2 exhibit a strong absorption maximum at about 330 nm and a second maximum either at 409 nm (P1) or 360 nm (P2). Compared with monomer M1, the absorption of P1 is red-shifted by 64 nm, which can be ascribed to the π -conjugation of the backbone. In contrast, the 360 nm maximum of P2 correlates with a shoulder in the absorption band of M2 at the same wavelength. This indicates a missing red-shift for P2, which can be explained with an interruption of π -conjugation at the N atoms of the lactam units, the backbone containing electronically isolated isoDPP and phenylene–fluorene–phenylene units. A similar effect was reported for regioisomeric DPP polymers, in which a tetraarylated diketopyrrolo[3,4-*c*]pyrrole unit was incorporated in the backbone via the 3- and 6-positions or the 1- and 4-positions.^{5g}

isomeric isoDPP- and DPP-containing polymers are displayed in Scheme 3.

It is striking that the absorption maxima of the isoDPPcontaining polymers occur at much shorter wavelengths than those of the related DPP polymers. It has its origin in a less efficient coupling of the aryl groups with the adjacent diketopyrrolopyrrole central unit in the isoDPP derivatives.²³ The UV/vis spectra also indicate that the absorption maxima of the thienyl-substituted polymers P3 and P4 are considerably red-shifted compared with the phenyl-substituted DPPpolymers P1 and P2 (see Table 1 and Figure 3). This can be ascribed to donor-acceptor interactions between the thienvl groups and the adjacent isoDPP core and between the comonomer units along the backbone. The four polymers exhibit a weak red fluorescence with maxima between 611 and 720 nm (Figure 3). The quantum yield is low and does not exceed 0.7% (for details see Table 1). Photographic images of the polymer solutions in different solvents are shown in Figure 4.

In order to determine the optical bandgaps of the polymers, thin films were cast from solution and the onset wavelength $\lambda_{abs,onset}$ of the absorption bands were determined. UV/vis absorption spectra of the films are shown in the Supporting Information, and the optical data are compiled in Table 2. It can be seen that the thienyl-substituted isoDPP polymers P3 and P4 exhibit bandgaps of about 1.5 eV, whereas the phenyl-substituted polymers P1 and P2 exhibit larger bandgaps of about 2 eV. The optical bandgap of P2 is about 0.15 eV larger than for P1 due to the lack of π -conjugation in the main chain.

Electrochemical Properties. In order to study the electrochemical properties, films of the four polymers were cast on ITO-coated glass slides, and cyclic voltammograms (CV diagrams) were recorded in the potential range from -2.5 to +1.5 V vs FOC. The CV diagrams are shown in Figure 5.

It can be seen that anodic oxidation of P3 and P4 sets in at low potentials of 0.38 and 0.48 V. Two anodic waves with maxima at 0.5 and 0.8 V occur. Anodic oxidation of P1 and P2 sets in at 0.59 and 0.42 V. Only single peaks occur with maxima at 0.8 and 0.7 V, respectively. Upon cathodic reduction, single peaks with maxima at -1.6 V (P1, P2), and -1.3 V (P3, P4) occur.

The oxidation and reduction behavior of all polymers is irreversible. From the onsets of the anodic and cathodic waves HOMO and LUMO values as well as electrochemical bandgaps were calculated. As shown in Table 2, the electrochemical bandgap values are similar to the optical ones. The thienylsubstituted isoDPP polymers exhibit the lowest bandgaps of about 1.4–1.5 eV, whereas the values for the phenyl-substituted isoDPP polymers are clearly higher (Table 2).

Table 2. Bandgap Data of P1-P4^a

polymer	$\lambda_{\mathrm{abs,onset}}$ of film [nm]	oxidation onset [V] {HOMO $[eV]$ }	reduction onset [V] {LUMO [eV]}	opt/electrochem bandgap [eV]
P1	640	0.59 { -5.39}	-1.36 { -3.44}	1.94/1.95
P2	599	0.42 { -5.22}	-1.41 { -3.39}	2.07/1.83
P3	746	0.38 {-5.18}	-1.04 { -3.76}	1.66/1.42
P4	698	0.48{ -5.28}	-0.99 { -3.81}	1.78/1.47

"Optical bandgap E_{opt} was measured at the onset of absorption of polymer film ($E_{opt} = 1240/\lambda_{onset}$ eV). HOMO–LUMO gap was calculated according to the equation $-E_{LUMO} = E_{onset(red)} + 4.8$ eV and $-E_{HOMO} = E_{onset(ox)} + 4.8$ eV, were $E_{onset(ox)}$ and $E_{onset(red)}$ are onset potentials for oxidation and reduction processes vs Fc/Fc⁺ couple.



Figure 5. Cyclic voltammograms of P1–P4 (a–d). Scan rate: 50 mV s⁻¹; temperature: 20 $^{\circ}$ C; electrolyte solution: 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile.

4. CONCLUSIONS

Our study shows that conjugated polymers containing 1,3,4,6tetraarylated diketopyrrolo[3,2-b]pyrrole (isoDPP) units can be prepared in only few reaction steps. For the synthesis of the monomers, the method described by Langer et al. can be applied. The polymers are subsequently prepared in one step using established palladium-catalyzed polycondensation procedures such as Suzuki coupling. Deeply colored polymers with absorption coefficients higher than 20 000 L mol⁻¹ cm⁻¹ are obtained. Variation of the chromophore structure by use of phenyl- or thienyl-substituted isoDPP units and incorporation of isoDPP units in conjugated polymers via the 3- and 6position or 1- and 4-position lead to remarkable differences in the optoelectronic and electrochemical properties. They qualitatively resemble those observed for the DPP polymers. However, less efficient coupling between aryl groups and the adjacent central pyrrolopyrrole unit²³ causes a blue-shift of the absorption maxima, and the colors of the polymers are less brilliant. Moreover, the quantum yields of fluorescence are not higher than 0.7%. Despite of these drawbacks the polymers exhibit a deep and broad absorption in the visible, which renders the compounds attractive for applications as dyes and colorants. They also might be useful as comonomers in photovoltaic polymers increasing the light absorption in the visible. Further studies will be concerned with the preparation of DPP/isoDPP copolymers, from which a very broad absorption in the visible can be expected.

ASSOCIATED CONTENT

S Supporting Information

¹H NMR spectra, UV/vis absorption spectra, fluorescence spectra of monomers M1–M3 and compound 3, and UV/vis

absorption spectra of films of P1-P4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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