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Synthesis of nitro- and amino-functionalized π-conjugated oligomers incorporating 3,4-ethylenedioxythiophene (EDOT) units

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ABSTRACT

Dissymmetric π-conjugated oligomers incorporating 3,4-ethylenedioxythiophene (EDOT) units and bearing nitro and amino end-groups were synthesized in good yields through Pd-catalyzed Suzuki coupling reactions and direct C–H bond arylation. Their spectroscopic properties show that they have a low HOMO–LUMO gap. They are easily oxidized at low potential and could be used in various applications ranging from photovoltaics to molecular electronics.

1. Introduction

Conjugated oligomers based on thiophene(T) are extensively used in plastic and organic electronics.[1,2] Such oligo(T) have been variously functionalized, and many reviews have described the wide range of π-conjugated materials derived from oligo (T).[3] Poly(3,4-ethylenedioxythiophene) (PEDOT) is an another widely used thiophene-based polymer.[4] It is characterized by a lower oxidation potential than poly(T), by a smaller intrinsic band gap and better processability.[5] EDOT incorporation into a π-conjugated chain enhances the π-donor ability and extends the properties of this class of material. Functionalized EDOT oligomers are thus of general interest. Oligo(EDOT) bearing a terminal amino group is of particular interest since it can be oxidized to yield an electroactive dimer or new conductive polymers.[6] It can also be transformed into the diazonium salt and grafted onto an electrode by diazonium salt electroreduction.[7] Such a modified surface associates a low oxidation potential with easy on/off switching of the transport properties across the grafted layer, and might be used in the design of new switchable devices[8] and metal/molecule/metal junctions in molecular electronics.[9]

In the present paper, we report the synthesis of various compounds based on EDOT and thiophene units, terminated by aniline or nitrobenzene. A first series having one to three EDOT units linked to nitrobenzene and aniline has been synthesized. A second series mixes EDOT and thiophene units.

2. Results and discussions

2.1. Synthesis

Among the organometallic reactions often used to synthesize oligothiophene derivatives, we have chosen the Suzuki reaction, since good yield, versatility, and easy removal of residual boronic salts by simple washing with water are reported.

Boronic derivatives **1** and **2** were firstly prepared from EDOT and biEDOT, respectively.[10] Then, reaction of 4-bromonitro-benzene with **1** and **2** led to compounds **3** and **4** in 74% and 76% yield, respectively (Scheme 1).

Compound **4** has also been prepared by an alternative one-step synthetic route using direct C–H arylation of EDOT (Scheme 2).[11] In spite of its potential interest, this method is not often used to prepare symmetrical oligothiophenes based on EDOT.[12] A few examples of mono arylation leading to unsymmetrical derivatives have also been reported but with poor to moderate yields (35–55%) after 8–12 h reaction. Catellani et al.[13] achieved satisfactory yields (72–82%) by increasing the reaction time (24 h). In our case, the direct arylation reaction between 4-bromonitrobenzene and a slight excess of biEDOT (1.1 equiv) was performed in DMF at 80 °C and catalyzed by 10% $Pd(OAc)_2$. The reaction mixture, initially pale yellow, turned orange after 10 min and red after 1 h, indicating an increase in the conjugation length. In this way, compound **4**

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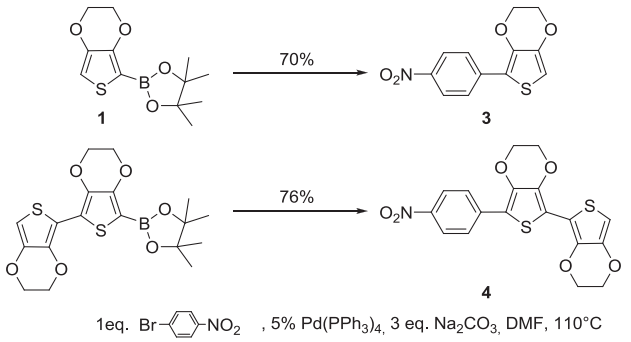
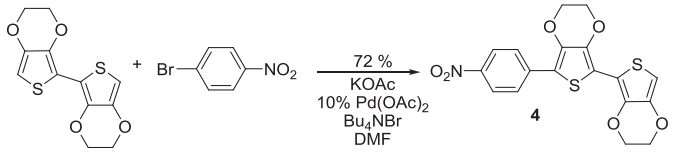


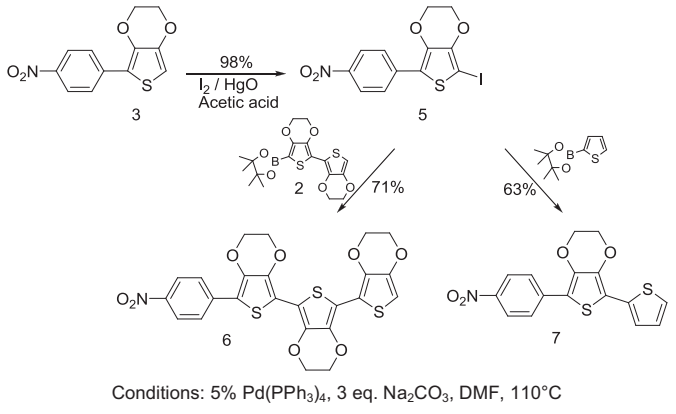
Scheme 1. Synthesis of nitrophenyl-EDOT derivatives using Suzuki coupling.



Scheme 2. Synthesis of nitrophenyl-biEDOT derivative using direct C–H arylation.

containing a biEDOT unit was obtained in 72% yield, and no trace of the symmetrical compound was observed by ^{1}H NMR. Suzuki reaction and C–H direct arylation of biEDOT led in both cases to compound **4** in good yields. We have chosen in this work to prepare other nitrophenyl precursors with boronic intermediates readily available. The use of direct C–H bond arylations to generate dissymmetric functionalized (EDOT)-based oligomers in good yields will be reported elsewhere.

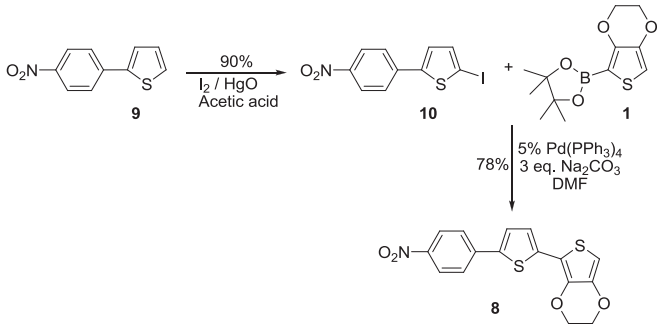
In order to increase the conjugation length, compound **6** bearing three EDOT units was synthesized. Two alternative approaches are possible. That used to generate compounds **3** and **4** requires the preparation of the boronic terEDOT derivative. An alternative two-step approach, described in Scheme 3, was preferred. Firstly, compound **3** was iodinated by reaction with iodine in the presence of mercuric oxide in 98% yield. The resulting intermediate **5** reacted then with boronic biEDOT **2** to give terEDOT **6** in good yield (71%) (Scheme 3).



Scheme 3. Increasing the conjugation length of nitrophenyl-EDOT oligomers by Suzuki coupling.

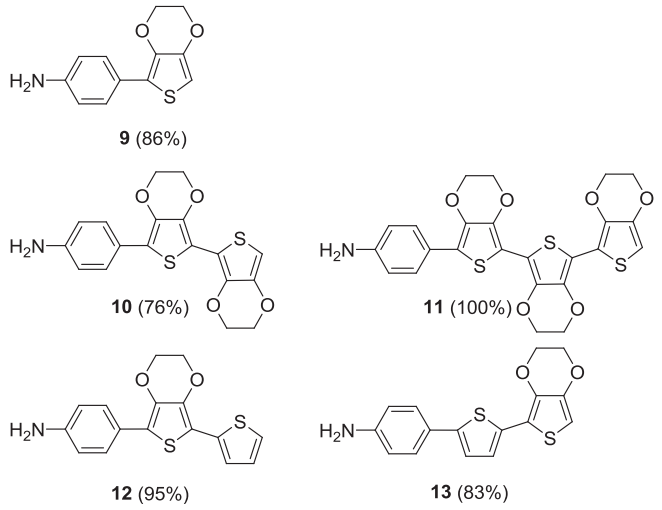
A second family of dissymmetric π-conjugated oligomers combining EDOT and thiophene units, and bearing the nitrobenzene end-group was prepared. The first compound has a terminal thiophene unit. Reaction between the iodide intermediate **5** and boronic thiophene gives compound **7** in 63% yield.

In order to study the influence of the position of EDOT on the physical properties of the oligomers, we have also prepared compound **8**, in which EDOT and thiophene are permuted compared to compound **7**. The synthetic approach is described in Scheme 4. Firstly, intermediate **9**, synthesized as previously reported,[14] was iodinated in excellent yield to compound **10**. Then, this latter was reacted with boronic EDOT **1** to give compound **8** in 78% yield (Scheme 4).



Scheme 4. Synthesis of nitrophenyl-thiophene-EDOT by Suzuki coupling.

Nitro compounds are push–pull molecules of interest but are also intermediates for amino derivatives. To this end, all the nitrobenzene derivatives were reduced in satisfactory yield by hydrazine[15] in the presence of Pd/C. The amino compounds are shown in Scheme 5.



Scheme 5. Aminophenyl-EDOT derivatives synthesized.

2.2. UV–visible spectroscopy

The UV–visible characteristics of the EDOT-based π-conjugated molecules bearing nitro groups are summarized in Table 1. All compounds are colored and display two absorption bands, between 384 and 481 nm, with the lowest energy band the stronger. This absorption involves the HOMO mainly localized on the EDOT units and the LUMO more centered on the nitrobenzene unit, as depicted for compound **4** in Fig. 1 (PM6 calculations). It is thus related to partial intramolecular charge transfer, and such molecules can be considered as push–pull systems. Nitrophenyl-bithiophene[14] (2-(4-nitrophenyl)-5,2′-bithiophene) **14** was taken as reference to compare the effect of biEDOT. Changing bithiophene to biEDOT leads to bathochromic shifts of 45 nm and 49 nm for the main and the minor peaks, respectively. This behavior is due to the presence of the electron-donating ethylendioxy groups on the thiophene units, which decreases the HOMO–LUMO gap of the molecules. In addition, increasing the number of EDOT units in the chain causes a bathochromic shift of 54 nm for two EDOTs (**4**) and 97 nm for three EDOTs (**6**) compared to a single EDOT (**3**). Contrary to several

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Table 1
UV–visible peak positions of various nitro- and amino-phenyl-EDOT oligomers (T=Thiophene, E=EDOT)[a]

Nitro compounds	λ_{max} (nm)	Amino compounds	λ_{max} (nm)
2TPhNO$_2$ (**14**)	393, 274	2TPhNH$_2$ (**15**)	358
EPhNO$_2$ (**3**)	384	EPhNH$_2$ (**9**)	309
2EPhNO$_2$ (**4**)	438, 323	2EPhNH$_2$ (**10**)	392, 371, 284
3EPhNO$_2$ (**6**)	481, 378	3EPhNH$_2$ (**11**)	435, 414
TEPhNO$_2$ (**7**)	419, 273	TEPhNH$_2$ (**12**)	367, 275
ETPhNO$_2$ (**8**)	412, 316	ETPhNH$_2$ (**13**)	365

[a] λ_{max} in acetonitrile 10^{-4} M, except for 3EPhNH$_2$: 10^{-5} M.

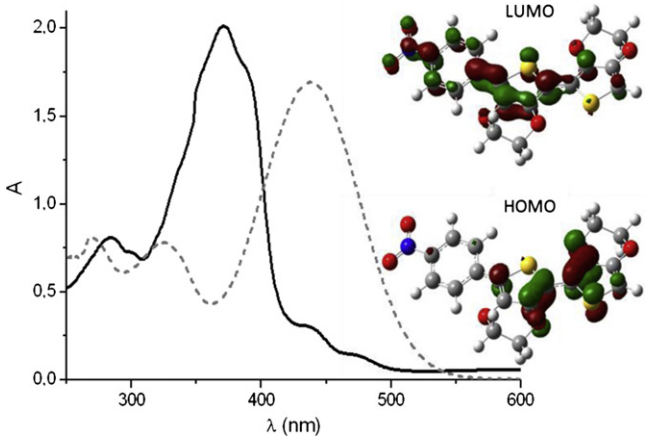

Fig. 1. UV spectra of **2EPhNO$_2$** (dash line) $C=10^{-4}$ M in acetonitrile, **2EPhNH$_2$** (straight line) $C=10^{-4}$ M in acetonitrile. Inset HOMO and LUMO of **2EPhNO$_2$**.

reported examples of oligoEDOT,[16] no vibronic fine structure, due to intramolecular S···O interactions, was observed in the UV–visible spectra.

When the nitrophenyl derivative combines one EDOT and one thiophene, as in **7** and **8**, the main absorption peaks (419 nm and 412 nm for **7** and **8**, respectively) are similar and lie between those for nitrophenyl-bithiophene **14** and nitrophenyl-biEDOT **4**. While the position of the EDOT unit in the structure does not influence the position of the main transition peak, it has a marked effect on the wavelength of the minor ones. Indeed, for this band, the terminal unit seems to be all-important. In compound **7**, thiophene is the terminal unit and the wavelength of the minor peak is similar to that of nitrophenyl-bithiophene **14**. For compound **8**, EDOT is the terminal unit and the wavelength of the minor peak is similar to that of nitrophenyl-biEDOT **4**.

Amino derivatives were also characterized by UV–visible spectroscopy (Table 2). If we compare a nitro precursor and the corresponding amino derivative, there is a hypsochromic shift of the absorption maximum close to 45 nm, except for the monoEDOT compound **9** for which it reaches 75 nm. This decrease is due to the replacement of the electron-attracting nitro group by a donor amino function. As a consequence, the push–pull system is replaced by a push-push system with LUMOs lying at higher energy and higher HOMO–LUMO gaps than observed for the nitro compounds. Contrary to the nitro precursors **7** and **8**, where there is one EDOT and one thiophene unit, the terminal units have no influence on the position of the absorption maximum for the amino derivatives **12** and **13**. In the case of amino compounds with more than one EDOT unit, hyperfine structure is observed; this indicates that there are intramolecular S···O interactions between two adjacent EDOTs even in solution.

Table 2
Electrochemical oxidation potential peak of various nitro-phenyl-EDOT oligomers (T=Thiophene, E=EDOT)

Amino compounds	E_{ox} (V/ECS)[a]
2TPhNH$_2$ (**14**)	0.59
EPhNH$_2$ (**9**)	0.53
2EPhNH$_2$ (**10**)	0.36
3EPhNH$_2$ (**11**)	0.20
TEPhNH$_2$ (**12**)	0.48
ETPhNH$_2$ (**13**)	0.49

[a] E_{ox} in acetonitrile 10^{-3} M, except for **3EPhNH$_2$**: $5\cdot10^{-4}$ M.

2.3. Electrochemical properties

In a preliminary investigation of the redox properties of these molecules, they were dissolved in 0.1 M LiClO$_4$ acetonitrile solution, and cyclic voltammetry performed using a carbon working electrode, stainless steel grid counter-electrode and SCE reference. All compounds were oxidized at low potential with an irreversible peak (Table 2).

Such low potential peaks can be compared to that of aminophenyl-bithiophene at 0.59 V. The replacement of two thiophenes by two π-electron donor EDOT units decreases the oxidation potential by 0.23 V. As expected, the increase in the conjugation length from one EDOT to three EDOT units decreases E_{ox} from 0.53 V/SCE for compound **9** to 0.20 V for compound **11** (Fig. 2). In the case of the mixed EDOT/thiophene series, there is no significant difference between aminophenyl derivatives **12** and **13**. Their oxidation potentials are intermediate between those of aminophenyl-bithiophene **15** and aminophenyl-biEDOT **10**, which correlates with their optical properties.

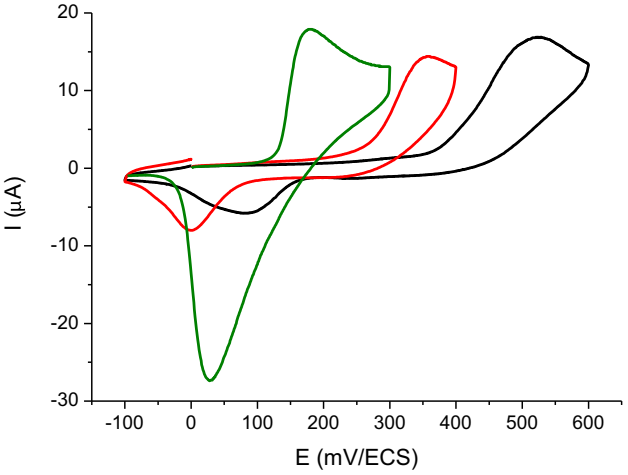

Fig. 2. CV of **EPhNH$_2$** (in black), **2EPhNH$_2$** (in red), **3EPhNH$_2$** (in green), $C=10^{-3}$ M in 0.1 M LiClO$_4$/acetonitrile, 100 mV s^{-1}/SCE.

Once oxidized, the radical cations of these molecules undergo coupling reactions and thin electroactive films are easily obtained using cyclic voltammetry or chronopotentiometry. Indeed, when a constant current of $I=1.4\cdot10^{-6}$ A is applied in a solution of **3EPhNH$_2$** ($5\cdot10^{-4}$ M) and 0.1 M LiClO$_4$ in acetonitrile solution, the potential of the electrode stabilizes at 0.120 mV indicating that a conductive material is generated. Fig. 3 shows the electroactivity of a film (generated during 80 s with a deposition charge Qd=0.112 mC) in 0.1 M HClO$_4$/water solution. A reversible redox systems with E_{ox}=0.2 V and E_{red}=−0.05 V is clearly observed. The charge involved in the switching of the film (Qs) is here of 0.1 mC, that is very close to that used to generate the film. As a consequence Qs/Qd is around 1 and strongly deviates from a value of 0.1 found when infinite chains are generated from a monomer or of 0.3 when the same chains are obtained from a trimer. Such value clearly shows that the generated insoluble oligomers are constituted of

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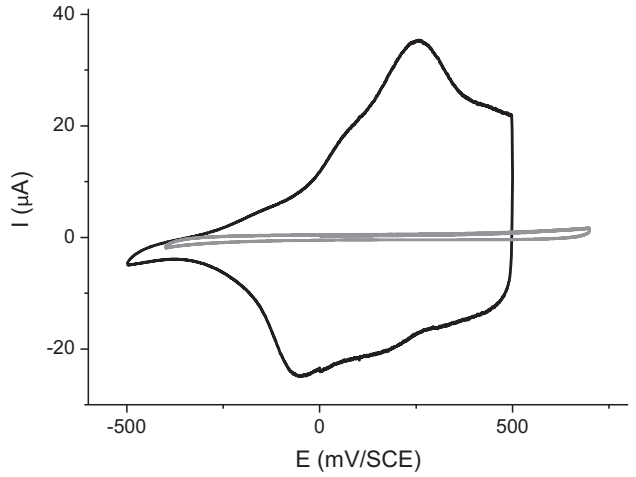

Fig. 3. CV of a GC bare electrode (in gray) and a GC modified electrode after deposition by chronoamperometry of **3EPhNH$_2$** (in black) (I=1.4·10^{-6} A, t=80 s) in 0.1 M $LiClO_4$/0.1 M $HClO_4$/water, 100 mV s^{-1}/SCE.

a small and finite numbers of **3EPhNH$_2$** units and suggests that mainly dimers with a plausible structure close to $H_2NPh(E)_6PhNH_2$ are obtained.

3. Conclusion

In summary, nitro- and amino-functionalized π-conjugated oligomers incorporating EDOT units have been synthesized in good yields. Dissymmetric π-conjugated oligomers bearing nitro end-groups have lower HOMO–LUMO gaps than those with amino end-groups; the latter have low oxidation potentials ranging from 0.20 V to 0.53 V/SCE and lead easily to thin electroactive films. Such molecules are of wide interest in materials science, in the design of new switchable devices and metal/molecule/metal junctions, and more generally in molecular and organic electronics.[17]

4. Experimental section

4.1. General

Reagents including EDOT, thiophene, triisopropylborate, pinacol, 4-bromonitrobenzene, palladium catalyst, *n*-butyllithium and hydrazine are commercially available. Bi-EDOT[18] and 1-(thien-2-yl)-4-nitrobenzene[14] were synthesized according to the literature. THF is distilled, under argon, over sodium and benzophenone. Other solvents were used without purification. Reactions were controlled by TLC (aluminum plates coated with silica gel, Merck 60, F-254) and UV light was used to show the spots. Purification by chromatography was carried out using silica gel 60 (63–210 μm) from VWR. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 300 MHz or 400 MHz instrument. The chemical shifts are calibrated on the reference value of the solvent.[19] Mass spectrum was recorded on Finigan 5890 coupled to DSQ1 spectrometer by electronic impact (EI). The high-resolution mass spectra were carried out by the service of CNRS in Vernaison. UV–visible spectra were recorded on a Cary 500 spectrometer and cyclic voltammetry was performed on a potentiostat CH Instrument 660.

4.2. Synthetic procedure

4.2.1. General procedure for the synthesis of boronic ester. Under Ar, a stirred solution of thiophenic compound (30 mmol) in distilled THF (100 mL) is cooled to −78 °C. A 2.5 M solution of butyllithium (12 mL, 1 equiv) is added dropwise and the solution is stirred at this temperature during 1 h. Triisopropylborate (21 mL, 3 equiv) is added and the reaction mixture is allowed to warm to room temperature. After 2.5 h, a solution of pinacol (10.6 g) in THF (30 mL) was added. The reaction is stirred during 30 min and then the solvent was removed in vacuo. The residue dissolved in diethyl ether is washed twice with water and dried over magnesium sulfate. The solvent is removed in vacuo. The product is used without further purification.

4.2.1.1. 4,4,5,5-Tetramethyl-2-thiophen-2-yl-1,3,2-dioxaboro-lane. This compound was prepared by the general procedure for the synthesis of boronic ester, starting with 30 mmol of thiophene. Yield: 5.3 g, 85%. White powder. ^{1}H NMR ($CDCl_3$): 1.36 (s, 12H, CH_3); 7.20 (dd, 1H, 3.6, and 4.8 Hz); 7.64 (d, 1H, 4.8 Hz); 7.66 (d, 1H, 3.6 Hz). ^{13}C NMR ($CDCl_3$): 24.8 (CH_3); 84.1; 128.2; 132.4; 137.2. MS ($M^{+\bullet}$): 210.

*4.2.1.2. 2-(2,3-Dihydrothieno[3,4-b][1,4]dioxin-5-yl)-4,4,5,5-tetramethyl-2-thiophen-2-yl-1,3,2-dioxaborolane **1**.* This compound was prepared by the general procedure for the synthesis of boronic ester starting with 50 mmol of EDOT. Yield: 11.13 g, 85%. White powder. ^{1}H NMR ($CDCl_3$): 1.34 (s, 12H, CH_3); 4.17–4.20 (m, 2H); 4.29–4.31 (m, 2H); 6.63 (s, 1H). ^{13}C NMR ($CDCl_3$): 24.7 (CH_3); 64.3 (CH_2–O); 65.1 (CH_2–O); 83.8 (C–OB); 107.5 (CH_{edot}); 142.3 (C_{IV}–O); 149.0 (C_{IV}–O). MS ($M^{+\bullet}$): 268.

*4.2.1.3. 4,4,5,5-Tetramethyl-2-(2,2′,3,3′-tetrahydro-5,5′-bithieno[3,4-b][1,4]dioxin-5-yl)-1,3,2-dioxaborolane **2**.* This compound was prepared by the general procedure for the synthesis of boronic ester, starting with 10 mmol of bi-EDOT. Yield: 3.94 g, 93%. Green solid. ^{1}H NMR ($CDCl_3$): 1.28 (s, 12H, CH_3); 4.23–4.25 (m, 2H); 4.32–4.34 (m, 6H); 6.31 (s, 1H). ^{13}C NMR ($CDCl_3$): 24.5 (CH_3); 64.6 (CH_2–O); 65.0 (CH_2–O); 83.2 (C–OB); 97.5; 109.9; 137.0; 141.2. MS ($M^{+\bullet}$): 408.

4.2.2. General procedure for iodation of thiophene derivatives. To a suspension of thiophene derivative (8 mmol) in acetic acid (150 mL) is added mercuric oxide (1.04 equiv, 8.32 mmol) and iodine (1.02 equiv, 8.16 mmol). The mixture is degassed in an ultrasounds bath during 20 min and then stirred overnight. The precipitate is filtered and then dissolved in dichloromethane. The organic phase is washed successively by a solution of potassium iodide, a solution of sodium hydrogenocarbonate and water. After drying over magnesium sulfate, the solvent is removed in vacuo. The product is used without further purification.

*4.2.2.1. 1-(5-Iodothien-2-yl)-4-nitrobenzene **9**.* This compound was prepared by the general iodation procedure, starting with 7 mmol of thiophene derivative. Yield: 2.10 g, 90%. Yellow powder. ^{1}H NMR ($CDCl_3$): 7.13 (d, 1 H, 3.6 Hz); 7.30 (d, 1 H, 3.6 Hz); 7.66 (d, 1H, 8.4 Hz, H_c); 8.23 (d, 1H, 8.4 Hz, H_b). ^{13}C NMR ($CDCl_3$): 76.1 (C_h); 124.5 (C_c); 125.9 (C_b); 127.0 (C_f); 138.5 (C_g); 139.4 (C_a); 146.9 (C_d); 147.5 (C_e). MS (M^+) 331.

*4.2.2.2. 1-(5-Iodo-3,4-ethylenedioxythien-2-yl)-4-nitrobenzene **5**.* This compound was prepared by the general iodation procedure, starting with 6.57 mmol of EDOT derivative. Yield: 2.52 g, 98%. Yellow powder. ^{1}H NMR ($CDCl_3$): 4.37 (m, 4H); 7.78 (d, 1H, 9.2 Hz); 8.21 (d, 1H, 9.2 Hz). ^{13}C NMR ($CDCl_3$): 52.1 (C_h); 64.9 and 64.9 (C_f and $C_{g'}$); 120.4 (C_e); 124.2 (C_b); 125.7 (C_c); 139.0 (C_a); 139.6 (C_f or C_g); 145.0 (C_f or C_g); 145.7 (C_d). MS (M^+) 389.

4.2.3. General procedure for the Suzuki coupling reaction. The boronic compound (2 mmol), the iodo derivative (2 mmol), the sodium carbonate (3 equiv, 6 mmol), tetrakis(triphenylphosphine) palladium (0) (5%) are successively introduced into a Schlenck containing 25 mL of DMF. The reaction mixture is heated at 110 °C from 2 to 3

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days. After return at room temperature, the solvent is removed in vacuo. The brown residue is dissolved in dichloromethane, washed twice with water, dried over magnesium sulfate and concentrated. The crude product is purified by chromatography.

4.2.3.1. 2-(4-Nitrophenyl)-3,4-ethylenedioxythiophene ***3***. This compound was prepared by the general Suzuki procedure starting with 15 mmol of boronic derivative. Yield: 2.79g, 70%. Yellow powder. ^{1}H NMR ($CDCl_3$): 4.28–4.40 (m, 2H, $H_{g'}$); 4.37–4.40 (m, 2H, $H_{f'}$); 6.48 (s, 1H, H_h); 7.86 (d, 9.0 Hz, 2H, H_c); 8.17 (d, 9.0 Hz, 2H, H_b). ^{13}C NMR ($CDCl_3$): 64.3 ($OC_{g'}H2$); 65.1 ($OC_{f'}H2$); 101.0 (C_h); 124.1 (C_b); 125.7 (C_c); 139.8 (C_a); 140.9 (C_g); 142.9 (C_f); 145.8 (C_d). MS ($M^{+\bullet}$): 263. UV (CH_3CN) (λ_{max} (nm)), [log ε (L mol^{-1} cm^{-1})]: 384 [4.26].

4.2.3.2. 2-(4-Nitrophenyl)-3,4,3′,4′-bis(ethylenedioxy)-5,2′-bithiophene ***4***. This compound was prepared by the general Suzuki procedure starting with 2 mmol of boronic derivative. The product was purified by chromatography on silica gel using petroleum ether/dichloromethane 3/7 as eluent. Yield: 316.3 mg, 36%. Dark powder. ^{1}H NMR ($CDCl_3$): 4.23–4.27 (m, 2H, OCH_2); 4.36–4.40 (m, 6H, 3x OCH_2); 6.36 (s, 1H, H_l); 7.84 (d, 9.2 Hz, 2H, H_c); 8.17 (d, 9.2 Hz, 2H, H_b). ^{13}C NMR ($CDCl_3$): 63.9, 64.0, 64.4, and 64.7 (4× OCH_2); 98.6 (C_l); 108.8, 111.5, 111.7 (C_e, C_h and C_i); 123.4 (C_b); 124.7 (C_c); 136.7, 137.4, 139.8, 140.7 (C_f, C_g, C_j, C_k); 139.3 (C_a); 144.4 (C_b); 145.0 (C_d). Mass exact $C_{18}H_{13}NO_6NaS_2$ [M+Na$^+$]: calculated: 426.0082, found: 426.0093. UV (CH_3CN) (λ_{max} (nm)), [log ε (L mol^{-1} cm^{-1})]: 438 [4.52], 323 [4.20].

4.2.3.3. 2-(4-Nitrophenyl)-3,4,3′,4′,3″,4″-ter(ethylenedioxy)-5,2′,5′,2″-terthiophene ***6***. This compound was prepared by the general Suzuki procedure starting with 1.2 mmol of boronic derivative. The product was purified by chromatography on alumina using dichloromethane as eluent. Yield: 465 mg, 71%. Dark powder. ^{1}H NMR ($CDCl_3$): 4.26 (m, 2H, OCH_2); 4.30–4.50 (m, 10H, 5× OCH_2); 6.33 (s, 1H, CH_p); 7.86 (d, 2H, 8.8 Hz, CH_c); 8.19 (d, 2H, 8.8 Hz, CH_b). Mass exact $C_{24}H_{17}NO_8S_3$ [M+H$^+$]: calculated: 543.0116, found: 543.0126. UV (CH_3CN) (λ_{max} (nm)), [log ε (L mol^{-1} cm^{-1})]: 481 [4.17], 378 [3.84].

4.2.3.4. 2-(4-Nitrophenyl)-3,4-ethylenedioxy-5,2′-bithiophene ***7***. This compound was prepared by the general Suzuki procedure starting with 2 mmol of boronic derivative. Yield: 690 mg, 63%. Orange powder. ^{1}H NMR ($CDCl_3$): 4.43 (s, 4H, 2× OCH_2); 7.08 (dd, 1H, 3.2 and 5.2 Hz, CH_k); 7.30 (d, 1H, 5.2 Hz, CH_l); 7.34 (d, 1H, 3.2 Hz, CH_j); 7.86 (d, 1H, 8.8 Hz, CH_c); 8.18 (d, 1H, 8.8 Hz, CH_b). ^{13}C NMR ($CDCl_3$): 64.7 and 65.0 (2× OCH_2); 112.1 (C_e); 113.8 (C_i); 124.0 (C_j); 124.1 (C_b); 125.0 (C_l); 125.6 (C_c); 127.4 (C_k); 133.9 (C_h); 137.9 and 140.9 (C_f and C_g); 139.4 (C_a); 145.3 (C_d). Mass exact $C_{16}H_{11}NO_4S_2$ [$M^{+\bullet}$]: calculated: 345.0130, found: 345.0139. UV (CH_3CN) (λ_{max} (nm)), [log ε (L mol^{-1} cm^{-1})]: 419 [4.44], 273.

4.2.3.5. 2-(4-Nitrophenyl)-3′,4′-ethylenedioxy-5,2′-bithiophe-ne ***8***. This compound was prepared by the general Suzuki procedure starting with 4 mmol of boronic derivative. Yield: 1.38g, 78%. Orange powder. ^{1}H NMR ($CDCl_3$): 4.28–4.31 (m, 2H, OCH_2); 4.40–4.42 (m, 2H, OCH_2); 6.23 (s, 1H, H_l); 7.25 (d, 4.0 Hz, 2H, H_f or H_g); 7.41 (d, 4.0 Hz, 2H, H_f or H_g); 7.73 (d, 8.8 Hz, 2H, H_c); 8.24 (d, 8.8 Hz, 2H, H_b). ^{13}C NMR ($CDCl_3$): 64.6 and 65.2 (2× OCH_2); 98.1 (C_l); 111.7 and 138.4 (C_j and C_k); 123.9 and 126.0 (C_f and C_g); 124.5 (C_b); 125.4 (C_c); 137.6 and 139.0 (C_h and C_i); 140.6 (C_a); 142.0 (C_e); 146.3 (C_d). $C_{16}H_{11}NO_4S_2$ [M+H$^+$]. Mass exact: calculated: 345.0130, found: 345.0145. UV (CH_3CN) (λ_{max} (nm)), [log ε (L mol^{-1} cm^{-1})]: 412 [4.40], 316 [3.92].

4.2.4. Alternative procedure to prepare 2-(4-nitrophenyl)-3,4,3′,4′-bis(ethylenedioxy)-5,2′-bithiophene. BiEDOT (1.87 g, 6.6 mmol, 1.1 equiv), 4-bromonitrobenzene (1.21 g, 6 mmol), potassium acetate (1.76 g, 18 mmol, 3 equiv), and tetrabuytyl-ammonium bromide (1.93 g, 6 mmol) were successively introduced into a Schlenck containing 20 mL of DMF. After complete dissolution, palladium acetate (134 mg, 0.6 mmol, 0.1 equiv) was added and the reaction mixture was heated at 80 °C during 1 h. After return to room temperature, ethanol was added and the red suspension was cooled. The precipitate was filtered and washed with cold ethanol. The nitro compound was then used without further purification. Yield: 72% (1.74 g).

4.2.5. General procedure for reduction of nitro in amino function. To the nitro derivative (0.86 mmol) dissolved in THF (20 mL), palladium (10%) on coal (0.086 mmol, 10%) and hydrazine (1 mL) is added. The reaction mixture is refluxed during 4 h. After return at room temperature, the suspension is filtered over Celite and then the solvent is removed in vacuo. The residue dissolved in dichloromethane is washed with water and dried over magnesium sulfate. The product is then used without further purification.

4.2.5.1. 2-(4-Aminophenyl)-3,4-ethylenedioxythiophene ***9***. This compound was prepared by the general reduction procedure starting with 0.65 mmol of nitro derivative. Yield: 130 mg, 86%. White powder. ^{1}H NMR ($CDCl_3$): 4.23–4.25 (m, 2H, $OCH_{f'2}$); 4.27–4.29 (m, 2H, $OCH_{g'}$); 6.20 (s, 1H, H_h); 6.69 (d, 2H, 8.8 Hz, CH_b); 7.51 (d, 2H, 8.8 Hz, CH_c). ^{13}C NMR ($CDCl_3$): 64.5 ($OC_{f'}H_2$); 64.7 ($OC_{g'}H_2$); 95.7 (C_h); 115.2 (C_b); 118.1 (C_e); 123.8 (C_a); 127.4 (C_c); 136.7 (C_g); 142.2 (C_f); 145.2 (C_d). UV (CH_3CN) (λ_{max} (nm)): 309.

4.2.5.2. 2-(4-Aminophenyl)-3,4,3′,4′-bis(ethylenedioxy)-5,2′-bithiophene ***10***. This compound was prepared by the general reduction procedure starting with 0.44 mmol of nitro derivative. Yield: 124 mg, 76%. Red powder. ^{1}H NMR ($CDCl_3$): 3.70–3.73 (large s, 2H); 4.24–4.27 (m, 2H); 4.33–4.37 (m, 6H); 6.27 (s, 1H); 6.69 (d, 2H, 8.4 Hz); 7.55 (d, 2H, 8.4 Hz). ^{13}C NMR ($CDCl_3$): 64.6, 64.6, 64.9, and 65.0 (4× CH_2O); 97.3 (C_lH); 106.2 (C_i or C_h); 110.2 (C_i or C_h); 115.2 (C_bH); 115.8 (C_e); 123.7 (C_a); 127.3 (C_cH); 136.3, 136.7, 137.5, and 141.3 (C_f, C_g, C_j and C_k); 145.0 (C_d). Mass exact $C_{18}H_{15}NO_4NaS_2$ [M+H$^+$]: calculated: 374.0521, found: 374.0515. UV (CH_3CN) (λ_{max} (nm)): 392, 371, 284.

4.2.5.3. 2-(4-Aminophenyl)-3,4,3′,4′,3″,4″-ter(ethylenedioxy)-5,2′,5′,2″-terthiophene ***11***. This compound was prepared by the general reduction procedure starting with 0.11 mmol of nitro derivative. Yield: 56 mg, quantitative. Red powder. ^{1}H NMR ($CDCl_3$): 4.21–4.40 (m, 12H); 6.27 (s, 1H, CH_p); 6.68 (d, 2H, 7.6 Hz, CH_b); 7.55 (d, 2H, 7.6 Hz, CH_c). Mass exact: $C_{24}H_{19}NO_6S_3$ [M+H$^+$] calculated: 513.0374, found: 513.0371. UV (CH_3CN) (λ_{max} (nm)): 435, 314.

4.2.5.4. 2-(4-Aminophenyl)-3,4-ethylenedioxy-5,2′-bithiophe-ne ***12***. This compound was prepared by the general reduction procedure starting with 0.86 mmol of nitro derivative. Yield: 270 mg, 95%. Yellow powder. ^{1}H NMR ($CDCl_3$): 4.32–4.35 (m, 2H); 4.37–4.39 (m, 2H); 6.70 (d, 2H, 8.8 Hz, H_b); 7.02 (dd, 1H, 3.6 and 5.0 Hz, H_k); 7.20 (d, 1H, 5.0 Hz, H_l); 7.22 (d, 1H, 3.6 Hz, H_j); 7.53 (d, 2H, 8.8 Hz, H_c). ^{13}C NMR ($CDCl_3$): 64.6 and 64.9 (2× OCH_2); 108.3 (C_e or C_h); 115.2 (C_b); 115.5 (C_a); 122.3 (C_j); 123.3 (C_l); 127.1(C_k); 127.3 (C_c); 135.0 (C_i); 136.7 (C_f or C_g); 137.9 (C_f or C_g); 145.3 (C_d). Mass exact $C_{16}H_9NO_2S_2$ [M+H$^+$]: calculated: 316.0466, found: 316.0466. UV (CH_3CN) (λ_{max} (nm)): 367, 275.

4.2.5.5. 2-(4-Aminophenyl)-3′,4′-ethylenedioxy-5,2′-bithio-phene ***13***. This compound was prepared by the general reduction procedure starting with 0.6 mmol of nitro derivative. Yield: 189 mg, 83%. Yellow powder. ^{1}H NMR ($CDCl_3$): 4.76 (s, 2H); 4.25–4.27 (m, 2H, $H_{j'}$); 4.34–4.37 (m, 2H, $H_{k'}$); 6.20 (s, 1H, H_l); 6.68 (d, 2H, 8.8 Hz, H_b); 7.06 (d, 1H, 4.0 Hz, H_f), 7.14 (d, 1H, 4.0 Hz, H_g); 7.41 (d, 2H,

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8.8 Hz, H_c). ^{13}C NMR ($CDCl_3$): 64.6 ($OC_{j'}H_2$); 65.0 ($C_{k'}H_2$); 96.5 (C_l); 112.6 (C_i); 115.3 (C_b); 121.3 (C_f); 123.8 (C_g); 125.0 (C_a); 126.8(C_c); 132.4 (C_h); 137.2 (C_k); 141.9 (C_j); 143.2 (C_e); 145.9 (C_d). Mass exact: $C_{16}H_9NO_2S_2$ [M+H$^+$] calculated: 316.0466, found: 316.0461. UV (CH_3CN) (λ_{max} (nm)): 365.

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