■ Synthesis Design

From-Core and From-End Direct C−H Arylations: A Step-Saving New Synthetic Route to Thieno[3,4-c]pyrrole-4,6-dione (TPD)-Incorporated D–π–A–π–D Functional Oligoaryls

Po-Han Lin, Kuan-Ting Liu, and Ching-Yuan Liu*[a]

Abstract: In contrast to the traditional multistep synthesis, herein an efficient and fewer-steps new synthetic strategy is demonstrated for the facile preparation of organic-electronically important D–π–A–π–D-type oligoaryls through sequential direct C−H arylations. This methodology has shown that the synthesis of thieno[3,4-c]pyrrole-4,6-dione (TPD)- or furano[3,4-c]pyrrole-4,6-dione (FPD)-centred target molecules could be accessed step-economically either from the core structure (acceptor) or from the end structure (donor), which supplied a more flexible and succinct new synthetic alternative to the preparation of the π-functional small-molecule semiconducting materials. In addition, optical and electrochemical properties of the synthesized oligoaryls were examined.

Figure 1. Thieno[3,4-c]pyrrole-4,6-dione (TPD)-based D–π–A–π–D-type oligoaryls for organic optoelectronic materials. Previous work: six-step synthesis including Suzuki and Stille coupling reaction.[4d] This work: two-step synthesis by sequential direct C−H arylations.

Linear D–π–A–π–D (D: donor; A: acceptor)-type symmetrical molecules constitute an important class of π-conjugated oligoaryls in modern organic electronics because their applications in organic photovoltaic cells (OPVCs) and organic field-effect transistors (OFETs) have attracted considerable attention.[1] For example, Nguyen reported high-performance bulk heterojunction solar cells using diketopyrrolopyrrole (DPP)-based D–π–A–π–D small molecules.[2] Fréchet reported similar small-molecule solar cells that exhibit interesting properties of pyrene-directed self-assembly.[3] Recently, the Zhan group disclosed a series of benzothiadiazole-,[4a,b] thiazolothiazole-,[4c] and thieno[3,4-c]pyrrole-4,6-dione[4d] (TPD)-centred oligomers with D–π–A–π–D structures for organic solar cell or field-effect transistor applications. The synthetic methods for the above-mentioned target compounds, however, must rely on traditional cross-coupling reactions that cannot avoid the process of pre-functionalizations/metalations, thereby leading to the frequent use and treatment with toxic reagents such as organotin species. Hence, we introduce herein a greener and fewer-steps synthetic approach for the facile preparation of TPD-incorporated symmetrical oligoaryls by sequential direct C−H arylations (Figure 1).
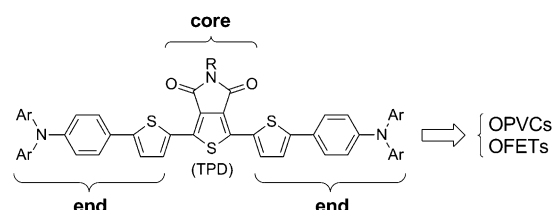
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To the best of our knowledge, target-oriented direct (hetero)arylation combining the concept of from-core or from-end synthetic strategy to access linear D–π–A–π–D-type π-functional molecules has not been reported to date (Schemes 1 and 2).

N-Alkyl TPD structures (1a, 1b) have exceptional planarity and solubility and they have been widely used as electron-accepting units in numerous π-functional materials.[5] Recently, we reported an efficient C−H arylation methodology using TPD as core substrate and functionalized aryl bromides as coupling partners, which led to the formation of various D–A–D- and A′–A–A′-type small molecules.[6] However, direct C−H coupling reaction of TPD with important heteroaryls (e.g., thiophenes) enabling the formation of synthetically versatile π–A–π-type building blocks (2a, 2b in Scheme 1) while leaving two further arylable C−H bonds at both ends still remains challenging because we envisaged that the self-oligomerization of 2-bromothiophene by C−H arylation would also take place and become a competitive side-reaction. Nevertheless, as the first part of this work (Scheme 1), we designed a sequential from-core synthesis, in which we found, under the condition of shortened reaction time (from 24 to 6 h), first C−H heteroarylation of TPD (1a, 1b) with 2-bromothiophene successfully proceeded with unexpected regioselectivity between two different C−H bonds and the useful terthiophene derivatives (2a, 2b) were obtained in moderate yields (66 and 51%, respectively). Subsequent C−H arylation of 2a or 2b with 4-bromotriphenylamine (3) was performed under similar reaction conditions described in previous step, giving the target D–π–A–π–D-type oligoaryls (7a, 7b) as from-core products, in 85 and 46% yields, respectively. More importantly, in order to further simplify the from-core strategy, the convenient two steps in one-pot reactions[7] (2a, 2b not isolated) were tested, and we found,

From-core synthetic strategy:
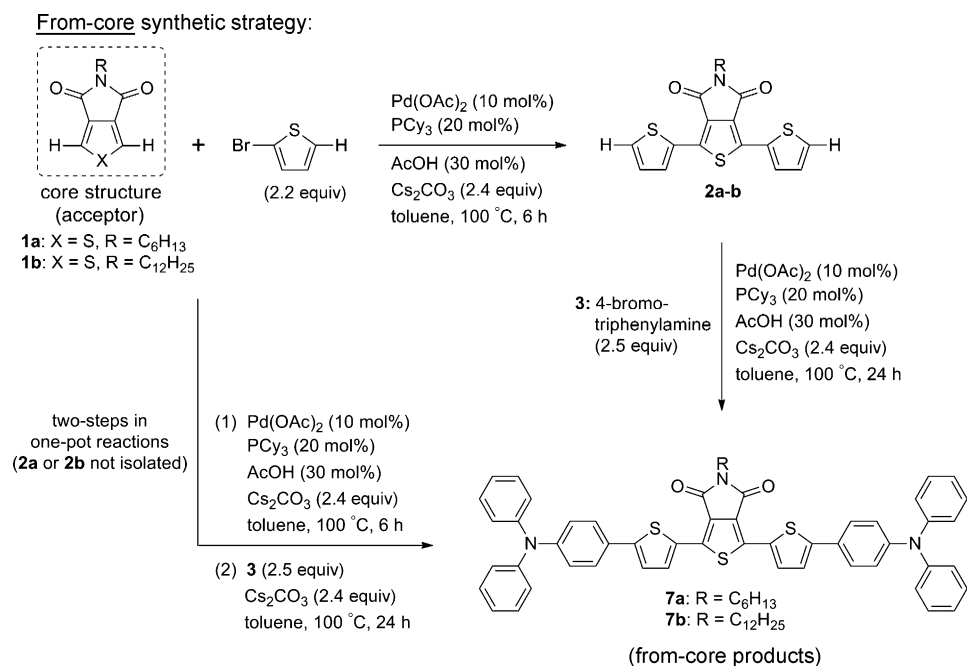
Scheme 1. From-core direct C–H arylation synthetic strategy: succinct synthesis of TPD- centred D–π–A–π–D-type oligoaryls.

surprisingly, the desired oligoaryls (**7a**, **7b**) could be successfully obtained by successive additions of the corresponding (hetero)aryl bromides as coupling partners (one-pot yields: 40% for **7a** and 31% for **7b**). On the other hand, we demonstrated a from-end synthetic strategy (Scheme 2), in which the key end-structure molecule (**5**) was prepared by the direct monoarylation of thiophene with a carbazole derivative (**4**) followed by NBS bromination, affording compound **5** in 41% overall yield (two steps). Second C–H arylation using **1b** or **6** as core and **5** as end proceeded smoothly to generate the interesting TPD- or furano[3,4-c]pyrrole-4,6-dione (FPD)-centred and carbazole-ended oligoaryls **8** and **9** in moderate to good isolated yields (68 and 75%, respectively).

The UV/Vis absorption spectra and the electrochemical properties examined by cyclic voltammetry of the synthesized oligoaryls (**7a**, **7b**, **8**, **9**) are demonstrated in Figure 2 and Figure 3, respectively, and relevant data and results are summarized in Table 1. In Figure 2, it was found that compounds terminated with triphenylamines (**7a**, **7b**)

displayed more red-shifted maximum absorbance ($\lambda_{max} = 480$ nm for **7a**; $\lambda_{max} = 475$ nm for **7b**) than those of the compounds terminated with carbazoles ($\lambda_{max} = 450$ nm for **8**; $\lambda_{max} = 430$ nm for **9**).

This implies that the charge transfer from carbazole group to the electron-deficient TPD or FPD is less efficient as a result of its rigid and planar structure with more restricted π-electrons.[8] Interestingly, we found that the molar extinction coefficient of **8** is exceptionally high (ε is close to 7.0×10^4 M^{-1} cm^{-1}), whereas other oligoaryls exhibited lower absorptivity ($\varepsilon = 4.1 \times 10^4$–$4.9 \times 10^4$ M^{-1} cm^{-1}). Compounds **7a** and **7b** have identical optical band gap ($E_g^{opt} = 1.89$ eV) since there is no difference in their conjugation lengths. In addition, we found furano[3,4-c]pyrrole-4,6-dione (FPD)-centred oligoaryl **9** has the largest E_g^{opt} (2.34 eV). Based on the cyclic voltammograms shown in Figure 3, the HOMO energy level (E_{HOMO}) was calculated by the half-wave potential ($E_{1/2}$) versus Ag/AgCl. More importantly, these oligoaryls (**7a**, **7b**, **8**, and **9**) show relatively

From-end synthetic strategy:
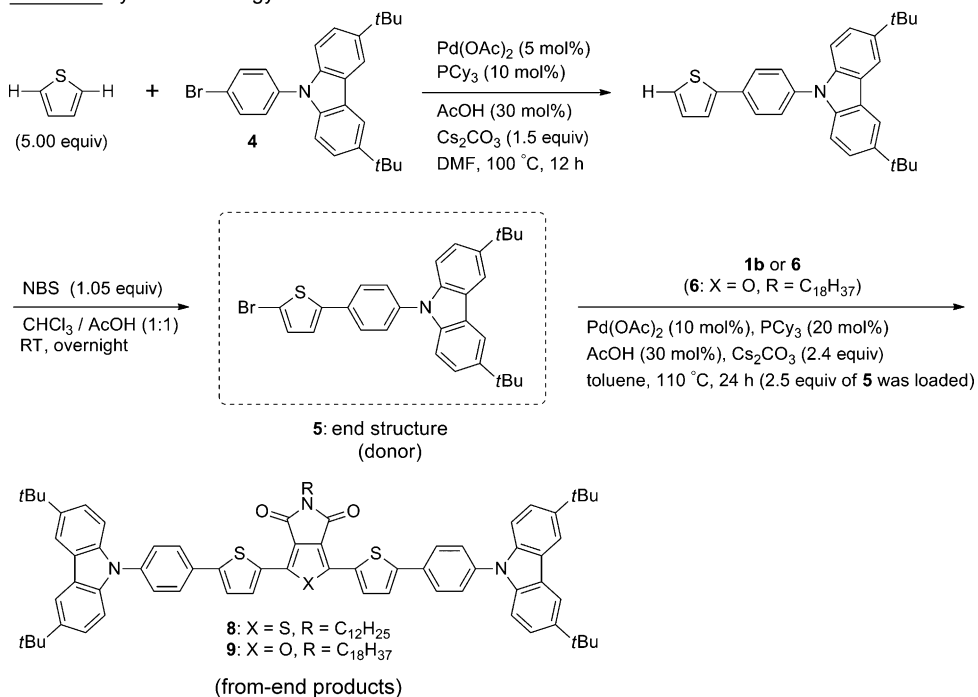
Scheme 2. From-end direct C–H arylation synthetic strategy: succinct synthesis of TPD- or FPD-centred D–π–A–π–D-type oligoaryls.
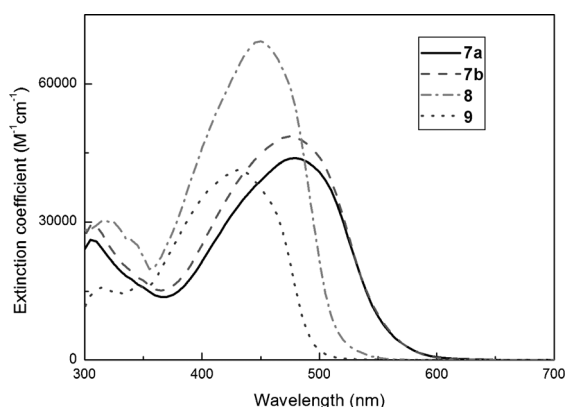
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Figure 2. Absorption spectra of the oligoaryls **7a**, **7b**, **8**, and **9**.

Table 1. Absorption and electrochemical parameters of **7a**, **7b**, **8**, and **9**.

	λ_{max} [nm][a]	ε [$M^{-1}cm^{-1}$][a]	E_g^{opt} [eV][b]	$E_{1/2}$ [V][c]	E_{HOMO}/E_{LUMO} [eV][d]
7a	480	43852	1.89	1.18	−5.88/−3.99
7b	475	48583	1.89	1.19	−5.89/−4.00
8	450	69238	2.18	1.47	−6.17/−3.99
9	430	41330	2.34	1.43	−6.13/−3.79

[a] Measured in THF solution (10^{-5} M); ε: extinction coefficient. [b] The optical band gap, E_g^{opt}, was calculated by $1240/\lambda^{onset}$. [c] The half-wave potential, $E_{1/2}$, was calculated by $(E_{pa}+E_{pc})/2$, where E_{pa} and E_{pc} are the potential energy of anodic and cathodic peaks, respectively. The measurements are conducted in THF solutions (10^{-4} M) containing (n-$C_4H_9)_4NPF_6$ as a supporting electrolyte under a scan-rate of 100 mVs^{-1}. [d] The HOMO energy level, E_{HOMO}, was calculated by $-(E_{1/2}+0.197+4.500)$ eV (vs. Ag/AgCl and NHE); $E_{LUMO}=E_{HOMO}+E_g^{opt}$.

deep-lying LUMO energy levels (E_{LUMO}, −3.79−−4.00 eV), which suggested that this class of oligomers would be potentially useful for n-type organic materials.

In summary, we have introduced a new synthetic design and economical route through Pd-catalysed direct C−H arylations, where the TPD- or FPD-containing D−π−A−π−D-type oligoaryls were efficiently constructed either from the core- or end-groups within three steps (traditionally, to access similar type

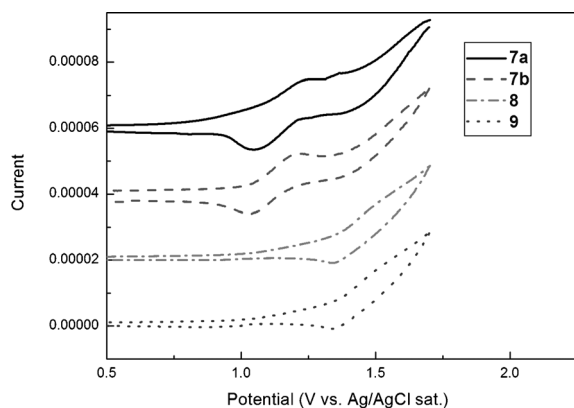of molecules would take at least six steps).[4d] More importantly, the synthesis of two target compounds (**7a**, **7b**) could be further simplified to two-steps in one-pot reactions with good regioselectivities by successive additions of the corresponding aryl bromides, which substantially reduced the synthetic transformations and avoided the generation of unnecessary by-products. The results of UV/Vis absorption and electrochemical analysis reveal that the obtained oligoaryls (**7a**, **7b**, **8**, **9**) are promising for further applications in organic semiconducting materials. Therefore, we expect this step-saving new approach would become a practical and greener synthetic tool/alternative for modern organic electronics.

Experimental Section

General procedure for compounds 2a and 2b

To a solution of Pd(OAc)$_2$ (10 mol%), PCy$_3$ (20 mol%), AcOH (30 mol%), and Cs$_2$CO$_3$ (2.40 mmol) in toluene (3.0 mL) in a flame-dried Schlenk tube (20 mL) were added **1a** or **1b** (1.00 mmol) and 2-bromothiophene (2.20 mmol) under N$_2$. The reaction mixture was then heated at 100 °C under N$_2$ for 6 h. After the reaction mixture had cooled to room temperature water (10 mL) was added. The mixture was extracted with ethyl acetate (2×30 mL), and the combined organic layers were washed with brine (50 mL), dried (Na$_2$SO$_4$) and concentrated in vacuo. Purification by flash chromatography yielded the desired products **2a** or **2b**. Detailed reaction procedures for other synthetic transformations shown in Scheme 1 and Scheme 2 are provided in the Supporting Information.
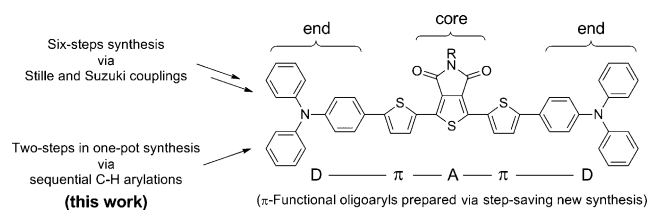
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Figure 3. Cyclic voltammograms of the oligoaryls **7a**, **7b**, **8**, and **9**.

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[7] Experimental procedures of the one-pot reactions are detailed in the Supporting Information.

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Six-steps synthesis via Stille and Suzuki couplings

Two-steps in one-pot synthesis via sequential C-H arylations **(this work)**

(π-Functional oligoaryls prepared via step-saving new synthesis)

■ **Synthesis Design**

P.-H. Lin, K.-T. Liu, C.-Y. Liu*

■■ – ■■

From-Core and From-End Direct C−H Arylations: A Step-Saving New Synthetic Route to Thieno[3,4-c]pyrrole-4,6-dione (TPD)-Incorporated D−π−A−π−D Functional Oligoaryls

Steps aside: A number of thieno[3,4-c]pyrrole-4,6-dione (TPD)- or furano[3,4-c]pyrrole-4,6-dione (FPD)-containing D–π–A–π–D type functional oligoaryls (see structure) were efficiently constructed either from the core- or end-groups by direct C−H arylations in three steps (tra-ditionally, to access similar type of mole-cules would take at least six steps). In addition, synthesis of two of the target compounds could be simplified to two steps in one-pot reactions with good re-gioselectivities.

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