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C–H activation: making diketopyrrolopyrrole derivatives easily accessible†

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Diketopyrrolopyrrole (DPP) derivatives are an important class of high-performance pigment used in inks, paints, plastics, and organic electronics. Until now, DPP derivatives containing sophisticated aryl units at the DPP core have usually been obtained *via* Suzuki, Stille, or Negishi cross-coupling reactions, which require organometallic precursors. In this work, a series of DPP-based π-conjugated molecules bearing diverse aryl substituents on the thiophene- or benzene-DPPs were facilely synthesized in moderate to excellent yields through the Pd-catalyzed direct arylation of C–H bonds. The synthetic procedures feature advantages over traditional C–C cross-coupling reactions such as: (1) avoidance of the use of organometallic reagents in the starting materials leading to simpler byproducts and higher atom economy, (2) fewer synthetic steps, (3) higher yields, (4) better compatibility with chemically sensitive functional groups, and (5) simpler catalytic systems free of phosphine ligands. These advantages make the present protocol an ideal and versatile strategy for the synthesis of DPP derivatives, especially for structurally complicated DPPs that may possess chemically sensitive functionalities. The optical and electrochemical properties of the synthesized DPPs (17 compounds) were systematically investigated using UV-vis spectroscopy, steady-state fluorescence spectroscopy, and cyclic voltammetry (CV).

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1 Introduction

Numerous diketopyrrolopyrrole (DPP) derivatives have been synthesized since DPP was discovered by Farnum *et al.* in 1974 (ref. 1) and the synthetic pathway was subsequently improved in the early 1980s, showing their technological and scientific importance.[2] DPP derivatives were first commercialized as pigments. In recent years, DPPs have also been widely explored for optoelectronic applications because of their unique π-conjugated systems as well as their exceptional stability.[3] For example, the DPP unit functions as an excellent electron-withdrawing unit in low-bandgap donor–acceptor copolymers for organic photovoltaic cells (OPVs)[4] and field effect transistors (FETs),[5] which display some of the highest mobilities reported due to the remarkable aggregating properties of the DPP moieties.[3c,d,5a] Small DPP-based molecules have also been widely used for small molecule bulk heterojunction (BHJ) OPVs,[6,7] FETs,[8] dye-sensitized solar cells (DSSCs),[9] and chemical sensors[10] in addition to their extensive applications in inks, paints, and the plastics industry.

Among various DPP derivatives that have been studied, thiophene-functionalized DPPs have attracted extensive attention for their applications in organic electronics.[3b–d,4–7] This is due to the fact that the electron richness of the thiophene moiety can induce strong intramolecular charge transfer with the electron-deficient DPP core and π–π stacking of the resulting conjugating units to create improved optical and electrochemical properties. For example, the derivatives of benzene-terminated thiophene-DPPs have been used either as electron donors or electron acceptors in small molecule based BHJ solar cells.[6a,d,e,7a] Recently, DPP-based small molecules with two bithiophene units connected to both sides of the DPP core have also been explored, generating very promising results in BHJ solar cells. Due to their bipolar charge-transporting properties, bithiophene-functionalized DPP compounds could be used both as electron donor[6c,f] and acceptor materials.[7b]

Usually, these thiophene-DPP functional molecules are synthesized *via* the Suzuki, Stille, or Negishi cross-coupling reactions, which involve the preparation of organoboron, organotin, or organozinc reagents, respectively.[6,7a,11] Nevertheless, thiophene has been regarded as an ideal moiety in synthetic organic chemistry for direct arylation with aryl halides due to the ease of palladation through a concerted

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† Electronic supplementary information (ESI) available: The detailed synthetic routes of all DPPs, ^{1}H NMR spectra of parent **DPP 1a–e**, PL, ^{1}H and ^{13}C NMR, and some MALDI-TOF MS spectra of **DPP 1–17**. See DOI: 10.1039/c2ta01318e

metalation–deprotonation (CMD) pathway.[12] This results in a highly selective reaction at the 2/5 positions on the thiophene ring. The excellent CMD pathway introduced by Fagnou *et al.*[12] and the similar proton abstraction mechanism proposed by Echavarren and Maseras[13] have enabled various electron-deficient aromatics and thiophene rings to be used as valid arene coupling partners for direct arylations.[14] These reactions possess numerous advantages over traditional cross-coupling reactions such as: (1) avoidance of the use of organometallic reagents in the starting materials leading to simpler byproducts and higher atom economy, (2) fewer synthetic steps, (3) higher yields, (4) better compatibility with chemically sensitive functional groups, and (5) simpler catalytic systems free of phosphine ligands.[15]

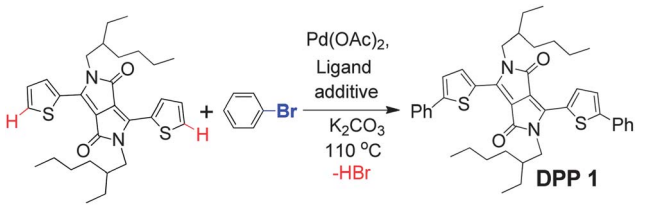
With these advantages, DPP-containing thiophene derivatives should be ideal candidates for the exploration of direct arylation reactions. However, there is very little information regarding the synthesis of DPP derivatives *via* direct arylation. During the preparation of this paper, Marder *et al.* recently reported the synthesis of several bis-arene-functionalized DPPs through direct arylation reactions.[16] In our independent study, we have systematically investigated the conditions of direct arylation for DPPs. Four types of DPP that are being extensively studied in the organic electronics field including various derivatives of benzene-thiophene-DPP, bithiophene-DPP, thiophene-benzene-DPP, pentafluorophenyl capped DPP, and sophisticated multi DPP cores, have all been synthesized *via* direct arylation. Most of these compounds could be obtained in moderate to excellent yields. The results from this study provide a generally applicable methodology for the broad application of direct arylation to synthesize DPPs and other useful π-conjugated materials.

2 Results and discussion

2.1 Optimization of reaction conditions for direct arylation of DPP

To determine the appropriate conditions for direct arylation, a model reaction involving the coupling between thiophene-DPP (**DPP 1a**, Table 1) and bromobenzene was carried out under three sets of conditions. The results are summarized in Table 1. Because tricyclohexylphosphine (PCy_3) has been reported as an effective ligand for the Pd-catalyzed direct arylation of thiophene derivatives in toluene,[17] the catalytic system combining $Pd(OAc)_2$ with PCy_3 was examined first. The catalysis using PCy_3 gave **DPP 1** with a 96% yield in 24 h (entry 1). During the reaction, a color change from red to purple was observed in the reaction mixture after 12 h. In addition to phosphine ligands, the direct arylation of thiophene derivatives using phosphine-free catalytic systems in polar solvents has been developed in recent years.[18] We have also examined the catalytic system without using phosphine ligands. Entry 2 in Table 1 shows that the use of $Pd(OAc)_2$, K_2CO_3 in dimethylacetamide (DMA) as a catalytic system gave **DPP 1** in 96% yield with a shorter reaction time (12 h). To our surprise, the reaction in this phosphine-free catalytic system could be further accelerated greatly in the presence of pivalic acid (PivOH). As shown in entry 3 in Table 1, with the addition of PivOH, the reaction time could be shortened to 2 h with 96% yield. The color change of the reaction mixture observed was obvious even after 0.5 h. This result demonstrates that pivalic acid plays a key role in direct arylation involving the CMD pathway.[12–14] The similar high reactivity in ligandless catalysis with pivalic acid in DMA solvent has also been observed by Hartwig and Tan.[15]

Table 1 Optimization of reaction conditions for the direct arylation of DPP[a]



Entry	Time	Solvent	Ligand	Additive	Yield[d]
1	24 h	Toluene	PCy_3[b]	PivOH[c]	96%
2	12 h	DMA	None	None	96%
3	2 h	DMA	None	PivOH[c]	96%

[a] **DPP 1a** (105 mg, 0.2 mmol), bromobenzene (78 mg, 0.5 mmol), anhydrous K_2CO_3 (69 mg, 0.5 mmol), anhydrous solvent 2 mL, $Pd(OAc)_2$ (2.3 mg, 0.010 mmol), carried out at 110 °C under an N_2 atmosphere. [b] $PCy_3 \cdot HBF_4$ (0.02 mmol, 7.4 mg). [c] PivOH (6.1 mg, 0.06 mmol, 30 mol%). [d] Isolated yields.

The optimized reaction conditions found in Table 1 (5 mol% $Pd(OAc)_2$, 30 mol% PivOH, 2.5 equiv. K_2CO_3, anhydrous DMA) were subsequently applied to the preparation of a series of DPP-based conjugated molecules starting from the five parent DPPs shown in Fig. 1 (**DPP 1a–e**) with various bromoarenes, thiophene derivatives, and pentafluorobenzene. The parent **DPP 1a**, **1b**, **1d** and **1e** were prepared according to our previous report and the literature;[4b,19,20] and **DPP 1c** was synthesized from the Suzuki coupling of phenylboronic acid with mono-bromothiophene DPP (see Experimental section and ESI, Scheme S1†). Fig. 1 shows the photos of the $CHCl_3$ solutions of each individual DPP made and their simplified synthetic routes. Interestingly, the seventeen DPP dyes synthesized from five parent DPPs cover a broad color spectrum ranging from yellow, orange, red-purple, purple, blue-purple, blue, to green as shown in Fig. 1.

Table 2 summarizes the substrates and the seventeen DPP derivatives synthesized from the five DPP cores. The seventeen synthesized DPPs, which are divided into four categories as benzene-derivative-thiophene DPPs (**DPP 1–9**), thiophene-derivative-thiophene or thiophene-derivative-benzene DPPs (**DPP 10–15**), pentafluorophenyl capped DPPs (**DPP 6** and **16**) and DPP–DPP-based oligomers (**DPP 9** and **17**), are described in detail later.

2.2 Direct arylation of thiophene-DPP with the bromides of benzene derivatives

Firstly, we investigated the arylation of **DPP 1a** using the bromides of benzene derivatives. As shown in entries 1–9 of

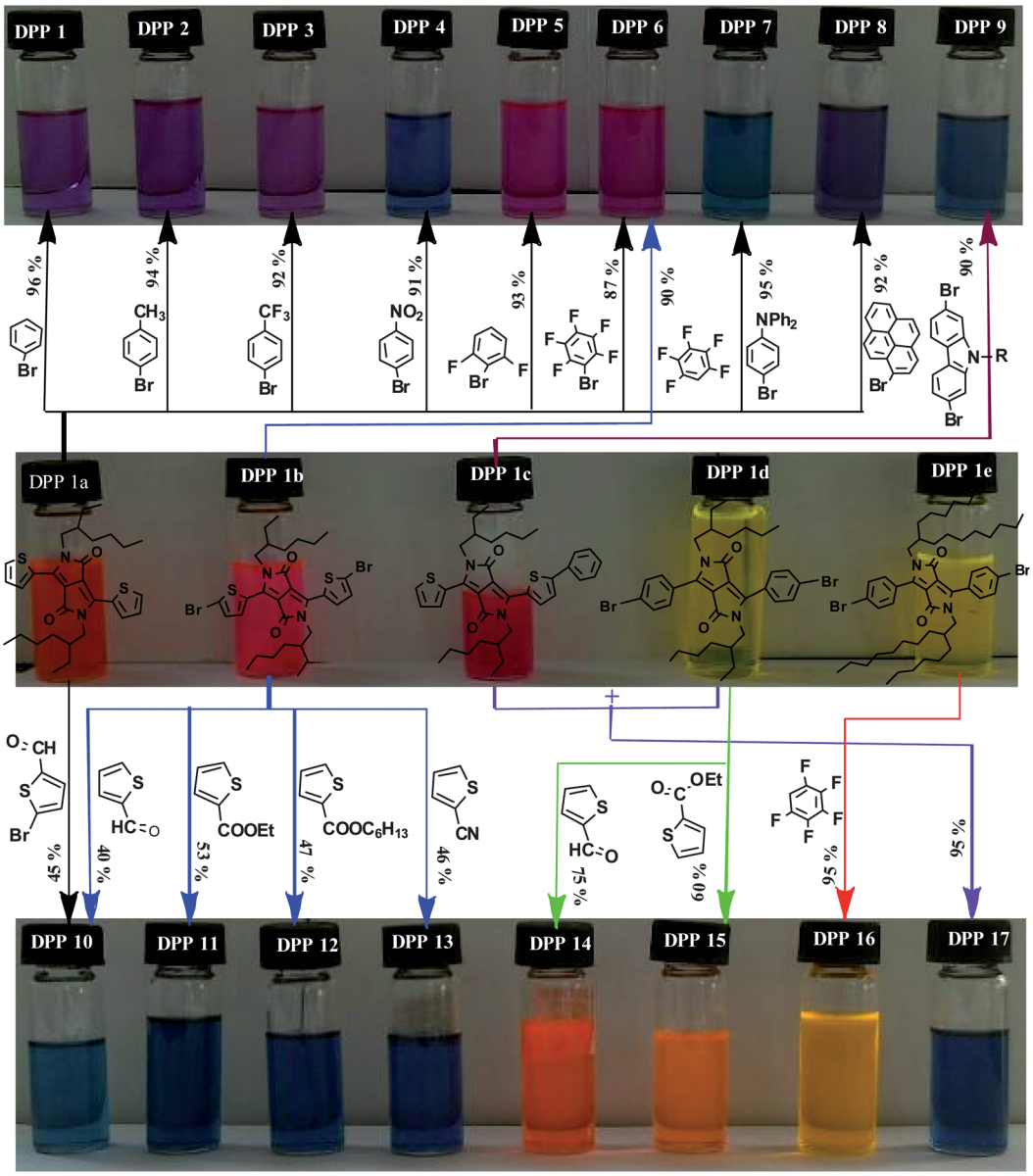


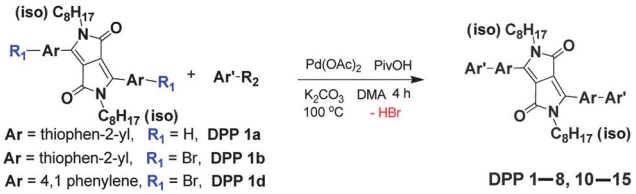
Fig. 1 Digital photos of $CHCl_3$ solutions of all the DPPs and the simplified synthetic routes for **DPP 1–17** from the corresponding reactants, the given values indicate the yields for the reactions.

Table 2, DPPs functionalized with various benzene derivatives were readily obtained through direct C–H arylation with good to excellent yields in short reaction times. The reaction time (4 h) is much shorter than that used for traditional Suzuki, Stille and Negishi cross coupling reactions, indicating that thiophene-DPPs are ideal substrates for direct arylation. It is noteworthy that no phosphine ligand is needed under these conditions.

In a previous report, **DPP 3** was used as an electron donor in small molecule BHJ solar cells devices.[6d] An analogue of **DPP 3** with dodecyl groups on N atoms has also been used as an electron acceptor in BHJ solar cells by the same research group.[7a] **DPP 3** was produced previously in 69% yield from a $Pd(PPh_3)_4$-catalyzed Suzuki coupling reaction between **DPP 1b** and 4-(trifluoromethyl) phenylboronic acid.[6d] However, using direct arylation, the aryl boronic acid and di-bromide **DPP 1b** could be replaced with an aryl bromide and the simpler **DPP 1a**, respectively. Entry 3 in Table 2 shows that the direct arylation proceeded smoothly using a catalytic amount of $Pd(OAc)_2$ with 30 mol% pivalic acid and 2.5 equiv. K_2CO_3 in DMA to give **DPP 3** in 92% yield (For comparison, see ESI, case 1 of Scheme S20†). The direct arylation of the activated C–H bond provides a more straightforward pathway employing simpler starting materials.

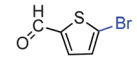
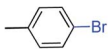
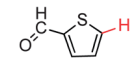
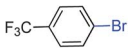
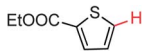
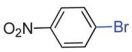
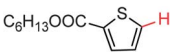
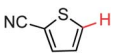
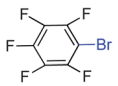
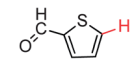
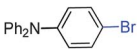
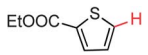
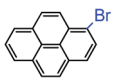
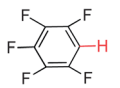
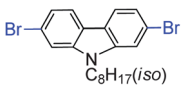
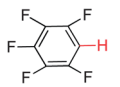
As indicated in entries 5 and 6, **DPP 5** and **DPP 6** containing fluorine atoms were synthesized by the direct arylation of **DPP 1a** with the corresponding bromoarenes in 93% and 87% yield, respectively. It should be noted that we also tried to prepare **DPP 5** using the Suzuki coupling of (2,6-difluorophenyl) boronic acid with **DPP 1b**, but no desired product was obtained. This is because the electron density on the carbon atom in the C–B bond is significantly reduced due to the strong

Table 2 Synthesis of the 17 DPP derivatives from five parent DPPs *via* direct arylation[a]



Ar = thiophen-2-yl, R_1 = H, **DPP 1a**
Ar = thiophen-2-yl, R_1 = Br, **DPP 1b**
Ar = 4,1 phenylene, R_1 = Br, **DPP 1d**

DPP 1—8, 10—15

Entry	Parent **DPP**	**Ar′–R$_2$**	Product	Yield[b] (%)	Entry	Parent **DPP**	**Ar′–R$_2$**	Product	Yield[b] (%)
1	**DPP 1a**		**DPP 1**[c]	96	10	**DPP 1a**		**DPP 10**	45[e] (10)[7b]
2	**DPP 1a**		**DPP 2**	94	11	**DPP 1b**		**DPP 10**	40[e]
3	**DPP 1a**		**DPP 3**	92 (69)[6d]	12	**DPP 1b**		**DPP 11**	53[e] (25)[6c]
4	**DPP 1a**		**DPP 4**	91	13	**DPP 1b**		**DPP 12**	47[e]
5	**DPP 1a**		**DPP 5**	93	14	**DPP 1b**		**DPP 13**	46[e] (31)[11]
6	**DPP 1a**		**DPP 6**	87	15	**DPP 1d**		**DPP 14**	75[e]
7	**DPP 1a**		**DPP 7**	95 (45)[6e]	16	**DPP 1d**		**DPP 15**	60[e]
8	**DPP 1a**		**DPP 8**	92 (98)[6e]	17	**DPP 1b**		**DPP 6**	95
9	**DPP 1c**		**DPP 9**	90[d]	18	**DPP 1e**		**DPP 16**	95 (13)[26]
					19	**DPP 1d**	**DPP 1c**	**DPP 17**	95[f]

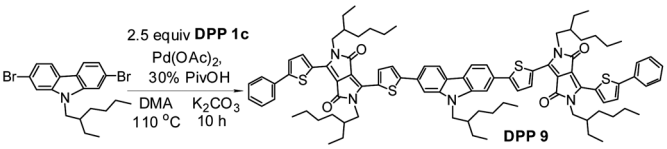
[a] Parent DPP (0.2 mmol), **Ar′–R$_2$** (0.5 mmol), anhydrous K_2CO_3 (69 mg, 0.5 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol), PivOH (6.1 mg, 0.06 mmol), anhydrous DMA 2 mL, carried out at 110 °C for 4 h under an N_2 atmosphere. [b] Isolated yield, the yields in parentheses are from the literature. [c] Reaction time 2 h. [d] Dibromo-carbazole (0.2 mmol), **DPP 1c** (0.5 mmol), reaction time 10 h. [e] Reaction temperature 100 °C. [f] **DPP 1d** (0.2 mmol), **DPP 1c** (0.5 mmol), reaction time 12 h.

electron-withdrawing effect of the two adjacent C–F bonds, leading to the reduced reactivity of the Suzuki coupling. A similar experimental result was also observed in (perfluorophenyl) boronic acid with no **DPP 6** being obtained from the corresponding Suzuki coupling. The cases of **DPP 5** and **DPP 6** demonstrate that direct arylation could proceed effectively with compounds that the commonly used C–C coupling reactions cannot work with.

DPP 7 and an analogue of **DPP 8** have previously been used as electron donors in small molecule BHJ solar cells.[6e] In this previous report, **DPP 7** and **DPP 8** were produced from the Suzuki coupling of dibromo-thiophene-DPP with an aryl boronic ester or acid with a total yield of 45% or 98%, respectively.[6e] Herein, **DPP 7** and **DPP 8** were obtained *via* the direct arylation of thiophene-DPP with the corresponding aryl bromides in yields of 95% and 92%, respectively (entries 7 and 8), with no organo-boron reagent used (ESI, cases 2 and 3 in Scheme S20†).

To obtain DPP derivatives containing multi DPP cores, a thiophene-DPP capped with a phenyl group on one side was designed (**DPP 1c**, Fig. 1). If the remaining 5′ C–H bond of the thiophene ring on **DPP 1c** could be arylated by a di-bromide, it would give a DPP derivative with two DPP cores. To test this idea, a 2,7-dibromo-carbazole derivative was chosen to couple with **DPP 1c**. Scheme 1 shows the route (entry 9, Table 2).

As expected, the target **DPP 9** was obtained in 90% yield (calculated from carbazole). Such a large molecule with a



Scheme 1 Synthesis of **DPP 9** from 2,7-dibromo-carbazole and **DPP 1c**.

molecular weight of 1477.14 was verified by ^{1}H and ^{13}C NMR, MALDI-TOF MS (found, 1477.04) and elemental analysis (see ESI, Fig. S16†). By extending this strategy to multi-bromide aryl analogs, DPP derivatives with multi-DPP cores can be obtained.

2.3 Direct arylation for the synthesis of bithiophene or thiophene-benzene-DPP

Previously, a DPP derivative containing two bithiophene units at the DPP core has been mentioned in a patent on DPP fluorophores[21] and its detailed synthesis was described in 2008.[22] Bithiophene-functionalized DPP compounds have been used as both electron donors[6c,f] and acceptors[7b] in BHJ solar cells. Bithiophene-functionalized DPPs are usually obtained by palladium-catalyzed cross coupling reactions. Recently, the improvement of synthetic procedures for DPP derivatives bearing bithiophene moieties has been investigated by several groups.[11,23] For example, Würthner and co-workers tried different C–C couplings to synthesize 5-carbonitrile-bithiophene functionalized DPP (**DPP 13** in Table 2). The synthesis proceeded smoothly to give the target DPP in 31% total yield, first by the deprotonation of **DPP 1a**, followed by the quenching of the reactive intermediate with a boronic ester to install the requisite boron for the subsequent Suzuki coupling reaction.[11] Alternatively, **DPP 13** could be obtained in one step (46% yield) by reacting **DPP 1b** with thiophene-2-carbonitrile through direct arylation (as shown in entry 14 (Table 2)), while avoiding organoboron reactants (for comparison of routes, see ESI, Scheme S20†).

As reported by Janssen *et al.*, a 5-carbaldehyde-bithiophene-DPP with a low-lying HOMO level can be synthesized and used as an acceptor in BHJ solar cells.[7b] In their reported synthetic procedure, the corresponding aldehyde-DPPs were prepared by the deprotonation of the Stille coupling-obtained bithiophene-DPP using lithium diisopropylamide (LDA), followed by the quenching of the dianion with *N*,*N*-dimethylformamide (DMF) to afford a total yield of <10%. In contrast, as shown in Table 2 (entry 10), 5-carbaldehyde-bithiophene-DPP (**DPP 10**) can be obtained in one step with a 45% yield using the direct arylation between 5-bromothiophene-2-carbaldehyde and **DPP 1a**, while avoiding organometallic intermediates and low-temperature conditions (ESI, case 4, Scheme S20†). Alternatively, **DPP 10** can be synthesized in 40% yield from the arylation of thiophene-2-carbaldehyde with **DPP 1b** (Fig. 1, and entry 11 in Table 2), demonstrating the versatility of the direct arylation methodology.

During the course of this study, an ester-functionalized bithiophene-DPP was synthesized and applied to BHJ solar cells by our group. An impressive power conversion efficiency (PCE) of 4.02% was achieved for this material.[6c] In that study, the 5-carboxylate-bithiophenyl-DPP (**DPP 11** in Table 2) was synthesized *via* a Stille coupling reaction between 3,6-bis[(5-(trimethylstannyl)thiophen-2-yl)]-DPP with ethyl 5-bromothiophene-2-carboxylate. The DPP tin precursor was obtained *via* the deprotonation of **DPP 1a** followed by quenching with Me_3SnCl. The synthetic procedure comprised of two key steps that afforded **DPP 11** in <25% yield.[6c] However, in our current study, **DPP 11** can be obtained straightforwardly *via* the direct arylation between ethyl thiophene-2-carboxylate and **DPP 1b** to afford **DPP 11** in 53% yield in one step (entry 12). Additionally, it was found that the analog hexyl thiophene-2-carboxylate could also be directly arylated by **DPP 1b** under the same conditions to give **DPP 12** in 47% yield (Table 2, entry 13).

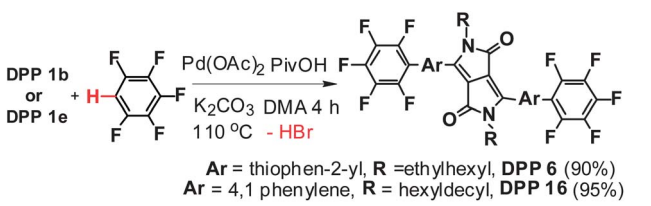
In this work, the direct arylation of the α-C–H bond of a thiophene by **DPP 1d** leading to the formation of thiophene-benzene-DPP was also investigated. Two thiophene derivatives, thiophene-2-carbaldehyde and ethyl thiophene-2-carboxylate, were arylated by **DPP 1d** and gave the targets **DPP 14** and **DPP 15** shown in Table 2 with yields of 75% and 60%, respectively (entry 15 and 16, Table 2), which are higher than those of their thiophene-DPP counterparts (entries 10–12).

2.4 Direct arylation of pentafluorobenzene for the synthesis of pentafluorophenyl functionalized DPPs

Like thiophene derivatives, pentafluorobenzene is also an ideal moiety for direct arylation *via* the CMD pathway, which renders the relatively acidic H on pentafluorobenzene highly reactive toward aryl bromide.[12,17,25] The introduction of electron-withdrawing substituents, such as fluoro groups, onto the DPP or other π-structures should provide the molecules with high electron affinities.[7a,24] The introduction of a pentafluorophenyl group onto a DPP is expected to produce a molecule with an improved electron affinity and a well-ordered stacking structure due to its electron-withdrawing ability and the π-conjugation extension. Herein, two bromides, **DPP 1b** and **DPP 1e**, were chosen as coupling partners to arylate pentafluorobenzene (entries 17 and 18 in Table 2). The routes are shown in Scheme 2. Gratifyingly, the arylation of pentafluorobenzene by **DPP 1b** and **DPP 1e** gave the targets **DPP 6** and **DPP 16**, respectively, with 90% and 95% yields under the optimized conditions.

As described above, **DPP 6** has also been obtained in high yield from the direct arylation of **DPP 1a** by pentafluorophenyl bromide (Fig. 1, and entry 6 in Table 2). The examples of entries 6 and 17 in Table 2 demonstrate that in cases where both arenes have been demonstrated to undergo direct arylation, such as with thiophenes and pentaflourobenzene, it is possible to switch the bromine substitution such that bromothiophene and a simple arene are utilized as coupling partners (ESI, Scheme S8†).[17] The examples also demonstrate that direct arylation is a versatile tool for the synthesis of functionalized DPPs.

It is noteworthy that an analogue of **DPP 16** has been previously synthesized by Kanbara *et al. via* Suzuki C–C coupling of the biphenyl-DPP boronic ester with pentafluorophenyl



Scheme 2 Direct arylation of pentafluorobenzene by **DPP 1b** and **1e**.

iodide.[26] However, the reported procedure was comprised of two key steps, with a total yield of only 13% (see ESI, case 6 of Scheme S20†).

2.5 Direct arylation between DPPs

Anthopoulos *et al.* have recently reported a DPP–DPP-based conjugated copolymer synthesized *via* a Suzuki reaction.[27] Due to the strong inter- and intra-molecular donor–acceptor interactions between DPP units, the copolymer exhibited a high electron mobility of over 1 $cm^2\ V^{-1}\ s^{-1}$. The intense donor–acceptor interactions should also be expected to improve the optical and electronic properties of DPP–DPP-based molecules or oligomers, whose synthesis has been rarely reported, however. For these reasons, we decided to prepare the DPP–DPP-based oligomer *via* direct arylation. The successful synthesis of **DPP 9** (entry 9 in Table 2 and Scheme 1) demonstrates that **DPP 1c** can be effectively arylated by a multi-brominated aromatic molecule, affording molecules with more extended π-conjugation containing multiple DPP cores. To obtain DPP–DPP-based oligomers, **DPP 1d**, as an aryl dibromide, was tested for the arylation of the 5′ C–H bond on the thiophene ring of **DPP 1c** (entry 19, Table 2). Scheme 3 shows the synthetic route. Interestingly, under the above-mentioned conditions, a π-conjugated molecule involving three DPP cores (**DPP 17**) was obtained in one step with 95% yield (calculated from **DPP 1d**).

The structure and molecular weight of **DPP 17** (1710.44) were verified by using ^1H and ^{13}C NMR, MALDI-TOF MS (found, 1710.39), and elemental analysis (see ESI, Fig. S24†). It is noteworthy that, if traditional C–C coupling was applied to the synthesis of **DPP 17**, either **DPP 1c** or **DPP 1d** should be further converted to organo-boronic or organo-tin compounds and more steps would be involved. The direct arylation provides a simpler and more efficient method. This example demonstrates that this methodology not only can be generally applicable to reactions between common aryl derivatives and DPPs, but also between DPPs themselves, leading to DPP–DPP-based oligomers.

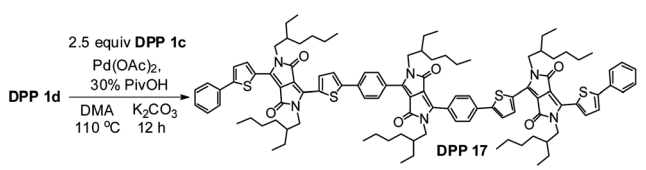
2.6 Optical and electrochemical properties of DPP 1–17

As shown in Fig. 1, the solutions of the synthesized **DPP 1–17** cover a broad color spectrum including various colors. The optical properties of **DPP 1–17** were studied by UV-vis and steady-state fluorescence spectroscopy. The significant optical properties are listed in Table 3.

Fig. 2 shows the UV-vis spectra. All the **DPPs** show a broad absorption band in the visible to near-infrared region. As shown in Fig. 2 and Table 3, the absorption peaks of **DPP 1–17** in $CHCl_3$ solution range from 482 nm to 626 nm, in accordance with the various colours observed. The structures of **DPP 1–6** are slightly different from each other. However, it is interesting to observe that the solution of **DPP 4** has a blue color, which differs much from that of **DPP 1–3**, **5** and **6** (Fig. 1). **DPP 4** exhibits an absorption peak at a longer wavelength of 623 nm (Fig. 2). This can be ascribed to the fact that the sp^2 N in the $-NO_2$ group extends the effective π-conjugation length of **DPP 4**, resulting in the red shift of the absorption.

The absorption band-edges (λ_{onset}) of the **DPPs** and the corresponding optical band-gaps (E_g^{opt}) calculated from $1240/\lambda_{onset}$ are also summarized in Table 3. The electrochemical properties of **DPP 1–17** were investigated by cyclic voltammetry (CV). The CV curves were recorded *versus* the potential of the SCE, which was calibrated by the ferrocene–ferrocenium (Fc/Fc^+) redox couple (4.8 eV below the vacuum level). The cyclic voltammograms of the seventeen **DPPs** are shown in Fig. 3, and the electrochemical data are summarized in Table 3. The HOMO energy levels were calculated from the CV and the corresponding LUMO levels were estimated from $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

The HOMO levels of **DPP 1–17** decrease with the increase of the electron-withdrawing ability of the substituents at the 3, 6 positions of the DPP cores. The electron-withdrawing abilities of the substituents follow the order **DPP 16** > **DPP 14** > **DPP 15** > **DPP 6** > **DPP 4** > **DPP 13** > **DPP 10** > **DPP 3** > **DPP 11** ≈ **DPP 12** > **DPP 5** > **DPP 8** > **DPP 1** > **DPP 2** > **DPP 17** > **DPP 9** > **DPP 7**. Accordingly, the HOMO levels of **DPP 1–17** obtained from the CV interestingly follow the order **DPP 16** < **DPP 14** < **DPP 15** < **DPP 6** < **DPP 4** < **DPP 13** < **DPP 10** < **DPP 3** < **DPP 11** ≈ **DPP 12** < **DPP 5** < **DPP 8** < **DPP 1** < **DPP 2** < **DPP 17** < **DPP 9** < **DPP 7** (Table 3).



Scheme 3 Direct arylation of **DPP 1c** by **DPP 1d**.

Table 3 Optical and electrochemical properties of **DPP 1–17**[a]

DPP	λ_{abs} (nm)	λ_{em} (nm)	HOMO (eV)	λ_{onset} (nm)	E_g^{opt} (eV)	LUMO (eV)
1	596.5	625	5.25	631	1.97	3.28
2	600.5	630	5.19	635	1.95	3.23
3	597.5	628	5.34	635	1.95	3.38
4	623.7	665	5.39	666	1.86	3.53
5	590.0	621	5.31	625	1.98	3.33
6	587.5	622	5.44	627	1.98	3.46
7	632.0	674	5.09	678	1.83	3.27
8	587.0	651	5.25	645	1.92	3.32
9	626.0	657	5.14	663	1.87	3.27
10	632.0	678	5.36	685	1.81	3.55
11	622.0	664	5.318	673	1.84	3.48
12	623.0	664	5.313	668	1.86	3.46
13	618.0	662	5.38	672	1.85	3.54
14	503.0	592	5.58	570	2.18	3.41
15	499.5	581	5.55	565	2.20	3.36
16	482.0	553	5.62	536	2.31	3.31
17	624.0	676	5.15	683	1.82	3.33

[a] All data were obtained from the solutions of the DPPs. UV-vis spectra were recorded in $CHCl_3$ solutions. CV was done with a Pt disk, a Pt plate, and an SCE as the working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol L^{-1} Bu_4NPF_6 CH_2Cl_2 solution.

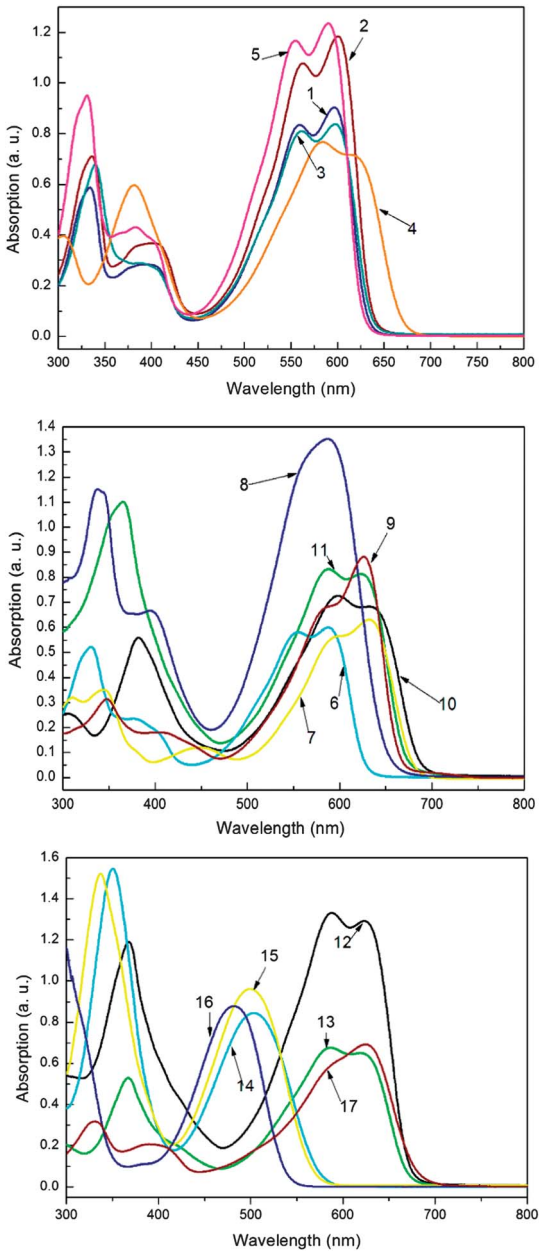


Fig. 2 UV-vis absorption spectra of **DPP 1–17** in $CHCl_3$.

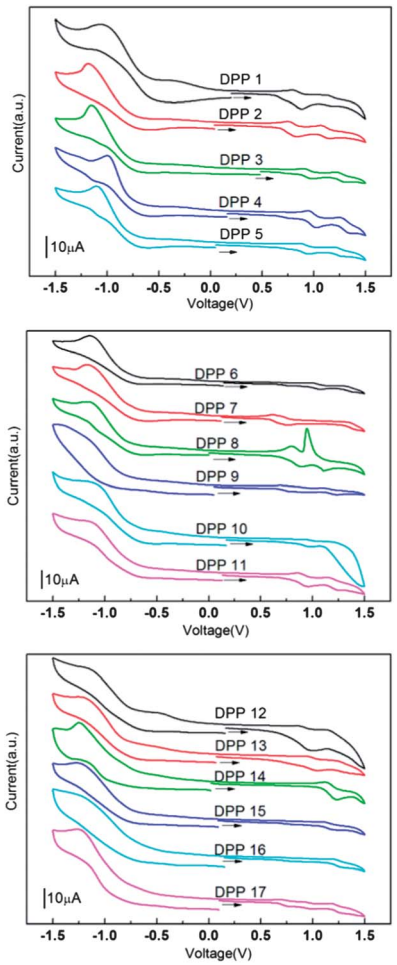


Fig. 3 Cyclic voltammograms of **DPP 1–17** in dry CH_2Cl_2 solution; scan rate 50 mV s^{-1} in 0.1 M NBu_4PF_6.

The low bandgap DPPs such as **DPP 4**, **DPP 9**, **DPP 11**, **DPP 12** and **DPP 17** may have applications in OPVs. The appropriate frontier orbital energy levels and good absorption in the NIR region would make **DPP 17** an ideal molecule for OPV applications. Alternatively, the **DPPs**, including **DPP 6**, **DPP 14**, **DPP 15** and **DPP 16**, with strong electron-withdrawing groups may serve as n-type and electron acceptor materials. Marks *et al.* reported an n-type semiconducting perfluorophenyl-capped quarterthiophene with HOMO and LUMO levels of −5.48 and −2.85 eV, respectively.[24a] Compared with Marks' molecule, **DPP 6** exhibited a comparable HOMO (−5.44 eV) but much lower LUMO (−3.46 eV) (Table 3). The structural difference between Marks' molecule and **DPP 6** is that the central bi-thiophene unit of the former is changed to a diketopyrrolopyrrole core. This comparison indicates that the LUMO can be more effectively lowered by the DPP core than the HOMO.

3 Conclusion

In summary, direct arylation has been demonstrated as a powerful, versatile and straightforward tool for the synthesis of diketo-pyrrolo-pyrrole dyes. Seventeen DPPs, including compounds that are unreactive for commonly used C–C couplings, benzene-thiophene-DPPs, thiophene-thiophene-DPPs, thiophene-benzene-DPPs, and DPP–DPP-based oligomers, have all been facilely synthesized *via* the direct arylation of C–H bonds in moderate to excellent yields. The obtained **DPPs** have broad absorption bands from the visible to near-infrared region, and some of them show suitable HOMO and LUMO energy levels for photovoltaic applications. It is believed that more DPP-based molecules or other functional materials could be synthesized *via* the direct arylation. Also, as a valuable alternative, direct arylation combined with traditional C–C coupling should make the synthesis of π-conjugated functional molecules or polymers more facile and versatile.

4 Experimental section

4.1 Synthesis of parent DPP 1a–e

DPP 1a (*2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*) was synthesized according to the reported literature.[4b,19] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.88 (dd, J = 3.9, 1.2 Hz, 2H), 7.62 (dt, J = 2.1, 1.1 Hz, 2H), 7.28–7.27 (m, 2H), 4.08–3.91 (m, 4H), 1.86 (m, 2H), 1.32–1.15 (m, 16H), 0.95–0.73 (m, 12H).

DPP 1b[19] (*3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). **DPP 1a** (2.62 g, 5 mmol) and *N*-bromosuccinimide (1.78 g, 10 mmol) were dissolved into chloroform (150 mL) in a two-necked round flask under argon protection, and then the solution was protected from light and stirred at room temperature. After 40 h, the mixture was poured into 200 mL of methanol and then filtered. The filter cake was washed by hot methanol twice. After drying in vacuum, the pure product was obtained as a purple-black solid (**DPP 1b**, 2.7 g, yield 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (d, J = 4.2 Hz, 2H), 7.25–7.18 (m, 2H), 3.93 (dd, J = 7.8, 3.6 Hz, 4H), 1.83 (s, 2H), 1.36 (m, 16H), 0.94–0.75 (m, 12H).

DPP 1c[19] (*2,5-bis(2-ethylhexyl)-3-(5-phenylthiophen-2-yl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). *N*-Bromosuccinimide (0.85 g, 4.76 mmol) was added in portions to a solution of **DPP 1a** (2.5 g, 4.76 mmol) in $CHCl_3$ (50 mL) in a two-necked flask at 5 °C. The mixture was warmed to room temperature and stirred overnight. CH_2Cl_2 was added and then the solution was washed with brine. The organic phase was dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The crude product was purified chromatographically (silica gel; CH_2Cl_2–petroleum ether, 2 : 1) to yield a red solid (1.70 g, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (d, J = 3.9 Hz, 1H), 8.64 (d, J = 4.2 Hz, 1H), 7.65 (d, J = 5.1 Hz, 1H), 7.29–7.18 (m, 2H), 4.03–3.92 (m, 4H), 1.84 (m, 2H), 1.38–1.23 (m, 16H), 0.91–0.83 (m, 12H).

The above mono-bromo-DPP (1.21 g, 2 mmol), phenylboronic acid (305 mg, 2.5 mmol), and K_2CO_3 (345 mg, 2.5 mmol) were dissolved in 30 mL of toluene and ethanol (3 : 1) followed by 1 mL H_2O and $Pd(PPh_3)_4$ (45 mg, 0.04 mmol), and was stirred for 24 h at 85 °C under a nitrogen atmosphere. The solvent was evaporated under vacuum and the residue was partitioned between CH_2Cl_2 and water; the organic phase was washed with brine and dried ($MgSO_4$) and then the solvent was evaporated. The residue was purified chromatographically (silica gel; CH_2Cl_2–petroleum ether, 1 : 1) and yielded a red purple solid (**DPP 1c**, 1.1 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (d, J = 4.1 Hz, 1H), 8.89 (d, J = 3.5 Hz, 1H), 7.68 (d, J = 7.4 Hz, 2H), 7.62 (d, J = 4.8 Hz, 1H), 7.42 (ddd, J = 33.7, 14.1, 5.7 Hz, 4H), 7.30–7.27 (m, 1H), 4.16–3.89 (m, 4H), 1.93 (d, J = 5.6 Hz, 2H), 1.37–1.25 (m, 16H), 0.88 (ddd, J = 20.0, 13.0, 7.0 Hz, 12H).

DPP 1d (*3,6-bis(4-bromophenyl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*) was synthesized according to the reported literature.[19a,20] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 8H), 4.12–3.94 (m, 4H), 1.46 (s, 2H), 1.07 (m, 16H), 0.88 (ddd, J = 20.0, 13.0, 7.5 Hz, 12H).

DPP 1e (*3,6-bis(4-bromophenyl)-2,5-bis(2-hexyldecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). The synthesis was similar to that for **DPP 1d** except that the 2-ethylhexyl bromide was changed to 2-hexyldecyl bromide. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 8H), 3.70 (d, J = 7.2 Hz, 4H), 1.49 (d, J = 19.2 Hz, 2H), 1.24–1.05 (m, 48H), 0.89–0.80 (m, 12H).

4.2 Synthesis of DPP derivatives DPP 1–17

A typical procedure for C–H arylation towards the seventeen **DPPs** (Table 2) is as follows. The parent DPP (0.2 mmol), **Ar–R$_2$** (0.5 mmol), anhydrous K_2CO_3 (69 mg, 0.5 mmol), pivalic acid (6.1 mg, 0.06 mmol), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) were stirred in anhydrous DMA (2 mL) for 2–4 h (**DPP 1**, 2 h; **DPP 2–8** and **10–16**, 4 h) at 100–110 °C (**DPP 1–8** and **16**, 110 °C; **DPP 10–15**, 100 °C) under a nitrogen atmosphere in a Schlenk tube. After cooling to room temperature, the mixture was poured into a 150 mL aqueous solution of NaCl to remove the salts and high boiling point solvent DMA. The precipitate was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with distilled water and dried over $MgSO_4$. Removal of the ethyl acetate by a rotary evaporator afforded the crude products, which were then purified by column chromatography on silica gel using the mixture of CH_2Cl_2 and petroleum ether as eluent and gave the product.

For **DPP 9**, 2,7-dibromo-9-(2-ethylhexyl)-9*H*-carbazole (0.2 mmol), **DPP 1c** (0.5 mmol), reaction time 10 h, reaction temperature 110 °C. The other conditions were similar to those above.

For **DPP 17**, **DPP 1d** (132 mg, 0.2 mmol), **DPP 1c** (300 mg, 0.5 mmol), reaction time 12 h, reaction temperature 110 °C. The other conditions were similar to those above.

DPP 1 (*2,5-bis(2-ethylhexyl)-3,6-bis(5-phenylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). Using CH_2Cl_2 and petroleum ether (2 : 1, v/v) as eluent gave a dark purple crystalline solid (129 mg, 96% yield), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (d, J = 4.1 Hz, 2H), 7.68 (dd, J = 7.1, 1.0 Hz, 4H), 7.51–7.29 (m, 8H), 4.16–4.00 (m, 4H), 1.94 (d, J = 5.9 Hz, 2H), 1.58–1.15 (m, 16H), 0.99–0.70 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.75, 149.67, 139.91, 136.78, 133.20, 129.16, 128.84, 128.81, 126.14, 124.49, 108.21, 45.99, 39.24, 30.35, 28.57, 23.70, 23.10, 14.05, 10.58; MALDI-TOF MS (m/z): $[M]^+$ calcd for $C_{42}H_{48}N_2O_2S_2$, 676.9727; found, 676.3343; elemental analysis: calcd for $C_{42}H_{48}N_2O_2S_2$, C, 74.52; H, 7.15; N, 4.14%. Found: C, 74.54; H, 7.14; N, 4.12%.

DPP 2 (*2,5-bis(2-ethylhexyl)-3,6-bis(5-(p-tolyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). Using CH_2Cl_2 and petroleum ether (2 : 1, v/v) as eluent gave a dark purple crystalline solid (132 mg, 94% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (d, J = 3.9 Hz, 2H), 7.57 (d, J = 8.0 Hz, 4H), 7.43 (d, J = 4.1 Hz, 2H), 7.24–7.19 (m, 4H), 4.13–3.95 (m, 4H), 2.40 (s, 6H), 1.94 (d, J = 5.5 Hz, 2H), 1.38–1.27 (m, 16H), 0.89 (dt, J = 13.9, 7.3 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.80, 149.96, 139.90, 139.05, 136.84, 130.50, 129.87, 128.37, 126.07, 124.02, 108.10, 45.99, 39.27, 30.39, 29.74, 28.66, 23.74, 23.15, 21.36, 14.10, 10.63; MALDI-TOF MS (m/z): $[M]^+$ calcd for $C_{44}H_{52}N_2O_2S_2$, 705.0259; found, 705.3841; elemental analysis: calcd for $C_{44}H_{52}N_2O_2S_2$, C, 74.96; H, 7.43; N, 3.97%. Found: C, 74.86; H, 7.42; N, 3.98%.

DPP 3 (*2,5-bis(2-ethylhexyl)-3,6-bis(5-(4-(trifluoromethyl) phenyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). Using CH_2Cl_2 and petroleum ether (2 : 1, v/v) as eluent gave a dark purple crystalline solid (149 mg, 92% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (dd, J = 12.7, 6.9 Hz, 2H), 7.79 (d, J = 8.2 Hz, 4H), 7.70–7.68 (m, 4H), 7.55–7.54 (d, 2H), 4.17–3.90 (m, 3H), 1.93 (d, J = 5.5 Hz, 2H), 1.47–1.28 (m, 16H), 0.94–0.87 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.65, 147.45, 139.84, 136.67, 136.46, 130.05, 126.24, 126.17, 125.72, 125.00, 122.83, 108.70, 46.03, 39.29, 30.37, 28.56, 23.72, 23.08, 14.05, 10.58; MALDI-TOF MS (*m*/*z*): $[M]^+$ calcd for $C_{44}H_{46}F_6N_2O_2S_2$, 812.9687; found, 813.3820; elemental analysis: calcd for $C_{44}H_{46}F_6N_2O_2S_2$, C, 65.01; H, 5.70; N, 3.45%. Found: C, 65.12; H, 5.72; N, 3.48%.

DPP 4 (*2,5-bis(2-ethylhexyl)-3,6-bis(5-(4-nitrophenyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). Using CH_2Cl_2 and petroleum ether (3 : 1, v/v) as eluent gave a dark blue crystalline solid (138 mg, 91% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (d, J = 4.2 Hz, 2H), 8.29 (d, J = 8.8 Hz, 4H), 7.82 (d, J = 8.8 Hz, 4H), 7.62 (d, J = 4.2 Hz, 2H), 4.08 (t, J = 7.2 Hz, 4H), 1.91 (s, 2H), 1.41–1.20 (m, 16H), 0.90 (dt, J = 14.0, 7.3 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.58, 147.42, 146.29, 139.79, 139.10, 136.79, 131.17, 126.83, 126.45, 124.65, 109.15, 46.07, 39.33, 30.35, 28.56, 23.71, 22.70, 14.11, 10.58; MALDI-TOF MS (*m*/*z*): $[M]^+$ calcd for $C_{42}H_{46}N_4O_6S_2$, 766.2859; found, 766.4314; elemental analysis: calcd for $C_{42}H_{46}N_4O_6S_2$, C, 65.77; H, 6.05; N, 7.30%. Found: C, 65.65; H, 6.07; N, 7.29%.

DPP 5 (*3,6-bis(5-(2,6-difluorophenyl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). Using CH_2Cl_2 and petroleum ether (2 : 1, v/v) as eluent gave a dark purple crystalline solid (139 mg, 93% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (d, J = 4.2 Hz, 2H), 7.76 (d, J = 4.2 Hz, 2H), 7.34–7.23 (m, 2H), 7.04 (t, J = 8.8 Hz, 4H), 4.16–3.97 (m, 4H), 1.94 (d, J = 5.6 Hz, 2H), 1.49–1.25 (m, 16H), 0.93–0.84 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.73, 160.78 (d), 158.76 (d), 140.09, 135.55, 134.99 (d), 130.41 (t), 129.25 (t), 112.18 (dd), 111.44 (t), 108.67, 46.09, 39.35, 30.31, 28.46, 23.64, 23.12, 14.02, 10.50; MALDI-TOF MS (*m*/*z*): $[M]^+$ calcd for $C_{42}H_{44}F_4N_2O_2S_2$, 748.9346; found, 749.1391; elemental analysis: calcd for $C_{42}H_{44}F_4N_2O_2S_2$, C, 67.36; H, 5.92; N, 3.74%. Found: C, 67.39; H, 5.93; N, 3.72%.

DPP 6 (*2,5-bis(2-ethylhexyl)-3,6-bis(5-(perfluorophenyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). Using CH_2Cl_2 and petroleum ether (2 : 1, v/v) as eluent gave a dark purple crystalline solid (154 mg, 90% yield), ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (dt, J = 4.2, 1.1 Hz, 2H), 7.71 (d, J = 4.3 Hz, 2H), 4.06 (dd, J = 7.7, 3.2 Hz, 4H), 1.90 (s, 2H), 1.47–1.25 (m, 16H), 0.99–0.83 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.68, 160.36, 145.18, 143.29, 139.91, 137.27, 135.51, 131.78, 131.17, 109.07, 46.13, 39.41, 30.33, 28.45, 23.58, 23.08, 13.97, 10.39; MALDI-TOF MS (*m*/*z*): $[M]^+$ calcd for $C_{42}H_{38}F_{10}N_2O_2S_2$, 856.8774; found, 856.9487; elemental analysis: calcd for $C_{42}H_{38}F_{10}N_2O_2S_2$, C, 58.87; H, 4.47; N, 3.27%. Found: C, 58.67; H, 4.49; N, 3.24%.

DPP 7 (*3,6-bis(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-2,5-bis(2-ethyl hexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). Using CH_2Cl_2 and petroleum ether (2 : 1, v/v) as eluent gave a dark purple crystalline solid (190 mg, 95% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 2H), 7.52 (d, J = 5.4 Hz, 4H), 7.36 (d, J = 3.8 Hz, 2H), 7.28 (dd, J = 16.6, 8.8 Hz, 8H), 7.18–7.02 (m, 16H), 4.20–3.82 (m, 4H), 1.94 (d, J = 5.6 Hz, 2H), 1.39–1.25 (m, 16H), 0.92–0.84 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.56, 147.10, 139.66, 137.04, 129.44, 127.90, 126.93, 125.00, 123.68, 122.82, 45.98, 39.22, 30.31, 28.52, 23.68, 23.11, 14.08, 10.61; MALDI-TOF MS (*m*/*z*): $[M]^+$ calcd for $C_{66}H_{66}N_4O_2S_2$, 1011.3858; found, 1011.1261; elemental analysis: calcd for $C_{66}H_{66}N_4O_2S_2$, C, 78.38; H, 6.58; N, 5.54%. Found: C, 78.27; H, 6.55; N, 5.58%.

DPP 8 (*2,5-bis(2-ethylhexyl)-3,6-bis(5-(pyren-1-yl)thiophen-2-yl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). Using CH_2Cl_2 and petroleum ether (2 : 1, v/v) as eluent gave a dark purple crystalline solid (170 mg, 92% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (d, J = 3.9 Hz, 2H), 8.57 (d, J = 9.3 Hz, 2H), 8.29–8.21 (m, 6H), 8.21–7.99 (m, 10H), 7.60 (d, J = 3.9 Hz, 2H), 4.28–3.85 (m, 4H), 2.06 (d, J = 5.4 Hz, 2H), 1.42–1.26 (m, 16H), 0.98–0.87 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.87, 148.47, 140.08, 136.31, 131.67, 131.42, 130.86, 130.40, 129.40, 128.99, 128.55, 128.26, 128.17, 128.15, 127.27, 126.37, 125.76, 125.42, 125.10, 124.69, 124.65, 124.47, 108.18, 46.11, 39.38, 30.36, 28.55, 23.69, 23.15, 14.09, 10.61; MALDI-TOF MS (*m*/*z*): $[M]^+$ calcd for $C_{62}H_{56}N_2O_2S_2$, 925.2502; found, 925.5685; elemental analysis: calcd for $C_{62}H_{56}N_2O_2S_2$, C, 80.48; H, 6.10; N, 3.03%. Found: C, 80.56; H, 6.14; N, 3.10%.

DPP 9 (*6,6′-(5,5′-(9-(2-ethylhexyl)-9H-carbazole-2,7-diyl)bis-(thiophene-5,2-diyl))bis(2,5-bis(2-ethylhexyl)-3-(5-phenylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). Using CH_2Cl_2 and petroleum ether (3 : 1, v/v) as eluent gave a dark blue crystalline solid (264 mg, 90% yield, calculated from dibromo-carbazole). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (s, 2H), 8.97 (s, 2H), 8.07 (d, J = 8.2 Hz, 2H), 7.64 (s, 4H), 7.56–7.52 (m, 6H), 7.42–7.34 (m, 8H), 4.07 (m, 10H), 2.00 (d, J = 37.4 Hz, 5H), 1.41–1.25 (m, 40H), 0.97–0.88 (m, 30H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.76, 161.63, 150.71, 141.99, 139.76, 139.55, 137.22, 136.80, 135.18, 133.07, 131.05, 129.12, 128.88, 128.73, 128.63, 126.04, 124.40, 124.30, 123.02, 120.99, 117.89, 108.16, 106.15, 45.99, 39.29, 31.93, 30.36, 30.17, 29.71, 29.37, 28.61, 24.48, 23.73, 23.15, 23.02, 22.69, 14.10, 11.00, 10.50; MALDI-TOF MS (*m*/*z*): $[M]^+$ calcd for $C_{92}H_{109}N_5O_4S_4$, 1477.1410; found, 1477.0412; elemental analysis: calcd for $C_{92}H_{109}N_5O_4S_4$, C, 74.81; H, 7.44; N, 4.74%. Found: C, 74.77; H, 7.45; N, 4.75%.

DPP 10 (*5′,5‴-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(([2,2′-bithiophene]-5-carbaldehyde))*). Using CH_2Cl_2 and petroleum ether (7 : 1, v/v) as eluent gave a dark blue crystalline solid (67 mg, 45% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (d, J = 19.5 Hz, 2H), 8.86 (d, J = 3.6 Hz, 2H), 7.64 (d, J = 3.1 Hz, 2H), 7.46–7.37 (m, 4H), 3.98 (d, J = 22.1 Hz, 4H), 1.88 (s, 2H), 1.35–1.25 (m, 16H), 0.83 (dd, J = 18.5, 11.0 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.34, 161.35, 145.10, 143.06, 140.83, 139.40, 137.05, 136.66, 130.43, 127.01, 125.50, 109.21, 46.04, 39.29, 30.29, 29.70, 28.46, 23.67, 23.07, 14.06, 10.54; MALDI-TOF MS (*m*/*z*): $[M]^+$ calcd for $C_{40}H_{44}N_2O_4S_4$, 745.0484; found, 745.3813; elemental analysis: calcd for $C_{40}H_{44}N_2O_4S_4$, C, 64.48; H, 5.95; N, 3.76%. Found: C, 64.54; H, 5.97; N, 3.69%.

DPP 11 (*diethyl-5′,5‴-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2′-bithiophene]-5-carboxylate)*). Using CH_2Cl_2 and petroleum ether (6 : 1, v/v) as

eluent gave a dark blue crystalline solid (88 mg, 53% yield), ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 8.91 (d, J = 4.1 Hz, 2H), 7.72 (d, J = 3.9 Hz, 2H), 7.39 (d, J = 3.9 Hz, 2H), 7.26 (d, J = 4.1 Hz, 2H), 4.37 (q, J = 7.1 Hz, 4H), 3.95–4.10 (m, 4H), 1.82–1.97 (m, 2H), 1.21–1.46 (m, 22H), 0.82–0.98 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 161.99, 161.73, 142.49, 141.57, 139.65, 136.87, 134.38, 133.73, 129.76, 126.34, 125.36, 109.09, 61.70, 46.12, 39.52, 30.58, 28.77, 23.92, 23.33, 14.56, 14.30, 10.79; MALDI-TOF MS (m/z): $[M]^+$ calcd for $C_{44}H_{52}N_2O_6S_4$, 833.1535; found, 833.8249; anal. calcd for $C_{44}H_{52}N_2O_6S_4$: C, 63.43; H, 6.29; N, 3.36%. Found: C, 63.54; H, 6.27; N, 3.21%.

DPP 12 (*dihexyl-5′,5‴-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2′-bithiophene]-5-carboxylate)*). Using CH_2Cl_2 and petroleum ether (6 : 1, v/v) as eluent gave a dark blue crystalline solid (88 mg, 47% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, J = 4.1 Hz, 2H), 7.73 (d, J = 3.9 Hz, 2H), 7.41 (d, J = 4.1 Hz, 2H), 7.28 (d, J = 3.9 Hz, 2H), 4.31 (t, J = 6.7 Hz, 4H), 4.04 (s, 4H), 1.93 (s, 2H), 1.76 (m, 4H), 1.39–1.25 (m, 28H), 0.89 (dt, J = 20.1, 7.1 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.85, 161.56, 142.25, 141.38, 136.62, 134.14, 133.60, 129.55, 126.15, 125.19, 108.91, 65.64, 46.02, 39.30, 31.42, 30.34, 29.69, 28.64, 28.58, 25.61, 23.69, 23.09, 22.53, 14.03, 10.55; MALDI-TOF MS (m/z): $[M]^+$ calcd for $C_{52}H_{68}N_2O_6S_4$, 945.3661; found, 944.8873; elemental analysis: calcd for $C_{52}H_{68}N_2O_6S_4$, C, 66.07; H, 7.25; N, 2.96%. Found: C, 66.10; H, 7.26; N, 2.89%.

DPP 13 (*5′,5‴-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(([2,2′-bithiophene]-5-carbonitrile))*). Using CH_2Cl_2 and petroleum ether (6 : 1, v/v) as eluent gave a dark blue crystalline solid (67 mg, 46% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (d, J = 4.1 Hz, 2H), 7.58 (d, J = 3.9 Hz, 2H), 7.41 (d, J = 4.2 Hz, 2H), 7.30 (m, 2H), 3.96 (t, J = 8.1 Hz, 4H), 1.60 (d, J = 5.5 Hz, 2H), 1.25–1.10 (m, 16H), 0.93–0.85 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.46, 142.87, 139.53, 139.41, 138.36, 136.46, 130.32, 126.90, 124.67, 113.72, 109.24, 109.18, 46.03, 39.30, 30.30, 28.45, 23.65, 22.99, 14.04, 10.54; MALDI-TOF MS (m/z): $[M]^+$ calcd for $C_{40}H_{42}N_4O_2S_4$, 739.0471; found, 739.3151; elemental analysis: calcd for $C_{40}H_{42}N_4O_2S_4$, C, 65.01; H, 5.73; N, 7.58%. Found: C, 64.95; H, 5.71; N, 7.60%.

DPP 14 (*5,5′-((2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(4,1-phenylene))bis(thiophene-2-carbaldehyde)*). Using CH_2Cl_2 and petroleum ether (7 : 1, v/v) as eluent gave a dark red crystalline solid (109 mg, 75% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (s, 2H), 7.85 (d, J = 8.4 Hz, 4H), 7.75 (dd, J = 10.9, 6.1 Hz, 6H), 7.46 (d, J = 3.9 Hz, 2H), 3.77 (dd, J = 7.1, 4.8 Hz, 4H), 1.25 (s, 2H), 1.10 (m, 16H), 0.78–0.71 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.73, 162.57, 152.54, 147.81, 143.28, 137.25, 135.19, 129.53, 129.09, 126.47, 124.99, 110.24, 45.06, 38.54, 30.32, 28.26, 23.77, 22.83, 13.93, 10.42; MALDI-TOF MS (m/z): $[M]^+$ calcd for $C_{44}H_{48}N_2O_4S_2$, 732.9929; found, 733.1593; elemental analysis: calcd for $C_{44}H_{48}N_2O_4S_2$, C, 72.10; H, 6.60; N, 3.82%. Found: C, 72.15; H, 6.58; N, 3.81%.

DPP 15 (*diethyl-5,5′-((2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(4,1-phenylene))bis(thiophene-2-carboxylate)*). Using CH_2Cl_2 and petroleum ether (7 : 1, v/v) as eluent gave an orange crystalline solid (98 mg, 60% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 4H), 7.72 (dd, J = 13.8, 6.1 Hz, 6H), 7.33 (d, J = 3.9 Hz, 2H), 4.39 (q, J = 7.1 Hz, 4H), 3.77 (dd, J = 7.0, 4.6 Hz, 4H), 1.60 (s, 2H), 1.38 (dt, J = 14.3, 6.4 Hz, 6H), 1.26–1.10 (m, 16H), 0.87–0.66 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.60, 162.02, 149.49, 147.86, 135.61, 134.19, 133.61, 129.44, 128.40, 126.10, 124.42, 110.02, 61.32, 45.00, 38.47, 30.30, 28.24, 23.76, 22.83, 14.35, 13.93, 10.42; MALDI-TOF MS (m/z): $[M]^+$ calcd for $C_{48}H_{56}N_2O_6S_2$, 821.0980; found, 821.2950; elemental analysis: calcd for $C_{48}H_{56}N_2O_6S_2$, C, 70.21; H, 6.87; N, 3.41%. Found: C, 70.17; H, 6.84; N, 3.43%.

DPP 16 (*2,5-bis(2-hexyldecyl)-3,6-bis(pentafluoro-[1,1′-biphenyl]-4-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione*). Using CH_2Cl_2 and petroleum ether (2 : 1, v/v) as eluent gave a bright yellow solid (203 mg, 95% yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 4H), 7.56 (d, J = 8.1 Hz, 4H), 3.77 (d, J = 7.3 Hz, 4H), 1.47 (d, J = 45.5 Hz, 2H), 1.25–1.15 (m, 48H), 0.86–0.80 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.60, 148.01, 145.13, 143.19, 138.87, 136.97, 130.57, 129.32, 128.97, 128.87, 110.27, 45.35, 37.27, 31.88, 31.68, 31.29, 31.33, 29.87, 29.64, 29.52, 29.42, 29.35, 26.14, 26.08, 22.62, 14.09, 14.05; MALDI-TOF MS (m/z): $[M]^+$ calcd for $C_{62}H_{74}F_{10}N_2O_2$, 1069.2472; found, 1069.2670; elemental analysis: calcd for $C_{62}H_{74}F_{10}N_2O_2$, C, 69.64; H, 6.98; N, 2.62%. Found: C, 69.56; H, 6.92; N, 2.64%.

DPP 17 (*6,6′-(5,5′-((2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(4,1-phenylene))bis(thiophene-5,2-diyl))bis(2,5-bis(2-ethylhexyl)-3-(5-phenylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione)*). Using CH_2Cl_2 and petroleum ether (4 : 1, v/v) as eluent gave a dark blue solid (324 mg, 95% yield, calculated from **DPP 1d**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 2H), 8.74 (s, 2H), 7.70 (d, J = 8.0 Hz, 4H), 7.52–7.45 (m, 8H), 7.35–7.29 (m, 8H), 7.13 (s, 2H), 4.05–3.95 (m, 8H), 3.70–3.60 (m, 4H), 1.87–1.83 (m, 4H), 1.64 (s, 2H), 1.38–1.25 (m, 32H), 1.10–0.99 (m, 16H), 0.90–0.80 (m, 24H), 0.77–0.70 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.29, 161.16, 161.05, 149.61, 147.85, 140.03, 138.37, 137.32, 135.92, 134.72, 133.00, 130.24, 129.77, 128.96, 128.86, 128.53, 127.91, 125.84, 125.04, 124.78, 124.04, 109.31, 108.35, 107.75, 45.94, 44.36, 39.20, 38.01, 30.36, 29.69, 28.66, 28.28, 23.77, 23.18, 23.09, 22.85, 14.08, 13.93, 10.67, 10.46; MALDI-TOF MS (m/z): $[M]^+$ calcd for $C_{106}H_{126}N_6O_6S_4$, 1710.4471; found, 1710.3909; elemental analysis: calcd for $C_{106}H_{126}N_6O_6S_4$, C, 74.52; H, 7.43; N, 4.92%. Found: C, 74.43; H, 7.40; N, 4.89%.

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