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Synthesis of diketopyrrolopyrrole (DPP) derivatives comprising bithiophene moieties

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ABSTRACT

Herein we disclose an easily applicable method for the synthesis of diketopyrrolopyrrole (DPP) derivatives comprising bithiophene moieties, with different substituents on the nitrogen atoms (Me, *n*-octyl, 3,5-di-*tert*-butylbenzyl, Boc) and on the thiophene rings (C_6H_{13}, $C_{12}H_{25}$), in good yields and purities. A comparison is made between the previously described method from literature and our more efficient approach regarding number of steps, overall yields and ease of synthesis and purification.

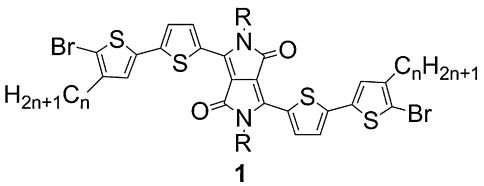
1. Introduction

3,6-Diaryl-2,5-dihydro-1,4-diketopyrrolo[3,4-*c*]pyrroles (DPPs) are known as high performance organic pigments used in paints, inks, lacquers, printings and plastics.[1] They are endowed with brilliant shades ranging from yellowish green to bluish red, depending on the aryl group attached to the chromophore unit, and exhibit outstanding chemical resistance, thermal stability, light and weather fastness, indicating high quality of colour retention.[2] Besides being a chromophore, DPP is also a fluorophore emitting in the visible region with a high fluorescence quantum yield.[3–5]

The DPP molecule is virtually planar, the two aryl rings being twisted out of the chromophore plane by merely a few degrees (e.g., 7° for phenyl). These heterocyclic compounds have been the object of several crystallographic studies and it was shown that the solid-state arrangement of DPP molecules occurs in parallel sheets.[6–9] The colour derives not only from the molecular structure, but also from the supramolecular order (π–π-interactions between the layer of molecules), since the colour in solid state differs from the colour in very dilute solutions.[10] The hydrogen bonding between neighbouring lactam-nitrogen and carbonyl-oxygen atoms is crucial for pigments in order to limit solubility. In fact, DPPs are insoluble in most common organic solvents, except in polar aprotic solvents (e.g., NMP, DMSO, DMF).

There is an increasing interest in DPP compounds for more advanced applications such as their use as charge-generating materials for laser printers, erasable optical information carriers or as electroluminescent elements.[11–15] To use DPPs in electronic devices, it is necessary to derivatize the DPP chromophore in order to prepare soluble and film forming compounds. To increase the solubility, the NH group of the DPP unit can be substituted and DPPs can be derivatized by incorporation in different materials such as conjugated polymers, liquid crystals and metal complexes.[16,17] In particular, DPP-containing conjugated polymers have been used as functional materials in OLEDs, OTFTs[18–20] and solar cells.[21–27]

Herein, we report the synthesis of DPP derivatives **1** comprising bithiophene moieties (Fig. 1). Previously reported syntheses of these DPP derivatives described in scientific journals[15–17,20,22,28] or patents[29–32] often lack experimental details. Moreover, in our hands certain synthetic steps were not reproducible. Therefore, we set out first to optimize the existing synthetic method and then to develop alternative pathways towards DPP derivatives **1**. Our goal is to develop a versatile and high-yielding synthesis of DPP molecules bearing bithiophene units. This synthetic pathway should also allow an easy derivatization by incorporating different substituents on the terminal thiophene units and on the *N*-atoms of the DPP moiety in order to modulate supramolecular order in solid state.



1

R = branched or linear alkyl, substituted benzyl, Boc
n = 6,12

Figure 1. Structure of DPP derivatives discussed in this paper.

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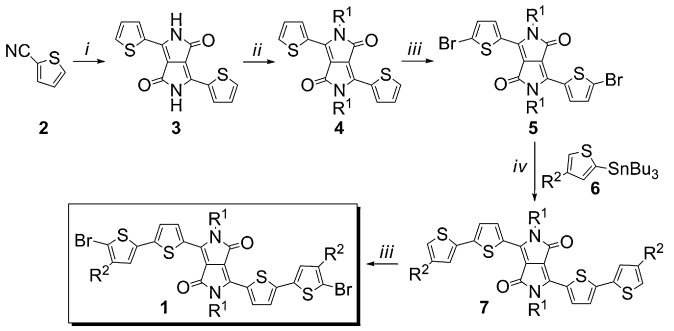
2. Results and discussion

2.1. Re-evaluation and optimization of previously reported synthetic route

The synthesis of 3,6-di(2,2′-bithiophen-5-yl)-1,4-diketopyrrolo[3,4-*c*]pyrroles **1** described in literature is summarized in Scheme 1.[15–17,20,31] We started with the careful *re*-investigation and, if needed, optimization of the published procedures for all synthetic steps.



R^1 = $(C_6H_{13})(C_8H_{17})CHCH_2$ (**a**), Me (**b**), *n*-octyl (**c**), 3,5-di-*t*-butylbenzyl (**d**), Boc (**e**)
R^2 = C_6H_{13} (**a**), $C_{12}H_{25}$ (**b**)

Scheme 1. Synthesis of 3,6-di(2,2′-bithiophen-5-yl)-1,4-diketopyrrolo[3,4-*c*]pyrroles **1** as described in literature. Reagents and conditions: (i) 0.5 equiv $(CH_2)_2(COOEt)_2$, 1.7 equiv $NaOC(CH_3)_2(CH_2CH_3)$, *tert*-amyl alcohol, reflux, 2 h, Ar-atmosphere, 72%; (ii) 4 equiv base, excess alkylating agent, Ar-atmosphere; (iii) 2.1 equiv NBS, anhydrous $CHCl_3$, rt, 48 h, Ar-atmosphere, dark; (iv) 20 mol % $Pd(PPh_3)_4$, 2.5 equiv **6**, anhydrous toluene, reflux, 2.5 h, Ar-atmosphere.

The first step consists of a condensation of thiophene-2-carbonitrile (**2**) with diethylsuccinate. We found the published procedure to be well reproducible,[15,28,30] yielding DPP **3** as a red solid (72% found versus 75% reported). Since DPP **3** is only soluble in polar aprotic solvents, it was in a second step solubilized by substituting the lactam-NH group.

In a first attempt, it was tried to derivatize DPP chromophore **3** with a branched alkyl chain in the same way as described in literature.[17,20,23,27,31] Therefore 1-bromo-2-hexyldecane was used as alkylating agent (Scheme S1, Supplementary data). According to the literature, potassium carbonate operates as base to deprotonate the amide-NH and alkylation in DMF[20] or NMP[31] results in yields around 45% of dialkylated DPP **4a**. Surprisingly, yields of only 12% in DMF and 19% in NMP of DPP **4a** were obtained in our hands. It was tried to optimize the reaction (Table S1, Supplementary data) by testing several aprotic solvents at different reaction temperatures (NMP, DMSO and DMF in a range of 120–150 °C) and by varying the base (K_2CO_3, Cs_2CO_3 and NaH), but the yields of pure **4a**, obtained after flash chromatography on silica gel, were always considerably lower than the yields claimed in literature. The highest yield of DPP **4a** (25%) was obtained in DMSO under Ar-atmosphere, with K_2CO_3 as base and with 6 equiv of alkyl bromide (Table S1, entry 14). The low yields can be explained by the multiple side reactions, which compete with the nucleophilic substitution of the alkyl bromide by deprotonated DPP (Scheme S2, Supplementary data). 2-Hexyl-1-decanol, probably formed via hydrolysis of the corresponding bromide with traces of water, and 7-methylenepentadecane, formed by elimination of HBr, were isolated as side compounds, as well as unreacted alkyl bromide. In the reactions in DMSO, 2-hexyl-1-decanal was present as side compound, resulting from reaction between the alkyl bromide and DMSO, which is mechanistically closely related to the Swern oxidation.[33] One or more other DPP derivatives were formed besides desired DPP compound **4a**. The structure of these products has not yet been identified since not very pure samples were isolated by chromatography. Possible DPP side compounds are monoalkylated DPP and derivatized DPPs where O-alkylation of the amide[34] occurred instead of N-alkylation. Another explanation for the low yields, besides the formation of side products, can be the lack of experimental data given in the experimental part of the patents, preventing accurate repetition of the synthetic procedure. Alkylation with 2-hexyldecyl methanesulphonate, a more reactive alkylating agent (Scheme S1, Supplementary data), was unsuccessful and produced a very complex mixture of products. Because alkylations of the DPP nitrogen with branched alkyl chains did not take place very smoothly, N-methylation was investigated. Reaction of DPP **3** with MeI (K_2CO_3, NMP, 55 °C) afforded the methylated derivative **4b** in 86% yield.[35,36] However, **4b** was very poorly soluble in organic solvents and therefore, N-methylation was not used anymore. Since methylated DPP **4b** was synthesized in good yield, but suffers from low solubility, and since alkylation with a branched alkyl chain offers good solubility to the corresponding DPP **4a**, although it was produced in low yields, it was tried to combine the positive aspects of both reactions by N-alkylation with a longer linear alkyl chain.[3,11,15,16] Reaction of *n*-octyliodide with DPP **3** (K_2CO_3, NMP, 140 °C) gave rise to dioctyl derivative **4c**, which precipitated as a dark red solid upon aqueous work-up (64% yield).[15,16] As expected, this compound was soluble in most organic solvents.

In contrast to the N-alkylations, some other reported *N*-functionalizations of DPP **3** were well reproducible. Derivative **4d** was obtained from reaction of **3** with 3,5-bis-*tert*-butylbenzyl bromide (K_2CO_3, NMP, 140 °C) in 74% yield.[37,38] Boc-protected DPP **4e** was prepared from **3**, *N*,*N*-dimethylaminopyridine (DMAP) and di-*tert*-butyl dicarbonate (THF, rt) in 68% yield.[9,22,39] Both DPPs (**4d** and **4e**) were isolated by simple precipitation from MeOH and the bulky substituents render these DPP derivatives well soluble in organic solvents.

The next step towards DPP derivatives **1** comprising bithiophene moieties is the bromination of the soluble DPP derivatives **4**. The previously reported bromination procedures[15,16,20,22,31] were slightly modified in order to obtain better yields. Bromination of DPP **4** with 2.1 equiv NBS occurred in dry $CHCl_3$ in 48 h, and gave moderate to good yields (**5a**, 20%; **5c**, 80%; **5d**, 51%; **5e**, 73%).[15] Precipitation of DPP **5** in methanol was sufficient to obtain highly pure compounds.

For the conversion of brominated DPPs **5** to bithiophene containing DPPs **7**, two cross coupling reactions were reported, namely the Suzuki coupling[12–15,22,23] and the Stille coupling[16,20,27,31], the former one being more abundantly described. We have selected the Stille coupling since it is generally the more efficient reaction for the synthesis of oligothiophenes.[40] Published Stille couplings with linear[16] and branched[20,31] alkyl-DPP compounds resulted in yields of 60–90%. Repeating the same literature method, led to yields of maximum 30% in our hands. Therefore, optimization of the reaction between dibromide **5e** and stannic compound **6a**[41] was undertaken. Different combinations of solvents, reaction temperatures and reaction times were evaluated (Table S2, Supplementary data). Yields of bithiophene containing DPP **7ea** (the first letter refers to R^1 and the second to R^2) given in Table S2, were obtained after precipitation of the product in methanol. The best result was achieved after reflux in toluene for 3 h. Longer times gave rise to side products, shorter reactions resulted in incomplete conversion (mono-coupled product). Optimized conditions were applied for the coupling of brominated DPPs **5c**, **5d** and **5e** with stannane **6a** to give the corresponding products **7ca**, **7da** and **7ea** in 73%, 78% and 85% yield, respectively.

In the final synthetic step, bromination of **7** was done in the same manner as bromination of **4** and yields between 50 and 60% of DPP derivatives **1** were obtained, while in literature yields of 83–97% are published.[20,31]

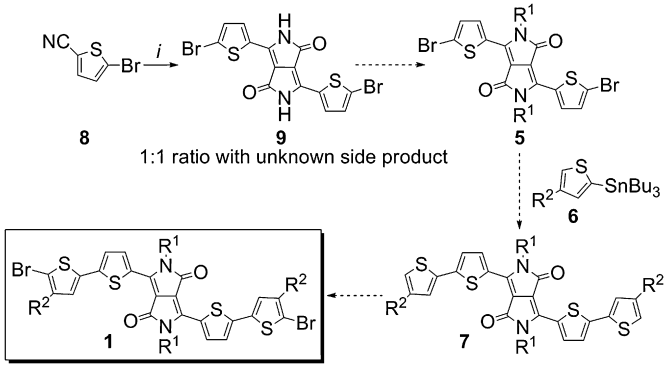
For the first pathway towards 3,6-di(2,2′-bithiophen-5-yl)-1,4-diketopyrrolo[3,4-*c*]pyrroles **1**, which already has been described in literature, following conclusions can be drawn. Several steps of the originally published synthesis were difficult to reproduce and required considerable optimization. Still, we were often unable to produce the reported yields. The synthetic route exists of five steps

for which we obtained overall yields between 11 and 17%, while the overall yields described in literature are slightly higher (26–33%).

Because of these not satisfying yields, we decided to develop alternative synthetic pathways. These pathways should possess high overall yields, high purities of the end product, a low number of steps and they should be easily applicable. Since several synthetic transformations (in particular the N-functionalization) on the DPP core proved problematic, our idea was to postpone the formation of DPP core to the later steps of the synthesis.

2.2. New synthetic routes towards DPP derivatives 1

A first alternative method (Pathway A) starts with the ring closure towards the DPP core with commercially available 5-bromothiophene-2-carbonitrile (**8**) (Scheme 2). This would immediately afford DPP chromophore **9** with bromo atoms on the thiophene units, decreasing the total number of steps from five to four. However, the ring closure towards DPP **9** did not occur smoothly. Analysis of the reaction mixture by ^{1}H NMR (DMSO-d_6) and MALDI-MS showed that besides desired DPP **9** a side product with DPP core (in ratio 1:1) was present, probably formed by nucleophilic aromatic substitution of the bromo atom on the thiophene unit by the deprotonated diethyl succinate. Since the first step in pathway A would already require intensive purification to remove the large amount of side product and thus would lead to a low yield of DPP core **9**, this route was not further explored.

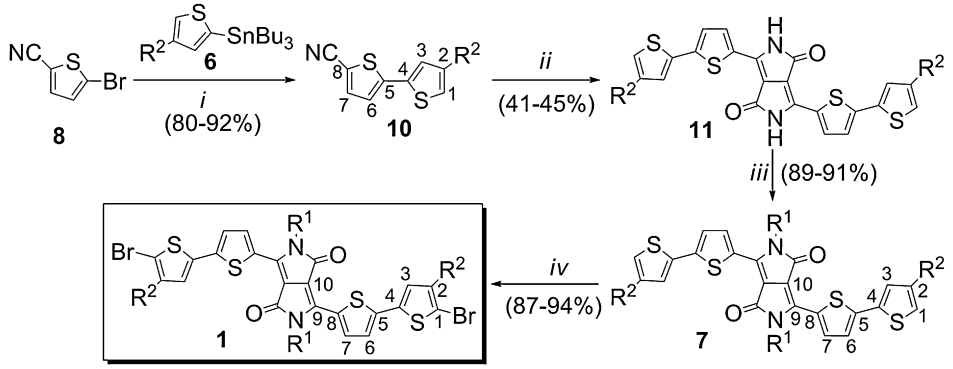


Scheme 2. Pathway A towards DPP derivatives **1**. Reagents and conditions: (i) 0.5 equiv $(CH_2)_2(COOEt)_2$, 1.7 equiv $NaOC(CH_3)_2(CH_2CH_3)$, *tert*-amyl alcohol, reflux, 2 h, Ar-atmosphere.

A second alternative pathway (Pathway B) starts with the synthesis of carbonitrile containing bithiophene unit **10**, which is then used to generate the DPP core. This would also lead to a route consisting of only four steps (Scheme 3). Synthesis of bithiophene **10** was accomplished by Stille coupling of 5-bromothiophene-2-carbonitrile (**8**) with stannic compounds **6**, resulting in yields of 80% for **10a** and 92% for **10b**. Using the bithiophene building blocks **10** in a reaction with diethyl succinate and sodium *tert*-amyl alcoholate yielded 41% and 45% of the corresponding DPP compounds **11a** and **11b**. Subsequent derivatization with Boc_2O was carried out by the same method as described for the Boc-protection of DPP chromophore **3** and gave rise to yields of 91% for **7ea** and 89% for **7eb**. The final step is a bromination with NBS, which was executed by the same experimental method as the bromination of DPPs **4**, leading to DPP analogues **1** (**1ea**, 94%; **1eb**, 87%). Pathway B consists of four steps with an overall yield for **1ea** of 28% and for **1eb** of 32%.

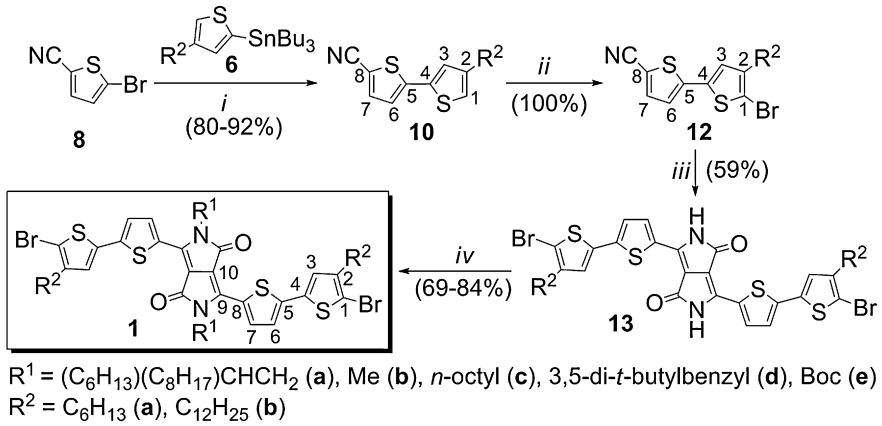
In a last proposed pathway (pathway C) towards bithiophene containing DPPs **1** (Scheme 4), bithiophene **10b** was also formed in a first step (yield of 92%), but was then quantitatively brominated into bithiophene **12b** before it was used in a reaction with diethylsuccinate and base towards DPP derivative **13b** (yield of 59%). The final step in this synthetic route was the N-functionalization of the DPP core. Towards this end, the same optimized conditions were applied as for the derivatization of DPP chromophore **3** into DPPs **4**, giving rise to DPPs **1bb**, **1cb**, **1db** and **1eb** with yields of 77%, 69%, 84% and 69%, respectively. Pathway C consists of four steps with an overall yield for **1bb** of 42%, for **1cb** of 37%, for **1db** of 46% and for **1eb** of 37%.

The overall yields of 3,6-di(2,2′-bithiophen-5-yl)-1,4-diketopyrrolo[3,4-*c*]pyrroles **1** in pathway B (28–32%) and pathway C (37–46%) were higher than the overall yields in the optimized method from literature (Scheme 1, 11–17%). Moreover, pathways B and C consist only of four steps instead of five. The bottleneck in these new routes is the generation of the DPP cores (yields of only 41% to 59%). The lower yields of DPP compounds **11** and **13** compared to DPP chromophore **3** prepared from unfunctionalized nitrile **2** in 72% yield, may be related to the presence of more bulky carbonitrile containing bithiophenes, causing more sterical hindrance and impeding ring closure towards the DPP core. Another problem encountered throughout this reaction is the fact that 4′-alkyl-2,2′-bithiophene-5-carbonitriles **10b** and **12b** are solid at room temperature. Therefore the described method for the synthesis of DPP **3** could not be performed, since it requires adding dropwise a mixture of diethyl succinate and (liquid) cyanothiophene to a boiling solution of base in *tert*-amyl alcohol.[39] After some experimenting, we discovered that highest yields of the corresponding DPPs (**11b** or **13b**) were obtained by adding diethyl succinate and base simultaneously and dropwise to a boiling solution of carbonitrile in



R^1 = $(C_6H_{13})(C_8H_{17})CHCH_2$ (**a**), Me (**b**), *n*-octyl (**c**), 3,5-di-*t*-butylbenzyl (**d**), Boc (**e**)
R^2 = C_6H_{13} (**a**), $C_{12}H_{25}$ (**b**)

Scheme 3. Pathway B towards DPP derivatives **1**. Reagents and conditions: (i) 10 mol % $Pd(PPh_3)_4$, 1.3 equiv **6**, anhydrous DMF, 80 °C, 4.5 h, Ar-atmosphere; (ii) 0.5 equiv $(CH_2)_2(COOEt)_2$, 1.7 equiv $NaOC(CH_3)_2(CH_2CH_3)$, *tert*-amyl alcohol, reflux, 2 h, Ar-atmosphere; (iii) 4 equiv base, excess alkylating agent Ar-atmosphere; (iv) 2.1 equiv NBS, anhydrous $CHCl_3$, rt, 48 h, Ar-atmosphere, dark.



Scheme 4. Pathway C towards DPP derivatives **1**. Reagents and conditions: (i) 10 mol % $Pd(PPh_3)_4$, 1.3 equiv **6**, anhydrous DMF, 80 °C, 4.5 h, Ar-atmosphere; (ii) 2.1 equiv NBS, anhydrous THF, 0 °C 1 h to rt 18 h, Ar-atmosphere, dark; (iii) 0.5 equiv $(CH_2)_2(COOEt)_2$, 1.7 equiv $NaOC(CH_3)_2(CH_2CH_3)$, *tert*-amyl alcohol, reflux, 2 h, Ar-atmosphere; (iv) 4 equiv base, excess alkylating agent, Ar-atmosphere.

the alcohol or by heating a one-pot mixture of all the compounds under reflux. The same procedures were applied by Horn et al. to synthesize pyrrolo[3,4-*c*]pyrrole-1,4-dione units from solid 4-cyanobiphenyls.[42] From this publication it can also be concluded that DPP core formation from solid biaryl carbonitriles results in lower yields (35%) than from liquid cyanoaryls (60–70%). This observation supports the presence of lower yields in the ring closing reactions of bithiophene carbonitriles **10b** and **12b** towards corresponding DPP units **11b** and **13b**. Additionally, we came across a difficult characterization of DPP molecules **11** and **13**. Since they are insoluble in most common organic solvents, it was not possible to record a proton NMR spectrum (tested deuterated solvents: $CDCl_3$, CD_2Cl_2, THF-d_8, TFA-*d*, $CDCl_3$+few drops of TFA-*d*, DMSO-d_6, DMF-d_7, D_2O, MeOD, CS_2+few drops of $CDCl_3$, benzene-d_6, NO_2Ph-d_5) and only MALDI-HRMS proved the formation of the desired bithiophene containing DPPs. Several interactions take place between adjacent molecules, such as π–π-interactions between the layer of molecules, hydrogen bonding between neighbouring lactam-N and carbonyl-O atoms and van der Waals contacts between therminal aryl groups. The same interactions are present for monothiophene comprising DPPs, but in case of bithiophene comprising DPPs even stronger π–π-interactions are present between the bithiophene units of adjacent molecules, resulting in very strong aggregates, insoluble in most common organic solvents. The formation of DPPs **11** and **13** was however not deniable when analyzing the results of the next step in the pathway: functionalization of these insoluble molecules on the nitrogen atom gave rise to perfectly soluble DPP derivatives **7** and **1** of which NMRs could easily be obtained ($CDCl_3$).

3. Conclusion

The best yields and highest purities of DPP derivatives **1** comprising bithiophene moieties were obtained in pathway C (Scheme 4), starting from commercially available 5-bromothiophene-2-carbonitrile (**8**). Stille coupling with stannic compounds **6** gave rise to intermediate products 4′-alkyl-2,2′-bithiophene-5-carbonitrile **10** (up to 92% yield). Subsequent bromination yielded quantitatively bromides **12**, which were then used in a reaction with diethyl succinate to form corresponding DPP chromophores **13** (up to 59% yield). In the last step, N-functionalization of **13** produced the target DPP derivatives **1** with yields of 69–84%.

This four-step pathway gave overall yields of 37–46% of DPP compounds **1**, which are much higher than the yields obtained in the optimized five-step pathway previously described in literature (11 to 17%). Therefore we believe that pathway C is the most efficient synthetic route towards DPP derivatives comprising bithiophene moieties. Moreover, our research showed that synthetic transformations on the DPP core proved problematic, but by applying pathway C, the formation of the DPP core is postponed to the one before last step and N-functionalization completes the synthesis. Route C allows an easy derivatization by incorporating different substituents on the terminal thiophene units and on the *N*-atoms of the DPP moiety in order to modulate supramolecular order in solid state. With this method, the desired functionalized DPPs **1** become available in large scale and with high purities, which are useful characteristics for further polymerization towards donor semiconducting materials that can be used in the development of photovoltaics.

4. Experimental

4.1. General methods

High resolution ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance 300 spectrometer. Chemical shifts are reported in parts per million downfield from TMS, coupling constants (*J*) are given in Hertz. ^{13}C NMR assignments were made using DEPT, HMQC and HMBC spectra. 2D-spectra were recorded on a Varian VNMRS 400 spectrometer. MALDI-HRMS measurements were made on a Waters MALDI-QTOF Premier mass spectrometer using a 350 mW laser and dithranol (1,8-dihydroxy-9,10-dihydroanthracen-9-one) as matrix. Infrared spectra were recorded with an Avatar 370 FTIR apparatus (Thermo Nicolet), using the attenuated total reflection technology (ATR). UV–vis absorption spectra were recorded on an Agilent 8453 spectrophotometer in a quartz cell (optical path of 1 cm). Melting points were measured by means of a Wild M3B Heerbrugg Switzerland microscope in combination with a Mettler Hot Stage (FP82) and a Mettler Central processor (FP80). Column chromatography was performed using Merck silica (diameter 40–63 μm) or Merck neutral alumina Brockmann grade I (diameter 50–200 μm), which was turned into activity grade III-IV by adding 8 wt % of water. TLC-analysis was performed on aluminium backed sheets (Merck) coated with 0.2 mm silica with UV-indicator $60F_{254}$ or on plastic backed sheets (Merck) coated with 0.2 mm neutral alumina with UV-indicator $60F_{254}$. Several anhydrous solvents were used throughout this work and they were dried as follows. THF was distilled from sodium metal, using benzophenone as indicator. 2-Methylbutan-2-ol (=*tert*-amyl alcohol) was dried by heating under reflux (T_b=102 °C) with sodium metal for 2 h followed by distillation on 4 Å molecular sieves. Freshly purchased NMP was

kept on molecular sieves (4 Å) under argon. Chloroform (HPLC-grade) was stored on $CaCl_2$. Anhydrous DMF (99.8%) and anhydrous DMSO (99.9%) were purchased from Aldrich.

4.2. Pathway B towards DPP derivatives comprising bithiophene moieties 1

*4.2.1. Tributyl(4-hexylthiophen-2-yl)stannane (**6a**)[41].* Tributyl(4-hexylthiophen-2-yl)stannane (**6a**) was synthesized according to the reported literature.[41] Yield: 72%, light yellow liquid. Complete spectral characterization: see Supplementary data.

*4.2.2. Tributyl(4-dodecylthiophen-2-yl)stannane (**6b**).* Tributyl(4-docedylthiophen-2-yl)stannane (**6b**) was synthesized by an analogues method as described for the synthesis of tributyl(4-hexylthiophen-2-yl)stannane (**6a**).[41]

To a solution of 3-dodecylthiophene (20 mmol, 5.05 g, 5.6 ml) in anhydrous THF (40 ml) cooled to −78 °C under argon, LDA in THF/ethylbenzene/heptane (1.8 M, 1 equiv, 20 mmol, 11.1 ml) was added dropwise. At the end of the addition the mixture was allowed to reach 0 °C in 3 h. The mixture was then cooled back down to −78 °C and Bu_3SnCl (1 equiv, 20 mmol, 6.51 g, 5.4 ml) was added in one portion. The mixture was kept for 15 min at −78 °C before it was allowed to reach room temperature at which temperature it was stirred for 2.5 h. Hexane (40 ml) was added and the reaction mixture was washed with water (4×20 ml). The water phase was extracted once again with hexane (40 ml) and the organic fractions were combined, dried ($MgSO_4$), filtered and evaporated. Kugelrohr distillation was performed as purification method. Unreacted Bu_3SnCl (T_b=171–173 °C/25 mmHg) and 3-dodecylthiophene (T_b=290 °C/760 mmHg) were distilled off at 170 °C/8.5 mmHg. The light yellow tributyl(4-dodecylthiophen-2-yl)stannane (7.98 g, 74% yield) distilled at 220 °C/8.5 mmHg and was stored at 2–4 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.19 (1H, d, J=0.8 Hz, $SCH_{thiophene}C_{quat.thiophene}C_{12}H_{25}$), 6.96 (1H, d, J=0.8 Hz, $SC_{quat.thiophene}(Sn)CH_{thiophene}$), 2.65 (2H, t, J=7.8 Hz, $C_{quat.thiophene}CH_2(C_{11}H_{23})$), 1.67–1.51 (12H, m, $3\times SnCH_2(CH_2)_2CH_3$), 1.40–1.26 (10×2H, m, $C_{quat.thiophene}CH_2(CH_2)_{10}CH_3$), 1.14–1.05 (3×2H, m, $3\times SnCH_2$), 0.89 (3×3H, t, J=7.2 Hz, $3\times SnCH_2(CH_2)_2CH_3$), 0.88 (3H, t, J=6.6 Hz, $C_{quat.thiophene}(CH_2)_{11}CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.4 ($C_{quat.thiophene}Sn$), 136.9 ($SCH_{thiophene}C_{quat.thiophene}C_{12}H_{25}$), 136.2 ($C_{quat.thiophene}C_{12}H_{25}$), 125.5 ($SC_{quat.thiophene}(Sn)CH_{thiophene}$), 31.9 ($C_{quat.thiophene}CH_2(C_{11}H_{23})$), 30.7, 30.0, 29.8, 29.69, 29.66, 29.6, 29.52, 29.49, 29.4, 29.0 ($C_{quat.thiophene}CH_2(CH_2)_{10}CH_3$), 27.3 ($3\times SnCH_2CH_2CH_2CH_3$), 22.7 ($3\times SnCH_2CH_2CH_2CH_3$), 14.1 ($C_{quat.thiophene}(CH_2)_{11}CH_3$), 13.7 ($3\times Sn(CH_2)_3CH_3$), 10.7 ($3\times SnCH_2(CH_2)_2CH_3$).

*4.2.3. Synthesis of 4′-alkyl-2,2′-bithiophene-5-carbonitrile (**10**).* A mixture of 5-bromothiophene-2-carbonitrile (**8**) (10 mmol, 1.88 g), $Pd(Ph_3P)_4$ (0.1 equiv, 1 mmol, 1.16 g) and stannane **6** (1.3 equiv, 13 mmol) in anhydrous DMF (60 ml) was brought under argon atmosphere and heated during 4.5 h at 80 °C. After cooling the mixture to room temperature, a saturated solution of NH_4Cl (100 ml) was added, and the medium was then extracted with CH_2Cl_2 (70 ml/50 ml/20 ml). The organic layers were combined, washed with water (50 ml), dried over and concentrated under vacuum.

*4.2.3.1. 4′-Hexyl-2,2′-bithiophene-5-carbonitrile (**10a**).* Compound (**10a**) was purified from the reaction mixture by flash chromatography on neutral alumina (Brockmann grade III-IV) with *n*Hex/CH_2Cl_2 (8:2) as eluents (R_f=0.31) resulting in 80% of 4′-hexyl-2,2′-bithiophene-5-carbonitrile (**10a**) (2.21 g) as a light yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.51 (1H, d, J=3.9 Hz, $CH_{thiophene}(6)$), 7.12 (1H, d, J=1.4 Hz, $CH_{thiophene}(1)$), 7.10 (1H, d, J=3.9 Hz, $CH_{thiophene}(7)$), 6.94 (1H, d, J=1.4 Hz, $CH_{thiophene}(3)$), 2.60 (2H, t, J=7.7 Hz, $C_{quat.thiophene}CH_2(C_5H_{11})$), 1.65–1.60 (2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_3CH_3$), 1.40–1.27 (3×2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_3CH_3$), 0.90 (3H, t, J=6.9 Hz, $C_{quat.thiophene}(CH_2)_5CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 145.2 ($C_{quat.thiophene}(5)$), 144.7 ($C_{quat.thiophene}(4)$), 138.2 ($CH_{thiophene}(7)$), 134.4 ($C_{quat.thiophene}(2)$), 127.3 ($CH_{thiophene}(6)$), 123.1 ($CH_{thiophene}(3)$), 121.7 ($CH_{thiophene}(2)$), 114.3 (CN), 107.1 ($C_{quat.thiophene}(8)$), 31.6 ($C_{quat.thiophene}CH_2$), 30.4, 30.3, 28.9 ($C_{quat.thiophene}CH_2(CH_2)_3CH_2CH_3$), 22.6 ($(CH_2)_4CH_2CH_3$), 14.1 ($(CH_2)_5CH_3$).

*4.2.3.2. 4′-Dodecyl-2,2′-bithiophene-5-carbonitrile (**10b**).* Compound (**10b**) was isolated from the reaction mixture by adding MeOH and storing the flask overnight in the fridge in order to fully precipitate the compound. The white precipitate was filtered off and washed with MeOH to yield 92% of 4′-dodecyl-2,2′-bithiophene-5-carbonitrile (**10b**) (3.30 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.50 (1H, d, J=3.9 Hz, $CH_{thiophene}(6)$), 7.11 (1H, d, J=1.3 Hz, $CH_{thiophene}(1)$), 7.09 (1H, d, J=3.9 Hz, $CH_{thiophene}(7)$), 6.93 (1H, d, J=1.3 Hz, $CH_{thiophene}(3)$), 2.59 (2H, t, J=7.8 Hz, $C_{quat.thiophene}CH_2(C_{11}H_{23})$), 1.67–1.57 (2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 1.37–1.26 (9×2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 0.88 (3H, t, J=6.7 Hz, $C_{quat.thiophene}(CH_2)_{11}CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 145.2 ($C_{quat.thiophene}(5)$), 144.8 ($C_{quat.thiophene}(4)$), 138.3 ($CH_{thiophene}(7)$), 134.5 ($C_{quat.thiophene}(2)$), 127.4 ($CH_{thiophene}(6)$), 123.2 ($CH_{thiophene}(3)$), 121.8 ($CH_{thiophene}(2)$), 114.4 (CN), 107.2 ($C_{quat.thiophene}(8)$), 32.0 ($C_{quat.thiophene}CH_2$), 30.5 ($C_{quat.thiophene}CH_2CH_2$), 29.9, 29.87, 29.85, 29.8, 29.7, 29.54, 29.48, 29.37 ($(CH_2)_2(CH_2)_8CH_2CH_3$), 22.8 ($(CH_2)_{10}CH_2CH_3$), 14.2 ($(CH_2)_{11}CH_3$).

*4.2.4. Synthesis of 3,6-bis(4′-alkyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**11**)*

*4.2.4.1. 3,6-Bis(4′-hexyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**11a**).* The same procedure as described for the synthesis of 3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**3**) was applied.[39]

A mixture of 4′-hexyl-2,2′-bithiophene-5-carbonitrile (**10a**) (4 mmol, 1.10 g) and 0.5 equiv diethyl succinate (2 mmol, 348 mg) was added dropwise over 1.3 h to a solution of 1.7 equiv sodium *tert*-amyl alcoholate (1 N solution, 6.8 mmol, 6.8 ml,) in boiling dry 2-methylbutan-2-ol (8 ml) under argon atmosphere. Stirring was continued for 1.5 h under reflux. The mixture was then cooled to room temperature before it was added to an ice-cooled mixture of methanol (25 ml) and concentrated (12.5 M) hydrochloric acid (1 ml). The mixture was stirred for 30 min and then left overnight in the fridge (2–3 °C) in order to fully precipitate the DPP derivative **11a**. The black precipitate was filtered off, washed with methanol and water, and then an overnight Soxhlet extraction with MeOH was performed to remove all MeOH-soluble side compounds. After drying of the solid in vacuo, 3,6-bis(4′-hexyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**11a**) was obtained as a dark blue solid in 41% yield (520 mg). IR (ATR, cm^{-1}): ν_{max} 3127 (aromatic C–H bending), 2955, 2924, 2850 (CH alkane stretch), 1641 (C=O amide stretch), 1595 (NH amide stretch), 1439, 1419 (aromatic C=C stretch), 1350 (CH alkane bending). UV_{max}(THF): λ (nm) 239, 346, 388, 554, 595. HRMS (MALDI): *m*/*z* calcd for $C_{34}H_{36}N_2O_2S_4$ ($M^{\bullet+}$) 632.1660; found 632.1673; ppm: 2.1. Mp: >300 °C.

*4.2.4.2. 3,6-Bis(4′-dodecyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**11b**).* A mixture of 4′-dodecyl-2,2′-bithiophene-5-carbonitrile (**10b**) (2.5 mmol, 899 mg), 1.7 equiv sodium *tert*-amyl alcoholate (1 N, 4.25 mmol, 4.25 ml, 4,25 mmol) and 0.5 equiv diethyl succinate (1.25 mmol, 218 mg) in anhydrous 2-methylbutan-2-ol (5 ml) was stirred under reflux under argon atmosphere during a period of 2.5 h. The mixture was added to an ice-cooled mixture of methanol (15 ml) and concentrated (12.5 M)

hydrochloric acid (0.75 ml). The mixture was stirred for 30 min and then stored overnight in the fridge (2–3 °C) in order to fully precipitate 3,6-bis(4′-dodecyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**11b**). The dark purple precipitate was filtered off, washed with methanol and water, and then dried in vacuo. An overnight Soxhlet extraction with MeOH was performed to remove all MeOH-soluble side compounds and after drying of the dark blue solid in vacuo, 45% (449 mg) of 3,6-bis(4′-dodecyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**11b**) was yielded. IR (ATR, cm^{-1}): ν_{max} 3125 (aromatic C–H bending), 2918, 2849 (CH alkane stretch), 1636 (C=O amide stretch), 1595 (NH amide stretch), 1452, 1431, 1413 (aromatic C=C stretch), 1351 (CH alkane bending). UV_{max}(THF): λ (nm) 238, 353, 375, 552, 597. HRMS (MALDI): *m*/*z* calcd for $C_{46}H_{60}N_2O_2S_4$ ($M^{\bullet+}$) 800.3538; found 800.3527; ppm: 1.4. Mp: >300 °C.

*4.2.5. Boc-protection of 3,6-bis(4′-alkyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**11**).* The Boc-protection of **11** was executed as described for the Boc-protection of DPP chromophore **3**, which was executed according to the reported literature.[22]

In a two-necked, oven-dried round bottom flask, 3,6-bis(4′-alkyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**11**) (2 mmol) was dissolved in 20 ml anhydrous THF and the resulting solution was purged with argon for 10 min. Then, 2.5 equiv of *N*,*N*-dimethylaminopyridine (5 mmol, 611 mg) dissolved in 7 ml anhydrous THF were added and the reaction mixture was stirred 15 min under argon atmosphere at room temperature. Next, 5 equiv of di-*tert*-butyl dicarbonate (10 mmol, 2.3 ml) were added (rinsed with 3 ml THF) and the mixture was stirred for 24 h at room temperature under argon. The mixture was concentrated under vacuum and the residue was dissolved in 12 ml MeOH and stored for 30 min in the fridge at 2–3 °C before the dark blue precipitate was filtered off. The precipitate was washed with MeOH and dried under vacuum to give pure dark blue Boc-protected DPP derivative **7**.

*4.2.5.1. Di-tert-butyl-3,6-bis(4′-hexyl-2,2′-bithiophen-5-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate (**7ea**).* Yield=91% (608 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.21 (2×1H, d, *J*=4.1 Hz, $CH_{thiophene}$(6)), 7.21 (2×1H, d, *J*=4.1 Hz, $CH_{thiophene}$(7)), 7.14 (2×1H, d, *J*=1.2 Hz, $CH_{thiophene}$(3)), 6.92 (2×1H, d, *J*=1.2 Hz, $CH_{thiophene}$(1)), 2.59 (2×2H, t, *J*=7.6 Hz, $C_{quat.thiophene}CH_2(CH_2)_4CH_3$), 1.64 (2×9H, s, 2×^{t}Bu), 1.63–1.61 (2×2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_3CH_3$), 1.32–1.26 (2×6H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_3CH_3$), 0.90 (2×3H, t, *J*=6.4 Hz, $C_{quat.thiophene}(CH_2)_5CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.1 (CO pyrrole-2-one), 148.9 (CO Boc), 144.7 ($C_{quat.thiophene}$(2)), 144.6 ($C_{quat.}$(9)), 136.7 ($C_{quat.thiophene}$(4)), 135.7 ($C_{quat.thiophene}$(5)), 135.2 ($CH_{thiophene}$(6)), 127.7 ($C_{quat.thiophene}$(8)), 126.9 ($CH_{thiophene}$(3)), 124.2 ($CH_{thiophene}$(7)), 121.4 ($CH_{thiophene}$(1)), 110.2 ($C_{quat.}$(10)), 86.0 ($C_{quat.}$ ^{t}Bu), 31.6 ($(CH_2)_3CH_2CH_2CH_3$), 30.4, 30.3, 28.9 ($(CH_2)_3CH_2CH_2CH_3$), 27.7 (CH_3 ^{t}Bu), 22.6 ($(CH_2)_4CH_2CH_3$), 14.1 ($(CH_2)_5CH_3$). IR (ATR, cm^{-1}): ν_{max} 3124, 3095 (aromatic C–H bending), 2953, 2920, 2851 (CH alkane stretch), 1740 (C=O ester stretch), 1685 (C=O amide stretch), 1559, 1540, 1431 (aromatic C=C stretch), 1366, 1305 (CH alkane bending), 1215, 1148, 1095 (C–O ester stretch). $UV_{max}(CH_2Cl_2)$: λ (nm) 230, 332, 405, 567. MALDI-HRMS: *m*/*z*: calcd for $C_{44}H_{52}N_2O_6S_4$ ($M^{\bullet+}$): 832.2708; found: 832.2708; ppm: 0.0. Mp: >300 °C, Boc-deprotection 167–173 °C.

*4.2.5.2. Di-tert-butyl-3,6-bis(4′-dodecyl-2,2′-bithiophen-5-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate (**7eb**).* Yield=89% (712 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.21 (2×1H, d, *J*=4.1 Hz, $CH_{thiophene}$(6)), 7.21 (2×1H, d, *J*=4.1 Hz, $CH_{thiophene}$(7)), 7.14 (2×1H, d, *J*=1.2 Hz, $CH_{thiophene}$(3)), 6.91(2×1H, d, *J*=1.2 Hz, $CH_{thiophene}$(1)), 2.59 (2×2H, t, *J*=7.7 Hz, $C_{quat.thiophene}CH_2(CH_2)_{10}CH_3$), 1.63 (2×9H, s, 2×^{t}Bu), 1.66–1.57 (2×2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 1.32–1.26 (2×18H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 0.88 (2×3H, t, *J*=6.6 Hz, $C_{quat.thiophene}(CH_2)_5CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.1 (CO pyrrole-2-one), 148.9 (CO Boc), 144.7 ($C_{quat.thiophene}$(2)), 144.6 ($C_{quat.}$(9)), 136.7 ($C_{quat.thiophene}$(5)), 135.7 ($C_{quat.thiophene}$(4)), 135.2 ($CH_{thiophene}$(6)), 127.7 ($C_{quat.}$(8)), 126.9 ($CH_{thiophene}$(3)), 124.2 ($CH_{thiophene}$(7)), 121.4 ($CH_{thiophene}$(1)), 110.2 ($C_{quat.}$(10)), 86.0 ($C_{quat.}$ ^{t}Bu), 31.9 ($(CH_2)_9CH_2CH_2CH_3$), 30.43, 30.38, 29.68, 29.67, 29.66, 29.60, 29.45, 29.36, 29.29 ($(CH_2)_9CH_2CH_2CH_3$), 27.7 (CH_3 ^{t}Bu), 22.7 ($(CH_2)_{10}CH_2CH_3$), 14.1 ($(CH_2)_{11}CH_3$). IR (ATR, cm^{-1}): ν_{max} 3111, 3083 (aromatic C–H bending), 2956, 2916, 2850 (CH alkane stretch), 1741 (C=O ester stretch), 1685 (C=O amide stretch), 1561, 1545, 1433 (aromatic C=C stretch), 1365, 1297 (CH alkane bending), 1213, 1149, 1100 (C–O ester stretch). $UV_{max}(CH_2Cl_2)$: λ (nm) 231, 333, 405, 572. HRMS (MALDI): *m*/*z*: calcd for $C_{56}H_{76}N_2O_6S_4$ ($M^{\bullet+}$): 1000.4586; found: 1000.4581; ppm: 0.5. Mp: >300 °C, Boc-deprotection 147–152 °C.

*4.2.6. Bromination of di-tert-butyl-3,6-bis(4′-alkyl-2,2′-bithiophen-5-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate **7**.* Bromination of **7** was executed by an analogue method as described for the bromination of DPP compound **4e**.[22]

In a two-necked, oven-dried 25 ml round bottom flask covered with aluminium foil, di-*tert*-butyl-3,6-bis(4′-alkyl-2,2′-bithiophen-5-yl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-dicarboxylate **7** (0.4 mmol) was dissolved in 24 ml anhydrous chloroform and stirred under argon for 15 min. 2.1 equiv of *N*-bromosuccinimide (0.84 mmol, 150 mg) were added in one portion at room temperature and the mixture was stirred for 48 h at rt. The reaction mixture was poured into 60 ml MeOH and the resulting suspension was stirred for 20 min at rt. The precipitation was completed in the fridge during 15 min. DPP derivatives **1** were collected as dark blue solids by vacuum filtration and were washed with several portions of hot distilled water and hot MeOH.

*4.2.6.1. Di-tert-butyl-3,6-bis(5′-bromo-4′-hexyl-2,2′-bithiophen-5-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate (**1ea**).* Yield=91% (377 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.18 (2×1H, d, *J*=4.1 Hz, $CH_{thiophene}$(6)), 7.15 (2×1H, d, *J*=4.1 Hz, $CH_{thiophene}$(7)), 7.00 (2×1H, s, $CH_{thiophene}$(3)), 2.55 (2×2H, t, *J*=7.5 Hz, $C_{quat.thiophene}CH_2(CH_2)_4CH_3$), 1.66–1.57 (2×2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_3CH_3$), 1.63 (2×9H, s, 2×^{t}Bu), 1.38–1.28 (2×6H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_3CH_3$), 0.90 (2×3H, t, *J*=6.5 Hz, $C_{quat.thiophene}(CH_2)_5CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.0 (CO pyrrole-2-one), 148.9 (CO Boc), 143.6 ($C_{quat.thiophene}$(2)), 143.3 ($C_{quat.}$(9)), 136.6 ($C_{quat.thiophene}$(4)), 135.5 ($C_{quat.thiophene}$(5)), 135.1 ($CH_{thiophene}$(6)), 128.1 ($C_{quat.thiophene}$(8)), 126.2 ($CH_{thiophene}$(3)), 124.3 ($CH_{thiophene}$(7)), 110.4 ($C_{quat.}$(10)), 109.6 ($C_{quat.thiophene}$(1)), 86.1 ($C_{quat.}$ ^{t}Bu), 31.6 ($(CH_2)_3CH_2CH_2CH_3$), 29.58, 29.57, 28.9 ($(CH_2)_3CH_2CH_2CH_3$), 27.8 (CH_3 ^{t}Bu), 22.6 ($(CH_2)_4CH_2CH_3$), 14.1 ($(CH_2)_5CH_3$). IR (ATR, cm^{-1}): ν_{max} 3065, 3052 (aromatic C–H bending), 2952, 2925, 2855 (CH alkane stretch), 1748 (C=O ester stretch), 1680 (C=O amide stretch), 1561, 1546 (aromatic C=C stretch), 1367, 1301 (CH alkane bending), 1213, 1145, 1100 (C–O ester stretch). $UV_{max}(CH_2Cl_2)$: λ (nm) 232, 342, 393, 572. MALDI-HRMS: *m*/*z*: calcd for $C_{44}H_{50}N_2O_6S_4Br_2$ ($M^{\bullet+}$): 988.0918; found: 988.0930; ppm: 1.2. Mp: >300 °C, Boc-deprotection 174–177 °C.

*4.2.6.2. Di-tert-butyl-3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate (**1eb**).* Yield=87% (483 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.18 (2×1H, d, *J*=4.1 Hz, $CH_{thiophene}$(6)), 7.15 (2×1H, d, *J*=4.1 Hz, $CH_{thiophene}$(7)), 6.99 ($CH_{thiophene}$(3)), 2.54 (2×2H, t, *J*=7.4 Hz, $C_{quat.thiophene}CH_2(CH_2)_{10}CH_3$), 1.69–1.63 (2×2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 1.63 (2×9H, s, 2×^{t}Bu), 1.36–1.26 (2×18H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 0.88 (2×3H, t, *J*=6.6 Hz, $C_{quat.thiophene}(CH_2)_{11}CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.0 (CO pyrrole-2-one), 148.9 (CO Boc), 143.6 ($C_{quat.thiophene}$(2)), 143.3

($C_{quat.}$(9)), 136.6 ($C_{quat.thiophene}$(4)), 135.5 ($C_{quat.thiophene}$(5)), 135.1 ($CH_{thiophene}$(6)), 128.1 ($C_{quat.thiophene}$(8)), 126.2 ($CH_{thiophene}$(3)), 124.3 ($CH_{thiophene}$(7)), 110.4 ($C_{quat.}$(10)), 109.6 ($C_{quat.thiophene}$(1)), 86.1 ($C_{quat.}$ ^{t}Bu), 31.9 ($(CH_2)_9CH_2CH_2CH_3$), 29.65, 29.57, 29.4, 29.4, 29.2 ($(CH_2)_9CH_2CH_2CH_3$), 27.8 (CH_3 ^{t}Bu), 22.7 ($(CH_2)_{10}CH_2CH_3$), 14.1 ($(CH_2)_{11}CH_3$). IR (ATR, cm^{-1}): ν_{max} 3063 (aromatic C–H bending), 2981, 2920, 2851 (CH alkane stretch), 1742 (C=O ester stretch), 1681 (C=O amide stretch), 1560, 1539, 1435 (aromatic C=C stretch), 1366, 1300 (CH alkane bending), 1215, 1149, 1101 (C–O ester stretch). $UV_{max}(CH_2Cl_2)$: λ (nm) 230, 341, 406, 572. MALDI-HRMS: *m/z*: calcd for $C_{56}H_{74}N_2O_6S_4Br_2$ ($M^{\bullet+}$): 1156.2796; found: 1156.2834; ppm: 3.3; *m/z*: calcd for $C_{46}H_{58}N_2O_6S_4Br_2$ ($[M^{\bullet+}]-(2\times Boc)$): 956.1748; found: 1156.1768; ppm: 2.1. Mp: >300 °C, Boc-deprotection 173–178 °C.

4.3. Pathway C towards DPP derivatives comprising bithiophene moieties 1

*4.3.1. Synthesis of 5′-bromo-4′-dodecyl-2,2′-bithiophene-5-carbonitrile (**12b**).* 4′-Dodecyl-2,2′-bithiophene-5-carbonitrile (5 mmol, 1.80 g) was dissolved in anhydrous THF (50 ml), covered from light with aluminium foil and cooled down to 0 °C. 1.06 equiv of *N*-bromosuccinimide (5.3 mmol, 943 mg) were added portionwise over a period of 1 h. The reaction mixture was stirred for 1 h in the ice-water bath before it was allowed to reach room temperature at which temperature the reaction was overnight stirred. The mixture is quenched with water (50 ml) and hexane (50 ml) is added. The organic phase was additionally extracted three times with water (3×50 ml). The combined water phase was once back-extracted with hexane (50 ml). The organic phases were combined, dried over $MgSO_4$ and concentrated in vacuo. 5′-Bromo-4′-dodecyl-2,2′-bithiophene-5-carbonitrile (**12b**) was obtained as a light yellow solid in quantitative yield (2.19 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.50 (1H, d, *J*=3.9 Hz, $CH_{thiophene}$(6)), 7.04 (1H, d, *J*=3.9 Hz, $CH_{thiophene}$(7)), 6.97 (1H, s, $CH_{thiophene}$(3)), 2.55 (2H, t, *J*=7.7 Hz, $C_{quat.thiophene}CH_2(C_{11}H_{23})$), 1.64–1.54 (2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 1.33–1.26 (9×2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 0.88 (3H, t, *J*=6.6 Hz, $C_{quat.thiophene}(CH_2)_{11}CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.9 ($C_{quat.thiophene}$(5)), 143.6 ($C_{quat.thiophene}$(2)), 138.2 ($CH_{thiophene}$(7)), 134.2 ($C_{quat.thiophene}$(4)), 126.7 ($CH_{thiophene}$(3)), 123.3 ($CH_{thiophene}$(6)), 114.0 (CN), 110.7 ($C_{quat.thiophene}$(1)), 107.6 ($C_{quat.thiophene}$(8)), 31.9 ($C_{quat.thiophene}CH_2$), 29.7 ($C_{quat.thiophene}CH_2CH_2$), 29.66, 29.63, 29.60, 29.50, 29.36, 29.35, 29.20, 29.18 ($(CH_2)_2(CH_2)_8CH_2CH_3$), 22.7 ($(CH_2)_{10}CH_2CH_3$), 14.1 ($(CH_2)_{11}CH_3$).

*4.3.2. Synthesis of 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**13b**).* 5′-Bromo-4′-dodecyl-2,2′-bithiophene-5-carbonitrile (**12b**) (7.40 mmol, 3.25 g) was suspended in 15 ml 2-methylbutan-2-ol under argon and the mixture is brought to 102 °C (bp *tert*-amyl alcohol). (When the mixture reached 70 °C, carbonitrile **12b** was dissolved in the alcohol.) Diethyl succinate (0.5 equiv, 3.70 mmol, 0.6 ml) and sodium *tert*-amyl alcoholate (1.7 equiv, 1 N, 12.6 mmol, 12.6 ml) were added dropwise to the boiling solution during a period of 2 h (12 portions of +/−1 ml base and +/−0.05 ml succinate). The mixture was then further refluxed for 3 h. The mixture was cooled to room temperature (30 min) and added to an ice-cooled mixture of methanol (50 ml) and concentrated (12.5 M) hydrochloric acid (2 ml). The mixture was stirred for 10 min and then overnight put in the fridge at 2–3 °C in order to fully precipitate DPP **13b**. The dark purple precipitate was filtered off, washed with methanol and water, and then dried in vacuo. The dried precipitate was put in a Soxhlet cellulose thimble and extracted overnight with MeOH in order to remove all the MeOH-soluble side compounds. After drying the solid in vacuo, 59% 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (2.11 g) was obtained. IR (ATR, cm^{-1}): ν_{max} 3128 (aromatic C–H bending), 2917, 2851 (CH alkane stretch), 1641 (C=O amide stretch), 1600 (NH amide stretch), 1453, 1420 (aromatic C=C stretch), 1340 (CH alkane bending). HRMS (MALDI): *m/z* calcd for $C_{46}H_{58}N_2O_2S_4Br_2$ ($M^{\bullet+}$) 956.1748; found 956.1751; ppm: 0.3. Mp: >300 °C.

*4.3.3. Functionalization of DPPs **13** at the nitrogen position*

*4.3.3.1. N-methylation of DPP **13b** towards 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)-2,5-dimethylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**1bb**).* The same method was applied as described for the N-methylation of DPP **3** into DPP derivative **4b**. This method is derived from a modified literature procedure.[35,36]

A solution of 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**13b**) (0.125 mmol, 120 mg) and potassium carbonate (4 equiv, 0.5 mmol, 69 mg) in 4 ml anhydrous NMP was brought under argon atmosphere and was stirred for 1 h at rt. Then, 12.8 equiv of iodomethane (1.6 mmol, 227 mg) were added in one portion. The mixture was stirred for 1 h at rt and then brought at 60 °C and 10 additional equivalents of MeI were added (177 mg) since MeI is very volatile (bp around 45 °C). The mixture was stirred for 2 h at 60 °C and then another 10 equiv of MeI (177.4 mg) were added and the mixture was left at 60 °C overnight (18 h). The mixture was cooled down to room temperature, washed with water (15 ml) and extracted with EtOAc (15 ml/10 ml/10 ml). The organic layers were collected and evaporated. The residue was suspended in 15 ml MeOH and a dark blue precipitate is formed. The mixture was stored in the fridge for 1 h and then the precipitate was filtered off, washed with fresh MeOH and dried in vacuo. A fast purification over alumina with CH_2Cl_2 as eluents was executed (R_f=0.67), resulting in 77% (95 mg) of 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)-2,5-dimethylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**1bb**). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.83 (2×1H, d, *J*=3.8 Hz, $CH_{thiophene}$(6)), 7.23 (2×1H, d, *J*=3.8 Hz, $CH_{thiophene}$(7)), 7.03 (2×1H, s, $CH_{thiophene}$(3)), 3.64 (2×3H, s, 2×N–CH_3), 2.55 (2×2H, t, *J*=7.6 Hz, $C_{quat.thiophene}CH_2(CH_2)_{10}CH_3$), 1.67–1.60 (2×2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 1.35–1.27 (2×18H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 0.88 (2×3H, t, *J*=6.4 Hz, $C_{quat.thiophene}(CH_2)_{11}CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 158.7 (CO pyrrole-2-one), 144.4 ($C_{quat.thiophene}$(2)), 140.9 ($C_{quat.}$(9)), 137.8 ($C_{quat.thiophene}$(4)), 136.6 ($C_{quat.thiophene}$(5)), 132.0 ($CH_{thiophene}$(6)), 125.0 ($CH_{thiophene}$(3)), 120.2 ($C_{quat.thiophene}$(8)), 115.5 ($CH_{thiophene}$(7)), 109.6 ($C_{quat.}$(10)), 103.4 ($C_{quat.thiophene}$(1)), 31.9 ($(CH_2)_9CH_2CH_2CH_3$), 29.7 (N–CH_3), 29.63, 29.59, 29.51, 29.45, 29.41, 29.36, 29.25, 29.21, 29.18 ($(CH_2)_9CH_2CH_2CH_3$), 22.7 ($(CH_2)_{10}CH_2CH_3$), 14.1 ($(CH_2)_{11}CH_3$). IR (ATR, cm^{-1}): ν_{max} 3069, 3043 (aromatic C–H bending), 2919, 2850 (CH alkane stretch), 1644 (C=O amide stretch), 1561, 1446, 1424 (aromatic C=C stretch). $UV_{max}(CH_2Cl_2)$: λ (nm) 235, 355, 408, 581, 622. MALDI-HRMS: *m/z*: calcd for $C_{48}H_{62}N_2O_2S_4Br_2$ ($M^{\bullet+}$): 984.2061; found: 984.2053; ppm: 0.8. Mp: 203.7–206.1 °C.

*4.3.3.2. N-octylation of DPP **13b** towards 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**1cb**).* The same method was applied as described for N-octylation of DPP **3** into DPP derivative **4c**.[15,16]

A solution of 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**13b**) (0.3 mmol, 288 mg) and potassium carbonate (1.2 mmol, 166 mg) in 8 ml anhydrous NMP was brought under argon atmosphere and was heated to 140 °C. After 30 min at that temperature, 3 equiv of *n*-octyliodide (0.9 mmol, 216 mg) were added in one portion. The mixture was further mixed at 140 °C during 5 h. The mixture was cooled down to room temperature (10 min) and then quenched with water (16 ml). A precipitate was formed and the mixture was stored in the fridge overnight to fully precipitate the compound.

The dark blue/black precipitate was filtered off, washed with water and MeOH and dried in vacuo. A fast purification over alumina with CH_2Cl_2 as eluents was executed (R_f=0.76), resulting in 69% (302 mg) of 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)-2,5-dioctyl-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**1cb**). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.85 (2×1H, d, J=4.2 Hz, $CH_{thiophene}$(6)), 7.22 (2×1H, d, J=4.2 Hz, $CH_{thiophene}$(7)), 7.01 (2×1H, s, $CH_{thiophene}$(3)), 4.07 (2×2H, t, J=7.3 Hz, $NCH_2(CH_2)_6CH_3$), 2.56 (2×2H, t, J=7.7 Hz, $C_{quat.thiophene}CH_2(CH_2)_{10}CH_3$), 1.79–1.73 (2×2H, m, $NCH_2CH_2(CH_2)_5CH_3$), 1.64–1.54 (2×2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 1.44–1.24 (2×16H, m, $NCH_2CH_2(CH_2)_5CH_3$+$C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 0.88 (2×3H, t, J=5.7 Hz, $N(CH_2)_7CH_3$), 0.87 (2×3H, t, J=6.7 Hz, $C_{quat.thiophene}(CH_2)_{11}CH_3$). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 161.2 (CO pyrrole-2-one), 143.6 ($C_{quat.thiophene}$(2)), 142.0 ($C_{quat.}$(9)), 138.9 ($C_{quat.thiophene}$(4)), 136.3 ($C_{quat.thiophene}$(5)), 135.5 ($CH_{thiophene}$(6)), 128.2 ($C_{quat.thiophene}$(8)), 125.9 ($CH_{thiophene}$(3)), 124.8 ($CH_{thiophene}$(7)), 110.1 ($C_{quat.}$(10)), 108.3 ($C_{quat.thiophene}$(1)), 42.3 ($NCH_2(CH_2)_6CH_3$), 31.9, 31.8, 30.0, 29.9, 29.71, 29.67, 29.66, 29.62, 29.58, 29.41, 29.36, 29.32, 29.26, 29.20, 26.9 ($NCH_2(CH_2)_5CH_2CH_3$+$C_{quat.thiophene}(CH_2)_{10}CH_2CH_3$), 22.7, 22.6 ($N(CH_2)_6CH_2CH_3$+$C_{quat.thiophene}(CH_2)_{10}CH_2CH_3$), 14.13, 14.12 ($N(CH_2)_7CH_3$+$C_{quat.thiophene}(CH_2)_{11}CH_3$). IR (ATR, cm^{-1}): ν_{max} 2954, 2918, 2849 (CH alkane stretch), 1656 (C=O amide stretch), 1556, 1545, 1510 (aromatic C=C stretch), 1450, 1407, 1367 (CH alkane bending). $UV_{max}(CH_2Cl_2)$: λ (nm) 231, 356, 381, 582, 621. MALDI-HRMS: *m*/*z*: calcd for $C_{50}H_{66}N_2O_2S_4Br_2$ ($M^{\bullet+}$): 1012.2374; found: 1012.2335; ppm: 3.9. Mp: 117–118 °C.

*4.3.3.3. N-benzylation of DPP **13b** towards 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)-2,5-bis(3,5-di-tert-butylbenzyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**1db**).* The same method was applied as described for the N-benzylation of DPP **3** into DPP derivative **4d**. This method is derived from a modified literature procedure.[37,38]

A solution of 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**13b**) (0.4 mmol, 384 mg) and potassium carbonate (4 equiv, 1.6 mmol, 221 mg) in 12 ml anhydrous NMP was brought under argon atmosphere and was heated to 60 °C. After 30 min at that temperature, 3 equiv of 1-(bromomethyl)-3,5-di-*tert*-butylbenzene (1.2 mmol, 340 mg) were added in one portion as a solution in 3 ml NMP (3,5-di-*tert*-butylbenzyl bromide is a white solid). The mixture was further mixed at 60 °C during 2 h and then it was brought at 80 °C and further stirred for 18.5 h. The mixture was cooled down to room temperature, washed with water (45 ml) and extracted with EtOAc (45 ml/30 ml/20 ml). The organic layers were collected and evaporated. The residue was suspended in 40 ml MeOH and a dark blue precipitate was formed. The mixture was overnight stored in the fridge in order to fully precipitate the DPP and then the precipitate was filtered off, washed with fresh MeOH and dried in vacuo. Further purification was not necessary and 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)-2,5-bis(3,5-di-*tert*-butylbenzyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**1db**) was obtained in 84% (465 mg) yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.60 (2×1H, d, J=4.2 Hz, $CH_{thiophene}$(6)), 7.28 (2×1H, t, J=1.6 Hz, ^{t}Bu-$C_{arom.quat.}CH_{arom.}C_{arom.quat.}$-^{t}Bu), 7.11 (2×1H, d, J=4.2 Hz, $CH_{thiophene}$(7)), 7.10 (2×2H, t, J=1.6 Hz, $CH_{arom.}C_{arom.quat.}(CH_2)CH_{arom.}$), 6.91 (2×1H, s, $CH_{thiophene}$(3)), 5.34 (2×2H, s, CH_2Benzyl), 2.51 (2×2H, t, J=7.6 Hz, $C_{quat.thiophene}CH_2(CH_2)_{10}CH_3$), 1.63–1.55 (2×2H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 1.34–1.26 (2×18H, m, $C_{quat.thiophene}CH_2CH_2(CH_2)_9CH_3$), 1.26 (4×9H, s, 4×^{t}Bu), 0.88 (2×3H, t, J=6.6 Hz, $C_{quat.thiophene}(CH_2)_{11}CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 161.5 (CO pyrrole-2-one), 151.1 ($C_{arom.quat.}$^{t}Bu), 143.5 ($C_{quat.thiophene}$(2)), 142.4 ($C_{quat.thiophene}$(5)), 139.5 ($C_{quat.}$(9)), 138.7 ($NCH_2CH_{arom.quat.}$), 135.8 ($CH_{thiophene}$(6)), 135.7 ($C_{quat.thiophene}$(4)), 128.2 ($C_{quat.thiophene}$(8)), 125.8 ($CH_{thiophene}$(3)), 124.6 ($CH_{thiophene}$(7)), 121.2 (^{t}Bu-$C_{arom.quat.}CH_{arom.}C_{arom.quat.}$-^{t}Bu), 120.7 ($CH_{arom.}C_{arom.quat.}(CH_2)CH_{arom.}$), 110.0 ($C_{quat.}$(10)), 108.1 ($C_{quat.thiophene}$(1)), 45.8 ($NCH_2$), 34.8 ($C_{quat.}$ ^{t}Bu), 31.9 ($(CH_2)_9CH_2CH_2CH_3$), 31.4 (CH_3 ^{t}Bu), 29.68, 29.67, 29.66, 29.64, 29.63, 29.56, 29.41, 29.36, 29.25 ($(CH_2)_9CH_2CH_2CH_3$), 22.7 ($(CH_2)_{10}CH_2CH_3$), 14.1 ($(CH_2)_{11}CH_3$). IR (ATR, cm^{-1}): ν_{max} 3072, 3018 (aromatic C–H bending), 2952, 2923, 2854 (CH alkane stretch), 1654 (C=O amide stretch), 1560, 1508, 1445, 1426 (aromatic C=C stretch), 1396, 1361, 1344 (CH alkane bending). $UV_{max}(CH_2Cl_2)$: λ (nm) 230, 356, 399, 582, 619. MALDI-HRMS: *m*/*z*: calcd for $C_{76}H_{102}N_2O_6S_4Br_2$ ($M^{\bullet+}$): 1360.5191; found: 1360.5167; ppm: 1.8. Mp: 187–193 °C.

*4.3.3.4. Boc-protection of DPP **13b** towards di-tert-butyl-3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate (**1eb**).* The Boc-protection of **13b** was executed as described for the Boc-protection of DPP chromophore **3**, which was executed according to the reported literature.[22]

In a two-necked, oven-dried round bottom flask, 3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)pyrrolo[3,4-*c*]pyrrole-1,4-(2*H*,5*H*)-dione (**13b**) (0.5 mmol, 480 mg) was dissolved in 15 ml anhydrous THF and the resulting solution was purged with argon for 10 min. Then, 2.5 equiv of *N*,*N*-dimethylaminopyridine (1.25 mmol, 153 mg) dissolved in 5 ml anhydrous THF were added and the reaction mixture was stirred for 15 min under argon atmosphere at room temperature. Next, 5 equiv of di-*tert*-butyl dicarbonate (2.5 mmol, 546 mg) were added (rinsed with 5 ml THF) and the mixture was stirred for 24 h at room temperature under argon. The mixture was concentrated under vacuum and the residue was dissolved in 20 ml MeOH and a very sticky dark blue precipitate was formed, which upon sonication broke up in small particles. The mixture was stored overnight in the fridge at 2–3 °C in order to fully precipitate the DPP before it was filtered off. A fast purification over alumina with CH_2Cl_2 as eluents was executed (R_f=0.82) resulting in 69% (406 mg) of di-*tert*-butyl-3,6-bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-dicarboxylate (**1eb**). Spectral analysis: vide supra.

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Supplementary data

Methods for the synthesis of all the described compounds in Scheme 1 were slightly modified compared to the literature procedures. Moreover, full spectral characterization (^{1}H NMR, ^{13}C NMR, IR, HRMS and UV–vis absorption) of all these products was performed. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.01.027.

References and notes

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