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Published on 19 February 2008 on http://pubs.rsc.org | doi:10.1039/B715568A

A versatile building block for EDOT or PEDOT functionalization†

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Received (in Montpellier, France) 11th October 2007, Accepted 21st January 2008
First published as an Advance Article on the web 19th February 2008
DOI: 10.1039/b715568a

A functionalized ethylenedioxythiophene (EDOT) derivative bearing a highly nucleophilic thiolate group has been synthesized. The efficiency of this new building block as a precursor to a wide range of EDOT-based monomers is demonstrated by reaction with different electrophilic species or by oxidation to a disulfide dimer. The corresponding electropolymerized PEDOT-based films, incorporating various side arms, have been prepared. In addition, the possibility to functionalize preformed PEDOT films obtained from these monomers, by nucleophilic substitution under heterogeneous conditions, was also checked thanks to the introduction of a tetrathiafulvalene redox probe.

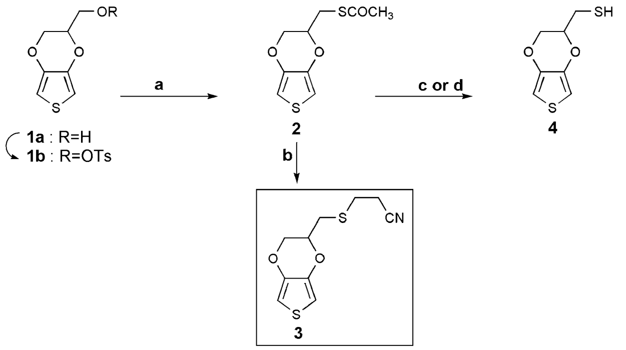
Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) has received a tremendous growth of interest in the last decade[1] and has become one of the most investigated conducting polymers for academic research and also for various industrial applications. Such interest results from its remarkable electroconducting properties associated with a high chemical stability. On this basis, and in order to obtain polymers combining PEDOT specificities to various additional properties, synthetic efforts have been devoted towards the preparation of substituted EDOT-based monomers (3,4-ethylenedioxythiophene).[1] Maintaining the integrity of the PEDOT polyconjugated backbone, implies that substitution of the monomer is carried out on the ethylenedioxy bridge. Many examples involve the hydroxymethyl-EDOT system **1a**,[2] which can be functionalized through direct esterification,[3] or by a Williamson ether reaction.[1,4,5] Nevertheless, generation of the alcoholate function of **1a** requires strong basic conditions and, depending on the nature of the electrophilic derivative which is opposed to EDOT–CH_2O^-, we experimented some difficulties in obtaining the corresponding *O*-alkylated product in good yields. Recently the synthesis of chloromethyl-EDOT was also described, which was conveniently used to prepare EDOT monomers functionalized with electron-accepting groups.[6] In this context, we decided to investigate the thiolate function in the preparation of new EDOT substituted monomers, since this anion combines the advantage of an easy generation under mild conditions, to a well-established highly nucleophile character. As demonstrated in tetrathiafulvalene chemistry,[7] or with the thiophene unit itself,[8] a key point of this strategy lies on an efficient protection of the thiolate anion with a cyanoethyl group, which then can be very easily cleaved by treatment under mild basic conditions.

In this manuscript, we describe the first application of this methodology to the preparation of EDOT derivatives, through the generation of a key nucleophilic thiolate EDOT anion **3′**. The high synthetic potential of this system for a straightforward access to various substituted EDOT derivatives is demonstrated. In addition, easy electropolymerization of the thiolate precursor **3** is shown, and the efficiency of the resulting PEDOT-based film to be functionalized under heterogeneous conditions is demonstrated, in particular with the use of a tetrathiafulvalene electrochemical probe.

Results and discussion

The synthesis of the new key EDOT derivative **3** starts from hydroxymethylEDOT **1a** synthesized according to literature[2,9] (Scheme 1). Tosylation of **1a** into **1b**[10] allows an access in high yields (95%) to thioester derivative **2** by reaction with potassium thioacetate in refluxing acetone for four days. The target EDOT derivative **3** is then obtained in 70% yield by treatment of **2** with 3-bromopropionitrile in the presence of sodium methanolate. Alternatively, compound **2** can also be transformed in good yields to the hitherto unknown EDOT methanethiol **4** by deprotection in basic medium (MeONa–MeOH, rt) or by reduction with DIBAL-H (dichloromethane, −80 °C).



Scheme 1 *Reagents and conditions*: (a) $KSCOCH_3$, acetone, reflux; (b) MeONa–MeOH, $BrCH_2CH_2CN$, THF; (c) DIBAL-H, CH_2Cl_2; (d) MeONa–MeOH, THF, HCl.

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† Electronic supplementary information (ESI) available: Electrochemical studies for compounds **5**, **7** and **8** and ^1H and ^{13}C NMR spectra for compound **8**. See DOI: 10.1039/b715568a

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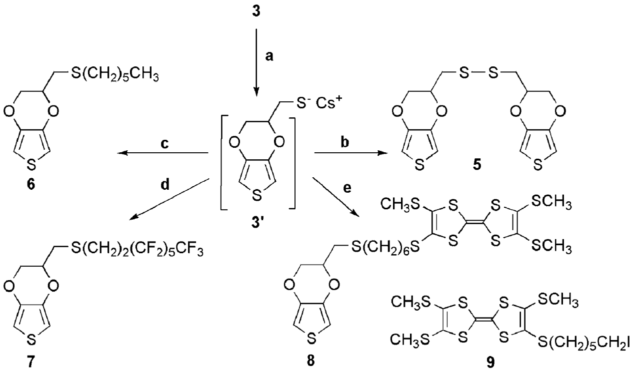

Scheme 2 *Reagents and conditions*: (a) CsOH, H_2O in MeOH; (b) O_2, DMF; (c) 1-bromohexane, DMF; (d) $I(CH_2)_2(CF_2)_5CF_3$, DMF; (e) **9**, DMF.

The synthetic versatility of **3** is illustrated by the following various examples of EDOT-based functionalized monomers (Scheme 2).

Functionalization of **3** requires first the generation of the corresponding methylene thiolate anion **3′** under mild basic conditions (cesium hydroxide). Oxidation of the latter in air produces the disulfide dimer **5** (60%). Alternatively, a similar result is obtained by treatment of mercaptan monomer **4** in the same conditions.

The cyclic voltammogram (CV) of **5** shows a typical irreversible anodic peak (E_{pa}) of EDOT derivatives at 1.71 V *vs.* Ag/AgCl (ESI†), and **5** could be easily electropolymerized by application of recurrent potential scans between 0.3 and 1.55 V in an acetonitrile solution (Fig. 1(a)). Fig. 1(b) shows the CV response of the resulting film, presenting the doping/undoping process of the substituted PEDOT skeleton between 0 and +1.2 V, as well as the expected linearity of the peak intensity with the scan rate (inset).

Another illustration of the synthetic versatility of **3** is given by the synthesis of compounds **6** and **7** which are obtained in 75 and 85% yields by treatment of **3** with cesium hydroxide monohydrate and subsequent addition of the corresponding 1-haloalkyl or perfluoroalkyl chain. Monomers **6** and **7** are oxidized at *ca.* 1.70–1.75 V (Table 1 and ESI†), and could be electropolymerized (10^{-3}–10^{-2} M in CH_3CN, Pt, Bu_4NPF_6 (0.1 M)) under potentiodynamic conditions (**6**: 0.30–1.50 V; **7**: 0.15–1.60 V). Similar oxidation potentials are observed for other monomers derived from **3** (compounds **4**, **8**). It appears from these oxidation potentials values that sulfanyl methyl derivatives **3–8** (general formula EDOT–CH_2XR with X = S and R alkyl) are oxidized at slightly higher potentials than the corresponding systems with X = O[4] (Table 1).

Following the same procedure, monomer **8** combining a redox-active tetrathiafulvalene (TTF) fragment to an EDOT moiety is obtained in 90% yield by reaction of **3′** with iodoalkyl-TTF **9**.[11] The TTF unit constitutes an internal redox probe within the polymer film. The CV of **8** shows the successive two-step reversible oxidation of TTF ($E_{ox}{}^1$ = 0.54 V, $E_{ox}{}^2$ = 0.85 V) besides the irreversible oxidation of the EDOT moiety (E_{pa} = 1.75 V). Electropolymerization of monomer **8** ((1 mM in CH_3CN, 25 cycles, 50 mV s^{-1}; Bu_4NPF_6 (0.1 M)) was carried out under potentiodynamic conditions from 0.10 to 1.65 V (see ESI†). Fig. 2(a) shows a typical electrochemical response of the resulting film poly(**8**), exhibiting in particular the signature of both TTF redox systems and, at a lower potential, the response of the redox-active PEDOT-based backbone (from 300 mV).

It is noteworthy that the key monomer **3**, which exhibits an irreversible oxidation peak at E_{pa} = 1.70 V (Fig. 3(a)), could also be very easily electropolymerized under potentiostatic (E_{appl} = 1.65 V) or potentiodynamic conditions (0.3–1.70 V), even at low concentration (1 mM) in CH_3CN. Fig. 3(b) and (c) illustrate the film growth of poly(**3**) (25 scans between 0.25 and 1.65 V at 50 mV s^{-1}) and the corresponding CV response. The CV exhibits an extended redox system from

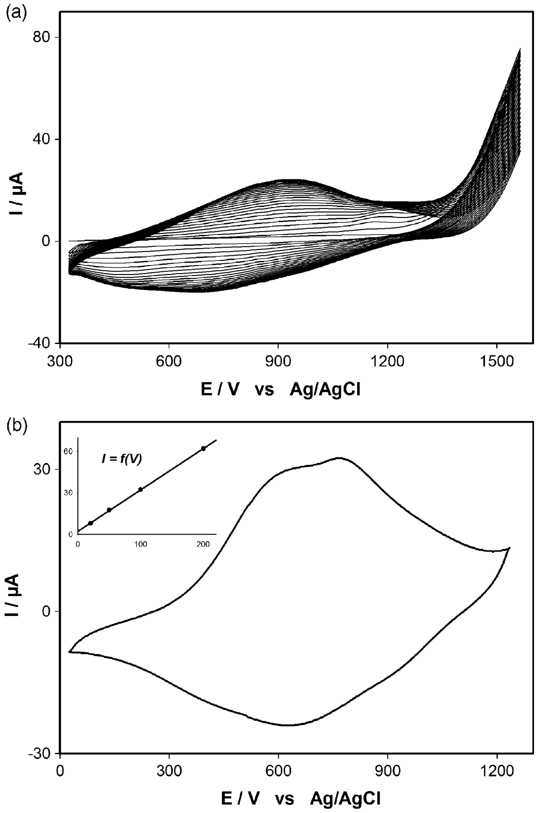

Fig. 1 (a) Electropolymerization of **5** (10 mM) in CH_3CN for 25 cycles at 50 mV s^{-1}; (b) CV response of poly(**5**). Inset: plot of the peak intensity as a function of the scan rate, CH_3CN 100 mV s^{-1}; CH_3CN, Bu_4NPF_6 (0.1 M), Pt diameter = 2 mm.

Table 1 Oxidation potentials for monomers derived from **3**

Monomer	$E_{pa}{}^a$/V
3	1.70
4	1.72
5	1.71
6	1.74
7	1.69
8	1.75
EDOT–CH_2OR[4]	1.60

[a] *vs.* Ag/AgCl, in 0.1 mol L^{-1} Bu_4NPF_6–MeCN, Pt working electrode (diameter: 2 mm) 100 mV s^{-1}.

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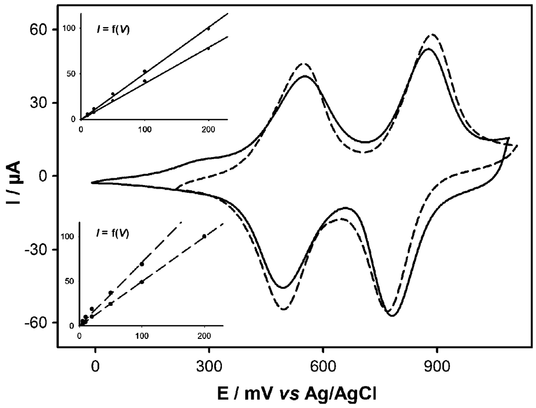


Fig. 2 (a) (--) CV response of poly(**8**); (b) (—) CV response of poly(**3**)-TTF (post-polymerization functionalization strategy); Inset: plot of the peak intensities (E^1 and E^2) as a function of the scan rate for both TTF redox systems. CH_3CN, Bu_4NPF_6 (0.1 M), 100 mV s^{-1}, Pt diameter = 2 mm.

+0.25 to +0.90 V, corresponding to the doping/undoping process of the substituted PEDOT skeleton.

A striking additional interest of the thiolato monomer **3** lies on the straightforward and efficient functionalization of the corresponding poly(**3**) films, subsequent to the polymerization step. We already described an efficient post-polymerization functionalization strategy involving EDOT monomers bearing terminal haloalkyl chains.[4] We propose here a more efficient route for the functionalization of PEDOT, using the highly nucleophilic thiolato functions of poly(**3**) films, likely to react with a broad range of electrophilic species. A description of the strategy for PEDOT film functionalization is given in Scheme 3, and involves in the present example compound **9** as a redox probe to control the substitution process.

A previously prepared poly(**3**)-modified Pt electrode, is successively immersed for 15 min under an inert atmosphere (glove-box) in a DMF–methanol solution of cesium hydroxide (10^{-2} M), and for 20 min in a DMF solution containing iodoalkylTTF **9** (10^{-2} M). Fig. 2(b) shows the CV response of the corresponding functionalized electrode poly(**3**)-TTF. The shape of the CV curve of poly(**3**)-TTF is very similar to that of poly(**8**) (Fig. 2(a)), with in particular two redox processes assigned to the reversible oxidation of TTF. As expected, a low intensity contribution of the conducting PEDOT backbone can be observed from 300 mV, and is essentially masked by the first redox TTF system (E^1). In particular, the peak intensity varies linearly with the scan rate for both TTF redox systems in poly(**8**) and poly(**3**)-TTF (insets of Fig. 2(a) and (b)) which, associated to the small anodic–cathodic peak potential separation for both TTF signals, is characteristic of surface-confined redox systems. Finally, comparing the CV responses of poly(**8**) and poly(**3**)-TTF in Fig. 2, we observe very similar peak intensities which could be attributed to similar coverage ratios ($\Gamma = 2.9 \times 10^{-9}$ and 2.6×10^{-9} mol cm^{-2} TTF units, respectively). In addition, we have observed that the coverage ratio in poly(**3**)-TTF depends directly on the charge used for the electropolymerization of monomer **3**,[12] and consequently depends on the thickness of the poly(**3**) film (Fig. 4). A direct consequence is that

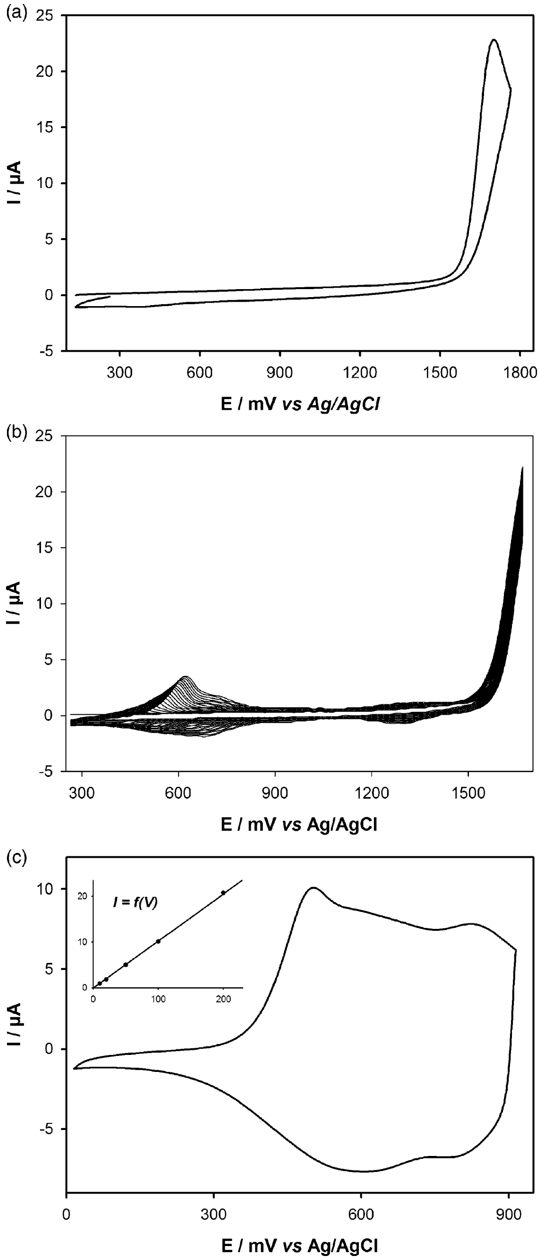
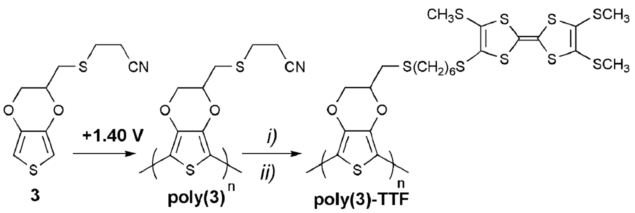


Fig. 3 (a) CV of **3**; (b) electropolymerization of **3** (1 mM), in 0.10 M Bu_4NPF_6–CH_3CN, 25 cycles at 50 mV s^{-1}, Pt diameter = 2 mm; (c) CV response of poly(**3**). Inset: plot of the peak intensity as a function of the scan rate; CH_3CN, Bu_4NPF_6 (0.1 M), 100 mV s^{-1}, Pt diameter = 2 mm.



Scheme 3 *Reagents and conditions*: (i) CsOH (DMF–MeOH) 15 min; (ii) **9**, DMF, 20 min.

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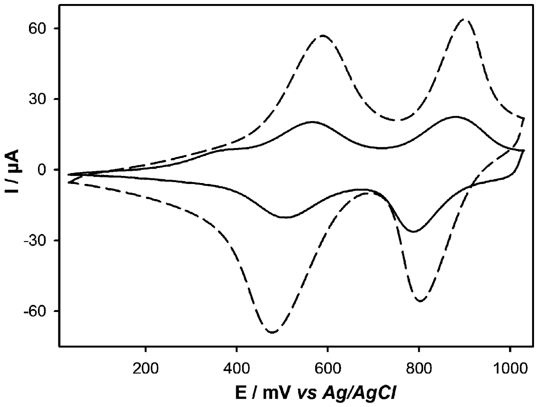

Fig. 4 CV response of poly(**3**)-TTF: (a) (—) Q_d = 0.84 mC cm^{-2} for poly(**3**); Γ = 3.6 × 10^{-9} mol TTF cm^{-2} in the corresponding poly(**3**)-TTF; (b) (--) Q_d = 2.88 mC cm^{-2} for poly(**3**); Γ = 10 × 10^{-9} mol TTF cm^{-2} in the corresponding poly(**3**)-TTF; CH_3CN, Bu_4NPF_6 (0.1 M), 100 mV s^{-1}, Pt diameter = 2 mm.

the yield of the covalent grafting between the conducting PEDOT backbone and the electrophilic TTF fragment **9** must be high, even though the reaction is operated under heterogeneous conditions. The post-polymerization functionalization process constitutes in this case a remarkably efficient tool to introduce an electrophilic fragment within the bulk of a PEDOT-based nucleophilic backbone.

Conclusions

In conclusion, we propose a key-building block in the EDOT family which, thanks to the richness of the thiolate chemistry, not only offers a broad range of perspectives to easily obtain new substituted EDOT monomers, but also for direct functionalization of PEDOT. Work is now in progress for exploring this strategy, as well as for studying potentialities from the thiol and disulfide monomers **4** and **5**.

Experimental

General experimental details

NMR spectra were recorded on a Bruker Advance DRX500 spectrometer operating at 500 and 125.7 MHz for ^{1}H and ^{13}C, respectively, δ values are given in ppm (relative to TMS). Mass spectra (MS) using electronic impact (EI) were achieved on a DSQ spectrometer (thermo).

Cyclic voltammetry experiments were performed on a potentiostat–galvanostat EG&G PAR models 273 or 273 A, with solvents and electrolytes of electrochemical grades, and at room temperature. Potentials are measured relative to a silver wire pseudo-reference electrode and then referenced to a AgCl/Ag electrode, and a platinum wire was used as the counter electrode. When necessary, electrochemical experiments were performed in a JACOMEX glove-box (O_2 and H_2O contents: 5 ppm).

Compounds **1a**[2] and **1b**[10] were prepared according to literature.

Syntheses

2-(Acetylsulfanylmethyl)-2,3-dihydrothieno[3,4,*b*]-1,4-dioxine (2). A large excess of potassium thioacetate (10 eq.) was added to EDOT derivative **1b** (1.04 g, 3.18 mmol) in acetone and the mixture was refluxed for 4 days. After the temperature was raised to rt, the solvent was removed *in vacuo* and the residue was dissolved in dichloromethane. The solution was washed with water, dried over sodium sulfate and concentrated *in vacuo*. The crude compound was purified by chromatography on a silica gel column (dichloromethane–petroleum ether 1 : 1). Red oil (0.70 g, 95%); ^{1}H NMR ($CDCl_3$): δ 2.38 (s, CH_3, 3H), 3.16 (dd, $^{\mathrm{gem}}J$ = 14.0 Hz, J = 6.2 Hz, SH_aH$_b$, 1H), 3.20 (dd, $^{\mathrm{gem}}J$ = 14.0, J = 6.0 Hz, SH$_a$$H_b$, 1H), 3.95 (dd, $^{\mathrm{gem}}J$ = 11.7 Hz, $^{trans}J$ = 7.2 Hz, =C(C)OCH$_2$, 1H), 4.19 (dd, $^{\mathrm{gem}}J$ = 11.7 Hz, ^{cis}J = 2.2 Hz, =C(C)OCH$_2$, 1H), 4.24 (m, (CH$_2$)$_2$CHO, 1H), 6.33 (d, J = 3.5 Hz, CH$_{\mathrm{thiophene}}$, 2H); ^{13}C NMR ($CDCl_3$): δ 29.2, 30.5, 66.9, 72.4, 99.8, 100.0, 141.1, 141.2, 194.8. Anal. for $C_9H_{10}O_3S_2$. Found (calc.): C, 47.14 (46.94); H, 4.46 (4.38); S, 27.78 (27.85%); EI-MS: m/z 230 [M$^{+\bullet}$].

2-(4-Cyano-2-thiabutyl)-2,3-dihydrothieno[3,4,*b*]-1,4-dioxine (3). A 1.2 M solution of sodium methoxide in methanol (4 mL), was added to EDOT thioester **2** (0.4 g, 1.73 mmol) dissolved in dry and degassed THF (40 mL). The mixture was stirred at room temperature for 2 h. 3-Bromopropionitrile (1.44 mL, 10 eq., 17.3 mmol) was added and the mixture was stirred for 2 h. The solvent was evaporated *in vacuo* and the residual oil was diluted with Et_2O and washed with water. After drying over magnesium sulfate, solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (dichloromethane–petroleum ether 1 : 1) affording the desired product **3** as a yellow oil (0.29 g, 70%).^{1}H NMR ($CDCl_3$): δ 2.69 (t, J = 7.2 Hz, CH$_2$CN, 2H), 2.83 (dd, $^{\mathrm{gem}}J$ = 10.2 Hz, J = 6.0 Hz, OCH$_2$CH_aH$_b$S, 1H), 2.89 (dd, $^{\mathrm{gem}}J$ = 10.2 Hz, J = 6.0 Hz, SH$_a$$H_b$, 1H), 2.91 (t, J = 8 Hz, SCH$_2$, 2H), 4.08 (dd, $^{\mathrm{gem}}J$ = 11.5 Hz, $^{trans}J$ = 7.0 Hz, =C(C)OCH$_2$, 1H), 4.22 (dd, $^{\mathrm{gem}}J$ = 11.5 Hz, ^{cis}J = 2.2 Hz, =C(C)OCH$_2$, 1H), 4.32 (m, (CH$_2$)$_2$CHO, 1H), 6.35 (s, CH$_{\mathrm{thiophene}}$, 2H); ^{13}C NMR ($CDCl_3$): δ 18.9, 28.7, 32.4, 66.9, 73.7, 100.1, 118.1, 140.9, 141.2. Anal. for $C_{10}H_{11}NO_2S_2$. Found (calc.): C, 49.93 (49.77); H, 4.56 (4.59); N 5.72 (5.80); O 13.32 (13.26); S 26.57 (26.52%); EI-MS: m/z 241 [M$^{+\bullet}$].

(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methanethiol (4). *By reduction of* **2** *with DIBAL-H*: A solution of EDOT thioester **2** (0.69 g, 3 mmol, 1 eq.) in distilled dichloromethane (180 mL) was cooled to −80 °C. A solution (1.0 M in toluene) of diisobutylaluminium hydride (15 mL, 5 eq.) was added dropwise. After stirring at −80 °C during 45 min, the reaction mixture was quenched with 12 mL of an aqueous solution of HCl (3 M). After the temperature has raised (rt), the organic layer was washed with water, dried over sodium sulfate and evaporated. The resulting oil was purified by chromatography on a silica gel column (dichloromethane–petroleum ether 1 : 4)). Colorless oil (0.54 g, 95%).

By deprotection of **2** *in basic medium*: A 1.2 M solution of sodium methoxide in methanol (2 mL), was added to EDOT thioester **2** (0.2 g, 0.86 mmol) dissolved in dry and degassed THF (20 mL). The mixture was stirred at room temperature

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for 2 h, and was then treated with an aqueous solution of HCl (3 M). The reaction mixture was concentrated *in vacuo* and methylene chloride was added. the organic layer was washed with water, dried over sodium sulfate and evaporated. The resulting oil was purified as above. Colorless oil (0.10 g, 65%).

^{1}H NMR (CDCl$_3$): δ 1.67 (dd, J = 9.5, 8.0 Hz, SH, 1H), 2.73 (ddd, ^{gem}J = 14.0 Hz, J = 9.5, 6.5 Hz, OCH$_2$CH_aH$_b$S, 1H), 2.85 (ddd, ^{gem}J = 14.0 Hz, J = 8.0, 6.0 Hz, OCH$_2$-CH$_a$$H_b$S, 1H), 4.10 (dd, ^{gem}J = 11.5 Hz, $^{trans}J$ = 6.7 Hz, =C(C)OCH$_2$, 1H), 4.21 (dd, ^{gem}J = 11.5 Hz, ^{cis}J = 2.0 Hz, =C(C)OCH$_2$, 1H), 4.32 (m, (CH$_2$)$_2$CHO, 1H), 6.34 (s, CH$_{thiophene}$, 2H); ^{13}C NMR (CDCl$_3$): δ 24.64, 66.59, 74.54, 99.81, 99.86, 141.16, 141.32. Anal. for $C_7H_8O_2S_2$. Found (calc.): C, 44.61 (44.66); H, 4.28 (4.28); O 17.03 (17.00); S 33.98 (34.06%); EI-MS: m/z 188 [M$^{+\bullet}$].

1,2-Bis((2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl)disulfane (5). Cesium hydroxide monohydrate (168 mg, 1.3 eq., 1.07 mmol) in solution in methanol (3 mL), was added to compound **3** (200 mg, 0.82 mmol) in DMF (20 mL). The reaction was stirred and refluxed for 2 h under oxygen bubbling. The DMF was removed *in vacuo* and the residue was dissolved in dichloromethane. The organic phase was washed with water, dried over sodium sulfate. After evaporation, the residue was purified by chromatography on a silica gel column (dichloromethane–petroleum ether 1 : 1). Yellow oil (0.10 g, 65%); ^{1}H NMR (CDCl$_3$): δ 2.98 (dd, ^{gem}J = 12.2 Hz, J = 6.2 Hz, SH_aH$_b$, 1H), 3.06 (dd, ^{gem}J = 12.2 Hz, J = 7.0 Hz, SH$_a$$H_b$, 1H), 4.08 (dd, ^{gem}J = 11.6 Hz, $^{trans}J$ = 7.0 Hz, =C(C)OCH$_2$, 1H), 4.27 (dd, ^{gem}J = 11.7 Hz, ^{cis}J = 1.7 Hz, =C(C)OCH$_2$, 1H), 4.44 (m, (CH$_2$)$_2$CHO, 1H), 6.35 (d, J = 3.5 Hz, CH$_{thiophene}$, 2H); ^{13}C NMR (CDCl$_3$): δ 39.0, 66.7, 72.1, 77.3, 100.1, 140.9, 141.2. Anal. for $C_{14}H_{14}O_4S_4$. Found (calc.): C, 44.96 (44.90), H, 3.72 (3.77), O, 17.11 (17.09), S, 34.21 (34.25%); EI-MS: m/z 374 [M$^{+\bullet}$].

2-(2-Thiaoctyl)-2,3-dihydrothieno[3,4,*b*]-1,4-dioxine (6). Cesium hydroxide monohydrate (168 mg, 1.3 eq., 1.07 mmol) in solution in methanol (3 mL) was added under N$_2$ to compound **3** (200 mg, 0.82 mmol) in dry and degassed DMF (20 mL). After 15 min of stirring, 1-bromohexane (0.14 mL, 1.2 eq., 0.98 mmol) diluted in DMF was added. The reaction was stirred for 2 h. DMF was removed *in vacuo* and the residue was dissolved in dichloromethane. The organic phase was washed with water, dried over sodium sulfate. After evaporation, the residue was purified by chromatography on a silica gel column (dichloromethane–petroleum ether 1 : 3). Yellow oil (0.19 g, 85%); ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.88 (t, J = 7.0 Hz, CH$_2$CH_3, 3H), 1.29 (m, CH$_2$, 4H), 1.38 (m, CH$_2$, 2H), 1.59 (m, CH$_2$, 2H), 2.60 (t, J = 7.5 Hz, SCH$_2$, 2H), 2.70 (dd, ^{gem}J = 14.0 Hz, J = 7.7 Hz, OCH$_2$CH_aH$_b$S, 1H), 2.84 (dd, ^{gem}J = 14.0 Hz, J = 5.5 Hz, OCH$_2$CHH_bS, 1H), 4.04 (dd, ^{gem}J = 11.5 Hz, $^{trans}J$ = 7.0 Hz, =C(C)OCH$_2$, 1H), 4.25 (m, (CH$_2$)$_2$CHO, 1H), 4.30 (dd, ^{gem}J = 11.7 Hz, ^{cis}J = 2.0 Hz, =C(C)OCH$_2$, 1H), 6.33 (d, J = 4.0 Hz, CH$_{thiophene}$, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.1, 22.6, 28.5, 29.6, 31.4, 32.07, 33.2, 67.1, 73.4, 99.7, 99.7, 141.4, 141.5. Anal. for $C_{13}H_{20}O_2S_2$. Found (calc.): C: 57.83 (57.31), H, 7.51 (7.40), O: 11.88 (11.75), S: 22.99 (23.54%); EI-MS: m/z 272 [M$^+$].

2-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-2-thiadecyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (7). Cesium hydroxide monohydrate (139 mg, 1.3 eq., 0.83 mmol) in solution in methanol (3 mL) was added under N$_2$ to compound **3** (155 mg, 0.64 mmol) in dry and degassed DMF (20 mL). After 15 min of stirring, 1-iodo-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane (0.19 mL, 1.2 eq., 0.77 mmol) diluted in DMF was added. The reaction was stirred for 2 h. DMF was removed *in vacuo* and the residue was dissolved in dichloromethane. The organic phase was washed with water, dried over sodium sulfate. After evaporation, the residue was purified by chromatography on a silica gel column (dichloromethane–petroleum ether 1 : 4). White solid (0.25 g, 75%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.43 (m, CH$_2$CF$_2$, 2H), 2.79 (dd, ^{gem}J = 14.5 Hz, J = 6.0 Hz, –OCH$_2$CH_aH$_b$S, 1H), 2.85–2.90 (m, CHHSCH_2, 3H), 4.07 (dd, ^{gem}J = 11.7 Hz, $^{trans}J$ = 6.7 Hz, =C(C)OCH$_2$, 1H), 4.23 (dd, ^{gem}J = 11.7 Hz, ^{cis}J = 2.2 Hz, =C(C)OCH$_2$, 1H), 4.32 (m, (CH$_2$)$_2$CHO, 1H), 6.35 (d, J = 3.7 Hz, CH$_{thiophene}$, 2H).^{19}F NMR (500 MHz, CDCl$_3$): δ −126.6, −123.9, −123.4, −122.4, −114.8, −81.2.^{13}C NMR (125 MHz, CDCl$_3$): δ 23.8, 31.2, 31.8, 66.9, 73.6, 99.9, 100.0, 140.9, 141.2. Anal. for $C_{15}H_{11}F_{13}O_6S_2$. Found (calc.): C, 33.76 (33.72), H, 2.05 (2.07) O, 6.01 (5.99), S, 11.97 (12.00%); EI-MS: m/z 534 [M$^{+\bullet}$].

2-(8-EDOT-7-Thiaoctylsulfanyl)-3,6,7-trimethylsulfanyl)-tetrathiafulvalene (8). Cesium hydroxide monohydrate (90 mg, 1.3 eq., 0.54 mmol) in solution in methanol (3 mL) was added under N$_2$ to compound **3** (100 mg, 0.41 mmol) in dry and degassed DMF (20 mL). After 15 min of stirring, ω-iodoalkyl-TTF **9**[11] (240 mg, 1 eq., 0.41 mmol) diluted in DMF was added. The reaction was stirred 2 h. The DMF was removed *in vacuo* and the residue was dissolved in dichloromethane. The organic phase was washed with water, dried over sodium sulfate. After evaporation, the residue was purified by chromatography on a silica gel column (dichloromethane–petroleum ether 1 : 1). Orange oil (0.24 g, 90%); ^{1}H NMR (CDCl$_3$): δ 1.42 (m, CH$_2$, 4H), 1.63 (m, CH$_2$, 4H), 2.41 (s, SCH$_3$, 9H), 2.61 (t, J = 7.5 Hz, SCH$_2$, 2H), 2.72 (dd, ^{gem}J = 10.8 Hz, J = 7.6 Hz, –OCH$_2$CH_aH$_b$S, 1H), 2.81 (t, J = 7.3 Hz, SCH$_2$, 2H), 2.85 (dd, ^{gem}J = 10.8 Hz, J = 7.6 Hz, –OCH$_2$CH$_a$$H_b$S, 1H), 4.05 (dd, ^{gem}J = 11.8 Hz, $^{trans}J$ = 7.1 Hz, =C(C)OCH$_2$, 1H), 4.27 (dd, ^{gem}J = 11.8 Hz, ^{cis}J = 2.0 Hz, 1H), 4.29 (m, (CH$_2$)$_2$CHO, 1H), 6.33 (s, CH$_{thiophene}$, 2H); ^{13}C NMR (CDCl$_3$): δ 19.3, 27.9, 28.2, 29.4, 29.5, 32.1, 33.0, 36.2, 67.1, 73.4, 99.7, 99.8, 127.4, 127.5, 129.7, 141.3, 141.3, 141.4. Anal. for $C_{22}H_{28}O_2S_{10}$. Found (calc.): C, 40.61 (40.96), H, 4.42 (4.37%); EI-MS: m/z 644 [M$^{+\bullet}$].

Acknowledgements

The authors are grateful to the "Agence Nationale de la Recherche" for financial support in the framework of NANOCONNECT project. M. B. is indebted to the Conseil general de Maine et Loire for a grant and M. S. thanks the Institut Universitaire de France (IUF) for financial support.

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