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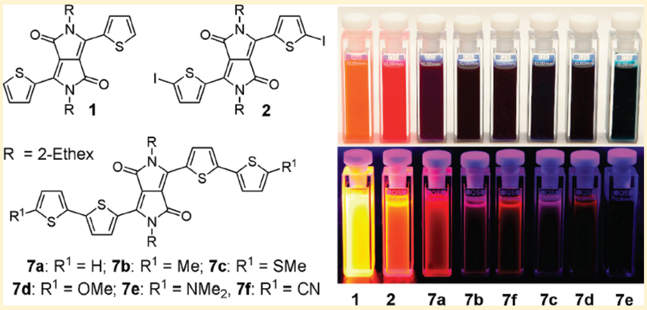
Synthesis and Characterization of Optical and Redox Properties of Bithiophene-Functionalized Diketopyrrolopyrrole Chromophores

Hannah Bürckstümmer, Annike Weissenstein, David Bialas, and Frank Würthner*

Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg, Germany

Supporting Information



ABSTRACT: A series of six new 2,2′-bithiophene-functionalized diketopyrrolopyrrole (DPP) dyes **7a**−**f** bearing different electron-donating and electron-withdrawing substituents at the terminal thiophene units was synthesized by palladium-catalyzed cross-coupling reactions. The to date unknown diiodinated DPP **2** and the corresponding boronic ester derivative **3** could be prepared in high yields, and these are shown to be versatile building blocks for the synthesis of DPP-based molecular materials by Negishi, Stille, and Suzuki coupling. The influence of the peripheral substituents on the optical and electrochemical properties of the present series of DPP dyes **7a**−**f** were investigated by UV/vis and steady-state fluorescence spectroscopy and cyclic voltammetry, revealing an appreciable effect on the electronic nature of these dyes. The diamino-substituted DPP derivative **7e** exhibits a strong absorption band reaching in the near-infrared (NIR) region, which is a highly desirable feature for application in organic photovoltaics.

INTRODUCTION

In recent years, 3,6-diaryl-2,5-dihydro-1,4-diketopyrrolo[3,4-*c*]pyrrole (DPP) pigments have experienced a remarkable innovation wave and are currently attracting considerable research efforts in the field of organic electronic materials.[1] Following the accidental discovery by Farnum et. al in 1974[2] and the significantly improved synthetic pathway by Iqbal, Cassar, and Rochat in the early 1980s,[3] DPP derivatives rapidly became an important class of high-performance pigments used in inks, paints, and plastics,[1a−d] owing to their brilliant shades and outstanding ambient stability. Further striking innovations include the development of DPP-based latent pigments,[4] where the time- and energy-consuming dispersion step can be circumvented, and because of their strong fluorescence and excellent photophysical stability, the construction of solid-state lasers.[5]

DPP pigments are usually highly insoluble in most common organic solvents because of strong intermolecular hydrogen bonding and $\pi-\pi$ interactions. The solubility of DPP compounds, however, can be drastically increased by substitution of the H atoms at the lactam nitrogens, e.g., with branched or linear long alkyl groups that prevent H-bonding. The resulting soluble molecular dyes or polymers containing such DPP dyes are often strong fluorophores[6] and found application for examples as chemosensors[7] or in light-emitting diodes.[8] In recent years, the potential of soluble DPP small molecules and polymers as organic semiconductors have been explored with highly promising results in organic thin-film transistors,[9] dye-sensitized solar cells,[10] and bulk heterojunction organic solar cells. In the latter devices, DPP compounds have been used as both electron-donor[11] and -acceptor material.[12]

For high-performance optoelectronic devices, in particular photovoltaic cells, semiconducting dyes with strong absorption in the visible spectral region are required. The optical properties of DPP chromophores, and their ability to aggregate as well, are dependent mainly on the electronic nature of aryl or heteroaryl groups such as phenyls, thiophenes, or thiazoles that are attached to the DPP core.[13] However, very little is known on tuning of optical properties of DPP dyes by systematic variation of peripheral substituents at aryl or heteroaryl groups.[14] Since optical and electrochemical properties of organic chromophores can be markedly improved by this approach,[15] we have decided to synthesize a systematic series of new chromophores having 2,2′-bithiophene moieties at the DPP core in common, but bearing different electron-donating groups or for the purpose of comparison one electron-withdrawing group, respectively, at the terminal thiophene units.

The basic DPP derivative containing two bithiophene units at the DPP core unit was first mentioned in a patent on DPP fluorophores in 2004,[16] and the synthetic details were described in 2008.[17] Usually, the bithiophene moieties are brominated in a subsequent reaction step and the dibrominated derivatives were used as versatile building blocks in palladium-catalyzed cross-coupling reactions to prepare polymeric materials for application as organic semiconductors.[9a,11a,11c,11d,17,18] Very recently, Geerts et al. have made great efforts to significantly improve the synthesis of dibrominated DPP derivatives bearing bithiophene moieties.[19] However, they have not explored the substitution

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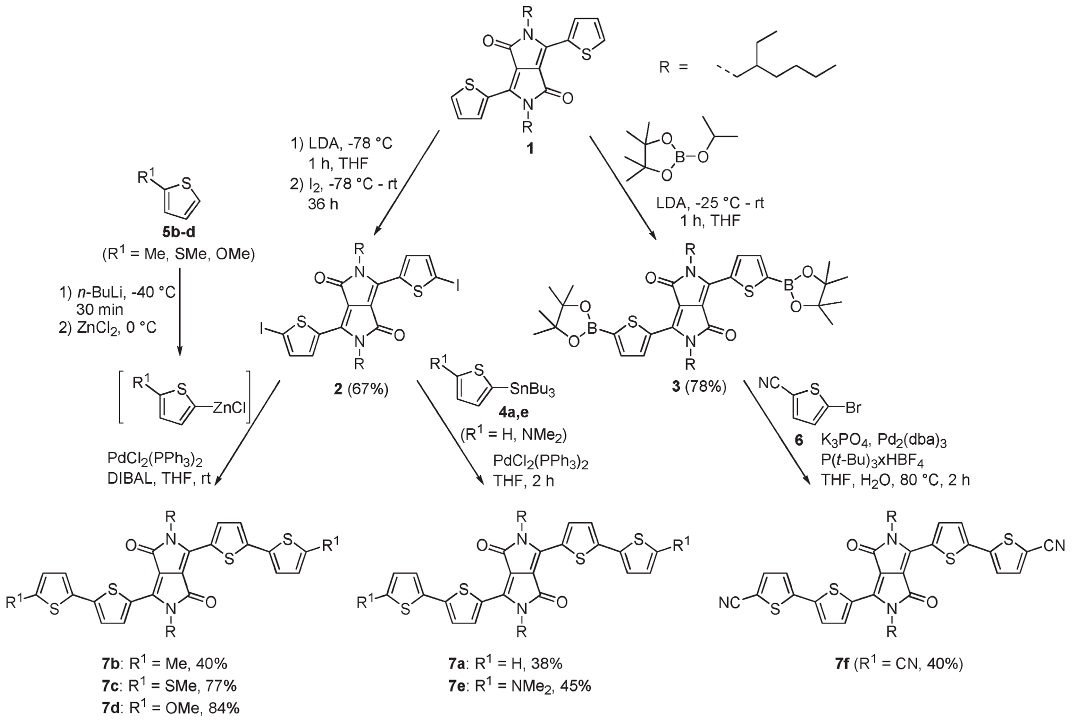

Scheme 1. Synthesis of 3,6-Bis(2,2′-bithiophene-5-yl)-1,4-diketopyrrolopyrroles 7a−f

effect on the optoelectronic properties of bithiophene-functionalized DPP derivatives by replacing the bromine atoms by electron-donating or electron-withdrawing groups.

Here we report the synthesis of a series of new bithiophene-functionalized DPP chromophores **7a**−**f** (Scheme 1) with varying electronic nature of the substituents at the 5′-position of terminal thiophene units. With this set of DPP derivatives we could explore the effect of peripheral substituents on the optical and electrochemical properties of this donor−acceptor−donor (bithiophene−DPP−bithiophene) system and found that the absorption of monomeric DPP dyes can be bathochromically shifted close to near-infrared region.

RESULTS AND DISCUSSION

Synthesis. The bithiophene-functionalized DPP dyes **7a**−**f** were synthesized by different palladium-catalyzed cross-coupling reactions as shown in Scheme 1.

The DPP derivative **1** containing two solubilizing 2-ethylhexyl groups at lactam nitrogen atoms was used as a starting compound and was synthesized according to the literature procedure.[11c] Although dibrominated DPP **1** was previously used for Pd-catalyzed cross-coupling reactions, to generate a more powerful DPP coupling component, we have developed a method to synthesize the unknown diiodinated DPP derivative **2**. First, we tried to iodize DPP **1** with *N*-iodosuccinimide in chloroform or chloroform/HOAc mixtures but could not obtain the desired product **2**. Then, in analogy to a previously reported procedure,[20] we treated compound **1** with freshly prepared LDA solution at low temperature (−78 °C), followed by the addition of iodine, which indeed afforded the diiodinated DPP **2** in 67% yield. Since the Negishi coupling reaction[21] was shown to be an efficient method to generate donor−acceptor-substituted bithiophene units,[22] we have applied this coupling reaction to synthesize the bithiophene-functionalized DPPs **7b**−**d** containing the electron-donating groups methyl, methylthio, and methoxy, respectively, at the terminal thiophene units. The respective zinc−thiophenes were generated in situ by lithiation of the corresponding electron-donor group substituted thiophenes **5b**−**d** with *n*-BuLi and subsequent reaction with $ZnCl_2$. The Pd-catalyzed cross-coupling reaction of DPP **2** with the in situ generated zinc-thiophenes at room temperature afforded DPP **7b** (Me) in 40% yield, while the DPPs **7c** (SMe) and **7d** (OMe) were obtained in significantly higher yields of 77% and 84%, respectively. The unsubstituted reference DPP **7a** (H) was prepared by a Stille coupling reaction of DPP **2** with commercially available tri-*n*-butylstannylthiophene at 65 °C in 38% yield. Cross-coupling of amino-substituted thiophenes by Negishi's method usually results in low yields.[22] Therefore, the bithiophene-functionalized DPP **7e** bearing two dimethylamino substituents at terminal thiophene units was synthesized by Stille coupling. First, the same reaction conditions (65 °C, 2 h) as for **7a** (H) were applied for the coupling reaction of **2** with dimethylamino-substituted stannyl thiophene **4e**. Although the starting materials were completely consumed under these conditions, only traces of the corresponding monocoupling product were obtained, and the desired product **7e** was not observed at all. Prolonging the reaction time to 15 h also did not yield the target compound. Thus, we increased the reaction temperature to 80 °C, and at this elevated temperature dye **7e** was obtained in 45% yield. To complete the series, we wanted to synthesize a DPP dye comprising bithiophene functionalities with an electron-withdrawing cyano group at terminal thiophene. We first attempted the synthesis by Negishi coupling using the non-nucleophilic base LDA to lithiate thiophene-2-carbonitrile, which was then treated with $ZnCl_2$ to generate the corresponding zinc organyl compound and added directly to the reaction mixture containing the palladium(0) species and DPP **2**. However, under varied reaction temperature and time, only unreacted starting materials could be recovered. Hence, we decided to apply Suzuki coupling[23] for the synthesis of dicyano-substituted DPP **7f**. First, we tried to react diiodinated DPP **2** with the commercially available 5-cyanothiophene-2-boronic acid by using $Pd(PPh_3)_4$ as catalyst. However, under varied reaction times (2−15 h) and temperatures (65−80 °C) only the dehalogenated monocoupling product was formed in poor yields. As the next approach, we generated the boronic ester DPP **3** by following a procedure reported recently for a related derivative.[18] For this purpose, a mixture of DPP **1** and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane was treated with freshly prepared LDA solution, resulting in boronic ester **3** with a yield of 78%. The latter was applied in a Suzuki coupling reaction with the commercially available 2-bromo-5-cyanothiophene **6** to give the targeted DPP dye **7f** (CN) with a yield of 40%. The synthesized compounds were purified by column chromatography and characterized by ^{1}H NMR, high-resolution mass spectroscopy, and elemental analysis.

Optical Properties. The optical properties of newly synthesized bis(bithiophene)-functionalized DPP **7a**−**f** and, for the purpose of comparison, those of thiophene-substituted compounds **1** and **2** were studied by UV/vis and steady-state fluorescence spectroscopy in dichloromethane. The absorption spectra are shown in Figure 1, and the significant optical properties are summarized in Table 1. All these DPP dyes show a broad absorption band in the visible to near-infrared region (about 450−800 nm).

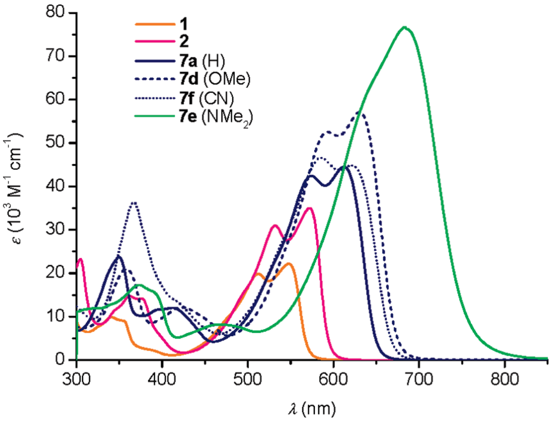

Figure 1. UV/vis absorption spectra of DPPs **1**, **2**, and **7a**,**d**−**f** in dichloromethane (2×10^{-5} M) at 20 °C. The spectra of **7b** (Me) and **7c** (SMe) are very similar to **7d** (OMe); thus, they are not depicted here.

The thiophene-substituted DPP **1** is orange in dichloromethane and features two absorption maxima in longer wavelength region at 548 and 512 nm (Figure 1). The vibronic structure of the absorption band and the high fluorescence quantum yield (Φ_{fl}) of 74% are typical for such DPP dyes,[13,24] while the relatively small Stokes shift of 342 cm^{-1} suggests a chromophore exhibiting similar geometry in the ground and the first excited state. The introduction of two iodine atoms in the thiophene moieties of **1** results in DDP **2**, which shows a pink color in dichloromethane with a bathochromic shift of the first absorption maximum from 548 nm (**1**) to 572 nm (**2**) and an enhanced absorption strength illustrated by the molar absorption coefficient (ε_{max}) as well as the square of the transition dipole moment $\mu_{eg}{}^2$ with an increase of 60% (Table 1). The fluorescence quantum yield and Stokes shift of **2** are similar to those of compound **1**. The conjugated π-systems of DPP **7** are enlarged by one thiophene unit at each side of DPP core. At terminal thiophene-unsubstituted DPP **7a** (H) entails a significant red-shift of the absorption band in longer wavelength region with a maximum at 613 nm and an even higher tinctorial strength of 77.9 D^2 compared with those of the precursors **1** and **2**. The blue dichloromethane solution of **7a** shows a significantly decreased fluorescence quantum yield of 36% but an increased Stokes shift of 600 cm^{-1}. The introduction of the weekly electron-donating methyl substituents at the bithiophene moieties in **7b** leads to a small red-shift of the absorption band of 8 nm compared to that of **7a** (H) and a higher absorption strength of 95.0 D^2, while Stokes shift with 610 cm^{-1} is comparable to that of **7a** (600 cm^{-1}), but the fluorescence is slightly decreased to 32%.

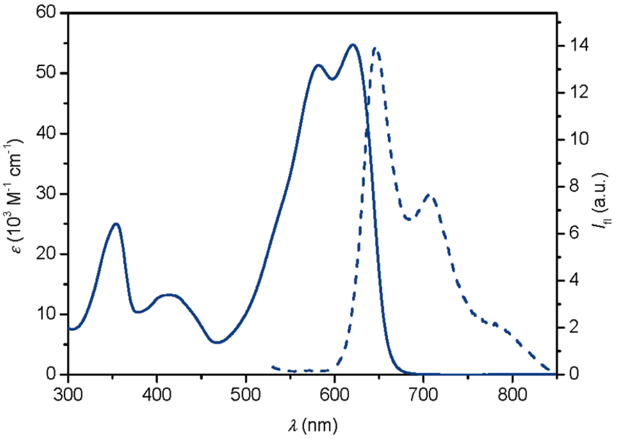

Figure 2. Absorption (solid line) and emission spectra (dashed line, excitation at 520 nm) of DPP **7b** (Me) in dichloromethane at 20 °C.

Table 1. Optical Properties of Diketopyrrolopyrroles 1, 2, and 7a−f in Dichloromethane (2×10^{-5} M) at 20 °C

	λ_{abs} (nm)[a]	ε_{max} (M^{-1} cm^{-1})	$\mu_{eg}{}^2$ (D^2)[b]	λ_{em} (nm)	Stokes shift (cm^{-1})	Φ_{fl} (%)
1	548	22200	32.7	559	342	74
2	572	35000	52.3	582	285	73
7a (H)	613	44500	77.9	637	600	36
7b (Me)	621	54700	95.0	646	610	32
7c (SMe)	627	57000	104.3	664	873	14
7d (OMe)	631	57100	99.1	662	740	22
7e (NMe$_2$)	684	76800	140.0	753	1322	3
7f (CN)	622	44800	89.9	656	795	32

[a] First absorption maxima. [b] Determined by integration of the absorption band.

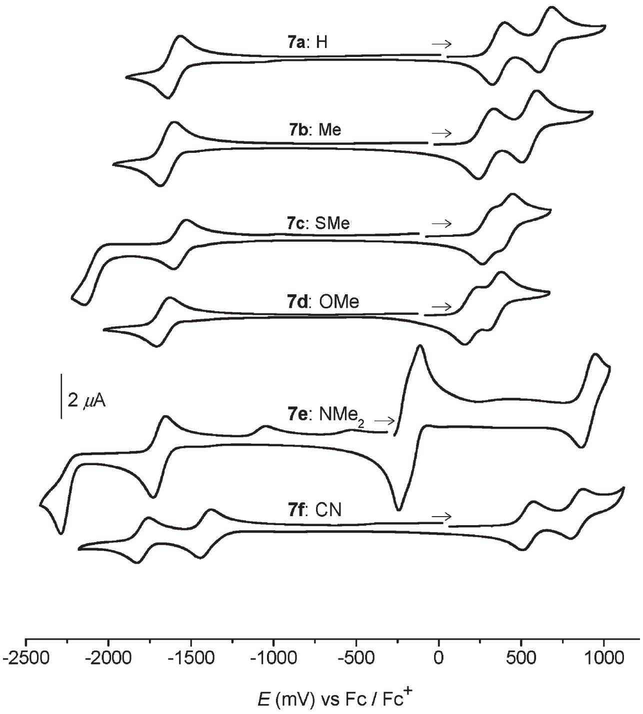

Figure 3. Cyclic voltammograms of DPPs **7a**−**f** in dry dichloromethane (10^{-4} M); scan rate 100 mV s^{-1}; supporting electrolyte: tetrabutylammonium hexafluorophosphate (NBu_4PF_6, 0.1 M).

The shape of the emission spectrum of **7b** shown in Figure 2 is representative for all fluorescence spectra of the presented series (Figure S1, Supporting Information) except for **7e** (NMe_2) and is typical for thiophene-functionalized DPP derivatives.[13]

The stronger electron-donating substituents in **7c** (SMe) and **7d** (OMe) compared to that in **7b** (Me) confer further bathochromic shift of absorption and emission maxima as expected for push−pull chromophores.[25] In accordance with the comparable electron-donating abilities of these two functional groups, both the absorption (**7c**: 627 nm, **7d**: 631 nm) and the fluorescence maxima (**7c**: 664 nm, **7d**: 662 nm) of DPP dyes **7c** and **7d** are quite similar. However, the introduction of the methylthio group in **7c** entails a larger Stokes shift of 873 cm^{-1} compared to that of **7d** (740 cm^{-1}) and a significantly reduced fluorescence quantum yield of only 14% (**7d**: 22%). The dimethylamino substituent in **7e** is the strongest electron-donor group used in this series of push−pull dyes leading to a green dye with a very broad and intense absorption band in dichloromethane reaching the near-infrared region (up to 800 nm) with a maximum at 684 nm. To our knowledge, this is the longest wavelength absorption maximum observed so far for a DPP dye by substitution at the aryl or heteroaryl residue. Notably, strong absorption in the NIR was also accomplished by incorporating electron-acceptor moieties directly at the DPP core.[26] In the case of **7e**, the fine structure is almost lost and the absorption strength of 140 D^2 is remarkably high. We suggest that the stronger electron-donating ability of the dimethylamino groups results in a planarization of the bithiophenes through extended conjugation to the electron acceptor DPP; hence, the absorption band is strongly bathochromically shifted. The fluorescence of **7e** is strongly quenched (Φ_{fl} = 3%), and the nonstructured emission band exhibits the largest Stokes shift of 1322 cm^{-1} of the present series of DPPs. For DPP **7f** with electron-withdrawing cyano groups a red-shift of the first absorption maximum (622 nm) by 9 nm compared to that of the reference compound **7a** (H) with a reversal of the intensities of first and second (586 nm) absorption maxima in visible region was observed. The emission spectrum of **7f** shows a similarly structured band like **7b** (Figure 2) with a fluorescence quantum yield of 32% and a Stokes shift of 795 cm^{-1}.

Table 2. Half-wave Potentials[a] of Diketopyrrolopyrroles 1, 2, and 7a−f

compd	$E_{1/2}^{red}$ (V)	$E_{1/2}^{ox}$ (V)
1	−1.70	0.50, 0.87
2	−1.59	0.55, 0.87
7a (H)	−1.60	0.36, 0.63
7b (Me)	−1.63	0.30, 0.55
7c (SMe)	−1.56, −2.14[b]	0.31, 0.41
7d (OMe)	−1.66	0.21, 0.34
7e (NMe_2)[c]	−1.70, −2.30[b]	−0.16[d], −0.21[d]
7f (CN)	−1.40, −1.78	0.54, 0.83

[a] All measurements were carried out in dry dichloromethane (10^{-4} M) using Fc/Fc^+ as reference and a scan rate of 100 mV s^{-1} with NBu_4PF_6 (0.1 M) as supporting electrolyte. [b] Peak potential of irreversible reduction. [c] $E_{1/2}^{ox}$ (X^{2+}/X^{3+}) = 0.90 V. [d] Estimated value; X/X^+ overlaps with X^+/X^{2+}; the exact value cannot be determined.

Redox Properties. The investigation of the optical properties of the present DPP series revealed a strong influence of the chosen electron-donating and electron-withdrawing peripheral substituents on the electronic properties of the chromophores. For potential application of such small molecule materials as organic semiconductors, not only the optical but also the electrochemical properties are of relevance. Therefore, we have explored the redox properties of the new DPP dyes by cyclic voltammetry in dichloromethane with NBu_4PF_6 as supporting electrolyte. The cyclic voltammograms of the six new dyes are displayed in Figure 3 and their half-wave oxidation and reduction potentials are compiled in Table 2.

At the core thiophene-substituted DPP **1** shows one reversible reduction at −1.70 V vs Fc/Fc^+ (Fc: ferrocene) and two reversible oxidation waves at 0.50 and 0.87 V. The iodine substituents in DPP **2** barely influence the reversible oxidation processes but facilitate the reduction ($E_{1/2}$ = −1.59 V). The bithiophene-substituted DPP **7a** (H) is also easier to reduce ($E_{1/2}$ = −1.60 V) and oxidize ($E_{1/2}$ = 0.36 and 0.63 V) than thiophene-substituted DPP **1**, reflecting the decreased bandgap of **7a**. The introduction of the methyl group in **7b** has almost no influence on the reduction potential ($E_{1/2}$ = −1.63 V) but shifts the oxidation potentials to lower values ($E_{1/2}$ = 0.30 and 0.55 V). This trend continues upon strengthening of the electron-donor ability of the peripheral substituents: the reduction processes occur in the range of −1.63 ± 0.07 V, while the two reversible oxidation processes are shifted continuously to lower values and get closer to each other. The extreme case is reached with **7e** (NMe_2) bearing the strongest electron-donating group in the present series, where the first and second oxidations overlap with each other (estimated potentials at −0.16 and −0.21 V, respectively). Moreover, a third reversible oxidation was detected at 0.90 V. In the case of **7c** (SMe) and **7e** (NMe_2), a second irreversible reduction potential at −2.14 and −2.30 V, respectively, is observed. We suppose that this reduction process also happens in the other cases, but is beyond the available potential range. In contrast, the cyano compound **7f** is easier to reduce but harder to oxidize than the other five dyes: two reversible reduction waves occur at −1.40 and −1.78 V, while the two reversible oxidation potentials were found at 0.54 and 0.83 V, respectively. For a potential application as donor material in organic solar cells with the most common phenyl-C_{61}-butyric acid methyl ester (PCBM) as acceptor, **7f** displays the most promising sets of redox properties in this work.

■ CONCLUSION

A series of six new bithiophene-functionalized diketopyrrolopyrrole (DPP) dyes with either electron-donating or electron-withdrawing groups at the terminal thiophene units was synthesized by several cross-coupling reactions such as Negishi, Stille, and Suzuki coupling. For the synthesis of the target bis(thiophene)-substituted DPPs, we have developed two new building blocks, namely the diiodinated DPP **2** and the boronic ester **3**, which are easily accessible and possess the potential to become valuable precursors for the synthesis of new molecular DPP dyes and polymers. Our studies illustrate the effect of the different substituents on the electronic properties of the respective DPP chromophores and reveal that the absorption and redox properties can be tuned by the choice of peripheral substituents. According to their absorption and redox properties, the newly synthesized DPP dyes are promising candidates for organic electronics and especially for organic photovoltaics (OPV): DPP **7e** (NMe_2), owing to its broad and intense absorption reaching in the NIR region, and **7f** (CN), owing to its high oxidation potential that is a prerequisite for achieving high open-circuit voltages.

■ EXPERIMENTAL SECTION

2,5-Bis(2-ethylhexyl)-3,6-bis(5-iodothiophene-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (2). *n*-Butyllithium in *n*-hexane (7.60 mL, 18.9 mmol) was added slowly at 0 °C to a solution of diisopropylamine (2.10 g, 2.90 mL, 20.8 mmol) in 30 mL of dry THF under argon atmosphere. The reaction solution was cooled to −78 °C, 2, 5-bis(2-ethylhexyl)-3, 6-dithiophene-2-yl-2, 5-dihydropyrrolo[3,4-*c*]-pyrrole-1,4-dione[11c] **1** (3.30 g, 6.29 mmol) in 35 mL of THF was added, and the mixture was stirred at −78 °C for 1 h. Then, iodine (6.36 g, 25.2 mmol) in 25 mL of THF was added, and the reaction mixture was stirred at −78 °C for an additional 1 h before it was allowed to slowly adjust to room temperature in the cooling bath for 36 h. After being quenched with NH_4Cl, the mixture was extracted with dichloromethane (3 × 40 mL), and the solvent was removed under vacuum. Column chromatography (CH_2Cl_2/*n*-pentane 1:1) afforded 3.26 g (4.02 mmol, 67%) of **2** as a dark violet solid. Mp: 186−189 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.50 (d, J = 4.1 Hz, 2H), 7.44 (d, J = 4.2 Hz, 2H), 3.92 (m, 4H), 1.81 (m, 2H), 1.30 (m, 16H), 0.87 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 161.9 (C), 139.5 (C), 138.9 (CH), 136.5 (C), 136.5 (CH), 108.5 (C), 81.6 (C), 46.4 (CH_2), 39.7 (CH), 30.7 (CH_2), 28.9 (CH_2), 24.1 (CH_2), 23.6 (CH_2), 14.4 (CH_3), 10.8 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{30}H_{38}I_2N_2O_2S_2$ $[M]^+$ 776.0464, found 776.0457. UV/vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 572 (35000). Anal. Calcd for $C_{30}H_{38}I_2N_2O_2S_2$: C, 46.40; H, 4.93; N, 3.61; S, 8.26. Found: C, 46.74; H, 5.18; N, 3.29; S, 7.90.

2,5-Bis(2-ethylhexyl)-3,6-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl)thiophene-2-yl]-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (3). *n*-Butyllithium in *n*-hexane (2.55 mL, 6.38 mmol) was added slowly at 0 °C to diisopropylamine (700 mg, 0.98 mL, 6.94 mmol) in 28 mL of dry THF under argon atmosphere. The freshly prepared LDA solution was added at −25 °C within 15 min to a 9 mL THF solution of 2,5-bis(2-ethylhexyl)-3,6-dithiophene-2-yl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione **1** (1.50 g, 2.86 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1.64 g, 1.80 mL, 8.79 mmol). After 1 h of stirring at 0 °C, the reaction was quenched with 10 mL of 1 M HCl solution. After extraction with chloroform (4 × 30 mL), the solvent was removed under vacuum. The residue was dissolved in 25 mL of dichloromethane, and the solution was poured into 400 mL of cold acetone under vigorous stirring. The precipitate was filtered off and washed with cold acetone to afford 1.74 g (2.25 mmol, 78%) of DPP **3** as a pink solid. Mp: 242−244 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.82 (d, J = 3.8 Hz, 2H), 7.67 (d, J = 3.8 Hz, 2H), 4.03 (m, 4H), 1.82 (m, 2H), 1.24−1.36 (m, 40H), 0.86 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 162.2 (C), 140.9 (C), 137.9 (CH), 136.4 (C), 136.1 (CH), 109.5 (C), 85.3 (C), 46.4 (CH_2), 39.7 (CH), 30.9 (CH_2), 29.1 (CH_2), 25.2 (CH_3), 25.1 (CH_3), 24.2 (CH_2), 23.6 (CH_2), 14.4 (CH_3), 10.8 (CH_3), 1.4 (C). HRMS (ESI): *m*/*z* calcd. for $C_{42}H_{63}B_2N_2O_6S_2$ $[M + H]^+$ 777.4314, found 777.4322. UV/vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 568 (29600). Anal. Calcd for $C_{42}H_{62}B_2N_2O_6S_2$: C, 64.95; H, 8.05; N, 3.61; S, 8.26. Found: C, 64.83; H, 8.19; N, 3.56; S, 7.90.

Dimethyl(5-tributylstannanylthiophene-2-yl)amine (4e). To a 30 mL dry THF solution of dimethylthiophene-2-ylamine[27] (1.90 g, 14.9 mmol) was added *n*-butyllithium in *n*-hexane (9.00 mL, 22.4 mmol) at −78 °C under argon atmosphere. The reaction mixture was first stirred for 45 min, while the temperature rose to −25 °C. Subsequently, it was stirred for 25 min at room temperature. Then, a 5.0 mL THF solution of Bu_3SnCl (6.30 g, 19.4 mmol) was added at −78 °C, and the reaction mixture was kept at this temperature for 2.5 h and afterward was allowed to warm slowly to room temperature in the cooling bath during ~60 h. The mixture was poured onto H_2O (dest) and extracted with diethyl ether (4 × 40 mL). After removal of the solvent under vacuum, distillation (4.7 × 10^{-1} mbar, 150 °C) of the residue yielded 1.51 g (3.62 mmol, 24%) of **4e** in sufficient purity for application in the next step. This reaction was carried out in a manner similar to the procedure reported in ref 22. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.81 (m, 1H), 6.03 (m, 1H), 2.89 (s, 6H), 1.56 (m, 6H), 1.33 (m, 6H), 1.05 (m, 6H), 0.90 (m, 9H). MS (EI): *m*/*z* calcd for $C_{18}H_{35}NSSn$ 417.2, found 417.1.

3,6-Bis(2,2′-bithiophene-5-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (7a). To a 8.6 mL dry THF solution of $PdCl_2(PPh_3)_2$ (18.0 mg, 0.03 mmol), were added 2,5-bis(2-ethylhexyl)-3,6-bis(5-iodothiophene-2-yl)-2,5-dihydropyrrolo-[3,4-*c*]pyrrole-1,4-dione **2** (200 mg, 0.38 mmol) and tributylthiophene-2-ylstannane **4a** (224 mg, 0.60 mmol) under argon atmosphere. After the mixture was heated to 65 °C for 2 h, the solvent was removed under vacuum. Column chromatography (CH_2Cl_2/*n*-pentane 4:6) of the crude product yielded 68.0 mg (0.10 mmol, 38%) of DPP **7a** as a dark blue solid. Mp: 191−193 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.90 (d, ^3J = 4.1 Hz, 2H), 7.37 (m, 6H), 7.11 (dd, ^3J = 5.1 Hz, ^3J = 3.7 Hz, 2H), 4.04 (m, 4H), 1.92 (m, 2H), 1.31 (m, 16H), 0.89 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 162.1 (C), 143.2 (C), 139.9 (C), 136.9 (CH), 136.8 (C), 128.9 (CH), 126.9 (CH), 125.8 (CH), 125.2 (CH), 109.0 (C), 46.4 (CH_2), 39.9 (CH), 30.9 (CH_2), 29.1 (CH_2), 24.2 (CH_2), 23.7 (CH_2), 14.4 (CH_3), 10.9 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{38}H_{44}N_2O_2S_4$ $[M]^+$ 688.2286, found 688.2279. UV/vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 613 nm (44500). Anal. Calcd for $C_{38}H_{44}N_2O_2S_4$: C, 66.24; H, 6.44; N, 4.07; S, 18.61. Found: C, 66.27; H, 6.51; N, 3.81; S, 18.73.

2,5-Bis(2-ethylhexyl)-3,6-bis(5′-methyl-(2,2′-bithiophene-5-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (7b). A solution of 2-methylthiophene **5b** (56.0 mg, 0.58 mmol) in 1.0 mL of dry THF was cooled to −40 °C, and *n*-butyllithium in *n*-hexane (0.29 mL, 0.73 mmol) was added slowly under argon atmosphere. After 30 min of stirring at −40 °C, $ZnCl_2$ (78.0 mg, 0.57 mmol) in 1.0 mL of THF was added at 0 °C to generate the organozinc compound. To a 2.0 mL THF solution of 2,5-bis(2-ethylhexyl)-3,6-bis(5-iodothiophene-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione **2** (200 mg, 0.26 mmol) was added a 1.0 mL THF solution of $PdCl_2(PPh_3)_2$ (4.00 mg, 5.00 μmol) and diisobutylaluminium hydride (0.01 mL, 0.01 mmol), followed by the dropwise addition of the organozinc compound (0.58 mmol, 1.3 mL). After being stirred at room temperature for 18 h, the reaction was quenched with cold 2 N HCl and extracted with dichloromethane (5 × 15 mL), and the organic phase was dried with Na_2CO_3. After removal of solvent under vacuum, column chromatography (CH_2Cl_2/*n*-pentane 7:3) and subsequent GPC (chloroform) afforded 75.0 mg (0.10 mmol, 40%) of the product **7b** as a dark blue solid. Mp: 239−242 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.89 (bs, 2H), 7.26 (d, ^3J = 4.2 Hz, 2H), 7.15 (bs, 2H), 6.76 (m, 2H), 4.02 (m, 4H), 2.52 (s, 6H), 1.91 (m, 2H), 1.32 (m, 16H), 0.89 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 162.1 (C), 143.7 (C), 142.3 (C), 139.8 (C), 136.9 (CH), 134.4 (C), 128.3 (C), 127.2 (CH), 125.8 (CH), 124.5 (CH), 108.8 (C), 46.4 (CH_2), 39.9 (CH), 30.9 (CH_2), 29.1 (CH_2), 24.2 (CH_2), 23.7 (CH_2), 15.8 (CH_3), 14.4 (CH_3), 10.9 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{40}H_{48}N_2O_2S_4$ $[M]^+$ 716.2599, found 716.2594. UV/vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 621 (54700). Anal. Calcd for $C_{40}H_{48}N_2O_2S_4$: C, 67.00; H, 6.75; N, 3.91; S, 17.89. Found: C, 66.65; H, 6.69; N, 3.84; S, 18.35.

2,5-Bis(2-ethylhexyl)-3,6-bis(5′-methylsulfanyl-(2,2′-bithiophene-5-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (7c). This compound was prepared according to the same procedure as described for **7b** by using 200 mg of 2,5-bis(2-ethylhexyl)-3,6-bis(5-iodothiophene-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione **2** (0.26 mmol) and 75.0 mg of 2-methylthiothiophene **5c** (0.57 mmol). Column chromatography (CH_2Cl_2/*n*-pentane 3:5) of the crude product and subsequent GPC (chloroform) afforded 157 mg (0.20 mmol, 77%) of the product **7c** as a dark blue solid. Mp: 182−184 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.90 (d, ^3J = 4.2 Hz, 2H), 7.30 (d, ^3J = 4.2 Hz, 2H), 7.21 (d, ^3J = 3.8 Hz, 2H), 7.02 (d, ^3J = 3.8 Hz, 2H), 4.02 (m, 4H), 2.56 (s, 6H), 1.91 (m, 2H), 1.34 (m, 16H), 0.90 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 162.0 (C), 142.6 (C), 140.1 (C), 139.7 (C), 138.0 (C), 137.0 (CH), 131.5 (CH), 128.9 (C), 125.9 (CH), 125.0 (CH), 109.0 (C), 46.4 (CH_2), 39.9 (CH), 30.9 (CH_2), 29.1 (CH_2), 24.2 (CH_2), 23.7 (CH_2), 21.9 (CH_3), 14.4 (CH_3), 10.9 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{40}H_{48}N_2O_2S_6$ $[M]^+$ 780.2040, found 780.2033. UV/vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 627 nm (57000). Anal. Calcd for $C_{40}H_{48}N_2O_2S_6$: C, 61.50; H, 6.19; N, 3.59; S, 24.63. Found: C, 61.58; H, 6.06; N, 3.50; S, 24.62.

2,5-Bis(2-ethylhexyl)-3,6-bis(5′-methoxy-(2,2′-bithiophene-5-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (7d). This compound was prepared according to the same procedure as described for **7b** by using 200 mg of 2,5-bis(2-ethylhexyl)-3,6-bis(5-iodothiophene-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione **2** (0.26 mmol) and 73.0 mg 2-methoxythiophene **5d** (0.64 mmol) and a reaction time of 90 min instead of 18 h. Column chromatography ($CHCl_3$/*n*-hexane 7:3) afforded 163 mg (0.22 mmol, 84%) of the product **7d** as a dark blue solid. Mp: 224−227 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.87 (d, *J* = 4.1 Hz, 2H), 7.15 (d, *J* = 4.1 Hz, 2H), 7.01 (d, *J* = 4.0 Hz, 2H), 6.22 (d, *J* = 4.1 Hz, 2H), 4.01 (m, 4H), 3.94 (s, 6H), 1.90 (m, 2H), 1.36 (m, 16H), 0.89 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 168.0 (C), 162.1 (C), 144.0 (C), 139.6 (C), 136.9 (CH), 127.6 (C), 124.0 (CH), 123.5 (CH), 123.0 (C), 108.6 (C), 105.6 (CH), 61.1 (CH_3), 46.4 (CH_2), 39.9 (CH), 30.9 (CH_2), 29.1 (CH_2), 24.2 (CH_2), 23.7 (CH_2), 14.4 (CH_3), 10.9 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{40}H_{48}N_2O_4S_4$ $[M]^+$ 748.2497, found 748.2493. UV/vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 631 (57100). Anal. Calcd for $C_{40}H_{48}N_2O_4S_4$: C, 64.14; H, 6.46; N, 3.74; S, 17.12. Found: C, 64.52; H, 6.46; N, 3.74; S, 16.42.

2,5-Bis(2-ethylhexyl)-3,6-bis(5′-dimethylamino-(2,2′-bithiophene-5-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (7e). To a 14 mL dry THF solution of $PdCl_2(PPh_3)_2$ (33.0 mg, 47.0 μmol) were added 2,5-bis(2-ethylhexyl)-3,6-bis(5-iodothiophene-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione **2** (400 mg, 0.52 mmol) and dimethyl(5-tributylstannylthiophene-2-yl)amine **4e** (536 mg, 1.29 mmol) was added under argon atmosphere. After being heated to 80 °C for 2 h, the solvent was removed under vacuum. Column chromatography (CH_2Cl_2/*n*-pentane 7:3) and subsequent GPC (chloroform) afforded 180 mg (0.23 mmol, 45%) of the product **7c** as a shiny golden solid. Mp: 217−220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (bs, 2H), 7.06 (m, 4H), 5.82 (bs, 2H), 4.03 (m, 4H), 3.00 (s, 12H), 1.95 (m, 2H), 1.33 (m, 16H), 0.89 (m, 12H). HRMS (ESI): *m*/*z* calcd for $C_{42}H_{54}N_4O_2S_4$ $[M]^+$ 774.3130, found 774.3122. UV/vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 684 nm (76800). Anal. Calcd for $C_{42}H_{54}N_4O_2S_4$: C, 65.08; H, 7.02; N, 7.23; S, 16.55. Found: C, 65.52; H, 7.23; N, 7.13; S, 16.77.

2,5-Bis(2-ethylhexyl)-3,6-bis(5′-dicarbonitrile-(2,2′-bithiophene-5-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (7f). A degassed 3.1 mL H_2O solution of K_3PO_4 (947 mg, 4.47 mmol) was added to a degassed 27 mL THF solution of 2,5-bis(2-ethylhexyl)-3,6-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl)thiophene-2-yl]-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione **3** (1.14 g, 1.46 mmol), $Pd_2(dba)_3$ (39.0 mg, 0.04 mmol), P(*t*-Bu)$_3$ × HBF_4 (23.0 mg, 0.08 mmol), and 2-bromothiophene-5-carbonitrile **6** (1.1 g, 5.85 mmol) under argon atmosphere. After the mixture was heated to 80 °C for 2 h, the solvent was removed under vacuum. Column chromatography (CH_2Cl_2) afforded 435 mg (0.59 mmol, 40%) of the product **7f** as a dark blue solid. Mp: 223−225 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.90 (d, ^3J = 4.2 Hz, 2H), 7.60 (d, ^3J = 4.0 Hz, 2H), 7.46 (d, ^3J = 4.2 Hz, 2H), 7.31 (m, ^3J = 4.2 Hz, 2H), 4.02 (m, 4H), 1.87 (m, 2H), 1.32 (m, 16H), 0.89 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 162.0 (C), 143.5 (C), 140.1 (C), 139.9 (C), 136.8 (CH), 131.1 (C), 127.5 (CH), 125.4 (CH), 114.3 (C), 109.9 (C), 109.7 (C), 46.5 (CH_2), 39.9 (CH), 30.9 (CH_2), 29.1 (CH_2), 24.3 (CH_2), 23.7 (CH_2), 14.4 (CH_3), 10.9 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{40}H_{43}N_4O_2S_4$ $[M + H]^+$ 739.2269, found 739.2261. UV/vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) 586 (46600). Anal. Calcd for $C_{40}H_{42}N_4O_2S_4$: C, 65.01; H, 5.73; N, 7.58; S, 17.35. Found: C, 65.03; H, 5.76; N, 7.41; S, 17.39.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** General experimental methods, ^{1}H of all new compounds, ^{13}C spectra of **2**, **3**, and **7a**−**d**,**f**, and fluorescence spectra of **2**, **3**, and **7a**,**c**−**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wuerthner@chemie.uni-wuerzburg.de.

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