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Facile one-pot microwave-assisted method of synthesis of novel functionalized arylenedioxythiophenes as promising building blocks for conjugated polymers with tuneable electronic properties is presented.
3,4-Phenylenedioxythiophenes (PheDOTs) functionalized with electron-withdrawing groups and their analogs for organic electronics. Remarkably efficient tuning the energy levels in flat conjugated polymers†‡

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Abstract

A novel, facile and efficient one-pot microwave-assisted method of synthesis allowing an access to a new series of 3,4-phenylenedioxy-thiophene derivatives with electron-withdrawing groups at the benzene ring (EWG-PheDOT) and their analogs (with expanded side π-system or with heteroaromatic rings, ArDOT) by reaction of 2,5-dialkoxy carbonyl-3,4-dihydroxythiophenes with electrophilic aromatic/heteroaromatic compounds in dipolar aprotic solvents has been described. Its applicability to a wide range of novel functionalized ArDOTs as promising building blocks for organic electronic materials have been demonstrated. The structures of selected ArDOTs have been determined by a single crystal X-ray diffraction. The electronic structure of conjugated polymers p[ArDOTs] based on synthesized novel thiophene monomers has been studied theoretically by DFT PBC/B3LYP/6-31G(d) method. The performed calculations reveal that while the side functional groups are formally not in conjugation with the polymer main chain, they have an unprecedentedly strong effect on the HOMO/LUMO energy levels of conjugated polymers, allowing their efficient tuning by over 1.6 eV range. In contrast to that, the energy gaps of the polymers are almost unaffected by such functionalizations and vary within a range of only ≤ 0.05 eV. Computational predictions have been successfully confirmed in experiments: cyclic voltammetry shows a strong anodic shift of p-doping for the electron-withdrawing CF₃ group functionalized polymer p[4CF₃-PheDOT] relative to the unsubstituted p[PheDOT] polymer(by 0.55 V; DFT predicted decrease of HOMO by 0.58 eV), while very similar Vis-NIR absorption spectra for both polymers in the undoped state indicate that their optical energy gaps near coincide (∆E₉ <0.04 eV).

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† We dedicate this paper to Prof. Fred Wudl in celebration of 50 years of his contributions to the field of π-conjugated organic materials.
‡ Electronic supplementary information (ESI) available: experimental procedures of synthesis of ArDOTs. ¹H, ¹³C and ¹⁹F NMR spectra and MS for characterized compounds; ¹³C DEPT, HSQC and HMBC NMR spectra for selected compounds; UV-Vis spectra for selected ArDOT compounds; data on DFT calculations for ArDOT oligomers and polymers; cyclic voltammograms and Vis-NIR absorption spectra for two p[ArDOT] polymers; single crystal X-ray structure data for 8 selected compounds (CCDC 1553610–1553617). For ESI and crystallographic data in CIF or other electronic formats see DOI: ##############
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Introduction

Polythiophenes are one of the most fascinating classes of conjugated polymers, and a large number of polythiophenes and oligothiophenes, as well as thiophene-based small molecules have been studied and used as materials for organic electronic applications, including organic light-emitting devices (OLED), field-effect transistors (OFET), photovoltaics (OPV), electrochromics, photochromics, electrode materials for batteries and capacitors, sensors and biosensors. Among them, poly(3,4-ethylenedioxythiophene) (PEDOT) is of special interest and importance due to its high electrical conductivity, optical transparency and stability in the doped state, and it has found many applications in organic electronics. Apart from the electronic effect of the ethylenedioxy substitution onto the thiophene moiety, an important reason for superior properties of PEDOT is the flat structure of its backbone due to the attractive S···O intermolecular interactions between the neighboring EDOT moieties, which was shown by X-ray crystallography for EDOT oligomers. This attracted substantial interest into EDOT derivatives and a large number of functionalized PEDOTs have been synthesized and studied. However, functionalization of EDOT monomer at the ethylene bridge does not provide means for tuning the properties of the polymers, because substituents attached to the bridge sp³ carbon atoms are not conjugated to the thiophene ring and are directed out of the polymer plane (thereby disturbing the π-π stacking between the polymer chains).

3,4-(1,2-Phenylenedioxy)thiophene (PheDOT), a benzo-fused analog of EDOT, represents a fascinating building block for π-functional oligo/polythiophene materials with the possibility of wider functionalization (at the benzene ring). Electrochemically prepared unsubstituted PheDOT polymer, pPheDOT, is oxidized at higher potentials (by 0.3–0.4 V) than PEDOT showing better environmental stability of its neutral form (highest occupied molecular orbital (HOMO) energy levels estimated from cyclic voltammetry data are −4.33 and −3.95 eV, respectively) and giving a slightly larger band gap (1.80 eV and 1.6 eV, respectively). In contrast to PEDOT, the hydrogen atoms on the benzene ring of pPheDOT lie in the monomer plane, and therefore substitution should not increase inter-chain spacing. Also, the electronic effect of substituents on the benzene ring of PheDOT is expected to be stronger because the sp² hybridization of the carbon atoms should allow better coupling of substituents with the oxygen atoms of the dioxine ring via resonance. Reynolds et al. first reported a soluble electroactive PheDOT polymer with dodecyl groups, p[(C₁₂₂)-PheDOT], which showed a remarkable degree of intra- and interchain order, both in solution and in the solid state. Other soluble alkyl-substituted pPheDOTs have been synthesized. The polymers showed hole mobility of 1.92 × 10⁻³ cm² V⁻¹ cm⁻¹ in OFET devices and up to 0.91% PCE (power conversion efficiency) in OPV with PC₇₀BM. The PheDOT building
block has also been used in the design of an efficient hole-transporting material for perovskite solar cells which showed encouraging power conversion efficiency (PCE) up to 10.64%.\(^{20}\) Another interesting behavior of some substituted PheDOTs was recently demonstrated by Darmanin and Guittard: on electropolymerization, they form well-ordered nanotubes of p[PheDOT] polymers on the surface without any template.\(^{21}\) Such nanotubes create parahydrophobic surfaces with extremely high water contact angles (up to \(\theta_W \sim 130–150^\circ\)) and high water adhesion, even if the nanotubes are prepared from the intrinsically hydrophilic polymers (i.e. Young’s angle \(\theta_Y \sim 60^\circ\)). This makes them attractive materials for advanced applications e.g. in membrane design, water transport and harvesting, as well as sensor design.

![PEDOT - pPheDOT - p[C6H5-PheDOT)](image)

PheDOT itself and alkyl-substituted PheDOTs (in a more general case, PheDOTs with electron-donating groups (EDGs) at the benzene ring) have been prepared by a common method of coupling of 3,4-dimethoxythiophene with catechols catalyzed by \(p\)-toluenesulfonic acid.\(^{16–19,21}\) However, synthesis of PheDOTs bearing electron-withdrawing groups (EWGs) by this route is problematic because even weak EWGs drastically decrease the nucleophilicity of the corresponding catechols and the yields of PheDOTs.\(^{22}\) An alternative multi-step method, widely used in the synthesis of functionalized EDOTs and related thiophenes, is based on the reaction of 3,4-dihydroxy-2,5-di(alkoxycarbonyl)thiophene (1) with dihaloalkanes, followed by removal of the carbalkoxy groups by reaction with lithium bromide\(^{23}\) or by alkali hydrolysis followed by high temperature decarboxylation in presence of copper chromite,\(^{24}\) copper oxide\(^{25}\) or silver carbonate.\(^{26}\) We have isolated PheDOT in a low yield by this reaction,\(^{16a}\) however its applicability toward a wider range of substituted PheDOTs is problematic (particularly because of problems with purification of intermediates). Also, this method required several synthetic steps and the use of highly toxic hexamethylphosphortriamide (in the case of decarboxyethylation with LiBr) that diminished its synthetic advantages.

Here we report the facile one-pot microwave-assisted synthesis of a wide range of substituted PheDOTs functionalized with EWGs at the benzene ring (EWG-PheDOTs) from thiophene 1. We have also successfully expanded this reaction to the synthesis of some analogues structures with pyridine (EWG-PyDOT) and pyrazine (PzDOT, QxDOT) rings, as well as polyfluorinated
arylendioxythiophenes ($F_4$-BnDOT, $F_6$-NaphDOT(1,2), $F_6$-NaphDOT(2,3)). We have analyzed the properties of the derived polymers by computational, electrochemical and Vis-NIR electron absorption methods. We demonstrate a remarkably strong effect of substituents in PheDOT and its heteroanalogs on the frontier orbital energies of derived polymers with surprisingly small influence on their band gaps.

Results and discussion

Synthesis

The synthetic approach to the one-pot microwave-assisted (MW) synthesis of PheDOT derivatives with EWG groups at the benzene ring, EWG-PheDOT, is illustrated in Scheme 1. Double nucleophilic aromatic substitution ($S_N$Ar) of the substituted benzenes 2–16 by anions generated from 3,4-dihydroxythiophene 1 by a weak base ($K_2CO_3$) led to the formation of intermediates 22 and 23, which at high temperature in the presence of lithium bromide underwent decarboxyethylation to form the target EWG-PheDOT compounds. The reaction proceeded well in dipolar aprotic solvents (generally, in $N$-$N$-dimethylacetamide (DMA), but $N$-$N$-dimethylformamide (DMF) and pyridine have also been tested).

For more detailed studies, the reaction of thiophene 1 was first tested with hexafluorobenzene (15) with monitoring by GC-MS (Table S2 in ESI). No product $F_4$-PheDOT or intermediates $F_4$-22 or $F_4$-23 were detected in the reaction with conventional heating in DMA even at prolonged time at 100 °C (Table S2 in ESI). In MW-assisted conditions, heating at 220 °C showed a formation of mixture of $F_4$-PheDOT and an intermediate $F_4$-23. Addition of LiBr substantially increased the rate
of decarboxyethylation of intermediate F₄-23, showing the yields of F₄-PheDOT of ca. 10–35% (Table S2, entries 6, 7). Further optimizations of the temperature, time and the amount of the solvent allowed to obtain F₄-PheDOT in 30–35% isolated yields in grams-scale reactions under MW conditions (Table S3 in ESI). Microwave irradiation is an important factor for the reaction: performing the reaction under similar conditions with conventional heating resulted in substantially lower yields of F₄-PheDOT (0–7%, Table S3 in ESI) and incomplete decarboxyethylation: apart from the target product F₄-PheDOT, substantial amounts of the intermediate F₄-23 were formed.

We have isolated an intermediate F₄-23 when the reaction was performed at temperatures of 140–160 °C and its structure was confirmed by a single crystal X-ray diffraction (Figure S4 in ESI).

Scheme 1. Microwave-assisted synthesis of EWG-PheDOT (the structures of reactants 2-16 and the products are shown in the Table 1).

A large series of electron-deficient aromatic compounds (3–16) have been investigated in the reaction with thiophene 1 and functionalized EWG-PheDOTs have been successfully obtained (Table 1, entries 3–15). The reaction worked well with fluoro-, chloro- and nitro-substituted aromatic compounds. While NO₂ is a poor leaving group, the intramolecular nature of the second step of cyclization to form the PheDOT moiety makes the reaction efficient. It should be mentioned that o-chloronitrobenzene under these conditions showed a very low yield of unsubstituted PheDOT of only 2% (Table 1, entry 2), presumably due to its lower reactivity in a S_NAr reaction in an absence of an additional EWG.

In the reaction of thiophene 1 with tetrafluorophtalic acid (14), spontaneous decarboxylation of CO₂H groups at the benzene ring was also observed under the reaction conditions resulting in 36F₂-PhedOT (Table 1, entry 13). For the reaction with octafluoronaphtalene (16), nucleophilic
substitution occurred at the both positions 2,3- and 1,2- of the naphthalene moiety to form two isomers (total yield 33%), symmetrical \( \text{F}_6\text{-NaphDOT(2,3)} \) and non-symmetrical \( \text{F}_6\text{-NaphDOT(1,2)} \) in a ratio of ca. 1.75:1 (Table 1, entry 15). In the case of dibromosubstituted 1,2-difluorobenzenes 24 and 25, we observed partial debromination in the reaction and mixtures of substituted \text{PheDOTs} were formed. The mixtures were difficult to separate, so were analyzed by GC-MS and \(^1\)H NMR, which indicated the removal of one or two bromine atoms in the products (see ESI).

After the successful synthesis of a series of \text{EWG-PheDOTs} with various electron-withdrawing substituents at the benzene ring, we expanded the reaction to other electrophiles, namely perfluorobenzylbromide (17), substituted pyridines (18, 19) and pyrazines (20, 21). The reaction worked well in these cases to give \text{PheDOT} analogs, i.e. \( \text{F}_4\text{-BnDOT}, \text{EWG-PyDOTs}, \text{PzDOT} \) and \( \text{QxDOT} \), correspondingly (Scheme 2 and Table 1, entries 16–20). Electron-deficient pyridine and pyrazine rings are activated for \( \text{S}_\text{N} \text{Ar} \) reactions and with these heterocycles the reaction worked well, even better than for EWG-functionalized benzenes, giving the target products in the yields of 17–74%.

![Scheme 2](image)

**Scheme 2.** Microwave-assisted synthesis of \text{PheDOT} analogs.

While the obtained yields in this one-pot microwave-assisted reaction (Schemes 1 and 2) were generally moderate to low, they are comparable with the total yields of the 3-steps “classical route”...
of condensation of $1 \rightarrow$ hydrolysis $\rightarrow$ decarboxylation (although for the reaction of pyridine $17$, we isolated $5\text{CF}_3\text{-PyDOT}$ with high yield of 74%). We should mention that in most the cases we did not optimize the yields towards the reaction conditions (e.g. temperature, time, ratio of reagents, concentrations etc., so the yields can be further improved) but focussed on demonstration of the applicability of this facile and simple method for a wide range of functionalized ArDOTs. In addition, even for the low yielding reactions, the target products could be very easily separated from the intermediates, by-products and tag by column chromatography on silica gel, as they always eluted first with non-polar/modest polarity solvents (usually, PE, toluene, DCM or their mixtures; see Table 1). The synthesized ArDOTs are colorless to yellowish crystalline materials (see Fig. S1 and S2 in ESI for their UV-Vis absorption spectra), generally well soluble in common organic solvents (except of $\text{F}_6\text{-NaphDOT(2,3)}$ and $\text{F}_6\text{-NaphDOT(1,2)}$, the solubility of which is much lower than for other compounds).

Table 1. Synthesis ArDOT derivatives by reaction of 3,4-dihydroxythiophene 1 under microwave-assisted conditions.$^{a,b}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactant (amount)</th>
<th>Conditions: (temperature, time)</th>
<th>Product</th>
<th>Yield, $%$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>200 °C, 1 h</td>
<td>2%</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>200 °C, 1 h</td>
<td>17%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>160 °C, 1 h</td>
<td>9%</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>200 °C, 1 h</td>
<td>19%</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>220 °C, 0.5 h</td>
<td>15%</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Structure</td>
<td>Temperature</td>
<td>Time</td>
<td>Yield</td>
</tr>
<tr>
<td>-----</td>
<td>-----------</td>
<td>-------------</td>
<td>------</td>
<td>--------</td>
</tr>
<tr>
<td>6</td>
<td><img src="1.10_eq." alt="Structure" /></td>
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<td>1 h</td>
<td>36%</td>
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<tr>
<td>7</td>
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</tr>
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<td>13%</td>
</tr>
<tr>
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<td>1.5 h</td>
<td>13%</td>
</tr>
<tr>
<td>10</td>
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<td>36%</td>
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<tr>
<td>No.</td>
<td>Structure</td>
<td>Conditions</td>
<td>Yield</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----------</td>
<td>------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td><img src="image" alt="Structure 15" /></td>
<td>200°C, 1 h</td>
<td>12%&lt;sup&gt;b&lt;/sup&gt; (PE)</td>
<td></td>
</tr>
<tr>
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<td><img src="image" alt="Structure 16" /></td>
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<td>11% (PE)</td>
<td></td>
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<tr>
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<td><img src="image" alt="Structure 17" /></td>
<td>155°C, 1.5 h</td>
<td>74% (PE:EA, 1:1, or DCM))</td>
<td></td>
</tr>
<tr>
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<td>200°C, 1 h</td>
<td>17% (toluene)</td>
<td></td>
</tr>
<tr>
<td>19</td>
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<td>38% (PE:EA, 9:1)</td>
<td></td>
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<tr>
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<td>42%&lt;sup&gt;i&lt;/sup&gt; (PE:DCM, 3:1 to DCM)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>ArDOT is a general abbreviation for all synthesized products, i.e. PheDOT, EWG-PheDOTs, and their analogs with aromatic/heteroaromatic side moieties.<sup>b</sup>Reaction conditions: DMA (2.6–3.1 mL/1 mmol of compound 1), K₂CO₃ (1.0 eq.), LiBr (0.6 eq.), MW irradiation 100–150W.<sup>c</sup>Isolated yields. Solvents used for column purification are indicated in brackets (PE = petrol ether, DCM = dichloromethane, EA = ethyl acetate).<sup>d</sup>The yield was decreased to 1.9% when AcONa was used as a base; 200 °C / 1 h.<sup>e</sup>2,5-Dicarbomethoxy-3,4-dihydroxythiophene disodium salt, DMF (6.9 mL / 1 mmol), AcOH (1.0 eq.), no LiBr.<sup>f</sup>In pyridine, 0.44 eq. LiBr.<sup>g</sup>The yield was decreased to 5% in the reaction at 155 °C for 1.5 h.<sup>h</sup>For the reaction at 165 °C / 1.5 h, the yields of Fr-NaphDOT(2,3) and Fr-NaphDOT(1,2) were lowered to 6.4% and 2.1%, respectively (1 g scale synthesis).<sup>i</sup>The yield was decreased to <26% for the reaction at 200 °C / 1h.
X-ray Crystallography of ArDOTs

For several synthesized EWG-PheDOTs and their analogs, we have confirmed their structures by X-ray crystallography. The molecular structures of single crystals for seven of the studied ArDOTs are shown in Figure 1 (see also Figure S3 in ESI for crystal packing).

Planar molecules of $36F_2$-PheDOT in the crystal structure form typical for polycyclic aromatic compounds inclined stacks with interplanar distances of 3.437(3) Å. C(thiophene)–H···O contacts link the stacks in layers, while weak C(Ph)–H···F interactions connect the layers in a 3D framework. In contrast to $36F_2$-PheDOT, molecules of $F_4$-PheDOT are arranged in an anti-parallel mode in stacks, probably due to the presence of two additional fluorine atoms creating an area of negative electrostatic potential. Only the heterocyclic parts of adjacent molecules are overlapped in stacks, the shortest interatomic distance between the molecules is 3.461(2) Å. The C(thiophene)-H···O interactions combine the stacks into corrugated layers.

![36F_2-PheDOT, F_4-PheDOT, 3NO_2,5CF_3-PheDOT, 56Cl_2-PyDOT, 5CF_3-PyDOT, PzDOT and QxDOT](image)

**Figure 1.** Molecular structures of $36F_2$-PheDOT, $F_4$-PheDOT, $3NO_2,5CF_3$-PheDOT, $56Cl_2$-PyDOT, $5CF_3$-PyDOT, PzDOT and QxDOT by a single crystal X-ray diffractometry ($3NO_2,5CF_3$-PheDOT showed some disorder of NO$_2$/CF$_3$ groups in a crystal and PzDOT contains two independent molecules in a unit cell).

The presence of bulky EWG groups in the phenyl ring (especially, nitrogroup’s oxygen atoms that are stronger acceptors of hydrogen bonds than heterocyclic oxygens), drastically change the packing motif. Instead of aromatic stacks, linked by CH···O interactions, the packing of
\(3\text{NO}_2\text{5CF}_3\text{-PheDOT}\) molecules is dominated by C(thiophene)–H···O(nitro) and C–F···O contacts. The planar moieties are barely overlapped and adjacent layers are shifted relatively to each other forming a step-like arrangement in order to accommodate the bulky substituents.

The structure \(\text{PzDOT}\) contains two virtually identical independent molecules. These two molecules form two separate layers with a different orientation relatively to the crystallographic \(\alpha\)-axis. The molecules are linked in layers by \(\pi\cdots\pi\) interactions between the dioxythiophene fragments of adjacent molecules and by C(Ph)–H···N contacts. A variety of potential acceptors of hydrogen bonds in this molecule makes the pattern of intermolecular interactions quite complex. Both independent molecules are involved in a number of C(thiophene)–H···N and C(thiophene)–H···S interactions that connect the molecules of different layers into a 3D-network. Interestingly, the C(thiophene)–H···O interactions, which are present in all other structures, are not present in structure \(\text{PzDOT}\).

The general packing motif of \(5\text{6Cl}_2\text{-PyDOT}\) is similar: the chains of the molecules are linked by \(\pi\cdots\pi\) interactions into layers. The peculiarity of the structure is the bonding between the molecules in the layer. Double C(thiophene)–H···N contacts are alternate with a combination of a pair of C(Py)–H···O interactions with another pair of C(thiophene)–H···Cl contacts. Weak Cl···Cl (and, probably, Cl···S) interactions exist between the layers.

The C(thiophene)–H···O and C(Py)···H···N interactions in \(5\text{CF}_3\text{-PyDOT}\) are far from being linear - the C–H···X angles are about 135°. Such deviation from linearity is apparently caused by the presence of the non-planar CF\(_3\) substituent, similarly to the structure of \(3\text{NO}_2\text{5CF}_3\text{-PheDOT}\). The packing motif of \(5\text{CF}_3\text{-PyDOT}\) is probably better described as layers of shifted stacks. No apparent direction-specific inter-layer contacts can be found in the structure and the layers interdigitate by terminal CF\(_3\) groups.

The extended polycyclic structure of \(\text{OxDOT}\) augments the formation of stacks in the crystal. Slightly shifted stacks are linked together in layers by pairs of bifurcated C(thiophene)–H···N,O contacts. C(Ph)–H···S contacts exist between the layers.

Generally, the packing of \(\text{PheDOT}\) derivatives is characterized by the presence of aromatic stacks (except for the cases, where the benzene ring is carrying non-planar groups \(3\text{NO}_2\text{5CF}_3\text{-PheDOT}\) and \(5\text{CF}_3\text{-PyDOT}\)) that are arranged in layers. The thiophene CH groups are the most active in the formation of weak C–H···X contacts that mainly determine the mutual arrangement of stacks within layers and orientation of the layers. It should be noted that the relative importance of the mentioned interactions and their role in the formation of crystal structures is impossible to estimate properly without calculations of pair-wise energies of intermolecular interactions. The geometrical parameters of intermolecular contacts alone cannot provide accurate description of packing motifs dominated by weak/non-directional interactions. For example, the chains of
molecules belonging to adjacent stacks may also be regarded as a basic motif of described structures.

**Computational Studies**

We have studied the geometries and the electronic structures of conjugated oligomers and polymers derived from synthesized ArDOT monomers by the density functional theory (DFT) method at the B3LYP/6-31G(d) level of theory in the gas phase. The structures of the dimers \((\text{ArDOT})_2\) optimized at B3LYP/6-31G(d) level have been used for calculations of the polymers by periodic boundary conditions (PBC) method at the same level of theory.\(^{28}\) Apart from synthesized ArDOTs, several other related molecules have also been included into these calculations to obtain a more comprehensive picture of the influence of the side arylenedioxy fragments on the structure, orbital energies and the band gaps of the polymers (namely, 4MeO-PheDOT, 4Me-PheDOT,\(^{21a}\) 4F-PheDOT, NaphDOT(2,3)\(^{17}\) and PyDOT).

The optimized geometries of \((\text{ArDOT})_n\) oligomers adopt an *anti* conformation of the adjacent monomer units and in the absence of steric repulsion between the side fragments in the monomer units (that are on the same side of the backbone\(^{29}\)) DFT calculations give planar oligomer chains (Figure 2a) with short S···O contacts between the thiophene sulphur atoms and dioxine oxygen atoms (see below for more details). Small steric repulsions between the fluorine atoms in \((\text{F}_4\text{-PheDOT})_n\) makes the oligomer backbone slightly twisted (average dihedral angles \(\sim 6.4^\circ\)), adopting a spiral conformation (Figure 2b), although this small twisting weakly effects the total energies or frontier orbital energies of the oligomers.\(^{30}\) So, we have compared an evolution of the HOMO and LUMO (highest occupied and lowest unoccupied molecular orbitals) energies and the HOMO–LUMO energy gaps \((\Delta E_{HL})\) for planar \((\text{PheDOT})_n\) and spiral \((\text{F}_4\text{-PheDOT})_n\) with an increase of the main chain length “n” of the oligomers.

Chain length dependences of the HOMO, LUMO and \(\Delta E_{HL}\), when plotted versus the reciprocal number of repeating units \((1/n)\), are linear for shorter oligomers \((n \sim 3–10)\) with deviation from the linearity and “saturation” for longer oligomers chains, as is commonly observed for \(\pi\)-conjugated oligomers (Figures S5, S6, S8a and Table S5 in ESI).\(^{31}\) This results in extrapolated (to \(1/n = 0\), i.e. n
$= \infty$) energy levels and the energy gaps that are substantially different (by ca 0.2 eV) from those calculated for these polymers by PBC method (Figures S6 and S8a in ESI). Using a function $1/(n+0.1n^2)$ that takes into account quadratic dependence on the chain length for longer oligomers\textsuperscript{32,33} gives excellent linear dependences (Figure 3 and Figures S7, S8b in ESI). The HOMO, LUMO and $\Delta E_{HL}$ energies extrapolated to $n = \infty$ nicely coincide with the highest occupied / lowest unoccupied crystal orbital energies (HOCO / LUCO) and the band gaps ($E_g$) for polymers calculated by PBC (deviations are ~5–21 meV only, Figure S7 in ESI).

(a) (PheDOT)$_{25}$

(b) (F$_4$-PheDOT)$_{20}$

Figure 2. B3LYP/6-31G(d) optimized structures of (a) (PheDOT)$_{25}$ and (b) (F$_4$-PheDOT)$_{20}$. Left structures – views perpendicular to the chain, right structures – views along the chain. Average dihedral angles / S···O distances between the adjacent monomer units are 0.0° / 2.947 Å [(PheDOT)$_{25}$] and 6.4° / 2.948 Å [(F$_4$-PheDOT)$_{20}$].

Figure 3. Chain length dependences of (a) HOMO and LUMO energies and (b) HOMO–LUMO energy gaps, $\Delta E_{HL}$, for B3LYP/6-31G(d) optimized geometries of (PheDOT)$_n$ and (F$_4$-PheDOT)$_n$ oligomers, plotted as a function of an empirical parameter $1/(n + 0.1n^2)$. Symbols ▬ and ▬ correspond to the energies (HOCO, LUCO, $E_g$) for polymers calculated by PBC.
Considering excellent coincidence between the oligomeric approach [linear fitting vs $1/(n + 0.1n^2)$] and less time-consuming PBC method, further calculations of the energy levels and the band gaps for polymers have been performed by PBC using the optimized dimers as the unit cells (Figures S9, S10 and Table S6, S7 in ESI). For $p[ArDOTs]$ without substantial steric repulsion in the side groups, planarization of the backbone is facilitated by attractive interactions between the thiophene sulphur atoms and oxygen atoms of the dioxine ring of the neighboring monomer units. This is manifested by shortening interatomic S···O distances, which for the studied polymers are in the range of ca. 2.9–3.0 Å (see Table S8 in ESI), i.e. substantially lower than the sum of van der Waals radii for sulphur and oxygen ($1.80 + 1.52 = 3.32$ Å). They are close to the experimental S···O distances from a single crystal X-ray diffraction structures of planar EDOT–EDOT (2.91–2.93 Å), EDOT–thiophene (2.96 Å, 3.02 Å), and EDOT–thieno[3,2-b]thiophene oligomers (2.87 Å) where non-covalent S···O interactions is also supposed to be an origin of planarization of these systems.

The energy levels calculated by PBC for the optimized geometries of the polymers, i.e. the highest occupied and lowest unoccupied crystal orbitals (HOCO and LUCO) and the band gaps ($E_g$) are presented in Figure 4. DFT calculations show that functionalization of PheDOT at the benzene ring efficiently tune the orbital energy levels of the polymers. Thus, for $p[EWG-PheDOT]$ polymers (first letter “p” designates the polymer), electron-withdrawing groups decrease the HOCO energy levels by up to 1.64 eV, from –4.374 eV for $p[PheDOT]$ to –6.017 eV for $p[45(CN)]_2-PheDOT]$ (Figure 4a and Table S7 in ESI). An intriguing feature found from these calculations is that LUCO energy levels are decreased by the near the same magnitude (from –2.239 eV to –3.847 eV, respectively). As a result, the band gaps of the polymers remains almost the same (with variations of less than 0.05 eV) and for all $p[X-PheDOT]$ polymers lie in the range of 2.123–2.170 eV (from $p[4Me-PheDOT]$ to $p[45(CN)]_2-PheDOT]$, Figure 4b and Table S7 in ESI)). This is contrasting with the effect of an introduction of electron-withdrawing substituents in other classes of conjugated polymers when intramolecular donor-acceptor interaction is observed. For example, an introduction of cyano-groups into poly($p$-phenylenevinylene) and their analogs or polythiophenes (onto vinylene or thiophene moieties, respectively) result both in decrease of the LUMO energy levels and the band gaps contraction.

Thus, our results demonstrate that structural variations at the benzene ring in $p[PheDOT]$ polymers might be an efficient way of controlling their frontier orbital energies and $p$-/n-doping abilities without affecting the band gaps of the polymers. These findings could also be exploited in the design of novel PheDOT-based copolymers, for which the fine tuning of their energy levels would be facilitated by functionalization of the PheDOT moieties at the benzene ring.
Figure 4. DFT B3LYP/6-31G(d) calculations in a gas phase (by PBC for polymers): (a) frontier orbital energies of \( p[\text{ArDOT}] \) polymers (HOCO and LUCO) and \((\text{ArDOT})_2\) dimers (HOMO and LUMO); bottom scale shows HOCO of \( p[\text{ArDOTs}] \) versus HOCO of \( p[\text{PheDOT}] \); (b) band gaps of \( p[\text{ArDOT}] \) polymers, \( E_g = \text{LUCO} - \text{HOCO} \); bottom axis shows \( E_g \) of \( p[\text{ArDOTs}] \) versus \( E_g \) of \( p[\text{PheDOT}] \).

Although the side benzene ring in \( p[\text{PheDOTs}] \) is not in direct conjugation with thiophene \( \pi \)-system, the resonance (and inductive) effects of the substituents in positions 4,5 of the benzene ring involving the oxygen atom of the dioxine ring strongly effect on the polymer backbone. This explains the efficient tuning of the frontier orbital energy levels of polymers (both HOMO and LUMO are on the main chain of the polymers). At the same time, the degree of this influence is incredibly high. For comparison: an attachment of the cyanogroups onto the main chain vinylene fragments of \((2,7\text{-carbazolylenevinylene})-(p\text{-phenylenevinylene})\) copolymer decreases the LUMO energy by 0.62 eV (with a band gap contraction of 0.10 eV).\(^{39}\) The effect of an attachment of one or two cyano-groups to the side benzene moiety of \text{PheDOT} (which are far from the main polymer chain and separated from it by the dioxine ring) is even more pronounced: in the series of \( p[\text{PheDOT}] \rightarrow p[4\text{CN-PheDOT}] \rightarrow p[45\text{(CN)}_2\text{-PheDOTs}] \), the calculated LUCO are decreased by 0.93 eV and 0.68 eV, respectively (Figure 4a).
Electron deficient nitrogen atoms in the side aromatic ring, i.e. pyridine and pyrazine, also lead to decrease in both the HOCO and LUCO energies (for \(p[PyDOT]\) and \(p[PzDOT]\)), decreases in HOCO/LUCO energies versus those in \(p[PhedOT]\) are 0.097/0.086 eV and 0.310/0.268 eV, respectively; (Figure 4 and Table S7 in ESI). Again, the band gaps are only weakly affected by these structural changes: \(E_g = 2.135\) eV \((p[PhedOT])\), 2.156 eV \((p[PyDOT])\), 2.177 eV \((p[PzDOT])\). On the other hand, an expanded conjugation at the side moiety by an additional annulated benzene ring (cf. \(p[NaphDOT(2,3)]\) and \(p[F_{6}-NaphDOT(2,3)]\) vs \(p[PhedOT]\) and \(p[QxDOT]\) vs \(p[PzDOT]\)) leads to more pronounced decrease in the band gaps by 79–106 meV to \(E_g \approx 2.029–2.056\) eV (Figure 4 and Table S7 in ESI). It was recently demonstrated by computational methods that an extension of conjugation into the second dimension leads to materials with smaller band gaps compared to parent 1D polymers.\(^{42}\)

**Electrochemistry and Vis-NIR absorption spectroscopy**

To confirm experimentally the predictions of DFT studies that functionalization of \(p[PhedOTs]\) at the benzene ring strongly effects on the HOMO/LUMO energies of the polymers while affording only minor changes in the band gaps, we have studied two polymers, \(p[PhedOT]\) and \(p[4CF_3-PhedOT]\), by cyclic voltammetry and Vis-NIR electron absorption spectroscopy methods. The polymers were prepared by electrochemical polymerization of the corresponding monomers to form insoluble polymer films, which were deposited onto Pt disks (for cyclic voltammetry experiments (CV), Figure S11 in ESI) or onto ITO (indium tin oxide) glass substrates (for spectroscopic studies) from the monomer solutions in DCM under potentiodynamic conditions. Previously, we have shown that electropolymerization of \(PhedOT\) is more difficult compared to \(EDOT\) due to lower positive charge /spin densities at the position 2,5- of the thiophene, and requires high concentration of the monomer and proper choice of the solvents (works better in DCM).\(^{16a}\) The selection of \(4CF_3-PhedOT\) as electron-deficient monomer, to compare it with \(PhedOT\), was conditioned by DFT prediction of observable decrease of the HOMO energy level of its polymer (by 0.58 eV, Figure 4) but still straightforward electropolymerization to form smooth and stable polymer films (Figures S11d and S12b in ESI). The CV studies on the polymer films in 0.1 M \(Bu_4NPF_6\) / acetonitrile demonstrated that both polymers are reversibly p-doped and show stable doping/dedoping on cycling (Figure 5a; see also Figure S12 in ESI). \(p[4CF_3-PhedOT]\) was oxidized (p-doped) at higher potential than \(p[PhedOT]\), confirming its weaker electron donor ability (Figure 5a). Its oxidation onset potential \((E_{ox})\) was anodically shifted by 0.55 V (from \(-0.36\) V to \(+0.19\) V vs Fc/Fc\(^+\) reference), which is in excellent agreement with DFT calculations (difference in HOCOs of \(p[PhedOT]\) and \(p[4CF_3-PhedOT]\) from DFT calculations is 0.58 V, Figure 4a). For \(p[4CF_3-PhedOT]\), we observed electrochemically irreversible n-doping at \(E_{red} = -1.57\) V (Figure 5a). From
the onsets of p- and n-doping processes, we estimated the band gap of this polymer as $E_g^{CV} = 1.76$ eV, which is close to estimation of $E_g \sim 1.8$ eV for p[PheDOT].

**Figure 5.** Comparison of properties of p[PheDOT] and p[4CF$_3$-PheDOT] in films: (a) cyclic voltammograms of polymer films (7 and 3 consecutive scans, respectively, are shown) in acetonitrile, 0.1 M Bu$_4$NPF$_6$, scan rate 100 mV/s (current for p[4CF$_3$-PheDOT] has been multiplied by a factor of $\times$6.5 for convenience of comparison); (b) Vis-NIR electron absorption spectra of p[PheDOT] and p[4CF$_3$-PheDOT] polymer films (electrodeposited on ITO glass substrate) in the undoped state; 0.1 M Bu$_4$NPF$_6$/acetonitrile; potentials are vs. Ag wire reference electrode.

Vis-NIR electron absorption spectra of p[PheDOT] and p[4CF$_3$-PheDOT] polymer films (deposited on ITO glass substrates) in undoped states were recorded in a spectroelectrochemical setup (SEC) with 0.1 M Bu$_4$NPF$_6$/acetonitrile, with applied negative potentials of $-(0.2-0.3)$ V, which correspond to the neutral states of the polymers. The results shown in Figure 5b demonstrate that the Vis-NIR spectra of two polymers near coincide (both by the maxima of absorption and by the red edge of the longest absorption band corresponding to the optical energy gaps of the polymers). The optical energy gaps of p[PheDOT] and p[4CF$_3$-PheDOT], estimated from their absorption onsets were found to be very similar, 1.83 eV (676 nm) and 1.87 eV (662 nm), respectively. These results confirm that the band gap of p[PheDOT] is unaffected by introduction of electron-withdrawing CF$_3$ groups and confirm the results of our DFT calculations and CV experiments. As the synthesized ArDOT monomers (Table 1) do not contain long-chain solubilizing groups, their polymers are expected to be insoluble materials (similar to p[PheDOT] and p[4CF$_3$-PheDOT]) that limits further expansion of these studies to chemically prepared polymers and requires synthesis of corresponding EWG-PheDOT analogs additionally decorated with linear or branched solubilizing groups.

**Conclusions**

We have reported a facile and efficient one-pot microwave-assisted method of synthesis of 3,4-phenylenedioxythiophene (PheDOT) derivatives substituted with electron-withdrawing groups at
the benzene rings and their analogs (with expanded side π-system or with heteroaromatic rings) by reaction of 2,5-dialkoxy carbonyl-3,4-dihydroxy thiophenes with electrophilic aromatic/heteroaromatic compounds in dipolar aprotic solvents under basic conditions in the presence of lithium bromide at high temperature. This general method provides an easy access to a wide range of novel ArDOT derivatives as attractive building blocks for conjugated molecular and polymeric materials for organic electronic applications, which are inaccessible by other current methods. The structures of eight selected compounds have been established by single crystal X-ray diffraction crystallography, shedding light on the molecular structure and crystal packing of these materials.

DFT calculations predict that the HOMO and LUMO energies for conjugated polymers derived from these monomers can be efficiently tuned by more than 1.6 eV, whereas the band gaps are expected to be near-identical for all of the studied polymers (variations in $\Delta E_{HL}$ are $\leq 0.05$ eV). This paves a way for efficient tuning of the HOMO energy levels of thiophene-based polymers in a wide range of over 1–1.5 eV without altering their band gaps.

These DFT predictions were further confirmed by cyclic voltammetry and Vis-NIR electron absorption spectroscopy experiments: an anodic shift by 0.55 V for p-doping of p[4CF$_3$-PheDOT] compared to p[PheDOT] corresponds well to the predicted difference in their HOCO orbital energies ($0.58$ eV), while good coincidence of their electron absorption spectra ($\lambda_{\text{max}} = 616$ and 609 nm, $E_{\text{onset}} = 1.83$ and $1.87$ eV, respectively) is in excellent agreement with very small changes in the DFT calculated band gaps ($E_g = 2.144$ and $2.135$ eV, respectively). On the other hand, an expansion of the π-system in the side moieties leads to the band gap contraction of the resulting polymers (an additional benzene ring decreases the $E_g$ by ca. 0.1 eV to $\approx 2.03$–$2.06$ eV).

The reported novel ArDOT molecules represent an interesting class of thiophene monomers for the design of conjugated homopolymers, with the ability to fine tune the optoelectronic properties of materials by side-chain functionalization. New ArDOTs also represent fascinating building blocks for incorporation into conjugated systems, including small conjugated molecules, cooligomers and copolymers, for design novel materials for organic electronic applications. The work on the synthesis of soluble conjugated oligomers and polymers/copolymers based on these ArDOTs as materials for electrochromic, field-effect transistor and photovoltaic applications is in progress and the results will be reported elsewhere.

**Experimental**

**Microwave-assisted synthesis of EWG-substituted ArDOTs. General procedure.** Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.000 g, 3.84 mmol, 1.00 eq.), K$_2$CO$_3$ (531 mg, 3.84 mmol, 1.00 eq.), electrophilic reagent 2–21 (1.0–1.3 eq.) and LiBr (210 mg, 2.42 mmol, 0.6 eq.)
were combined in a 35 mL microwave tube, and DMA (10–12 mL) was added. The tube was sealed and bubbled with N\textsubscript{2} under stirring for ca. 5 min. The mixture was then heated with stirring in a microwave reactor (initially for 5–20 min at 80–100°C (for dissolution and homogenization of the reaction mixture), then at 150–200 °C for 0.5–1.5 h; see Table 1 in the paper). After cooling to room temperature, the dark brown mixture was diluted with water (100 mL) and extracted with DCM (3 × 100 mL). The combined organic layers were washed with water (2–3 times), dried over MgSO\textsubscript{4}, and the solvent was evaporated. The residue was purified by column chromatography on silica gel with an appropriate solvent as an eluent (PE, toluene, DCM, PE/DCM or PE/EA). For full details on the experimental procedures and characterizations of novel compounds see ESI.

Conflict of Interests
There are no conflicts of interests to declare.

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References and Notes


In PBC calculations of non-symmetrical moieties, which are on the same side of the polymer backbone (as in the case of PheDOT, see X-ray crystallography section below), the calculations of the polymers with HT and HH-TT (head-to-head / tail-to-tail) arrangement gave very close total energies (differences are 0.00 – 0.39 kcal/mol), as well as HOCO, LUCO and E_g (differences are 0 – 5 kcal/mol) from the dimers as unit cells, we used head-to-tail (HT) connectivity of the monomer units in all the cases. In an absence of steric repulsions between the side aromatic moieties, which are on the same side of the polymer backbone (as in the case of p4R-PheDOTs and p5Cl2-PheDOTs) with low yields of only 1.3% and 5%, respectively (M. A. Krompiec, S. N. Baxter and I. F. Perepichka, unpublished results), compared to the yield of 20–25% for unsubstituted PheDOT [Ref. 16a].
meV) (Table S1 in ESI). Of course, these differences are substantially higher in the case of polymers with large steric repulsion between the side moieties, i.e. \( \text{p}[3\text{NO}_2,5\text{CF}_3-\text{PheDOT}], \text{p}[3\text{NO}_2,5\text{CF}_3-\text{PheDOT}] \) and \( \text{p}[\text{Fc}-\text{NaphDOT}(1,2)] \).

(ArDOT)\(_n\) oligomers with bulky side aryl groups, i.e. \( \text{Cl}_4-\text{PheDOT}, 3\text{NO}_2,5\text{CF}_3-\text{PheDOT}, 3\text{NO}_2,5\text{CF}_3-\text{PheDOT}, \text{F}_6-\text{NaphDOT}(1,2) \) and \( \text{F}_6-\text{BnDOT} \) showed substantial deviation from the planarity, with large dihedral angles between the adjacent ArDOT moieties and therefore they have not been used in further calculations.

For example, fully flat conformation of hexamer (F\(_6\)-PheDOT)\(_6\) has been calculated (local minimum, no frozen coordinates have been used) to have a total energy of 0.59 kcal/mol higher than that for the optimized spiral structure and very close frontier orbital energy levels: HOMO = −5.238 / −5.236 eV, LUMO = −2.580 / 2.562 eV, \( \Delta E_{\text{HOMO}} = 2.658 / 2.675 \) eV, for flat / spiral (F\(_6\)-PheDOT)\(_6\) optimized structures.


An extrapolation of EDOT and PheDOT oligomers to the polymers limit (\( n = \infty \)) using different physical models was recently considered in: J. Torras, J. Casanovas and C. Alemán, J. Phys. Chem. A, 2012, 116, 7571–7583.

Similar results have been obtained by us recently for calculations of EDOT–thieno[3,2-b]thiophene copolymers, see Ref. 32b.

Basing on the computational studies, Gierschner et al. assume that short S···O contacts in EDOT oligomers are non-bonding and vibrationally resolved absorption/emission spectra of oligo-EDOTs (as opposite to non-resolved spectra of oligothiophenes) are not due to self-rigidification by attractive S···O interactions, but due to very similar out-of-plane modes in the electronic ground (S\(_g\)) and first excited (S\(_1\)) state, which exhibit surprisingly low frequencies: B. M. Medina, D. Wasserberg, S. C. J. Meskers, E. Mena-Osteritz, P. Bäuerle and J. Gierschner, J. Phys. Chem. A, 2008, 112, 13282–13286.

In the case of monosubstituted non-symmetric ArDOTs, the polymer main chain can be arranged in HT (head-to-tail) and HH-TT (head-to-head / tail-to-tail) fashion. The total energies, HOCO, LUCO and \( E_g \) are almost the same for both regioisomers (Table S1 in ESI). The values reported in the paper are for HT-p-[R-ArDOT] regioisomers.

The calculated band gap for \( \text{p}[\text{PheDOT}] \) (\( E_g = 2.135 \) eV, \( \Delta E_{\text{HOMO}} = 2.120 \) eV) is ca. 0.3 eV higher than the experimental value for this polymer (1.8 eV [Ref. 17], 1.87 eV [this paper, see below]). However, it should be noted that the calculations have been performed for the isolated molecules in the gas phase and do not take into account the polarity of the environment and the solid state effect. Good correlations have been demonstrated between the experimental (cyclic voltammetry, Vis-NIR spectroscopy) and PBC/B3LYP/6-31G(d) calculated frontier orbital energy levels and band gaps for structurally related polythiophenes [Ref. 17], so changes in the HOMO, LUMO and \( E_g \) with the structural changes in \( \text{p}[\text{ArDOTs}] \) should be predicted by DFT with a high accuracy.


The tail absorption of \( \text{p}[\text{PheDOT}] \) in NIR region (900–1200 nm) is presumably due to trapped charges in the polymer as is sometimes observed for low band gap polymers. This might result in somewhat higher estimation of its band gap (see e.g. Ref. 32b).
3,4-Phenylenedioxythiophenes (PheDOTs) functionalized with electron-withdrawing groups and their analogs for organic electronics. Remarkably efficient tuning the energy levels in flat conjugated polymers

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S1
Experimental Part

Materials

All starting materials were purchased from Aldrich, Fisher Scientific or Alfa Aesar and were used without further purification. Diethyl 3,4-dihydroxy-2,5-dicarboxylate (1) and dimethyl 3,4-dihydroxy-2,5-dicarboxylate (27) were synthesized according to the method described by Hinsberg\(^1\) (syntheses by this protocol have also been described in later publications\(^2\)). Disodium 2,5-bis(methoxy carbonyl)thiophene-3,4-bis(olate) (26) was obtained as an intermediate in synthesis of compound 27 by this method.

![Chemical structures of compounds 1, 26, and 27](image)

Instruments

\(^1\)H, \(^13\)C, and \(^19\)F NMR spectra were recorded using a Bruker Avance 400 instrument in CDCl\(_3\). Tetramethylsilane (TMS) (\(\delta_H, \delta_C = 0.00\) ppm) and C\(_6\)F\(_6\) (\(\delta_F = -163.0\) ppm) were used as internal standards. For assigning H and C signals, DEPTQ and 2D NMR (\(^1\)H-\(^1\)H COSY, \(^13\)C-\(^1\)H HSQC and HMBC spectroscopy have been used). Enumerations of H and C atoms used in description of \(^1\)H and \(^13\)C NMR spectra are shown below:

![Assignments of H and C atoms in NMR spectra](image)

Electron impact mass spectra (positive mode) were recorded on a GC-MS system consisting of a HP 5890 gas chromatograph with a HP 8971 EI-MS detector, operating at 70KeV. Thin layer chromatography (TLC) was carried out throughout all syntheses using Merck TLC silica gel 60 aluminium sheets. Microwave assisted reactions were carried out in a CEM Discover SP microwave reactor, with a maximum power output of 300 W and controlling the temperature of the reaction mixture. Purification of synthesised compounds by flash chromatography was performed manually on glass columns or on Teledyn ISCO CombiFlash RF 200 flash chromatograph on silica gel 40-60 \(\mu\)m (40–250 mesh). UV-Vis electron absorption spectra of ArDOT monomers were recorded on a Shimadzu UV-3600 spectrophotometer in dichloromethane in quartz cells of 10 mm path length.

Computational methodology

Computational studies were carried out using density functional theory (DFT) with the Gaussian 09\(^3\) package of programs. Becke's three-parameter hybrid exchange functional\(^4\) with the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP)\(^5\) and Pople's 6-31G split valence basis set supplemented by d-polarization functions for heavy atoms were employed [B3LYP/6-31G(d)]. The restricted Hartree-Fock formalism was used. The geometries of the oligomers, (ArDOT)\(_n\), were fully optimized for isolated molecules in a gas phase, with no constraints, and the electronic structures for the optimised geometries were calculated at the same level of theory.

Optimization of the geometries of the polymers, \(p[\text{ArDOTs}]\), and calculation of their electronic structures were performed using periodic boundary conditions formalism (PBC) at the PBC/B3LYP/6-31G(d) level, which generally gives a good estimate of the band gaps of conjugated
polymers, including polythiophenes. The unit cells for PBC calculations of the polymers presented in the paper have been prepared from the optimized structures of corresponding dimers. Presented in the paper PBC calculations of non-symmetrical ArDOTs (as in the case of p[4R-PheDOT] and p[5CF3-PyDOT]) from the dimers as unit cells, are for head-to-tail (HT) connectivity of the monomer units in all the cases. For comparison, we also performed calculations for head-to-head/tail-to-tail (HH-TT) arrangement of the monomer units in the polymer backbone. The results show that in the absence of steric repulsions between the side aromatic moieties, which are on the same side of the polymer backbone (as in the case of p[4R-PheDOT] and p[5CF3-PyDOT]), the calculations of the polymers with HT and HH-TT arrangement give very close total energies (differences are 0.00 – 0.39 kcal/mol), as well as HOCO, LUCO and $E_g$ (differences are 0 – 5 meV) (Table S1). Of course, these differences are substantially higher in the case of polymers with substantial steric repulsion between the side moieties, i.e. p[3NO2,5CF3-PheDOT], p[3NO2,5CF3-PheDOT] and p[F6-NaphDOT(1,2)], and PBC calculations for these polymer were not performed.

Table S1. Total energies ($E_{\text{total}}$), HOCO/LUCO energy levels and the band gaps ($E_g$) of regioisomeric p[ArDOTs] by PBC/B3LYP/6-31G(d) calculations in the gas phase

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Regioisomer$^a$</th>
<th>$E_{\text{total}}$, hartree</th>
<th>$\Delta E_{\text{total}}$ (HT-HH), kcal/mol</th>
<th>HOCO, eV</th>
<th>LUCO, eV</th>
<th>$E_g$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>p[4Me-PheDOT]</td>
<td>HT</td>
<td>−1942.8090085</td>
<td>−0.08</td>
<td>−4.270</td>
<td>−2.147</td>
<td>2.123</td>
</tr>
<tr>
<td></td>
<td>HHTT</td>
<td>−1942.8088779</td>
<td></td>
<td>−4.268</td>
<td>−2.139</td>
<td>2.129</td>
</tr>
<tr>
<td>p[4F-PheDOT]</td>
<td>HT</td>
<td>−2062.6355280</td>
<td>0.00</td>
<td>−4.644</td>
<td>−2.511</td>
<td>2.133</td>
</tr>
<tr>
<td></td>
<td>HHTT</td>
<td>−2062.6355222</td>
<td></td>
<td>−4.644</td>
<td>−2.512</td>
<td>2.132</td>
</tr>
<tr>
<td>p[4Br-PheDOT]</td>
<td>HT</td>
<td>−7006.3793017</td>
<td>0.00</td>
<td>−4.770</td>
<td>−2.631</td>
<td>2.139</td>
</tr>
<tr>
<td></td>
<td>HHTT</td>
<td>−7006.3793007</td>
<td></td>
<td>−4.770</td>
<td>−2.631</td>
<td>2.140</td>
</tr>
<tr>
<td>p[4Cl-PheDOT]</td>
<td>HT</td>
<td>−2783.3613276</td>
<td>0.00</td>
<td>−4.790</td>
<td>−2.650</td>
<td>2.140</td>
</tr>
<tr>
<td></td>
<td>HHTT</td>
<td>−2783.3613268</td>
<td></td>
<td>−4.790</td>
<td>−2.650</td>
<td>2.140</td>
</tr>
<tr>
<td>p[4CF2-PheDOT]</td>
<td>HT</td>
<td>−2538.2463064</td>
<td>−0.39</td>
<td>−4.953</td>
<td>−2.809</td>
<td>2.144</td>
</tr>
<tr>
<td></td>
<td>HHTT</td>
<td>−2538.246926</td>
<td></td>
<td>−4.955</td>
<td>−2.806</td>
<td>2.149</td>
</tr>
<tr>
<td>p[4MeSO2-PheDOT]</td>
<td>HT</td>
<td>−3039.9466487</td>
<td>−0.09</td>
<td>−4.980</td>
<td>−2.831</td>
<td>2.149</td>
</tr>
<tr>
<td></td>
<td>HHTT</td>
<td>−3039.9465101</td>
<td></td>
<td>−4.982</td>
<td>−2.834</td>
<td>2.147</td>
</tr>
<tr>
<td>p[4CN-PheDOT]</td>
<td>HT</td>
<td>−2048.6563942</td>
<td>−0.01</td>
<td>−5.324</td>
<td>−3.173</td>
<td>2.152</td>
</tr>
<tr>
<td></td>
<td>HHTT</td>
<td>−2048.6563817</td>
<td></td>
<td>−5.325</td>
<td>−3.174</td>
<td>2.151</td>
</tr>
<tr>
<td>p[4NO2-PheDOT]</td>
<td>HT</td>
<td>−2273.1744023</td>
<td>−0.03</td>
<td>−5.370</td>
<td>−3.230</td>
<td>2.140</td>
</tr>
<tr>
<td></td>
<td>HHTT</td>
<td>−2273.1743528</td>
<td></td>
<td>−5.371</td>
<td>−3.235</td>
<td>2.136</td>
</tr>
<tr>
<td>p[5CF3-PyDOT]</td>
<td>HT</td>
<td>−2570.3264606</td>
<td>−0.10</td>
<td>−5.055</td>
<td>−2.887</td>
<td>2.169</td>
</tr>
<tr>
<td></td>
<td>HHTT</td>
<td>−2570.32631</td>
<td></td>
<td>−5.055</td>
<td>−2.891</td>
<td>2.164</td>
</tr>
</tbody>
</table>

$^a$HT – head-to-tail arrangement of 4R groups in the polymer backbone. $^b$HH-TT – head-to-head / tail-to-tail arrangement of 4R groups in the polymer backbone.
The PBC calculated HOCO/LUCO and $E_g$ of p[ArDOTs] were compared with the results based on the oligomers approach of extrapolations of HOMO/LUMO energies and the HOMO–LUMO energy gaps ($\Delta E_{HL}$) of (ArDOT)$_n$ to the infinite chain length to ($n = \infty$) by linear fitting of $E$ vs $1/(n + 0.1n^2)$, showing good coincidence.

X-Ray crystallography

Single crystals of studied ArDOTs have been obtained by recrystallization of pure samples from appropriate solvents (petrol ether, dichloromethane, toluene, ethylacetate or their mixtures) or by slow evaporation of their solution at room temperature. The X-ray single crystal data have been collected using $\lambda$MoK$\alpha$ radiation ($\lambda = 0.71073\AA$) on a Bruker D8Venture (Photon100 CMOS detector, I$_{\text{cr}}$S-microsource, focusing mirrors; compounds F$_4$-23, 36F$_2$-PheDOT, and PzDOT) and Agilent XCalibur (Sapphire-3 CCD detector, fine-focus sealed tube, graphite monochromator; comounds F$_4$-PheDOT, 3NO$_2$CF$_3$-PheDOT, 56Cl$_2$-PyDOT, 5CF$_3$-PyDOT and Q$_8$DOT) diffractometers equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperature 120.0(2) K. The crystals of compound 3NO$_2$CF$_3$-PheDOT shuttered during the flash-freezing, so the crystal of this compound was placed on a goniometer at 250 K and slowly cooled down to 200 K where the data were collected. All structures were solved by direct method and refined by full-matrix least squares on $F^2$ for all data using Olex2$^7$ and SHELXTL$^8$ software. All non-disordered non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the structures of F$_4$-PheDOT and PzDOT were placed in the calculated positions and refined in riding mode. The hydrogen atoms in the other structures were refined isotropically. The disordered atoms in the structure of 3NO$_2$CF$_3$-PheDOT were refined isotropically with fixed SOF = 0.5. Crystal data and parameters of refinement are listed in Table S4 and molecular structures and crystal packings are shown in Figures S3 and S4.

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1553610–1553517.

Electrochemistry and Vis-NIR electron absorption spectroscopy of polymers.

Electrochemical experiments were carried out using an Autolab PGSTAT-302N potentiostat-galvanostat. Cyclic voltammetry (CV) measurements were performed in a three-electrode cell equipped with a platinum disk (d = 1.6 mm) as the working electrode, platinum wire as a counter electrode and a non-aqueous Ag/Ag$^+$ reference electrode (0.01 M AgNO$_3$ and 0.1 M Bu$_4$NPF$_6$ in MeCN). Cyclic voltammograms of monomers PheDOT and 4CF$_3$-PheDOT were recorded at room temperature in dichloromethane (DCM) at low concentrations (~1mM) with 0.2 M Bu$_4$NPF$_6$ as supporting electrolyte, with ohmic drop compensation (Figure S9a,c). The potentials were corrected with ferrocene/ferrocenium redox pair (Fc/Fc$^+$) as an internal standard. At such low monomer concentrations, no electropolymerization was observed on cycling (we have observed previously that electropolymerization of PheDOT is more difficult than EDOT and requires higher concentrations of the monomer$^{9,10}$). Their electropolymerization was performed under potentiodynamic conditions in 0.2 M Bu$_4$NPF$_6$ / DCM at higher monomer concentrations of ~100 mM, cycling between 0 and +1.3 V for PheDOT, and between 0 and +1.6 V for 4CF$_3$-PheDOT (vs. Ag/Ag$^+$ reference electrode) (Figure S9b,d). After being electrodeposited onto working electrodes, the films of the polymers p[PheDOT] and p[4CF$_3$-PheDOT] were rinsed with acetonitrile and their electrochemical response was recorded in dry acetonitrile with 0.1 M Bu$_4$NPF$_6$ as supporting electrolyte.

For measurements of Vis-NIR electron absorption spectra, the films of p[PheDOT] and p[4CF$_3$-PheDOT] were electrodeposited on ITO glass substrate working electrodes in the same manner as described above. As the polymers have low oxidation potentials, they can be partly self-doped under air. Therefore, their Vis-NIR spectra were measured (Shimadzu UV-3600 spectrophotometer) in a spectroelectrochemical setup (0.1 M Bu$_4$NPF$_6$ / acetonitrile, ITO working...
electrode, Ag wire reference electrode) applying potentials corresponding to the neutral state of the polymers.

**Synthesis**

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.000 g, 3.84 mmol, 1.00 eq.), K$_2$CO$_3$ (531 mg, 3.84 mmol, 1.00 eq.), electrophilic reagent 2–21 (1.0–1.3 eq.) and LiBr (210 mg, 2.42 mmol, 0.60 eq.) were combined in a 35 mL microwave tube, and DMA (10–12 mL) was added. The tube was sealed and bubbled with N$_2$ under stirring for ca. 5–10 min. The mixture was then heated with stirring in a microwave reactor (initially for 5–20 min at 80–100°C (for dissolution and homogenization of the reaction mixture), then at 150–200 °C for 0.5–1.5 h). After cooling to room temperature, the dark brown mixture was diluted with water (100 mL) and extracted with DCM (3 × 100 mL). The combined organic layers were washed with water (2–3 times), dried over MgSO$_4$, and the solvent was evaporated. The residue was purified by column chromatography on silicagel with an appropriate solvent as an eluent (PE, toluene, DCM, PE/DCM or PE/EA).

**Microwave-assisted synthesis of PheDOTs and their analogs. General procedure.**
Benzo[b]thieno[3,4-e][1,4]dioxine (PheDOT)

\[
\text{HO} + \text{NO}_2 \xrightarrow{\text{K}_2\text{CO}_3, \text{LiBr, DMA}} \text{PheDOT}
\]

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.004 g, 3.86 mmol, 1.00 eq.), K₂CO₃ (0.533 g, 3.86 mmol, 1.00 eq.), 1-chloro-2-nitrobenzene (2) (0.632 g, 4.01 mmol, 1.04 eq.), LiBr (0.200 g, 2.30 mmol, 0.60 eq.) and DMA (10 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min. 4) 200 °C / 1 h. The reaction was repeated at the same conditions using diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.002 g, 3.85 mol, 1.00 eq.), K₂CO₃ (0.548 g, 3.97 mol, 1.03 eq.), 1-chloro-2-nitrobenzene (2) (0.653 g, 4.14 mol, 1.08 eq.) and LiBr (0.211 g, 2.43 mol, 0.63 eq.) in DMA (10 mL). The combined mixtures from both syntheses were poured into water (200 mL), stirred and the precipitate was filtered off. The solid was dissolved in DCM (200 mL), stirred for 1 h, dried over MgSO₄, filtered and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: PE) to yield compound PheDOT (24.1 mg, 1.6%) as a white solid.

Analytical data (¹H and ¹³C NMR, MS) were consistent with the data published in the literature.¹

¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.92 (4H, m, H¹⁻⁴), 6.43 (2H, s, H¹²⁻⁵).

FTIR (cm⁻¹): 3102, 3075.

6-Chlorobenzo[b]thieno[3,4-e][1,4]dioxide (4Cl-PheDOT)

\[
\text{HO} + \text{NO}_2 \xrightarrow{\text{K}_2\text{CO}_3, \text{LiBr, DMA}} \text{Cl-PheDOT}
\]

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.001 g, 3.85 mmol, 1.00 eq.), K₂CO₃ (0.542 g, 3.92 mmol, 1.02 eq.), 2,5-dichloronitrobenzene (3) (0.804 g, 4.19 mmol, 1.09 eq.), LiBr (0.218 g, 2.51 mmol, 0.65 eq.) and DMA (10 mL) were placed in a 35 mL MW reaction tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min. 4) 200 °C / 1 h. After cooling to room temperature, the mixture was poured into DCM (100 mL) and stirred for 1 h before adding water (100 mL). The mixture was filtered, the organic layer was separated, washed with water (4 × 50 mL), dried over MgSO₄ and the solvent was evaporated. The residue was purified by flash chromatography on silica gel (eluent: PE) to yield compound 4Cl-PheDOT (0.145 g, 16.8%) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.93 (1H, d, J_B₃-B₅ = 2.3 Hz, H²₃), 6.90 (1H, dd, J_B₅-B₆ = 8.6 Hz, J_B₃-B₅ = 2.3 Hz, H⁸₅), 6.84 (1H, d, J_B₅-B₆ = 8.6 Hz, H⁸₆), 6.46 (1H, d, J_T₂-T₅ = 3.6 Hz, H¹⁰⁻⁵), 6.44 (1H, d, J_T₂-T₅ = 3.6 Hz, H¹⁰⁻⁵).

¹³C NMR (DEPTQ, 100 MHz, CDCl₃): δ (ppm) 141.29, 139.70, 138.61, 138.32, 128.16 (C⁻⁴), 123.55 (CH, C⁻⁵), 117.57 (CH, C⁻⁶), 117.07 (CH, C⁻⁹), 101.57 (CH, C¹²⁻⁵), 101.38 (CH, C¹²⁻⁵).

MS (EI⁺): m/z 223.95 (M⁺, 100%), 225.95 (37.61%); calcd. for C₁₀H₅ClO₂S: 223.97 (100.0%), 225.97 (37.0%).
6-Bromobenzo[b]thieno[3,4-c][1,4]dioxine (4Br-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.500 g, 5.76 mmol, 1.00 eq.), K₂CO₃ (0.840 g, 6.08 mmol, 1.05 eq.), 2-chloro-5-bromonitrobenzene (4) (1.781 g, 6.34 mmol, 1.10 eq.), LiBr (0.320 g, 3.68 mmol, 0.64 eq.) and DMA (15 mL) were placed in a 35 mL MW reaction tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min, 4) 160 °C / 1 h. The mixture was cooled to room temperature, diluted with DCM (100 mL) and filtered. The filtrate was washed with water (3 × 200 mL), dried over MgSO₄ and the solvent was evaporated. The residue was purified by flash chromatography on silica gel (eluent: PE) to yield compound 4Br-PheDOT (139 mg, 9.0%) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.07 (1H, d, J₈₋₅₋₆ = 2.3 Hz, H₅), 7.03 (1H, dd, J₆₋₅₋₆ = 8.6 Hz, J₈₋₅₋₆ = 2.3 Hz, H₆), 6.79 (1H, d, J₆₋₅₋₆ = 8.6 Hz, H₆), 8.46 (1H, d, J₁₋₂₋₅ = 3.6 Hz, H₂), 6.44 (1H, d, J₁₋₂₋₅ = 3.6 Hz, H₂), 3.6 Hz, H₂).

¹³C NMR (DEPTQ, 100 MHz, CDCl₃): δ (ppm) 141.5 (C₁), 140.2 (C₂), 138.6 (C₃), 138.3 (C₄), 126.5 (CH₂C₅), 119.9 (CH, C₆), 118.0 (CH, C₆), 115.1 (C₆), 101.6 (CH, C₅), 101.4 (CH, C₄).

MS (EI+): m/z 267.95 (M⁺, 100.0%), 79Br, 270.00 (M⁺, 99.47%), 81Br; calcd. for C₁₁H₅BrO₂S: 267.92 (97.8%, 79Br), 269.92 (100.0%, 81Br).

Benzo[b]thieno[3,4-c][1,4]dioxine-6-carbonitride (4CN-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.508 g, 5.79 mmol, 1.00 eq.), K₂CO₃ (0.802 g, 5.80 mmol, 1.00 eq.), 1-chloro-2-nitro-4-cyanobenzene (5) (1.150 g, 6.30 mmol, 1.09 eq.), LiBr (0.215 g, 2.48 mmol, 0.43 eq.) and DMA (15 mL) were placed in a 35 mL MW reaction tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min, 4) 200 °C / 1 h. After cooling, the mixture was diluted with DCM (100 mL), filtered and the filtrate was washed with water (5 × 100 mL). The organic phase was dried over MgSO₄, filtered and evaporated to dryness. The residue was purified by flash chromatography on silica gel (eluent: toluene) to yield compound 4CN-PheDOT (242 mg, 19.4%) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.24 (1H, dd, J₆₋₅₋₆ = 8.4 Hz, J₈₋₅₋₆ = 1.9 Hz, H₅), 7.19 (1H, d, J₆₋₅₋₆ = 1.9 Hz, H₆), 6.98 (d, J₆₋₅₋₆ = 8.4 Hz, H₆), 6.52 (d, J₁₋₂₋₅ = 3.6 Hz, H₂), 6.50 (d, J₁₋₂₋₅ = 3.6 Hz, H₂), 3.6 Hz, H₂).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 144.68 (C₁), 141.30 (C₂), 137.75 (C₃), 137.67 (C₄), 128.24 (CH, C₅), 120.63 (CH, C₆), 117.95 (CN), 117.85 (CH, C₆), 107.17 (C₆), 102.53(CH, C₅), 102.27 (CH, C₄).

MS (EI+): m/z 214.95 (M⁺, 100.0%); calcd. for C₇H₅NO₂S: 215.00.
6-Nitrobenzo[b]thieno[3,4-e][1,4]dioxide (4NO$_2$-PheDOT)

![Chemical structure of 4NO$_2$-PheDOT]

Dimethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate disodium salt (26) (201 mg, 0.73 mmol, 1.00 eq.), 1-chloro-2,4-dinitrobenzene (6) (147 mg, 0.73 mmol, 1.00 eq.), acetic acid (44 mg, 0.73 mmol, 1.00 eq.) and DMF (5 mL) were placed in a 10 mL microwave tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor at 220 °C for 30 min. After cooling, the mixture was poured into water (25 mL) and extracted with ethyl acetate (2 × 20 mL). The organic layer was dried over MgSO$_4$, evaporated to dryness and purified by flash chromatography on silica gel (eluent: toluene) to afford 4NO$_2$-PheDOT (23.6 mg, 15%) as a light yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.87 (1H, dd, $J_{B5-B6} = 8.9$ Hz, $J_{B3-B5} = 2.6$ Hz, H$^B$), 7.82 (1H, d, $J_{B3-B5} = 2.6$ Hz, H$^B$), 7.02 (1H, d, $J_{B5-B6} = 8.9$ Hz, H$^B$), 6.56 (1H, d, $J_{T2-T5} = 3.6$ Hz, H$^{T2/5}$), 6.54 (1H, d, $J_{T2-T5} = 3.6$ Hz, H$^{T2/5}$).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm) 146.08, 143.52, 140.92, 137.55, 137.10 (C$^B$), 119.72 (CH, C$^{B3/5/6}$), 116.99 (CH, C$^{B3/5/6}$), 112.96 (CH, C$^{B3/5/6}$), 102.81 (CH, C$^{T2/5}$), 102.43 (CH, C$^{T2/5}$).

MS (EI+): m/z 235.05 (M$^+$, 100%); calcd. for C$_{10}$H$_5$NO$_3$S: 234.99.

6-(Trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxide (4CF$_3$-PheDOT)

![Chemical structure of 4CF$_3$-PheDOT]

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.021 g, 3.92 mmol, 1.00 eq.), K$_2$CO$_3$ (0.537 g, 3.88 mmol, 1.00 eq.), 4-chloro-3-nitrobenzotrifluoride (7) (0.976 g, 4.33, 1.12 eq.), LiBr (0.221 g, 2.54, 0.66 eq.) and DMA (10 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min, 4) 200 °C / 1 h. Another batch of diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.021 g, 3.92 mmol, 1.00 eq.), K$_2$CO$_3$ (0.537 g, 3.89 mmol, 1.01 eq.), 4-chloro-3-nitrobenzotrifluoride (7) (0.976 g, 4.33, 1.12 eq.), LiBr (0.221 g, 2.54, 0.66 eq.) and DMA (10 mL) was run under the same conditions. The two reaction mixtures were combined, diluted with DCM (200 mL), stirred and filtered to remove insoluble material. The filtrate was washed with water (6 × 150 mL), dried over MgSO$_4$ and the solvent was evaporated to dryness. The crude product was purified by flash chromatography on silica gel (eluent: PE) to yield compound 4CF$_3$-PheDOT (0.715 g, 35.8%) as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.19 (2H, m, H$^{B3/5}$), 6.98 (1H, d, $J_{B5-B6} = 8.4$ Hz, H$^B$), 6.49 (1H, d, $J_{T2-T5} = 3.6$ Hz, H$^{T2/5}$), 6.48 (1H, d, $J_{T2-T5} = 3.6$ Hz, H$^{T2/5}$), 13C NMR (100 MHz, CDCl$_3$): δ (ppm) 143.46 (C$^{B1/2}$), 141.00 (C$^{B1/2}$), 138.24 (C$^{T3/4}$), 138.18 (C$^{T3/4}$), 126.12 (q, $J_{C-F} = 33.4$ Hz, C$^B$), 123.51 (q, $J_{C-F} = 271.6$ Hz, CF$_3$), 120.89 (CH, q, $J_{C-F} = 3.9$ Hz, C$^B$), 117.21 (CH, C$^B$), 114.44 (CH, q, $J_{C-F} = 3.9$ Hz, C$^B$), 101.97 (CH, C$^{T2/5}$), 101.82 (CH, C$^{T2/5}$).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ (ppm) –63.52 (s, CF$_3$).

MS (EI+): m/z 258.05 (M$^+$, 100%); calcd. for C$_{11}$H$_5$F$_3$O$_2$S: 258.00.
6-(Methylsulfonyl)benzo[b]thieno[3,4-e][1,4]dione (4MeSO₂-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.001 g, 3.85 mmol, 1.00 eq.), K₂CO₃ (0.566 g, 4.10 mmol, 1.06 eq.), 2-chloro-5-methylsulfonyl-1-nitrobenzene (8) (1.009 g, 4.28 mmol, 1.11 eq.), LiBr (0.217 g, 2.49 mmol, 0.65 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 140 °C / 15 min (80 W), 2) 200 °C / 1 h. After cooling, the mixture was diluted with DCM (50 mL) and water (100 mL) and filtered. The organic phase was washed with water (3 × 50 mL), dried over MgSO₄, filtered and the solvent was evaporated. The residue was dissolved in hot toluene (50 mL) and passed through a short silica gel column eluting with DCM. After solvent evaporation the solution, the crude product was purified by flash chromatography on silica gel (eluent: DCM) to afford compound 4MeSO₂-PheDOT (216 mg, 20.9 %) as a white solid (purity 98%, by ¹H NMR). Analytically pure product (193 mg, 18.7%) was obtained by recrystallization from heptane/chloroform (7:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.52 (1H, dd, J₈₅-B₅ = 8.4 Hz, J₆₃-B₅ = 2.0 Hz, H₅₃), 7.50 (1H, d, J₆₃-B₅ = 2.0 Hz, H₆₃), 7.07 (1H, d, J₈₅-B₅ = 8.4 Hz, H₈₅), 6.54 (1H, d, J₇₂-T₅ = 3.6 Hz, H₇₂/T₅), 6.52 (1H, d, J₆₃-T₅ = 3.6 Hz, H₆₃/T₅), 3.05 (3H, s, CH₃).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 145.19, 141.32, 137.84, 137.71, 135.69, 123.39, 117.74, 116.57, 102.51, 102.27, 44.63 (CH₃).

MS (El⁺): m/z 268.10 (M⁺, 100%); calcd. for C₁₁H₄O₄S₂: 267.99.

5-Nitro-7-(trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dione (3NO₂,5CF₃-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.004 g, 3.86 mmol, 1.00 eq.), K₂CO₃ (0.531 g, 3.84 mmol, 1.00 eq.), 4-chloro-3,5-dinitrobenzotrifluoride (9) (1.144 g, 4.23 mmol, 1.10 eq.), LiBr (0.200 mg, 2.30 mmol, 60 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) and heated with stirring in a microwave reactor in 2 steps: 1) 100 °C / 10 min, 2) 155 °C / 1.5 h. After cooling, the mixture was diluted with DCM (50 mL) and water (50 mL), stirred and filtered to remove insoluble material. The organic layer was washed with water (3 × 50 mL), dried over MgSO₄, filtered and evaporated to dryness. The crude product was purified by flash chromatography on silica gel (eluent: PE:DCM, 7:3) to yield compound 3NO₂,5CF₃-PheDOT (150 mg, 12.8%) as a light yellow solid.

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.83 (1H, d, J₈₅-B₅ = 2.0 Hz, H₅₃/B₅), 7.39 (1H, d, J₆₃-B₅ = 2.0 Hz, H₆₃/B₅), 6.72 (1H, d, J₆₃-T₅ = 3.6 Hz, H₆₃/T₅), 6.59 (1H, d, J₆₃-T₅ = 3.6 Hz, H₆₃/T₅).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 142.92, 138.56, 138.25, 136.76, 136.02, 122.35 (q, J₇₋₈₅ = 272.7 Hz, CF₃), 125.31 (q, J₈₃₋₇ = 35.2 Hz, C₈₅), 118.13 (CH₃, q, J₈₃₋₇ = 3.5 Hz, C₈₅/B₅), 117.24 (CH₃, q, J₈₃₋₇ = 4.0 Hz, C₈₅/B₅), 104.50, 103.07.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) −64.13 (s, CF₃).

MS (El⁺): m/z: 303.05 (100); calcd. for C₁₁H₄F₃NO₄S: 302.98.
7-Nitro-5-(trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxine (3CF₃,5NO₂-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.007 g, 3.87 mmol, 1.00 eq.), K₂CO₃ (0.537 g, 3.89 mmol, 1.00 eq.), 2-chloro-3,5-dinitrobenzotrifluoride (10) (1.144 g, 4.23 mmol, 1.09 eq.), LiBr (0.217 mg, 2.50 mmol, 0.65 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 100 °C / 10 min, 2) 155 °C / 1.5 h. After cooling, the mixture was diluted with DCM (70 mL) and water (50 mL), stirred and filtered to remove insoluble material. The organic layer was washed with water (2 × 50 mL), dried over MgSO₄, filtered and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: DCM) to yield compound 3CF₃,5NO₂-PheDOT (175 mg, 14.9%) as a light yellow solid. An analytically pure sample was obtained by recrystallization from heptane (154 mg, 13.1%).

³¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.16 (1H, d, J_B3-B5 = 2.6 Hz, H_B3)/3), 7.98 (1H, d, J_B3-B5 = 2.6 Hz, H_B3)/3), 6.71 (1H, d, J_T2-T5 = 3.6 Hz, H_T2)/5), 6.60 (1H, d, J_T2-T5 = 3.6 Hz, H_T2)/5).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 144.35, 142.39, 142.02, 136.65, 136.20, 121.55 (q, ¹¹J_C-F = 273.8 Hz, CF₃), 119.18 (CH, q, ¹¹J_C-F = 34.0 Hz, C⁵⁵), 117.28 (q, ¹¹J_C-F = 5.3 Hz, C⁴⁴), 115.95, 104.34 (CH, C⁷²), 103.17 (CH, C⁷²).

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) –63.63 (s, CF₃).

MS (EI+): m/z 303.05 (M⁺, 100%); calcd. for C_{11}H_{23}F_{3}NO₅S: 302.98.

5,6,7,8-Tetrachlorobenzo[b]thieno[3,4-e][1,4]dioxine (Cl₄-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (904 mg, 3.47 mmol, 1.00 eq.), K₂CO₃ (486 mg, 3.52 mmol, 1.01 eq.), pentachloronitrobenzene (11) (112 mg, 0.38 mmol, 1.09 eq.), LiBr (187 mg, 2.15 mmol, 0.62 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 140 °C / 15 min (80 W), 2) 200 °C / 1 h. After cooling, the mixture was diluted with DCM (100 mL), washed with water (3 × 50 mL), dried with MgSO₄, and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: hot heptane) to yield compound Cl₄-PheDOT (105 mg, 9.2%) as a white powder.

³¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.65 (1H, s, H_T²5).

¹³C NMR (DEPTQ, 100 MHz, CDCl₃): δ (ppm) 137.87, 136.91, 127.08, 120.40, 103.16 (CH, C_T²5).

MS (EI+): m/z 325.90 (80%), 327.95 (100%), 329.90 (51%) [M⁺ with ³⁵Cl/³⁷Cl distribution]; calcd. for C_{10}H_{20}Cl₄O₃S (for natural ³⁵Cl/³⁷Cl distribution): 325.85 (78.2%), 327.85 (100.0%), 329.85 (47.9%).
Benzo[b]thieno[3,4-e][1,4]dioxine-6,7-dicarbonitrile (45(CN)2-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.502 g, 5.77 mmol, 1.00 eq.), 4,5-dichlorophthalonitrile (12) (1.238 g, 6.28 mmol, 1.09 eq.), LiBr (0.220 g, 2.55 mmol, 0.44 eq.) and pyridine (15 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps (MW 150 W): 1) 100 °C / 15 min, 150 °C / 15 min, 170 °C / 1 h. After cooling, the mixture was diluted with water (100 mL) and extracted with DCM (8 × 25 mL). The combined DCM layers were washed with concentrated HCl (4 mL), water (2 × 25 mL) and filtered through a silica gel plug. The solvent was evaporated to yield the crude product (750 mg, 54%) as an orange solid. The crude product was purified by flash chromatography on silica gel (eluent: toluene) to yield pure compound 45(CN)2-PheDOT (208 mg (15 %) as a light yellowish solid. 

1H NMR (400 MHz, CDCl3): δ (ppm) 7.29 (2H, s, H B3,6), 6.61 (2H, s, H T2,5).

13C NMR (100 MHz, CDCl3): δ (ppm) 144.65, 136.54, 122.12, 114.56, 111.32, 103.85.

MS (EI+): m/z 240.08 (M+ +, 100%); calcd. for C12H4N2O2S: 240.0.

6,7-Difluorobenzo[b]thieno[3,4-e][1,4]dioxine (45F2-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.001 g, 3.86 mmol, 1.00 eq.), K2CO3 (0.562 g, 4.07 mmol, 1.06 eq.), 1,2,4,5-tetrafluorobenzene (13) (0.640 g, 4.26 mmol, 1.11 eq.), LiBr (0.199 g, 2.29 mmol, 0.60 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 140 °C / 15 min, 2) 165 °C / 1 h. After cooling, the mixture was diluted with DCM (100 mL) and filtered to remove insoluble material. The filtrate was washed with water (3 × 50 mL), dried with MgSO4, filtered and evaporated to dryness. The crude product was purified by flash chromatography on silica gel (eluent: PE) to yield compound 45F2-PheDOT (17 mg, 2%) as a white solid.

1H NMR (400 MHz, CDCl3): δ (ppm) 6.78 (2H, dd, J = 9.2 Hz, 8.8 Hz, H B3,6), 6.61 (2H, s, H T2,5).

13C NMR (100 MHz, CDCl3): δ (ppm) 145.70 (dd, 1Jc-f = 246.1 Hz, 2Jc-f = 15.8 Hz, C B4,5), 138.06 (C T3,4), 136.53 (dd, J = 6.4 Hz, J = 6.3 Hz), 105.74 (m), 101.62 (CH, C T2,5).

19F NMR (376 MHz, CDCl3): δ (ppm) –143.85 (s, F B4,5).

MS (EI+): 226.00 (M+ +, 100%); calcd. for C10H4F2O2S: 225.99.
5,8-Difluorobenzo[b]thieno[3,4-e][1,4]dioxine (36F₂-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.005 g, 3.86 mmol, 1.00 eq.), K₂CO₃ (0.546 g, 3.95 mmol, 1.02 eq.), tetrafluorophthalic acid (14) (1.021 g, 0.004 mmol, 1.11 eq.), LiBr (0.207 g, 2.38 mmol, 0.62 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 100 °C / 10 min (80 W), 2) 155 °C / 1.5 h. After cooling, the mixture was diluted with DCM (100 mL) and water (100 mL), stirred and filtered to remove insoluble material. The filtrate was acidified with a few drops of concentrated HCl, organic layer was separated, washed with water (3 × 50 mL), dried with MgSO₄, filtered and the solvent evaporated. The crude product was purified by flash chromatography on silica gel (eluent: PE to PE:EA, 95:5) to yield compound 36F₂-PheDOT (58.5 mg, 6.7%)* as a white powder.

*Note: The yield in the reaction is low (lower than e.g. in the case of F₂-PheDOT, see below). We can’t guarantee that full decarboxylation took place in the reaction and possibly the products with one or two CO₂H on the benzene ring were formed as well but were lost with a tag during the column chromatography purification. Thus, CO₂H group at the benzene ring of PheDOT seems to be more stable toward decarboxylation than those at the 2,5-positions of the thiophenes ring.

1H NMR (400 MHz, CDCl₃): δ (ppm) 6.74–6.69 (2H, m, H₆,7,8), 6.60 (2H, s, HT²,₃), 3.86 (2H, m, H₁,₂), 1.00 (3H, t, J = 7.0 Hz, CH₃), 1.00 (3H, t, J = 7.0 Hz, CH₃).

MS (EI+): m/z 226.05 (M⁺, 100%); calcd. for C₁₀H₇F₂O₂S: 225.99 (100.0%).

5,6,7,8-Tetrafluorobenzo[b]thieno[3,4-e][1,4]dioxine (F₄-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (2.002 g, 7.69 mmol, 1.00 eq.), K₂CO₃ (1.068 g, 7.73 mmol, 1.00 eq.), hexafluorobenzene (15) (1.837 g, 9.87 mmol, 1.28 eq.), LiBr (0.400 g, 4.61 mmol, 0.60 eq.) and DMA (20 mL) were placed in a 35 mL microwave reaction tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor at 172 °C for 30 min. The mixture was cooled down to room temperature, poured into DCM (100 mL) and filtered to remove insoluble material. The filtrate was washed with water (5 × 50 mL), dried over MgSO₄, filtered and evaporated to dryness. The crude product was purified by flash chromatography on a silica gel (eluent: toluene) to yield compound F₄-PheDOT (0.719 g, 35.6% yield) as a white solid.

1H NMR (400 MHz, CDCl₃): δ (ppm) 6.63 (2H, s, HT²,₃), 3.86 (2H, m, H₁,₂), 1.00 (3H, t, J = 7.0 Hz, CH₃), 1.00 (3H, t, J = 7.0 Hz, CH₃).

MS (EI+): m/z 262.05 (M⁺, 100%); calcd. for C₁₀H₇F₄O₂S: 261.97.
Optimization of the reaction conditions in synthesis of F₄-PheDOT

For more detailed studies in our initial experiments, the reaction of thiophene 1 was tested with hexafluorobenzene (15) with monitoring by GC-MS (Table S2). No product F₄-PheDOT or intermediates F₄-22 or F₄-23 were detected in the reaction with conventional heating even at prolonged time at 100 °C (Table S2, entries 1, 2). In MW-assisted conditions, heating with K₂CO₃ in DMA at 220 °C showed formation of the target product F₄-PheDOT along with intermediate F₄-23 (entries 3, 4). However, the yield was drastically decreased when the temperature was raised to 245 °C indicating decomposition of F₄-PheDOT at higher temperatures (entry 5). Addition of LiBr substantially increased the rate of decarboxyethylation of intermediate F₄-23, giving the yields of F₄-PheDOT of ca. 30% (entries 6, 7), although entry 8 indicates that decomposition of F₄-PheDOT occurs upon prolonged heating at 220 °C. Finally, variations in the amount of DMA solvent showed that the highest yields are achieved when the reaction temperature does not exceed 200 °C and ca. 10 mL of a solvent is used per 1 g of thiophene 1 (entries 10, 11).

Table S2. Reaction of thiophene 1 with hexafluorobenzene (15) at different conditions.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>T, °C</th>
<th>Time, h</th>
<th>LiBr, eq.</th>
<th>V DMA/1c mL/g</th>
<th>Yield, b %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>100</td>
<td>16</td>
<td>0</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>2e</td>
<td>100</td>
<td>18</td>
<td>0</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>220</td>
<td>1.5</td>
<td>0</td>
<td>25</td>
<td>19.2</td>
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<td>25</td>
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<td>0.6</td>
<td>30</td>
<td>10.5</td>
</tr>
<tr>
<td>7</td>
<td>220</td>
<td>0.5</td>
<td>0.6</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
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<td>1.5</td>
<td>0.6</td>
<td>25</td>
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</tr>
<tr>
<td>9</td>
<td>200</td>
<td>1.5</td>
<td>0.6</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>1</td>
<td>0.6</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>200</td>
<td>0.5</td>
<td>0.6</td>
<td>9.5</td>
<td>0</td>
</tr>
</tbody>
</table>

aReactions: thiophene 1 (1.0 eq.), hexafluorobenzene 15 (1.1 eq.), K₂CO₃ (1.0 eq.), LiBr (0–0.6 eq.), in DMA, MW irradiation. bYields by GC-MS analysis. The intermediate F₄-22 (with two CO₂Et groups at the thiophene ring) was not detected in any experiment. cAmount of DMA per 1 g of thiophene 1. δIn DMF, conventional heating, 3 eq. Cs₂CO₃ instead of 1 eq. K₂CO₃.

Microwave irradiation is an important factor for the reaction: performing the reaction under similar conditions with conventional heating resulted in substantially lower yields of F₄-PheDOT (0–7%, Table S3) and incomplete decarboxyethylation: apart from the target product F₄-PheDOT, substantial amount of the intermediate F₄-23 was formed. It was isolated and is characterized below.
Table S3. Optimization of the reaction conditions and the yields of F₄-PheDOT in MW-asisted reaction of thiophene 1 with hexafluorobenzene (15):a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Thiophene 1</th>
<th>C₆F₆ (15)</th>
<th>Base (1.0 eq.)</th>
<th>Solvent: DMA</th>
<th>MW, temp./time</th>
<th>Yield, b%</th>
<th>Number of reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.00 g</td>
<td>1.1 eq.</td>
<td>K₂CO₃</td>
<td>20 mL</td>
<td>172 °C / 0.5 h</td>
<td>35.6%</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1.50 g</td>
<td>1.1 eq.</td>
<td>t-BuOK</td>
<td>10 mL</td>
<td>178 °C / 1 h</td>
<td>31.7%</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>2.00 g</td>
<td>1.1 eq.</td>
<td>K₂CO₃</td>
<td>20 mL</td>
<td>160–170 °C / 1 h</td>
<td>32.3%</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>1.50 g</td>
<td>1.1 eq.</td>
<td>K₂CO₃</td>
<td>10 mL</td>
<td>164 °C / 1 h</td>
<td>29.3%</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>1.00 g</td>
<td>1.1 eq.</td>
<td>K₂CO₃</td>
<td>10 mL</td>
<td>190–200 °C / 1 h</td>
<td>23%</td>
<td>3</td>
</tr>
<tr>
<td>6c</td>
<td>2.00 g</td>
<td>1.0 eq.</td>
<td>K₂CO₃</td>
<td>20 mL</td>
<td>120 °C / 38 h/ 140 °C / 18 h</td>
<td>4%</td>
<td>1</td>
</tr>
<tr>
<td>7e</td>
<td>1.00 g</td>
<td>1.1 eq.</td>
<td>K₂CO₃</td>
<td>9 mL</td>
<td>160 °C / 2.5 h</td>
<td>7%</td>
<td>1</td>
</tr>
<tr>
<td>8e</td>
<td>8.00 g</td>
<td>1.1 eq.</td>
<td>K₂CO₃</td>
<td>72 mL</td>
<td>180 °C / 2.5 h</td>
<td>6%</td>
<td>1</td>
</tr>
<tr>
<td>9e</td>
<td>5.00 g</td>
<td>1.5 eq.</td>
<td>K₂CO₃</td>
<td>40 mL (DMF)</td>
<td>149 °C / 28 h</td>
<td>0%</td>
<td>1</td>
</tr>
</tbody>
</table>

a0.6 eq. LiBr has been used in all reactions. bIsolated yields. Average yields from several reactions (where appropriate). cConventional heating in an autoclave.

Ethyl 5,6,7,8-tetrafluorobenzo[b]thieno[3,4-e][1,4]dioxine-1-carboxylate (F₄-23)

Compound F₄-23 was isolated from a tag after an isolation of F₄-PheDOT. After purification of F₄-PheDOT, the residue from the column was washed with DCM, the crude product was collected and was purified twice by flash chromatography on a silica gel (eluent: gradient from PE to PE:DCM, 1:1) to afford pure compound F₄-23.

Rf (PE:DCM, 1:1) = 0.32.

1H NMR (400 MHz, CDCl₃): δ (ppm) 6.83 (1H, s, HT₅), 4.38 (2H, q, J = 7.1 Hz, CH₂), 1.40 (3H, t, J = 7.1 Hz, CH₃).

13C NMR (100 MHz, CDCl₃): δ (ppm) {only thiophene aromatic carbons have been detected; benzene carbons appear as very low intensity multiplets due to H–F coupling}, 160.12 (s, C=O), 139.00 (s, C), 139.0–137.8 (m, C–F, Cᵦ)136.36 (s, C), 137.0–135.5 (m, C–F, Cᵦ), 128.2–127.8 (m, C–F, Cᵦ), 108.12 (s, CH, C₅), 61.65 (CH₂), 14.19 (CH₃).

19F NMR (376 MHz, CDCl₃); δ (ppm) –161.64 (1F, ddd, J = 21.6, 5.7, 2.9 Hz, Fᵦᵢ), –163.13 (1F, ddd, J = 21.5, 5.6, 3.3 Hz, Fᵦᵢ), –164.75 (1F, td, J = 21.7, 2.8 Hz, Fᵦᵣ), –165.30 (1F, td, J = 21.7, 3.3 Hz, Fᵦᵣ).

MS (EI+): m/z 334.01; caleld for C₁₃H₁₆F₄O₄S: 333.99.
1,2,3,4,5,6-Hexafluoronaphtho[2,1-b]thieno[3,4-e][1,4]dioxine \{F_6-NaphDOT(1,2)\} and
5,6,7,8,9,10-hexafluoronaphtho[2,3-b]thieno[3,4-e][1,4]dioxine \{F_6-NaphDOT(2,3)\}

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (101 mg, 0.39 mmol, 1.00 eq.), K_2CO_3 (55.7 mg, 0.40 mmol, 1.03 eq.), octafluoronaphthalene (16) (115 mg, 0.42 mmol, 1.09 eq.), LiBr (20 mg, 0.23 mmol, 0.60 eq.) and DMA (1.0 mL) were placed in a 10 mL MW reaction tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor at 200 °C for 30 min. The mixture was cooled to room temperature and poured into DCM (20 mL). The solution was filtered from insoluble material, the filtrate was washed with water (5 × 15 mL), dried over MgSO_4, filtered and the solvent was removed by evaporation. The residue, which contains a mixture of isomers F_6-NaphDOT(1,2) and F_6-NaphDOT(2,3) (two closely spaced spots on TLC in non-polar solvents, which are not separated in more polar solvents) was purified by column chromatography on silica gel (eluent: PE) first eluting compound F_6-NaphDOT(1,2) (16.6 mg, 12.2% yield, white solid), followed by compound F_6-NaphDOT(2,3) (28.9 mg, 21.3% yield, white solid). The total combined yield of both isomers was 33.5% (with a ratio of F_6-NaphDOT(1,2):F_6-NaphDOT(2,3) ≈ 1:2). Both isomers, especially F_6-NaphDOT(2,3), are very insoluble materials, so their flash chromatography separation can only be performed on a small scale.

Non-symmetric compound F_6-NaphDOT(1,2):

\(^1\)H NMR (400 MHz, CDCl_3): δ (ppm) 6.64 (1H, d, J_{T2-T5} = 3.6 Hz, H^{T2/5}), 6.62 (1H, d, J_{T2-T5} = 3.6 Hz, H^{T2/5}).

\(^1\)H NMR (100 MHz, CDCl_3): δ (ppm) 137.22, 136.40, 103.32 (2C, C^{T2/5}), \{identification of other peaks in the region of 133–144 ppm was difficult because of low solubility of the compound and low intensity of the signals due to C–F coupling\}.

\(^1\)F NMR (376 MHz, CDCl_3): δ (ppm) –144.0–144.2 (m, 1F), –144.5–147.9 (m, 1F), –150.3–150.6 (m, 1F), –155.1–155.2 (m, 1F), –157.0–157.2 (m, 1F), –157.4–157.6 (m, 1F).

MS (EI+): m/z 348.01 (M^+, 100.0%); calcd. for C_{14}H_{14}F_{10}O_5S: 347.97.

Symmetric compound F_6-NaphDOT(2,3):

\(^1\)H NMR (400 MHz, CDCl_3, TMS): δ (ppm) 6.74 (2H, s, H^{T2/5}).

\(^1\)C NMR (DEPTQ, 100 MHz, CDCl_3): δ (ppm) 103.5 (2C, C^{T2/5}), \{an identification of other peaks was difficult because of very low solubility of the compound and low intensity of the signals due to C–F coupling\}.

\(^1\)F NMR (376 MHz, CDCl_3): δ (ppm) –146.5–146.8 (m, 2F), –147.7–148.1 (m, 2F), –157.6–157.8 (m, 2F).

MS (EI+): m/z 348.05 (M^+, 100.0%); calcd. for C_{14}H_{14}F_{10}O_5S: 347.97.
5,6,7,8-Tetrafluoro-9H-benzo[e]thieno[3,4-b][1,4]dioxepine (F₄-BnDOT)

\[
\begin{align*}
\text{EtO}_2C & \quad \text{S} & \quad \text{CO}_2\text{Et} \\
\text{HO} & \quad \text{OH} & \quad \text{Br} & \quad \text{F} & \quad \text{F} & \quad \text{F}
\end{align*}
\]

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.018 g, 3.91 mmol, 1.00 eq.), K₂CO₃ (0.558 g, 4.04 mmol, 1.03 eq.), 2,3,4,5,6-pentafluorobenzylbromide (17) (1.170 g, 4.48 mmol, 1.15 eq.), LiBr (0.215 g, 2.48 mmol, 0.63 eq.) and DMA (10 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 1) 50 °C / 5 min; 2) 80 °C / 15 min; 3) 100 °C / 15 min, 4) 200°C / 1 h. After cooling, the mixture was diluted with water (100 mL), stirred for 1 h and the solid was filtered off by suction. The solid was transferred into DCM (150 mL), stirred for 30 min, dried over MgSO₄, filtered and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: PE to yield compound F₄-BnDOT (0.120 g, 11.1%) as a white solid.

1H NMR (400 MHz, CDCl₃): δ (ppm) 6.87 (1H, d, J₁₂₋₁₅ = 4.2 Hz, H₁₅), 6.44 (1H, d, J₁₂₋₁₅ = 4.2 Hz, H₁₅), 5.24 (2H, d, J₁₋₁₅ = 1.5 Hz, CH₂).

13C NMR (100 MHz, CDCl₃): δ (ppm) 145.35 (s), 145.0 (m), 142.7 (m), 142.31 (s), 140.8 (m), 140.3 (m), 138.5 (m), 136.2 (m), 114.40 (dd, J = 16.1 Hz, J = 3.6 Hz), 108.76 (CH, s, H₁₅), 104.39 (CH, s, H₁₅), 60.38 (d, J₃₋₋₅ = 4.3 Hz, CH₂).

19F NMR (376 Hz): δ (ppm) -146.16 (1F, ddd, J = 22.5 Hz, 11.1 Hz, 1.9 Hz), -154.91 (1F, td, J = 20.8 Hz, 19 Hz), -157.61 (1F, dd, J = 21.1 Hz, 10.5 Hz), -162.65 (1F, dd, J = 22.2 Hz, 20.7 Hz).

MS (EI+): m/z 276.05 (M⁺, 100%); calcd. for C₁₁H₂₅F₄O₂S: 275.99.

3-Trifluoromethylthieno[3',4':5,6][1,4]dioxino[2,3-b]pyridine (5CF₃-PyDOT)

\[
\begin{align*}
\text{EtO}_2C & \quad \text{S} & \quad \text{CO}_2\text{Et} \\
\text{HO} & \quad \text{OH} & \quad \text{Br} & \quad \text{F} & \quad \text{F} & \quad \text{F}
\end{align*}
\]

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.000 g, 3.84 mmol, 1.00 eq.), K₂CO₃ (531 mg, 3.84 mmol, 1.00 eq.), 2,3-difluoro-6-trifluoromethylpyridine (18) (778 mg, 4.25 mmol, 1.11 eq.), LiBr (210 mg, 2.42 mmol, 0.63 eq.) and DMA (11 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 2 steps: 1) 100°C / 10 min, 155°C / 90 min. After cooling, a clear, almost colorless layer was formed at the bottom of the tube. The mixture was partitioned between DCM (80 mL) and water (70 mL) (full dissolution was observed). The organic layer was separated, washed with water (3 × 25 mL), dried over MgSO₄, filtered and the solvent was evaporated. The crude product was analyzed by GC-MS, which showed the desired product, together with small amount of one by-product. The crude product was purified by flash chromatography on silica gel (eluent: PE to PE:EA, 9:1) to yield a relatively pure sample of compound 5CF₃-PyDOT (841 mg, 96%) followed by an impure fraction (71 mg). The first fraction was additionally purified by flash chromatography on silica gel (eluent: PE:EA, 1:1) to afford pure compound 5CF₃-PyDOT (641 mg, 74%) as a white solid.
**1H NMR** (400 MHz, CDCl3): δ (ppm) 8.16 (br.s, H5/6), 7.44 (d, J4-5 = 1.9 Hz, H5/6), 6.65 (1H, d, J2-T5 = 3.6 Hz, H2/5), 6.55 (1H, d, J2-T5 = 3.6 Hz, H2/5).

**13C NMR** (100 MHz, CDCl3): δ (ppm) 150.55 (C2), 139.02 (CH, q, JCF = 4.5 Hz, C5/6), 137.90 (C3/4), 137.04 (C3/4), 136.85 (C3/4), 136.01 (C3/4), 127.06 (CH, C5), 124.89 (C5/6), 103.75 (CH, C2/5), 102.61 (C3, C3/4).

**MS (EI+):** m/z 259.00 (M+, 100%); calcd. for C10H4F3NO2S: 258.99.

2,3-Dichlorothieno[3',4':5,6][1,4]dioxino[2,3-b]pyridine (56Cl2-PyDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.001 g, 3.85 mmol, 1.00 eq.), K2CO3 (0.544 g, 3.94 mmol, 1.02 eq.), 2,3,5,6-tetrachloropyridine (19) (0.920 g, 4.24 mmol, 1.10 eq.), LiBr (0.222 g, 2.56 mmol, 0.66 eq.) and DMA (10 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min, 2) 80 °C / 15 min, 3) 100 °C / 15 min, 4) 200°C / 1 h. After cooling, the mixture was poured into water (100 mL) and stirred for 1 h. The solid was filtered off, dissolved in DCM (150 mL), dried over MgSO4, filtered and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: toluene) to yield compound 56Cl2-PyDOT (166 mg, 16.6%) as light-yellow crystals. An analytically pure sample was obtained by repeated flash chromatography with PE:DCM, 2:1.

**1H NMR** (400 MHz, CDCl3): δ (ppm) 7.36 (1H, s, H3), 6.61 (1H, d, J2-T5 = 3.6 Hz, H2/5), 6.53 (1H, d, J2-T5 = 3.6 Hz, H2/5).

**13C NMR** (100 MHz, CDCl3): δ (ppm) 145.50 (C2/3/5/6), 139.01 (C2/3/5/6), 137.76 (C3/4), 136.85 (C3/4), 136.01 (C2/3/5/6), 127.06 (CH, C5), 124.89 (C2/3/5/6), 103.66 (CH, C2/5), 102.71 (CH, C2/5).

**MS (EI+):** m/z 259.00 (M+, 100%, 35Cl/37Cl), 261.00 (68%, 35Cl/37Cl), 262.95 (13%, 37Cl/37Cl), calcd. for C9H8Cl2NO2S: 258.93 (100.0%), 260.92 (68.4%), 262.92 (13.2%).
Thieno[3',4':5,6][1,4]dioxino[2,3-b]pyrazine (PzDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (999 mg, 3.84 mmol, 1.00 eq.), K₂CO₃ (534 mg, 3.86 mmol, 1.01 eq.), 2,3-dichloropyrazine (20) (839 mg, 4.22 mmol, 1.0 eq.), LiBr (195 mg, 2.25 mmol, 0.6 eq.) and DMA (12 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min, 2) 80 °C / 5 min, 3) 100 °C / 15 min, 4) 200 °C / 1 h. After cooling, the mixture was diluted with DCM (120 mL), stirred for 1 h and filtered to remove insoluble materials. The filtrate was washed with water (6 × 150 mL), dried over MgSO₄, filtered and the solvent was evaporated to dryness. The crude product was purified by flash chromatography on silica gel (eluent: PE:EA, 9:1) to yield compound PzDOT (0.283 g, 38.2%) as a white crystalline solid.

[^1]H NMR (400 MHz, CDCl₃, TMS): δ (ppm) 7.88 (2H, dd, J = 6.3 Hz, 3.5 Hz, H[^P5,6]), 6.66 (2H, s, H[^T2,5]).
[^13]C NMR (100 MHz, CDCl₃): δ (ppm) 144.91 (C[^P2,3]), 137.51 (C[^T3,4]), 137.09 (CH, C[^P5,6]), 103.54 (CH, C[^T2,5]).
MS (EI+): m/z 192.01 (100%); calcd. for C₈H₈N₂O₂S: 192.00.

Thieno[3',4':5,6][1,4]dioxino[2,3-b]quinoxaline (QxDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (999 mg, 3.84 mmol, 1.00 eq.), K₂CO₃ (534 mg, 3.86 mmol, 1.01 eq.), 2,3-dichloroquinoxaline (21) (839 mg, 4.22 mmol, 1.0 eq.), LiBr (195 mg, 2.25 mmol, 0.6 eq.) and DMA (12 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor in 4 steps: 1) 50 °C / 5 min, 2) 80 °C / 5 min, 3) 100 °C / 15 min, 4) 155 °C / 1.5 h. After cooling, the mixture was diluted with DCM (120 mL) and water (25 mL), stirred and filtered through glass wool to remove insoluble materials. The organic layer was separated, washed with water (3 × 25 mL), dried with MgSO₄, filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (eluent: gradient from PE to DCM) to yield compound QxDOT (388 mg, 41.7%) as a yellowish powder.

[^1]H NMR (400 MHz, CDCl₃): δ (ppm) 7.85 (2H, dd, J = 6.3 Hz, 3.5 Hz, H[^B3,6/B4,5]), 7.62 (2H, dd, J = 6.3 Hz, 3.5 Hz, H[^B3,6/B4,5]), 6.75 (2H, s, H[^T2,5]).
[^13]C NMR (100MHz, CDCl₃): δ (ppm) 143.15 (C[^P2,3]), 138.66 (C[^P5,6]), 137.18 (C[^T3,4]), 129.09 (CH, C[^B3,5/B4,5]), 127.34 (CH, C[^B3,5/B4,5]), 103.70 (CH, C[^T2,5]).
MS (TOF EI+): m/z 242.09 (M⁺, 100%); calcd for C₁₂H₈N₂O₂S: 242.01.
6-Bromo-5,8-difluorobenzo[b]thieno[3,4-e][1,4]dioxine (3Br,45F₂-PheDOT) and 5,8-difluorobenzo[b]thieno[3,4-e][1,4]dioxine (45F₂-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.031 g, 3.96 mmol, 1.00 eq.), K₂CO₃ (0.546 g, 3.95 mmol, 1.00 eq.), 1,4-dibromo-2,3,5,6-tetrafluorobenzene (24) (1.216 g, 3.95 mmol, 1.00 eq.), LiBr (0.208 g, 2.40 mmol, 0.61 eq.) and DMA were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor (80 W) in 4 steps: 1) 50 °C / 5 min, 2) 80 °C/ 5 min, 3) 100 °C/ 15 min, 4) 200 °C / 1 h. After cooling, the reaction mixture was transferred into water (100 mL), stirred for 1 h and the precipitate was filtered off. This solid was transferred into DCM (150 mL), stirred for 1 h for dissolution, dried over MgSO₄, filtered and the solvent was evaporated. The crude was purified by column chromatography on silica gel (eluent: PE) to yield a light-cream color solid (0.055 g, ~5%). The GC-MS analysis of the sample showed a mixture of two products, 3Br,45F₂-PheDOT and 45F₂-PheDOT, in a ratio of ca. 1.6:1. The sample showed one spot on TLC (with the same R_f as authentic 45F₂-PheDOT synthesized independently in another experiment, see above) and we were unable to separate these products by flash chromatography. As the yield was low, partial debromination occurred during the reaction and the experiment did not give the expected 36Br₂,45F₂-PheDOT, we did not make further attempts to separate the products.

3Br,45F₂-PheDOT:  
MS (EI⁺): m/z 305.95 (M⁺, 100%, ⁷⁹Br), 303.90 (95.5%, ⁸¹Br); calcd. for C₁₀H₃BrF₂O₂S: 305.90 (100.0%, ⁷⁹Br), 303.90 (97.8%, ⁸¹Br).

45F₂-PheDOT:  
MS (EI⁺): m/z 226.00 (M⁺, 100%); calcd. for C₁₀H₁₄F₂O₂S: 225.99.
6,7-Dibromobenzo[b]thieno[3,4-e][1,4]dioxine (45Br₂-PheDOT), and 6-bromobenzo[b]thieno[3,4-e][1,4]dioxine (4Br-PheDOT)

Diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.013 g, 3.89 mmol, 1.00 eq.), K₂CO₃ (0.552 g, 3.99 mmol, 1.03 eq.), 1,2-dibromo-4,5-difluorobenzene (25) (1.106 g, 4.07 mmol, 1.04 eq.), LiBr (0.222 g, 2.56 mmol, 0.66 eq.) and DMA (10 mL) were placed in a 35 mL MW tube. The tube was sealed, degassed by bubbling with nitrogen (stirring) for 3 min and heated with stirring in a microwave reactor (80 W) in 4 steps: 1) 50 °C / 5 min, 2) 80 °C / 5 min, 3) 100 °C / 15 min, 4) 200 °C / 1 h. Another batch of diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate (1) (1.012 g, 3.89 mmol, 1.00 eq.), K₂CO₃ (0.539 g, 3.90 mmol, 1.00 eq.), 1,2-dibromo-4,5-difluorobenzene (29) (1.137 g, 4.18 mmol, 1.08 eq.), LiBr (0.209 g, 2.41 mmol, 0.62 eq.) and DMA (10 mL) was run at the same conditions. After cooling, the combined reaction mixtures were poured into water (200 mL), stirred for 1 h and the precipitate was filtered off. This solid was transferred into DCM (200 mL), stirred for 1 h, dried over MgSO₄, filtered and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (eluent: PE) to yield an off-white (light cream color) solid (0.258 g, ~10%). The GC-MS and ¹H NMR analyses of the sample showed a mixture of two products, 45Br₂-PheDOT and 4Br-PheDOT, in a ratio of ca. 4:1. The sample showed one spot on TLC and we were unable to separate these products by flash chromatography. In the ¹H NMR of the mixture, partly debrominated compound 4Br-PheDOT was identified by comparison with an authentic sample prepared independently (see above) and 45Br₂-PheDOT was identified by comparison with an authentic sample prepared by reaction of 4,5-dibromocatechol with 3,4-dimethoxythiophene.¹³ As partial debromination occurred during the reaction and the experiment did not give the expected 45Br₂-PheDOT in a pure form, we did not make further attempts to separate these products.

**45Br₂-PheDOT:**
MS (EI⁺): m/z 347.95 (M⁺, 100%, ⁷⁹Br/⁷⁹Br), 349.90 (53.3%, ⁷⁹Br/⁸¹Br), 345.90 (50.2%, ⁸¹Br/⁸¹Br); calcd. for C₁₀H₄Br₂O₂S: 347.92 (100.0%, ⁷⁹Br/⁷⁹Br), 345.92 (97.8%, ⁸¹Br/⁸¹Br).

**4Br-PheDOT:**
MS (EI⁺): m/z 270.00 (M⁺, 100%, ⁷⁹Br), 267.95 (90.0%, ⁸¹Br); calcd. for C₁₀H₅BrO₂S: 269.92 (100.0%, ⁷⁹Br), 267.92 (97.8%, ⁸¹Br).
Figure S1. UV-Vis electron absorption spectra of mono- and disubstituted (at the benzene ring) EWG-PheDOT monomers in dichloromethane. The spectra are normalized to the maxima in the region of 260–280 nm (45Br2-PheDOT and 45Cl2-PheDOT have been synthesized according to Ref. 13).
Figure S2. UV-Vis electron absorption spectra of ArDOT monomers in dichloromethane. The spectra are normalized to the maxima in the region of 240–280 nm.
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<th>Compound</th>
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<th>$3NO_25CF_2$-PheDOT</th>
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Figure S3 (4 pages): Molecular and crystal structures of compounds F$_4$-23, 36F$_2$-PheDOT, F$_4$-PheDOT, 3NO$_2$4CF$_3$-PheDOT, 56Cl$_2$PyDOT, 5CF$_3$-PheDOT, PzDOT and QxDOT.

(non-centrosymmetric structure; second polymorph crystal is seen)
(some disorder of NO\textsubscript{2}/CF\textsubscript{3} in a crystal)
(twin crystals; two independent molecules in a unit cell)
We were also able to isolate the $\text{F}_4\text{-23}$ intermediate from the reaction mixture in synthesis by Scheme 1 in the paper, and its structure was confirmed by a single crystal X-Ray diffraction (Figure S4). In the crystal structure of $\text{F}_4\text{-23}$ planar (with the exception of the terminal methyl group) molecules are arranged in layers perpendicular to the c-axis. Each layer is formed out of anti-parallel chains of molecules linked by C(thiophene)–H⋯O and F⋯O contacts. Weaker C(methylene)–H⋯S contacts exist between the layers. The polycyclic fragments of the molecules in adjacent parallel chains do not overlap, meaning the absence of “classical” aromatic π⋯π stacking in the structure. Nevertheless, the distance between molecules in parallel chains is quite short: the shortest interatomic distance is O⋯O 3.132(1) Å. Most probably electrostatic interactions between numerous heteroatoms are responsible for such an unusual (for planar tricyclic molecules) packing arrangement. A proper analysis of these interactions requires quantum-chemical calculations and is impossible on the basis of geometrical information obtained by X-ray method only.

Figure S4. Molecular structure and crystal packing of compound $\text{F}_4\text{-23}$. 
Figure S5. Chain length dependences of (a) HOMO and LUMO energies and (b) HOMO–LUMO energy gaps $\Delta E_{\text{HL}}$ for B3LYP/6-31G(d) optimized geometries (in the gas phase) of (PhedOT)$_n$ and (F$_4$-PhedOT)$_n$ oligomers, plotted versus a number of repeating units “n”.
Figure S6. Chain length dependences of (a) HOMO and LUMO energies and (b) HOMO–LUMO energy gaps $\Delta E_{HL}$ for B3LYP/6-31G(d) optimized geometries (in the gas phase) of $(\text{PheDOT})_n$ and $(\text{F}_4\text{-PheDOT})_n$ oligomers, plotted versus a reciprocal number of repeating units, $1/n$. Symbols ▲ and ▼ correspond to the energies (HOCO, LUCO, $E_g$) for polymers calculated by PBC/B3LYP/6-31G(d).
Figure S7. Chain length dependences of (a) HOMO and LUMO energies and (b) HOMO–LUMO energy gaps $\Delta E_{\text{HL}}$ for B3LYP/6-31G(d) optimized geometries (in the gas phase) of (PheDOT)$_n$ and (F$_4$-PheDOT)$_n$ oligomers, plotted as a function of $1/(n + 0.1n^2)$. Symbols ▲ and ▼ correspond to the energies (HOCO, LUCO, $E_g$) for polymers calculated by PBC/B3LYP/6-31G(d).
In contrast to dependences of energies (HOMO, LUMO, ΔE_{HL}) versus 1/n, which show deviation from the linearity (saturation) with an elongation of the oligomers length, the use of the function $1/(n + 0.1n^2)$ gives excellent linear dependences (see Figure S7 for magnified graphs) with correlation coefficients $R \geq 0.9998$, and the extrapolated (to the infinite polymer length, $n = \infty$) energies excellently coincide with the energies for the polymers calculated by PBC/B3LYP/6-31G(d).

$$E_n = E_{n=\infty} + \alpha \cdot [1/(n + 0.1n^2)]$$

(PheDOT)$_n$:
- LUMO [eV] = -(2.244 ± 0.001) + (2.655 ± 0.011)·[1/(n + 0.1n^2)]
  
  $R = 0.9999$, $N = 18$ (points $n = 3...18, 20, 25$)

- HOMO [eV] = -(4.364 ± 0.001) - (2.454 ± 0.008)·[1/(n + 0.1n^2)]
  
  $R = 0.9999$, $N = 18$ (points $n = 3...18, 20, 25$)

- ΔE_{HL} [eV] = (2.120 ± 0.002) + (5.109 ± 0.017) · [1/(n + 0.1n^2)]
  
  $R = 0.9999$, $N = 18$ (points $n = 3...18, 20, 25$)

p[PheDOT], calculations by PBC:
- LUCO = -2.239 eV
- HOCO = -4.374 eV
- $E_g = 2.135 eV$

(F$_4$-PheDOT)$_n$:
- LUMO [eV] = -(2.868 ± 0.002) + (2.889 ± 0.012)·[1/(n + 0.1n^2)]
  
  $R = 0.9999$, $N = 18$ (points $n = 3...20$)

- HOMO [eV] = -(5.015 ± 0.001) - (2.143 ± 0.010)·[1/(n + 0.1n^2)]
  
  $R = 0.9998$, $N = 18$ (points $n = 3...20$)

- ΔE_{HL} [eV] = (2.147 ± 0.001) + (5.032 ± 0.015) · [1/(n + 0.1n^2)]
  
  $R = 0.9999$, $N = 18$ (points $n = 3...20$)

p[F$_4$-PheDOT], calculations by PBC:
- LUCO = -2.882 eV
- HOCO = -5.033 eV
- $E_g = 2.151 eV$
**Figure S8.** Magnified graphs (for $n = 4 – 25$, from Figures S4 and S5) of B3LYP/6-31G(d) calculated energy gaps $\Delta E_{HL}$ for (PheDOT)$_n$ and (F$_4$-PheDOT)$_n$: comparison of correlations versus (a) $1/n$ and (b) $1/(n + 0.1n^2)$. 

$\Delta E_{HL}$ [eV] vs. $1/n$ (a) and $1/(n + 0.1n^2)$ (b) for various polymer lengths $n$. Graphs illustrate the correlation between the calculated energy gap and the inverse of the polymer length, highlighting the trend for both PheDOT and (F$_4$-PheDOT) polymers with and without fluorine substitution.
Table S5. Total energies, HOMO/LUMO energy levels and the HOMO–LUMO gaps for (PheDOT)$_n$ and (F$_4$-PheDOT)$_n$ oligomers by B3LYP/6-31G(d) calculations in the gas phase.

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<th>LUMO, eV</th>
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Table S6. HOMO, LUMO energy levels and the HOMO–LUMO energy gaps (ΔE_{HL}) of dimers (ArDOT)₂ by B3LYP/6-31G(d) calculations in the gas phase.

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<tr>
<td>7 (4Br-PheDOT)₂</td>
<td>-7007.565927</td>
<td>-5.563</td>
<td>-1.463</td>
<td>4.100</td>
</tr>
<tr>
<td>8 (4Cl-PheDOT)₂</td>
<td>-2784.5474279</td>
<td>-5.572</td>
<td>-1.468</td>
<td>4.104</td>
</tr>
<tr>
<td>9 (45F₂-PheDOT)₂</td>
<td>-2262.2698477</td>
<td>-5.612</td>
<td>-1.512</td>
<td>4.100</td>
</tr>
<tr>
<td>10 (4CF₃-PheDOT)₂</td>
<td>-2539.4325592</td>
<td>-5.701</td>
<td>-1.582</td>
<td>4.119</td>
</tr>
<tr>
<td>11 (4MeSO₂-PheDOT)₂</td>
<td>-3041.1303425</td>
<td>-5.843</td>
<td>-1.729</td>
<td>4.114</td>
</tr>
<tr>
<td>12 (F₄-PheDOT)₂</td>
<td>-2659.1424161</td>
<td>-5.864</td>
<td>-1.742</td>
<td>4.122</td>
</tr>
<tr>
<td>13 (45Cl₂-PheDOT)₂</td>
<td>-3703.7258360</td>
<td>-5.766</td>
<td>-1.658</td>
<td>4.108</td>
</tr>
<tr>
<td>14 (Cl₄-PheDOT)₂</td>
<td>-5542.0642800</td>
<td>-5.990</td>
<td>-1.869</td>
<td>4.120</td>
</tr>
<tr>
<td>15 (3NO₂,5CF₃-PheDOT)₂</td>
<td>-2948.4047350</td>
<td>-6.148</td>
<td>-2.842</td>
<td>3.306</td>
</tr>
<tr>
<td>16 (4CN-PheDOT)₂</td>
<td>-2049.8433341</td>
<td>-5.917</td>
<td>-1.845</td>
<td>4.073</td>
</tr>
<tr>
<td>17 (4NO₂-PheDOT)₂</td>
<td>-2274.3601970</td>
<td>-6.003</td>
<td>-2.587</td>
<td>3.416</td>
</tr>
<tr>
<td>18 (3CF₃,5NO₂-PheDOT)₂</td>
<td>-2352.9989481</td>
<td>-5.947</td>
<td>-2.513</td>
<td>3.434</td>
</tr>
<tr>
<td>19 (45(CN)₂-PheDOT)₂</td>
<td>-2234.3133927</td>
<td>-6.415</td>
<td>-2.582</td>
<td>3.833</td>
</tr>
<tr>
<td>20 (NaphDOT(2,3))₂</td>
<td>-2172.6473759</td>
<td>-5.260</td>
<td>-1.313</td>
<td>3.947</td>
</tr>
<tr>
<td>21 [(F₆-NaphDOT(2,3))]₂</td>
<td>-3363.3433721</td>
<td>-5.773</td>
<td>-1.874</td>
<td>3.899</td>
</tr>
<tr>
<td>22 [(F₆-NaphDOT(1,2))]₂</td>
<td>-3363.3378313</td>
<td>-5.798</td>
<td>-1.918</td>
<td>3.881</td>
</tr>
<tr>
<td>23 (PyDOT)₂</td>
<td>-1897.4408713</td>
<td>-5.509</td>
<td>-1.365</td>
<td>4.145</td>
</tr>
<tr>
<td>24 (5CF₃-PyDOT)₂</td>
<td>-2571.5109075</td>
<td>-5.899</td>
<td>-1.754</td>
<td>4.145</td>
</tr>
<tr>
<td>25 (56Cl₂-PyDOT)₂</td>
<td>-3735.8092468</td>
<td>-5.966</td>
<td>-1.825</td>
<td>4.141</td>
</tr>
<tr>
<td>26 (PzDOT)₂</td>
<td>-1929.5159146</td>
<td>-5.764</td>
<td>-1.641</td>
<td>4.124</td>
</tr>
<tr>
<td>27 (QxDOT)₂</td>
<td>-2236.8167607</td>
<td>-5.701</td>
<td>-1.968</td>
<td>3.734</td>
</tr>
<tr>
<td>28 (F₄-BnDOT)₂ cisoid⁵</td>
<td>-2737.7710399</td>
<td>-5.437</td>
<td>-1.340</td>
<td>4.097</td>
</tr>
<tr>
<td>29 (F₄-BnDOT)₂ transoid⁵</td>
<td>-2737.7710008</td>
<td>-5.439</td>
<td>-1.343</td>
<td>4.096</td>
</tr>
</tbody>
</table>

ΔE_{HL} = LUMO – HOMO.

⁵ “Cisoid” and “transoid” belongs to the relative orientation of non-planar seven-member rings in the dimers.
Table S7. HOCO, LU CO energy levels and the band gaps ($E_g$) of p[ArDOT] polymers by PBC/B3LYP/6-31G(d) calculations in the gas phase

<table>
<thead>
<tr>
<th>p[ArDOT]</th>
<th>Total energy, a hartree</th>
<th>HOCO, eV</th>
<th>LU CO, eV</th>
<th>$E_g$, b eV</th>
<th>$\Delta$HOCO, c eV</th>
<th>$\Delta$E_g, d meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>p[4MeO-PheDOT]</td>
<td>–2093.2153646</td>
<td>–4.329</td>
<td>–2.204</td>
<td>2.126</td>
<td>0.040</td>
<td>–10</td>
</tr>
<tr>
<td>p[PheDOT]</td>
<td>–1864.1731432</td>
<td>–4.374</td>
<td>–2.239</td>
<td>2.135</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>p[36F2-PheDOT]</td>
<td>–2261.076465</td>
<td>–4.552</td>
<td>–2.390</td>
<td>2.162</td>
<td>–0.178</td>
<td>26</td>
</tr>
<tr>
<td>p[4F-PheDOT]</td>
<td>–2062.6355280</td>
<td>–4.644</td>
<td>–2.511</td>
<td>2.133</td>
<td>–0.27</td>
<td>–2</td>
</tr>
<tr>
<td>p[4Cl-PheDOT]</td>
<td>–2783.3613276</td>
<td>–4.790</td>
<td>–2.650</td>
<td>2.144</td>
<td>–0.579</td>
<td>9</td>
</tr>
<tr>
<td>p[4MeSO2-PheDOT]</td>
<td>–3039.9466487</td>
<td>–4.980</td>
<td>–2.831</td>
<td>2.149</td>
<td>–0.606</td>
<td>14</td>
</tr>
<tr>
<td>p[F4-PheDOT]</td>
<td>–2657.9557189</td>
<td>–5.033</td>
<td>–2.882</td>
<td>2.151</td>
<td>–0.659</td>
<td>16</td>
</tr>
<tr>
<td>p[4Cl2-PheDOT]</td>
<td>–3702.5384422</td>
<td>–5.059</td>
<td>–2.919</td>
<td>2.140</td>
<td>–0.685</td>
<td>5</td>
</tr>
<tr>
<td>p[NaphDOT(2,3)]</td>
<td>–2351.8121007</td>
<td>–4.393</td>
<td>–2.364</td>
<td>2.029</td>
<td>–0.019</td>
<td>–106</td>
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<tr>
<td>p[F6-NaphDOT(2,3)]</td>
<td>–2233.1177820</td>
<td>–4.950</td>
<td>–2.913</td>
<td>2.037</td>
<td>–0.576</td>
<td>–98</td>
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<tr>
<td>p[5CF3-PyDOT]</td>
<td>–3362.1576614</td>
<td>–5.055</td>
<td>–2.887</td>
<td>2.169</td>
<td>–0.681</td>
<td>33</td>
</tr>
<tr>
<td>p[56Cl2-PyDOT]</td>
<td>–3362.1542424</td>
<td>–5.157</td>
<td>–2.988</td>
<td>2.169</td>
<td>–0.783</td>
<td>34</td>
</tr>
<tr>
<td>p[QxDOT]</td>
<td>–2570.3264606</td>
<td>–4.639</td>
<td>–2.583</td>
<td>2.056</td>
<td>–0.265</td>
<td>–79</td>
</tr>
</tbody>
</table>

a Absolute energies per unit cell.

b $E_g =$ LU CO – HOCO.

c $\Delta$HOCO = HOCO(p[ArDOT]) – HOCO(p[PheDOT])

d $\Delta$E_g = $E_g$(p[ArDOT]) – $E_g$(p[PheDOT])
Table S8. Short S···O contacts and selected bond distances in p[ArDOTs] for optimized polymer structures by PBC/B3LYP/6-31G(d).

<table>
<thead>
<tr>
<th>p[ArDOT]</th>
<th>S···O (lowest-highest)</th>
<th>(Ph)C1···O (Ph)C2-O</th>
<th>O···C3(Th)</th>
<th>O···C4(Th)</th>
<th>(Th···Th)</th>
<th>Thiophene C2···C3</th>
<th>Thiophene C3···C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>p[4MeO-PheDOT]</td>
<td>2.944–2.949</td>
<td>1.385</td>
<td>1.372</td>
<td>1.437</td>
<td>1.378</td>
<td>1.413</td>
<td></td>
</tr>
<tr>
<td>p[4Me-PheDOT]</td>
<td>2.947</td>
<td>1.384</td>
<td>1.372</td>
<td>1.437</td>
<td>1.379</td>
<td>1.413</td>
<td></td>
</tr>
<tr>
<td>p[PheDOT]</td>
<td>2.947</td>
<td>1.384</td>
<td>1.372</td>
<td>1.437</td>
<td>1.379</td>
<td>1.413</td>
<td></td>
</tr>
<tr>
<td>p[36F2-PheDOT]</td>
<td>2.951</td>
<td>1.377</td>
<td>1.374</td>
<td>1.442</td>
<td>1.378</td>
<td>1.413</td>
<td></td>
</tr>
<tr>
<td>p[4F-PheDOT]</td>
<td>2.947</td>
<td>1.383</td>
<td>1.373</td>
<td>1.437</td>
<td>1.378</td>
<td>1.412</td>
<td></td>
</tr>
<tr>
<td>p[4Br-PheDOT]</td>
<td>2.943–2.952</td>
<td>1.382</td>
<td>1.373</td>
<td>1.436</td>
<td>1.378</td>
<td>1.412</td>
<td></td>
</tr>
<tr>
<td>p[4Cl-PheDOT]</td>
<td>2.944–2.951</td>
<td>1.382</td>
<td>1.373</td>
<td>1.437</td>
<td>1.378</td>
<td>1.412</td>
<td></td>
</tr>
<tr>
<td>p[45F2-PheDOT]</td>
<td>2.947</td>
<td>1.382</td>
<td>1.373</td>
<td>1.437</td>
<td>1.378</td>
<td>1.412</td>
<td></td>
</tr>
<tr>
<td>p[4CF3-PheDOT]</td>
<td>2.943–2.954</td>
<td>1.381</td>
<td>1.373</td>
<td>1.437</td>
<td>1.378</td>
<td>1.412</td>
<td></td>
</tr>
<tr>
<td>p[4MeSO2-PheDOT]</td>
<td>2.894–2.996</td>
<td>1.380</td>
<td>1.375</td>
<td>1.435</td>
<td>1.378</td>
<td>1.411</td>
<td></td>
</tr>
<tr>
<td>p[F4-PheDOT]</td>
<td>2.951</td>
<td>1.376</td>
<td>1.375</td>
<td>1.441</td>
<td>1.378</td>
<td>1.413</td>
<td></td>
</tr>
<tr>
<td>p[45Cl2-PheDOT]</td>
<td>2.948</td>
<td>1.380</td>
<td>1.373</td>
<td>1.437</td>
<td>1.378</td>
<td>1.412</td>
<td></td>
</tr>
<tr>
<td>p[4CN-PheDOT]</td>
<td>2.934–2.965</td>
<td>1.380</td>
<td>1.373</td>
<td>1.437</td>
<td>1.378</td>
<td>1.411</td>
<td></td>
</tr>
<tr>
<td>p[4NO2-PheDOT]</td>
<td>2.916–2.980</td>
<td>1.379</td>
<td>1.373</td>
<td>1.436</td>
<td>1.378</td>
<td>1.411</td>
<td></td>
</tr>
<tr>
<td>p[45(CN)2-PheDOT]</td>
<td>2.955</td>
<td>1.376</td>
<td>1.374</td>
<td>1.438</td>
<td>1.378</td>
<td>1.411</td>
<td></td>
</tr>
<tr>
<td>p[NaphDOT(2,3)]</td>
<td>2.950</td>
<td>1.382</td>
<td>1.371</td>
<td>1.436</td>
<td>1.379</td>
<td>1.411</td>
<td></td>
</tr>
<tr>
<td>p[F6-NaphDOT(2,3)]</td>
<td>2.951</td>
<td>1.374</td>
<td>1.373</td>
<td>1.438</td>
<td>1.379</td>
<td>1.410</td>
<td></td>
</tr>
<tr>
<td>p[PyDOT]</td>
<td>2.948–2.932</td>
<td>1.380</td>
<td>1.374</td>
<td>1.435</td>
<td>1.378</td>
<td>1.411</td>
<td></td>
</tr>
<tr>
<td>p[5CF3-PyDOT]</td>
<td>2.944–2.938</td>
<td>1.376</td>
<td>1.375</td>
<td>1.435</td>
<td>1.378</td>
<td>1.410</td>
<td></td>
</tr>
<tr>
<td>p[56Cl2-PyDOT]</td>
<td>2.935–2.946</td>
<td>1.375</td>
<td>1.375</td>
<td>1.436</td>
<td>1.378</td>
<td>1.411</td>
<td></td>
</tr>
<tr>
<td>p[PzDOT]</td>
<td>2.942</td>
<td>1.374</td>
<td>1.376</td>
<td>1.438</td>
<td>1.378</td>
<td>1.411</td>
<td></td>
</tr>
<tr>
<td>p[QxDOT]</td>
<td>2.945</td>
<td>1.373</td>
<td>1.374</td>
<td>1.437</td>
<td>1.379</td>
<td>1.409</td>
<td></td>
</tr>
</tbody>
</table>

Figure S9. Unit cells for the optimized structures of $p$[EWG-PheDOT] polymers calculated at PBC/B3LYP/6-31G(d). Replication of the unit cells is shown as shadow atoms/bonds. Absolute energies (per unit cell), HOCO and LUCO energies and the band gaps $E_g$ are given in the Table S7.
Figure S10. Unit cells for the optimized structures of other p[Ar-DOT] polymers calculated at PBC/B3LYP/6-31G(d). Replication of the unit cells is shown as shadow atoms/bonds. Absolute energies (per unit cell), HOCO and LUCO energies and the band gaps $E_g$ are given in the Table S7.
Figure S11. (a,c) Cyclic voltammograms of PheDOT and 4CF₃-PheDOT (~1 mM) in dichloromethane, 0.2 M Bu₄NPF₆, scan rate 100 mV/s. (b,d) Potentiodynamic electropolymerization of PheDOT and 4CF₃-PheDOT (~100 mM) in dichloromethane, 0.2 M Bu₄NPF₆, scan rate 100 mV/s.

Figure S12. Cyclic voltammograms of p[4CF₃-PheDOT] films in DCM solution, 0.1 M Bu₄NPF₆, scan rate 100 mV/s. (a) Six consecutive scans on p-doping / dedoping. (b) Recurrent p-doping / dedoping of p[4CF₃-PheDOT] to different maximal p-doping potentials: the polymer shows good reversibility and stability on cycling up to potentials of ~1.2–1.3 V. Overdoping the films by applying the potentials of >1.4 V leads to some degradation of the polymer films.
References

1. O. Hinsberg, Berichte, 1910, 43, 901.


11. We have isolated an intermediate $F_4$ when the reaction was performed at higher temperature of 140–160 °C (see below).

12. Easier decarboxyethylation of the first CO$_2$Et group in the intermediate 22 (without EWG) was observed before [Ref. 9 above]: in conventional heating reaction of thiophene 1 with o-chloronitrobenzene (2) at 100 °C, a mixture of mono- and disubstituted thiophenes (22 and 23) were formed. An absence of such products in the reaction with hexafluorobenzene (15) (Table S2, entries 1–2) is indicative of its substantially lower reactivity in SN$_2$Ar reaction.

13. 45Br$_2$PheDOT and 45Cl$_2$PheDOT were synthesized by reflux of 4,5-dibromocatechol or 4,5-dibromocatechol with 3,4-dimethoxythiophene in benzene or toluene in the presence of p-toluenesulfonic acid, similarly to unsubstituted PheDOT (Ref. 6a, 9) and isolated with low yields of 1.3 and 5%, respectively (M. P. Krompiec, S. N. Baxter and I. F. Perepichka, unpublished results).
6-Chlorobenzo[b]thieno[3,4-e][1,4]dioxine (4Cl-PheDOT)
C NMR DEPTQ (101 MHz, CDCl₃)

\[ \text{Cl} \quad \text{O} \quad \text{S} \quad \text{Cl} \]

\[ \text{O} \quad \text{S} \quad \text{O} \]

\[ ^{1}H\text{-NMR in CDCl}_{3} \]

\[ ^{13}C\text{-NMR DEPTQ (101 MHz, CDCl}_{3}) \]
SpinWorks 3: Supervisor Name IP
SNB-408
HSQC_TOCSY.b CDCl3 \{C:\Bruker\TopSpin3.1\} IP 26

file: ...
transmitter freq: 400.131670 MHz
width (F2): 3032.05 Hz = 7.5723 ppm = 1.4796 Hz/pt
number of scans: 8

SpinWorks 3: Supervisor Name IP
SNB-408
HSQC_TOCSY.b CDCl3 \{C:\Bruker\TopSpin3.1\} IP 26

file: ...
transmitter freq: 400.131670 MHz
width (F2): 3032.05 Hz = 7.5723 ppm = 1.4796 Hz/pt
number of scans: 8
6-Bromobenzol[b]thieno[3,4-e][1,4]dioxine (4Br-PheDOT)
SpinWorks 3: Supervisor Name IP
MPK-71A11
HMBC.b CDCl₃ (C:\Bruker\TopSpin3.2) sam 12

file: ...\PhEDOT\51-MPK-71A11-HMBC.b\ser
expt: <hmbcetgpl3nd>
transmitter freq: 400.131582 MHz
time domain size: 2048 by 256 points
width (F2): 2808.99 Hz = 7.0202 ppm = 0.6858 Hz/pt
number of scans: 4

F2: freq. of 0 ppm: 400.1300106 MHz
processed size: 1024 complex points
window function: Sine
shift: 90.0 degrees
Hz/cm: 468.870    ppm/cm: 4.65968

F1: freq. of 0 ppm: 100.612769 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 223.400    ppm/cm: 3.11408
Benzo[b]thieno[3,4-e][1,4]dioxine-6-carbonitrile (4CN-PheDOT)
$^{13}$C DEPTQ NMR in CDCl$_3$
6-Nitrobenzo[b]thieno[3,4-e][1,4]dioxine (4NO$_2$-PheDOT)

$^1$H-NMR in CDCl$_3$

$^{13}$C-NMR in CDCl$_3$
6-(Trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxine (4CF₃-PheDOT)
$^{13}$C DEPTQ NMR in CDCl$_3$

$^{19}$F NMR (in CDCl$_3$)
$^{13}$C-$^1$H HSQC NMR in CDCl$_3$

$^{13}$C-$^1$H HMBC NMR in CDCl$_3$
6-(Methylsulfonyl)benzo[b]thieno[3,4-e][1,4]dioxine (4MeSO_2-PheDOT)
5-Nitro-7-(trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxine (3NO$_2$5CF$_3$-PheDOT)
$^{19}$F NMR in CDCl$_3$

$[\delta (C_6F_6) = -163.00 \text{ ppm}]$
7-Nitro-5-(trifluoromethyl)benzo[b]thieno[3,4-e][1,4]dioxine (3CF₃,5NO₂-PheDOT)
$^{19}$F NMR in CDCl$_3$

$[\delta (C_6F_5) = -163.00 \text{ ppm}]$
5,6,7,8-Tetrachlorobenzo[b]thieno[3,4-e][1,4]dioxine (Cl₄-PheDOT)
Benzo[b]thieno[3,4-e][1,4]dioxine-6,7-dicarbonitrile \((45(CN)_2\text{-PheDOT})\)
$^{13}$C NMR (in DMSO-$d_6$)
6,7-Difluorobenzo[b]thieno[3,4-e][1,4]dioxine (45F2-PheDOT)
$^{19}$F NMR in CDCl$_3$

$\delta$ (C$_6$F$_6$) = -163.00 ppm
5,8-Difluorobenzo[b]thieno[3,4-e][1,4]dioxine (36F₂-PheDOT)
$^{19}$F NMR in CDCl$_3$

$[5 \text{ (C}_6\text{F}_5) = \text{-}163.00 \text{ ppm}]$
5,6,7,8-Tetrafluorobenzo[b]thieno[3,4-e][1,4]dioxine (F₄-PheDOT)

\[ F\text{-PheDOT} \]

\[ \text{H-NMR in CDCl}_3 \]

\[ \text{C-NMR in CDCl}_3 \]
SpinWorks 3: Supervisor Name IP
TP-27D
HSQC.b CDCl₃ (C:\Bruker\TopSpin3.1) IP 11

file: ...
experiment: <hsqcedetgpsisp2.3>
transmitter freq: 400.131549 MHz
time domain size: 2048 by 256 points
width (F2): 2762.43 Hz = 6.9038 ppm = 1.3488 Hz/pt
number of scans: 2

F2: freq. of 0 ppm: 400.1300094 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 15.901 ppm/cm: 0.03974

F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 459.036 ppm/cm: 4.56208

19F NMR in CDCl₃ with C₆F₆ as standard

13C-1H HSQC NMR in CDCl₃
Ethyl 5,6,7,8-tetrafluorobenzothieno[3,4-e][1,4]dioxine-1-carboxylate (F₄-23)
1,2,3,4,5,6-Hexafluoronaphtho[1,2-b]thieno[3,4-e][1,4]dioxine \( \text{Fe-NaphDOT(1,2)} \)
5,6,7,8,9,10-Hexafluoronaphtho[2,3-b]thieno[3,4-e][1,4]dioxine \( \{\text{F}_6\text{-NaphDOT(2,3)}\} \)

\[ \text{1H NMR in CDCl}_3 \]

\[ \text{19F NMR in CDCl}_3 \]
(with \( \text{C}_6\text{F}_6 \) as standard)
DEPTQ $^{13}$C NMR in CDCl$_3$
5,6,7,8-Tetrafluoro-9H-benzo[e]thieno[3,4-b][1,4]dioxepine (F4-BnDOT)
3-Trifluoromethylthieno[3',4';5,6][1,4]dioxino[2,3-b]pyridine (5CF₃-PyDOT)
$^{13}$C DEPTQ NMR in CDCl$_3$

$^{19}$F NMR in CDCl$_3$
2,3-Dichlorothieno[3’,4’:5,6][1,4]dioxino[2,3-b]pyridine (56Cl2-PyDOT)
SpinWorks 3: Supervisor Name IP  
SNB-47BP  
HSQC.b CDCl3 {C:\Bruker\TopSpin3.2} sam 10

![SpinWorks 3: HSQC NMR in CDCl3](image1)

**F2:** freq. of 0 ppm: 400.1300097 MHz  
processed size: 1024 complex points  
window function: Sine Squared  
shift: 90.0 degrees  
Hz/cm: 16.571 ppm/cm: 0.04141

**F1:** freq. of 0 ppm: 100.6127684 MHz  
processed size: 1024 complex points  
window function: Sine Squared  
shift: 90.0 degrees  
Hz/cm: 281.170 ppm/cm: 2.79438

SpinWorks 3: Supervisor Name IP  
SNB-47BP  
HMBC.b CDCl3 {C:\Bruker\TopSpin3.2} sam 10

![SpinWorks 3: HMBC NMR in CDCl3](image2)

**F2:** freq. of 0 ppm: 400.1300098 MHz  
processed size: 2048 complex points  
window function: Sine  
shift: 45.0 degrees  
Hz/cm: 16.881 ppm/cm: 0.04219

**F1:** freq. of 0 ppm: 100.6127679 MHz  
processed size: 1024 complex points  
window function: Sine Squared  
shift: 90.0 degrees  
Hz/cm: 468.609 ppm/cm: 4.65708

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S83
Thieno[3',4':5,6][1,4]dioxino[2,3-b]pyrazine (PzDOT)

$^1$H-NMR in CDCl$_3$

$^{13}$C NMR in CDCl$_3$
$^{13}$C DEPTQ NMR in CDCl$_3$
SpinWorks 3: HMBC spectrum of SNB-398
Thieno[3',4':5,6][1,4]dioxino[2,3-b]quinoxaline (QxDOT)
DEPTQ $^{13}$C-NMR in CDCl$_3$
SpinWorks 3: Supervisor Name IP
MPK-57B4
HSQC.b CDCl3 {C:\Bruker\TopSpin3.1} IP 34

file: ...

expt: <hsqcedetgpsisp2.3>
transmitter freq: 400.131763 MHz
time domain size: 2048 by 256 points
width (F2): 3184.71 Hz = 7.9592 ppm = 1.5550 Hz/pt
class: 2

number of scans: 2

F2: freq. of 0 ppm: 400.1300084 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 21.302 ppm/cm: 0.05324

F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 283.687 ppm/cm: 2.81940

SpinWorks 3: Supervisor Name IP
MPK-57B4
HMBC.b CDCl3 {C:\Bruker\TopSpin3.1} IP 34

file: ...

expt: <hmbcetgpl3nd>
transmitter freq: 400.131763 MHz
time domain size: 4096 by 256 points
width (F2): 3184.71 Hz = 7.9592 ppm = 0.7775 Hz/pt
class: 2

number of scans: 4

F2: freq. of 0 ppm: 400.1300084 MHz
processed size: 2048 complex points
window function: Sine
shift: 45.0 degrees
Hz/cm: 23.096 ppm/cm: 0.05772

F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 435.681 ppm/cm: 4.32984

13C-1H HSQC NMR in CDCl3

13C-1H HMBC NMR in CDCl3