Broadly Applicable Synthesis of Arylated Dithieno[3,2-b:2’,3’-d]pyrroles as Building Blocks for Organic Electronic Materials

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Abstract: A novel and versatile method for the N-arylation of dithieno[3,2-b:2’,3’-d]pyrrole (DTP) is presented. By Pd- or Cu-catalyzed coupling a variety of aryls and acenes were directly attached at the DTP–nitrogen yielding a variety of functionalized DTPs. Investigations on optical and redox properties led to valuable structure-property relationships, which were corroborated by quantum chemical calculations. Further functionalization and elongation of the conjugation of an acceptor-substituted DTP was elaborated to result in complex cruciform-type donor–acceptor oligomers, which were investigated and implemented in single material organic solar cells.

Introduction

Dithieno[3,2-b:2’,3’-d]pyrroles (DTP) represent an interesting multi-functional and electron-rich building block for organic semiconductors, for example, as donor unit in low bandgap donor–acceptor polymers[11] or conjugated oligomers,[2,3] which are applied in organic electronic devices, in particular in organic solar cells.[4] Due to the reactive α-positions, DTPs can be oxidatively polymerized into conductive polymers,[5] which for example can be applied as electrode material in rechargeable batteries.[6,7] The frequently used N-alkyl and N-aryl DTPs are effectively synthesized via Pd-catalyzed Buchwald-Hartwig amination/cyclization of 3,3’-dibromo-2,2’-bithiophene precursors and alkyl or aryl amines to form the central pyrrole ring (Scheme 1).[8,9] In this respect, some N-phenylated DTPs have been described, whereby only very few examples of DTPs bearing larger aryls or polycyclic aromatic hydrocarbons such as truxene[10] or 1-naphthalene[11] are known.

We have recently disclosed a straightforward and safe method for the large-scale synthesis of basic 4H–dithieno[3,2-b:2’,3’-d]pyrrole 1 (H–DTP).[11] This progress now allowed us to test and optimize the synthesis of a variety of arylated DTPs comprising larger aryls and acenes by Pd- or Cu-catalyzed coupling of H–DTP 1 and well available aryl and acene halides 2a–k (Scheme 1). The resulting N-arylated and N-acene-substituted DTPs represent interesting building blocks for functional materials applicable in organic electronics.

Results and Discussion

4H–DTP 1 can be seen as electron-rich analogue of 9H-carbazole and intermediate 8H–thieno[3,2-b]indole. Direct N-arylations are well known for carbazole derivatives, which are well represented in natural products or in organic materials. Typical methods include reaction of carbazole with diaryliodonium salts without metal catalysts,[12] with aryl halides and Cu-catalysis (CuI),[13] or Pd-catalysis (Pd(dba₂/ligand).[14] Mostly phenyl substituents were coupled, but sterically hindered aryls[15] or heteroaryl[13a-1] could only very rarely be attached. With respect to thienoindoles only one example is known, and Driver et al. described the coupling of the heteroacene and 1-bromo-4-butylbenzene with the catalyst system Pd(OAc)₂/Bu₃P. The resulting N-arylated thienoindole was used as a building block for the preparation of heteroheptacenes with good charge transport properties.[15] As in the case of arylated DTPs, a broad series of corresponding thienoindoles were prepared by Langer et al. by Buchwald-Hartwig amination of dibrominated...
Discarded diaryliodonium salts as arylation reagents (see above), 'inverse' arylation of phenyl halides and tosylate as model reagents under Pd(OAc)$_2$ to screen the possible catalyst system and the leaving group of because the scope of available derivatives is restricted. In order to screen the possible catalyst system and the leaving group of the arylation reagent, H−DTP 1 was firstly reacted various phenyl halides and tosylate as model reagents under Pd(OAc)$_2$ catalysis and NaOTBu as base in toluene. A brief screening of the ligand revealed tBu$_2$P > tBuXPhos > P(o-Tol)$_2$ and of the substrate Br > I > Cl > OTos (Table S1, Supporting Information). In the following, we therefore used the well available broad scope of arylation reagents and acene bromides. Thus, the arylation of H−DTP 1 with 2-bromo-1,1′-biphenyl 2f and DTP 3f could be isolated in lower 33% yield mostly due to steric hindrance of the biphenyl unit in the catalytic cycle. In the following, we reacted acene bromides 2g and 2h with H−DTP 1 yielding 2-naphthyl−DTP 3g and 2-anthryl−DTP 3h. Here, Pd$_2$dba$_2$/tBu$_2$P gave slightly better results compared to the other catalysts. We also tested functionalized and electron-deficient acene bromides, among them 4-bromo-1,8-naphthalimide 2i (N−Anh), N-hexyl-4-bromo-1,8-naphthalimide 2j.

Although N-phenyl DTP 3a can be conveniently prepared via amination of 3,3′-dibromo-2,2′-bithiophene and aniline in 84% yield, we investigated in initial studies the alternative 'inverse' arylation of H−DTP 1 as amine precursor. A priori, we discarded diaryliodonium salts as arylation reagents (see above), because the scope of available derivatives is restricted. In order to screen the possible catalyst system and the leaving group of the arylation reagent, H−DTP 1 was firstly reacted with various phenyl halides and tosylate as model reagents under Pd(OAc)$_2$ catalysis and NaOTBu as base in toluene. A brief screening of the ligand revealed tBu$_2$P > tBuXPhos > P(o-Tol)$_2$ and of the substrate Br > I > Cl > OTos (Table S1, Supporting Information). In the following, we therefore used the well available broad scope of arylation reagents and acene bromides. Thus, the reaction of H−DTP 1 and bromobenzene 2a Ph−DTP 3a was isolated in 78% yield with the catalytic system Pd(OAc)$_2$/tBu$_2$P.

The change to Pd$_2$dba$_2$/tBu$_2$P or Cul under microwave-assisted conditions as catalysts gave slightly higher or the same yield. Having established the frame conditions, we then examined the scope of the arylation of H−DTP 1 and further tested additional electronically and sterically different aryl and acene bromides 2b–2k with all three catalytic systems. The results are compiled in Table 1.

As with bromobenzene 2a, the aryl substrates 2b–e bearing electron-donating (2b), electron-withdrawing (2c), and extended conjugated π-systems (2d–e) readily reacted with H−DTP 1 to the targeted arylated DTPs 3b–e in acceptable to good yields (52–94%) with moderate variations for the three catalysts. In particular, Cul was the only catalyst to promote reaction of H−DTP 1 with 2-bromo-1,1′-biphenyl 2f and DTP 3f could be isolated in lower 33% yield most probably due to steric hindrance of the biphenyl unit in the catalytic cycle. In the following, we reacted acene bromides 2g and 2h with H−DTP 1 yielding 2-naphthyl−DTP 3g and 2-anthryl−DTP 3h. Here, Pd$_2$dba$_2$/tBu$_2$P gave slightly better results compared to the other catalysts. We also tested functionalized and electron-deficient acene bromides, among them 4-bromo-1,8-naphthalimide 2i (N−Anh), N-hexyl-4-bromo-1,8-naphthalimide 2j.

Table 1. Arylation reaction of H−DTP 1 with aryl bromides 2a–k to arylated DTPs 3a–k.[a]

| Ar-Br | [Pd] (0–94%) | [Cu] (0–94%) |
|-------|-------------|-------------|
| 2a | 78% (76%/76%) |
| 2b | 54% (89%/61%) |
| 2c | 59% (85%/52%) |
| 2d | 66% (87%/69%) |
| 2e | 72% (94%/72%) |
| 2f | 0% (0%/33%) |
| 2g | 59% (89%/87%) |
| 2h | 41% (61%/45%) |
| 2i | 11% (18%/0%) |
| 2j | 64% (93%/45%) |
| 2k | 69% (59%/9%) |

[a] Yields are given as isolated yields of purified substance with Pd(OAc)$_2$/tBu$_2$P, Pd$_2$dba$_2$/tBu$_2$P, Cul/microwave as catalyst. Detailed conditions are given in the experimental part.
(N–Imi), and extended 9-bromoperylene-3,4-dicarboximide (PDCI) 2k. Whereas anhydride 2i reacted very slowly and gave only low yields of DTP 3i with the Pd-catalysts, no reaction with CuI was observed. Dicarboximides 2j and 2k were much more reactive and were converted to corresponding covalently linked push-pull donor (D)-acceptor (A) DTPs 3j and 3k in good to excellent yields after purification. These promising results prompted us to further investigate in particular PDCI–DTP 3k as building block for the synthesis of advanced photoactive materials and their application in single material organic solar cells (see below).

The use of various catalytic systems and various aryl and acene bromides showed that Pd$_2$(dba)$_3$/tBu$_3$P had the broadest applicability with continuous good to excellent yields. The other Pd-catalyst Pd(OAc)$_2$/tBu$_3$P is as well broadly applicable, but by trend give somewhat lower yields. The only exception in the series was the completely failed reaction of sterically hindered 2-bromo-1,1'-biphenyl 2f with H–DTP 1, for which CuI worked to some degree. In general, CuI under microwave-assistance gave more or less equal results. The only reaction, which failed was with anhydride 2i. The structures of the novel aryl and acene-substituted DTPs 3a–3k were fully characterized by NMR-spectroscopy (Figures S1–S9, Supporting Information) and high-resolution mass spectra (HRMS) (Figures S15–S20, Supporting Information). Thus, we can conclude that with respect to electronic effects and tolerance of functional groups the presented arylation method of H–DTP 1 with aryl bromides is quite broadly applicable leading to interesting functionalized DTP derivatives. The more challenging examples, bromides 2f and 2i, could be improved further by optimizing the applied catalyst system.\[18\]

Quantum chemical DFT-calculations on DTPs

DFT calculations were performed on parent Ph–DTP 3a in comparison to PDCI–DTP 3k in order to rationalize the electronic and steric influence of the substituents on the distribution of electron density in the frontier molecular orbitals. Thus, HOMO and LUMO of Ph–DTP 3a and donor–acceptor PDCI–DTP 3k are depicted in Figure 1. Previously, it was shown that in alkyl-substituted DTPs the HOMO is only located at the DTP backbone with the nitrogen residing at a node.\[19\] Herein, the same observation was made for the DTPs under investigation and substituents only slightly influence the HOMO energy level by inductive effects. In contrast, the LUMO in Ph–DTP 3a extends over the whole molecule with the expected quinoidal reorganization of the electron density in the DTP unit. The electron-withdrawing perylene dicarboximide residue in PDCI–DTP 3k strongly influences the LUMO, which is fully localized on the π-conjugated part of the PDCI moiety (Figure 1). Whereas the calculated torsion angle of the phenyl unit versus the DTP plane amounts to 37°, the respective calculated angle with the more sterically demanding PDCI-substituent is 51°.

Optical and redox properties of arylated DTPs 3a–3k

Optical investigations on the various arylated DTPs were performed by UV-vis absorption spectra in THF solution. Representative absorption spectra of DTPs 3a, 3f, and 3h are depicted in Figure 2 (left) and full data is listed in Table 2. In general, all DTPs exhibited a strong, mostly structured absorption band in the UV-regime between 275–325 nm, which we address to the π–π* transition of the DTP unit and corresponds to the HOMO-LUMO energy gap. The absorption maximum for this transition is gradually red-shifted from 294 nm for parent...
H–DTP 1 to 320 nm for fluorenyl–DTP 3e due to increasing conjugation of the substituent at the nitrogen. Substituents with extended $\pi$-conjugation superimpose their specific absorption signature, which is most prominent for 2-anthryl derivative 3h (Figure 2, left). The strong absorption band at 256 nm and the weaker absorption at 343 nm, 361 nm, 376 nm, and 394 nm can be attributed to the anthracene unit.\[20\]

Sterical hindrance works in the opposite direction which can be seen for biphenyls 3d and 3f. Whereas linear 4'-substituted biphenyl in 3d exerts additional conjugation to the system and absorbs at 311 nm, the sterically hindered and twisted 2'-biphenyl in 3f blue-shifts the main absorption band to 297 nm and an additional band at 245 nm arises due to the biphenyl unit (Figure 2, left).

On the other hand, electron-withdrawing units in DTPs 3i, 3j, and 3k cause substantial red-shifts of the longest wavelength band up to 513 nm for 3k due to partial charge-transfer character in the transition (Figure 4, left). A smaller red-shift of around 20 nm...
can be seen for the main absorption of cyanophenyl–DTP 3c compared to Ph–DTP 3a, whereas the electron-donating anisyl-substituent in MeOPh–DTP 3b practically does not influence absorption. This effect can be rationalized with the findings from electrochemistry and quantum chemical calculations (see below). Accordingly, the optical energy gaps $E_{opt}$ of the acceptor-substituted DTPs are substantially lower compared to the arylated derivatives.

In order to get information about the redox properties and energetics of the frontier orbitals, arylated DTPs 3a–3k were studied by cyclic voltammetry in dichloromethane and tetrabutylammonium hexafluorophosphate (0.1 M) as electrolyte and all potentials were referenced against the ferrocene/ferriocinium couple (Fc/Fc'). Representative examples are depicted in Figure 2 (right) and data is compiled in Table 3. All derivatives gave irreversible oxidation waves due to the reactive α-positions of the DTP unit and the follow-up polymerization of the radical cations to form conducting DTP–polymers.[23] The peak potentials vary in a relatively small window from 0.49 V for Ph–DTP 3a to 0.75 V for naphthalic anhydride 3i. In the reductive potential regime, acceptor-substituted DTPs 3i, 3j, and 3k showed reversible reduction waves at $-1.57 \text{ V}$, $-1.78 \text{ V}$, and $-1.40 \text{ V}$ due to the formation of stable radical anions according to the acceptor strength (Figure 2, right). In this respect, the measurements showed that the anhydride residue in DTP 3i represents the stronger electron-withdrawing group compared to the corresponding alkylic dicyanobenzoimide in DTP 3j.

HOMO energy levels were determined from the onset of the oxidation wave and are only marginally influenced by the substituents and range from $-5.49 \text{ eV}$ to $-5.72 \text{ eV}$ due to a node at the DTP–nitrogen in this orbital. On the contrary, the LUMO energies are substantially influenced by the electron-withdrawing power of the aryl and acen groups. With increasing acceptor strength, the LUMO is increasingly destabilized and energies decrease from $-1.54 \text{ eV}$ for Ph–DTP 3a to $-3.79 \text{ eV}$ for PDCI–DTP 3k concomitant with a decrease of the electrochemical energy gap $E_{opt}$ from 3.95 eV to 1.88 eV. A resulting schematic energy level diagram of the frontier orbitals and the optical transitions in the series of investigated DTPs 3a–3k was derived and is shown in Figure 3.

**Synthesis of ambipolar donor–acceptor dyads for organic electronic application**

As already mentioned, DTP-units have been frequently used as building block in conjugated materials for application in organic electronics, in particular for organic solar cells.[14] In this respect, over the years we have developed DTP-based co-oligomers, which in conjunction with fullerene acceptors (PCBM) reached power conversion efficiencies (PCE) of 7–8% in solution-processed bulk-heterojunction organic solar cells (BHJ-OSC).[21] In order to further develop this structural concept, we implemented PDCI–DTP 3k as a core unit into enlarged oligomers, which are terminated with dicyanovinylene (DCV) acceptor groups and should strongly absorb in the visible regime of the solar spectrum. For the synthesis of enlarged D–A oligomers, PDCI–DTP 3k was brominated at the α-positions with NBS to give dibromo–DTP 4 in 96% yield, which was subsequently coupled with various stannylated dicyanovinylene (DCV)-substituted thiophene and bithiophene units (Scheme 2). In this respect, DTP 4 was reacted with stannylated thiophene S[23] under Pd-catalysis in a Stille-type coupling reaction to give D–A dyad 6 in 57% yield. Due to the resulting moderate solubility hexyl side chains were implemented at the outer thiophene units and DTP 4 was reacted with the corresponding 3-hexyl derivative 7[21] to give analogous D–A dyad 8 in 31% yield. Further enlargement of the donor moiety with additional 3-hexylthiophene units was obtained by reaction of brominated PDCI–DTP 4 and stannylated DCV–bithiophene 10, which was synthesized in 74% yield from corresponding aldehyde 9 and malononitrile. Cruciform-type D–A dyad 11 was isolated as a black solid in moderate 14% yield after purification. Structures and purities of D–A dyads 6, 8, and 11 were fully characterized by NMR-spectroscopy (Figures S10–S14, Supporting Information) and HRMS (Figures S21–S25, Supporting Information).

The optical properties of D–A dyads 6, 8, and 11 were determined by UV-vis absorption in dichloromethane solution and spectra are shown in comparison to those of basic DTP 3k and substituent PDCI in Figure 4 (left), data is collected in Table 4. The absorption spectra reflect more or less the specific absorptions of the subunits, which are superimposed. The spectra are dominated by the strong absorptions of the PDCI.

| Table 3. Electrochemical data of arylated DTPs 3a–3k. |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| DTP            | R              | $E^{\text{Onset}}$ | $E^{\text{Red 1/2}}$ | $E^{\text{Red 1/2}}$ | $E^{\text{HOMO}}$ | $E^{\text{LUMO}}$ |
| 3a             | Ph             | 0.49            | –               | –               | –              | –              | 3.95            |
| 3b             | MeOPh          | 0.56            | 0.48            | –               | –              | –              | 3.84            |
| 3c             | NCPH           | 0.65            | 0.56            | –               | –              | –              | 3.65            |
| 3d             | 4′-BPh         | 0.74            | 0.58            | –               | –              | –              | 3.70            |
| 3e             | Flu            | 0.71            | 0.57            | –               | –              | –              | 3.62            |
| 3f             | 2′-BPh         | 0.60            | 0.50            | –               | –              | –              | 3.83            |
| 3g             | 2-Naph         | 0.64            | 0.54            | –               | –              | –              | 3.50            |
| 3h             | 2-Anth         | 0.64            | 0.56            | –               | –              | –              | 2.99            |
| 3i             | N-Anh          | 0.75            | 0.62            | $-1.57$         | $-1.49$        | $-5.72$        | 2.11            |
| 3j             | N-Iso          | 0.70            | 0.58            | $-1.78$         | $-1.70$        | $-5.68$        | 2.28            |
| 3k             | PDCI           | 0.71            | 0.56            | $-1.40$         | $-1.31$        | $-5.67$        | 1.88            |

[a] Onset voltage determined by applying a tangent line. [b] Calculated from the onset value of the oxidation wave; Fc/Fc' was set to $-5.1 \text{ eV}$ vs. vacuum. [c] Calculated from the onset value of the reduction wave or with $E^{\text{HOMO}}$ and $E^{\text{LUMO}}$ sol. [d] Calculated $E^{\text{HOMO}}$, $E^{\text{LUMO}}$.
acceptor unit at around 265 nm and 500–530 nm. The absorptions of the donor units rather appear as shoulders, which is at 295 nm for the DTP unit of 3k in accordance with the UV-vis spectra of the other arylated DTPs.

With increasing conjugation length of the donor block in 6, 8, and 11, these π-π* transitions, which comprise partial charge-transfer (CT) character due to the terminal DCV-substitution, appear as shoulders at lower energies of the main PDCI band and are red-shifted to 570–582 nm. These values well correlate with the main absorption bands of the corresponding DCV-substituted tetrameric[23] and hexameric[24] co-oligomers without PDCI group at the DTP unit (560–612 nm). For the longest oligomer 11 an additional band with a maximum at 397 nm is visible which corresponds to the π-π* transition of the pure oligothiophene subunit without attached DCV groups.[25]

The optical gaps, which were determined from the onset of the longest wavelength absorption, gradually decrease

| Oligomer | λ_{max}^{sol} [nm] | log ε | ε_{max}^{sol} [M^−1 cm^−1] | λ_{max}^{film} [nm] | ε_{max}^{film} [M^−1 cm^−1] | E_g [eV] |
|----------|--------------------|-------|-----------------------------|--------------------|-----------------------------|--------|
| 3k       | 266, 295, 513      | 4.57  | 2.14                        | 268, 297 (sh), 521 | 2.05                        |        |
| 6        | 264, 304, 527      | 4.97  | 1.93                        | 268, 533 (sh), 603 | 1.65                        |        |
| 8        | 264, 314, 523      | 4.94  | 1.90                        | 265, 538           | 1.77                        |        |
| 11       | 264, 397, 517      | 4.94  | 1.86                        | 265, 430 (sh), 529 | 1.61                        |        |
| PDCI     | 265, 486, 509      | 4.52  | 2.25                        | 265, 488           | 2.17                        |        |

[a] Absolute maximum is underlined, (sh) shoulder. [b] Energy gaps E_g determined by applying a tangent line and the formula E_g = 1240/λ_{onset} (nm). [c] Films were spin-coated from chloroform solution.

Table 4. Optical properties of D-A dyads 6, 8, and 11 in comparison to DTP 3k and perylene-3,4-dicarboximide (PDCI) in dichloromethane solution and in thin films.

Figure 4. UV-vis absorption spectra of D-A dyads 6 (blue), 8 (black), and 11 (red) in comparison to DTP 3k (magenta) and perylene-3,4-dicarboximide (PDCI, green) in dichloromethane solution (left); in thin films spin-coated from chloroform solution and normalized to the highest energy absorption (right).
from 2.25 eV for pure PDCI to 1.86 eV for the most extended oligomer 11.

Thin films, which were prepared by spin-coating on glass slides from chloroform solutions (Figure 4, right; Table 3), showed the typical broadening and bathochromic shift of the absorption bands compared to the solution spectra. This behavior is most pronounced for D–A dyad 11, where now the \( \pi^* - \pi \) transition of the donor part is shifted to 629 nm and promoted to the most intensive band. We address this behavior to partial ordering and \( \pi - \pi \) stacking of the oligothiophene backbone. Compared to the values determined from the solution spectra, the optical gaps are concomitantly decreased for each derivative and range from 2.17 eV for PDCI to 1.61 eV for 11.

The redox properties of D–A oligomers 6, 8, and 11 were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in dichloromethane and tetrabutylammonium hexafluorophosphate (0.1 M) as electrolyte, potentials were referenced against the ferrocene/ferricenium couple (Fc/Fc\(^+\)) and data is compiled in Table 5. Exemplarily, the CV of oligomer 11 is shown in Figure 5, while those of 6 and 8 are depicted in Figure S26 (Supporting Information). Four reversible redox waves can be identified, two in the oxidative, two in the reductive potential range. We could address the various redox waves by comparing the CVs of individual subunits. The first one-electron oxidation occurs at \( E_{1/2}^{\text{Ox1}} = 0.32 \text{ V} \), whereas the second oxidation occurs at \( E_{1/2}^{\text{Ox2}} = 0.65 \text{ V} \). The latter corresponds to the formation of stable radical cations and dications, respectively, which are located on the extended oligomeric DTP–donor part.[25] The first reduction wave at \( E_{1/2}^{\text{Red1}} = -1.46 \text{ V} \) reflects a superimposition of the reversible one-electron reduction of the PCDI-substituent[25] and the irreversible reduction of the terminal DCV groups.[26] The second reversible one-electron reduction at \( E_{1/2}^{\text{Red2}} = -1.96 \text{ V} \) is addressed to the further reduction of the PDCI unit under the formation of stable dianions.

**Photovoltaic properties of cruciform-type D–A oligomers 8 and 11 in single material organic solar cells**

Covalently linked, ambipolar molecular donor (D)-acceptor (A) dyads have been used as sole photoactive component in single material organic solar cells (SMOSC).[26] We could recently demonstrate power conversion efficiencies (PCE) of around 4% by linking the same DTP-based oligothiophene donor as in novel dyad 11 and fullerene PC\(_{61}\)BM with alkyl ester spacers of variable length.[27] However, directly connected and \( \pi \)-conjugated D–A systems have been rarely described and reached lower PCEs of 0.35% to 1.75%.[28–30] A cruciform-type D–A molecule comprising a benzodithiophene core and a calculated distortion of 56° between the D and A-axes in the molecule showed ambipolar semiconducting behavior in organic field-effect transistors.[31] In this respect, our DTP oligomer 3k, in which the PDCI acceptor is tilted by 51° with respect to the DTP donor (see above) represents an interesting alternative of a cruciform-type core system. We assume that in the related extended structures of dyads 6, 8, and 11 the PDCI unit is similarly tilted. Due to their broad and strong absorption in the

**Table 5. Electrochemical properties of D–A dyads 6, 8, and 11 in comparison to DTP 3k and perylene-3,4-dicarboximide (PDCI) in dichloromethane/tetrabutylammonium hexafluorophosphate (0.1 M) at 100 mV/s. Potentials vs. ferrocene/ferricenium (Fc/Fc\(^+\)).**

| Oligomer | \( E_{1/2}^{\text{Ox1}} \) [V] | \( E_{1/2}^{\text{Ox2}} \) [V] | \( E_{1/2}^{\text{Red1}} \) [V] | \( E_{1/2}^{\text{Red2}} \) [V] | \( E_{\text{onset}Ox} \) [V] | \( E_{\text{onsetRed}} \) [V] | \( E_{\text{peakOx}} \) [eV](a) | \( E_{\text{peakRed}} \) [eV](b) | HOMO [eV](c) | LUMO [eV](d) | \( E_{\text{CV}} \) [eV](e) |
|----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 3k       | 0.71           | -              | -              | -              | -              | -              | -1.31           | -5.66           | -3.79           | 1.87           |
| 6        | 0.66           | 1.13           | -1.34          | -1.83          | -1.22          | -5.69           | -3.88           | 1.81           |
| 8        | 0.59           | 1.06           | -1.35          | -1.83          | -1.23          | -5.63           | -3.87           | 1.76           |
| 11       | 0.32           | 0.65           | -1.46          | -1.96          | -1.32          | -5.31           | -3.78           | 1.53           |
| PDCI     | 0.95           | -              | -1.46          | -1.95          | -1.33          | -5.97           | -3.77           | 2.20           |

Data were determined by applying a tangent line. [a] Calculated from the onset value of the oxidation wave; Fc/Fc\(^+\) was set to -5.1 eV vs. vacuum. [b] Calculated from the onset value of the redox wave. [c] Calculated by \( E_{\text{onsetOx}} - E_{\text{LUMO}} \). [d] Determined by DPV. [f] Values from Ref. [25].

**Figure 5. Cyclic voltammogram of D–A dyad 11 in dichloromethane/tetrabutylammonium hexafluorophosphate (0.1 M) at 100 mV/s. Potentials vs. ferrocene/ferricenium (Fc/Fc\(^+\)).**
visible and appropriate HOMO/LUMO energy levels, these dyads should be appropriate candidates for SMOSCs.

Because oligomer 6 was only barely soluble in organic solvents, we implemented the better soluble derivatives 8 and 11 as sole photoactive component in SMOSCs with the standard device structure glass/ITO/PEDOT:PSS/dyad 8 or 11/LiF/Al. SMOSCs were built by spin-coating solutions with concentrations of 10–15 mg mL\(^{-1}\) under ambient conditions. Thereby, various solvents, additives, and post-treatment methods, such as solvent vapor annealing (SVA) or thermal annealing (TA) were tested. The best performing solar cells unfortunately showed very low performances and we could not exceed PCEs of 0.05\% for both dyads (Table 6, Supporting Information). We assume that despite beneficial optoelectronic properties, the crossed subunits of the dyads hamper a favorable arrangement of the molecules in the photoactive film for the formation of suitable channels for the separate charge transport of holes and electrons which explains the rather moderate fill factor (FF) and low photocurrent densities \(J_{SC}\). Therefore, thermal deactivation of the excitons formed under illumination and recombination of charges seem to be dominating processes. A further drawback was the moderate solubility of dyad 8 and 11 not allowing for the preparation of optimal films. From these rather disappointing results in SMOSCs, we can conclude that for good performance in SMOSCs, the connection of donor and acceptor units by flexible insulating linkers\(^{[27]}\) seems to be more favorable than a direct cruciform-type connection.

### Conclusion

In summary, we have presented a novel, direct and versatile N-arylation method of dithienopyrrole–H–DTP 1 with widely available aryl or acene bromides 2a–k by efficient Pd- or Cu-catalyzed coupling. The direct introduction of various aryls and acenes with different electronic and steric properties at the DTP nitrogen yielded intriguing functionalized DTPs 3a–k. The use of three catalytic systems, Pd(OAc)\(_2\)/Bu\(_3\)P, Pd(dbq)/Bu\(_3\)P, or Cu under microwave-assistance, showed different selectivities and provided a broad scope of products with mostly good to excellent yields. Investigations on optical and redox properties of the functionalized DTPs led to valuable structure-property relationships. Absorption spectra and cyclic voltammograms were typically a superimposition of the DTP properties and the specific signatures of the substituent. The results were corroborated by quantum chemical calculations revealing that the substituents at the DTP nitrogen have only little influence on the HOMO, whereby the distribution of electron density in the LUMO is rather delocalized on the substituent, in particular for the electron acceptors. Perylene dicarboximide-substituted DTP 3k was further elaborated to result in conjugated cruciform-type donor–acceptor oligomers, which were characterized and tested in single material organic solar cells.

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### Conflict of Interest

The authors declare no conflict of interest.

### Keywords:

cross-coupling · dithienopyrrole · heterocycles · organic solar cell · structure-property relationship

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**Table 6. Photovoltaic parameters of SMOSCs with glass/ITO/PEDOT:PSS/dyad 8 or 11/LiF/Al\(^{[a]}\)**

| Solvent   | SVA/TA         | \(V_{OC}\) [V] | \(J_{SC}\) [mA/cm\(^2\)] | FF  | PCE [%] |
|-----------|----------------|----------------|----------------------------|-----|---------|
| Dyad 8    | CF, r.t.       | 0.98 ± 0.02    | 0.21 ± 0.00                | 0.24 ± 0.00 | 0.05 ± 0.00     |
|           | (1.02)         |                | (0.21)                     | (0.24) | (0.05)   |
| Dyad 11   | CB, 80°C       | 0.72 ± 0.04    | 0.24 ± 0.01                | 0.23 ± 0.00 | 0.04 ± 0.00     |
|           | 100°C, 10 min  |                | (0.23)                     | (0.23) | (0.04)   |

\([a]\) Average values for 4 devices ± standard deviation (best value). CF = chloroform; CB = chlorobenzene.
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