Crown-Tetrathiafulvalenes Attached to a Pyrrole or an EDOT Unit: Synthesis, Electropolymerization and Recognition Properties

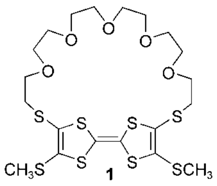
Gaëlle Trippé, Franck Le Derf, Joël Lyskawa, Miloud Mazari, Jean Roncali,
Alain Gorgues, Eric Levillain,* and Marc Sallé*[a]

Abstract: A crown-tetrathiafulvalene electroactive receptor has been covalently linked to electropolymerizable pyrrole or 3,4-ethylenedioxythiophene monomers. The synthetic route to the monofonctionalized tetrathiafulvalene (TTF) ligand has been optimized. Two derivatives of pyrrole (N- and 3-substituted) were synthesized. The various substituted monomers have been electropolymerized to produce polypyrrole (PP) and poly(ethylenedioxothiophene) (PEDOT) films bearing the electroactive TTF moiety. The electroactivity of the polymer films is efficiently controlled by the well-defined two-step redox behavior of the TTF unit. In the case of PEDOT, an alternative post-polymerization derivatization strategy has been used, involving the grafting of the crown-TTF ligand on the previously grown PEDOT backbone. Though chemical derivatization is realized under heterogeneous conditions, in the bulk of the film, this strategy proved to be particularly efficient. These electrodes constitute the first examples of conducting polymer-based modified electrodes incorporating a TTF electrochemical probe, able to interact with a guest ion, such as Ba^{2+}. The cation recognition properties of these various electrodes have been analyzed by cyclic voltammetry and their electroactivity in water as well as their regeneration capability have been investigated.

Keywords: crown compounds · cyclic voltammetry · electrochemistry · polypyrrole · tetrathiafulvalene

Introduction

Much effort has been devoted over the last years to the preparation of switchable macrocyclic ligands able to recognize given guests via the generation of a physico-chemical response (e.g., photo- or electrochemical).[1] Redox responsive ligands have been widely explored, because of their ability to undergo a change in their electrochemical response upon complexation of suitable ions.[2] In the case of a metallic cation recognition, most of these systems are built by covalent association of a ligating subunit to an electrophore. In this context, we and others have demonstrated[3,4] the ability of the strong π-donating tetrathiafulvalene (TTF) unit[5] to act as a redox probe based on the sequential formation of two stable oxidized states (TTF^{+} and TTF^{2+}). Indeed, since the control of the association constant in redox-responsive ligands is essentially governed by electrostatic interactions, the TTF moiety offers a unique opportunity to monitor not only the binding (neutral TTF) but also the progressive releasing of the metal cation (TTF^{+} and then TTF^{2+}). An exciting step towards applications of such a system, lies in the preparation of a modified surface able to reproduce at a solid electrode liquid interface the recognition process observed in homogeneous solutions.[6] Electrode surface modification with TTF derivatives has already been described by formation of self-assembly monolayers (SAMs) from mercapto or disulfide TTF derivatives,[7] or by electropolymerization of TTF functionalized thiophene-based precursors.[8] In the course of our studies on related aspects dedicated to electrode surface modifications with TTF moieties, we have developed the preparation of crown-TTF SAMs,[9] and we have also carried out an original film electrodeposition of TTF-based dendrimers.[10] Furthermore, we have preliminary demonstrated the high efficiency of a post-polymerization surface functionalization process.[11]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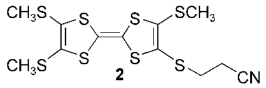
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[a] Dr. G. Trippé, Dr. F. Le Derf, Dr. J. Lyskawa, Dr. M. Mazari,
Dr. J. Roncali, Prof. A. Gorgues, Dr. E. Levillain, Prof. M. Sallé
Laboratoire de Chimie et Ingénierie Moléculaire
des Matériaux d'Angers (CIMMA)
Groupe Synthèse Organique et Matériaux Fonctionnels
UMR CNRS 6200, Université d'Angers
2 Bd Lavoisier, 49045 Angers (France)
Fax: (+33) 2 4173-5405
E-mail: marc.salle@univ-angers.fr

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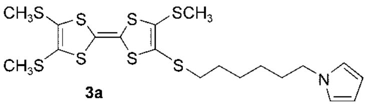
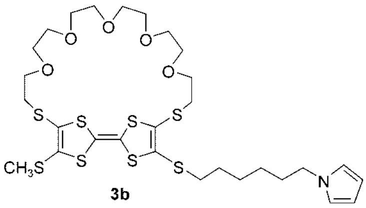
Here, we report on the synthesis of a series of molecular assemblies associating a crown-TTF host unit **1** to various electropolymerizable pyrroles or 3,4-ethylenedioxythiophene derivatives (**3**–**5**). These systems have been electropolymerized and the resulting modified electrodes have been electrochemically characterized. Also, the alternative post-polymerization derivatization strategy has been used and the films obtained compared to the ones prepared by direct electropolymerization of crown-TTF substituted monomers. Finally, the recognition properties of related electrodes have been investigated by cyclic voltammetry.



3a



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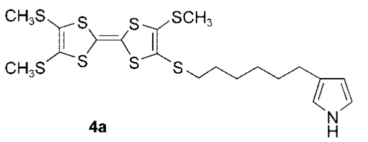
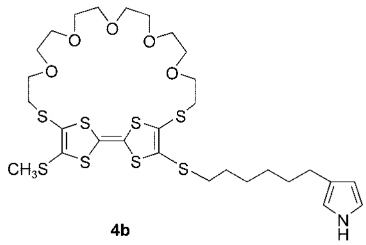


4a



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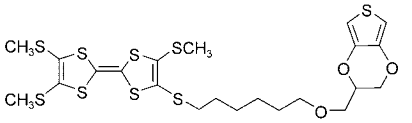
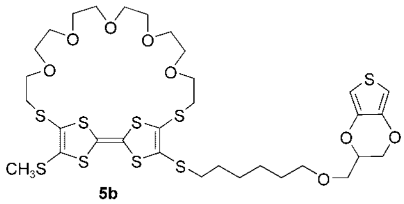


5a



5b

Results and Discussion

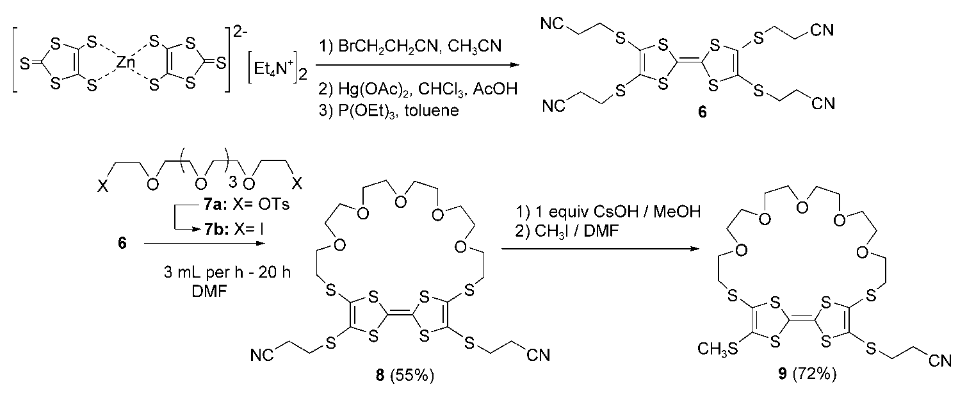
Synthesis: We have recently shown[3a,b] that crown-TTF **1** exhibits a good affinity and complexation selectivity for Ba^{2+} in homogeneous solution, and that this affinity decreases upon electrochemical oxidation to $\mathbf{1}^{\cdot+}$ and $\mathbf{1}^{2+}$. Such a behavior is explained by the repulsive electrostatic interactions between the ligand and the metal cation, upon oxidation of TTF. This phenomena is illustrated by cyclic voltammetry (CV) experiments, for which the first redox wave (E^1_{ox}) shifts toward a higher potential upon progressive addition of barium (the electroactive TTF unit being more difficult to oxidize because of the proximity of the coordinated metal cation), whereas the second potential (E^2_{ox}) remains constant, therefore illustrating the expulsion of the metal outside the cavity.

With the subsequent grafting of this model ligand onto a solid substrate in mind, we have modified the synthetic strategy previously used for **1**, in order to introduce various types of anchorage sites prone to interact with the solid surface.

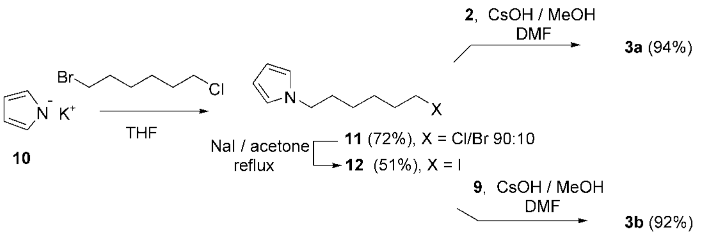
The tetraalkysulfanylTTF [$(RS)_4$TTF] skeleton was built from the so-called zincate salt through the preparation of the TTF intermediate **6** (Scheme 1). The cyanoethyl fragment is known to be selectively cleaved upon addition of stoichiometric amounts of base, to produce the corresponding thiolato derivative.[12] Different synthetic methods based on the addition order of the electrophilic species, can be used to reach the target disymmetrical crown-TTF **9**. We found that the best results involve first the [1+1] cyclocondensation step between **6** and the 1,ω-diodo polyether chain **7b**, and then a methylation of one of the residual thiolato sites of **8**. The diiodo derivative **7b** was quantitatively obtained by refluxing ditosylate **7a** prepared according to reference [13] in acetone with NaI (excess). Equimolar amounts of the dianion resulting from treatment of **6** with two equivalents of cesium hydroxide on the one hand, and the polyether chain **7b** on the other hand, were both transferred into two distinct syringes connected to a perfursor pump. Simultaneous addition (3 mLh^{-1}) to dry DMF was then operated (final theoretical concentration in **8** was ca. 5 mM), and allowed formation of the [1+1] macrocycle **8** (55% yield) (neither higher order macrocycles nor oligomers were formed). Compound **8** was then monodeprotected with $CsOH{\cdot}H_2O$ (1 equiv) and addition of an excess of iodomethane (excess) led to the formation of the key derivative **9** (72% yield, as a 60:40 *Z*/*E* isomeric mixture as determined by ^1H NMR ($CDCl_3$)). An analogous TTF derivative **2**,[14] devoid of coordinating unit, was synthesized for comparison studies.

According to a convergent strategy, crown-TTF **9** (as well as model compound **2**) was then linked to various suitably functionalized polymerizable units.

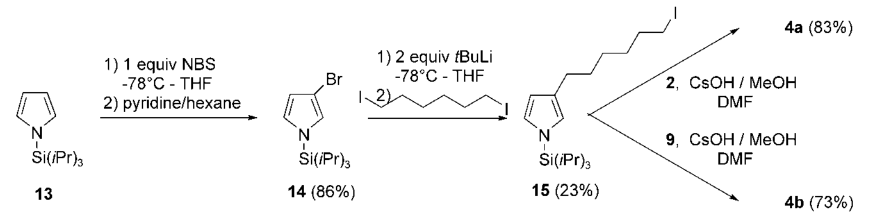
N-Substituted pyrroles (Scheme 2) were obtained starting from the pyrryl salt **10**, quantitatively prepared by deprotonation of pyrrole with metallic potassium in xylene (100°C).[15] Salt **10**, dissolved in DMSO was then slowly added onto a THF solution of 1-bromo-6-chlorohexane, producing N-alkylpyrrole **11** with a 90:10 relative amount of X = Cl/Br. Transhalogenation in the presence of an excess of sodium iodide afforded compound **12** in 51% yield. The 3-substituted pyrrole derivative **15** (Scheme 3) was obtained by N-protection of pyrrole by a triisopropylsilyl group to produce **13**, subsequent bromination with NBS (compound **14**)[16] and treatment of the bromo intermediate **14** with *t*BuLi (2 equiv) and a large excess of 1,6-diiodo-hexane.



Scheme 1. Synthesis of the key crown-TTF system.

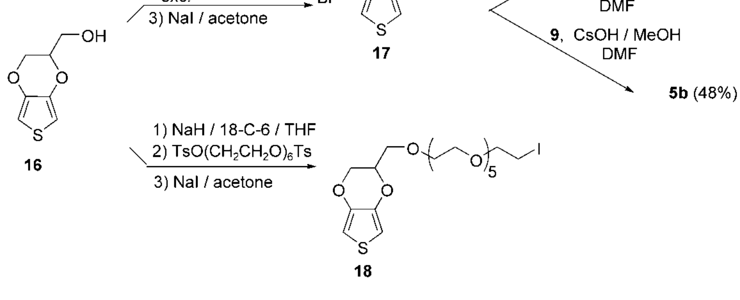


Scheme 2. Synthesis of *N*-pyrryl substituted TTF derivatives.



Scheme 3. Synthesis of 3-pyrryl substituted TTF derivatives.

The synthesis of monomers derived (3,4-ethylenedioxythiophene) (Scheme 4), was realized through the preparation of compounds **17** and **18**, obtained from hydroxymethyl(3,4-ethylenedioxythiophene) (hydroxymethyl-EDOT **16**).[17]



Scheme 4. Synthesis of (3,4-ethylenedioxythiophene)-substituted TTF derivatives.

The target systems (**3**–**5**) associating the redox-active TTF unit to an electropolymerizable unit were obtained by nucleophilic substitution between the cesium thiolate salt derived from key intermediates **9** (or **2**) and the corresponding pyrrole or thiophene derivative (**12**, **15**, **17**, **18**).

Electrochemistry: All electrochemical experiments were carried out under inert atmosphere with an initial millimolar concentration of monomer in acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. For the three families (N-substituted pyrrole, 3-substituted pyrrole, and EDOT derivatives), electropolymerization conditions were optimized with the corresponding model compound devoid of crown ether unit.

N-Substituted pyrroles 3a,b: Pyrrole derivatives are known for their ability to generate electroactive substituted polypyrroles (PP), and therefore constitute excellent candidates to graft our TTF systems onto an electrode.[18] This monomer has already been extensively used for immobilisation of many different redox active sites onto electrode surfaces. For example, ferrocene covalently linked to a suitable host binding site, can produce an efficient ferrocene-based cation sensor.[19] In our case, the cyclic voltammogram (CV) of monomers **3a** and **3b**, shows two reversible redox systems corresponding to the two reversible oxidation steps of TTF ($E^1_{1/2}$ and $E^2_{1/2}$) followed by an irreversible anodic wave related to the oxidation of the monomer (peak potential E^3_{pa}) (**3a**: $E^1_{1/2} = 0.54$ V, $E^2_{1/2} = 0.79$ V, $E^3_{pa} = 1.48$ V; **3b**: $E^1_{1/2} = 0.56$ V, $E^2_{1/2} = 0.77$ V, $E^3_{pa} = 1.50$ V). The similarity between oxidation potentials of monomers **3a** and **3b** illustrates the small influence of the outer-S substitution on the HOMO level of these tetraalkyl(sulfanyl)TTF derivatives.

Nevertheless, both monomers behave differently upon electropolymerization. The best results for the films growing of the methyl substituted **3a** were obtained for an applied potential of $E = 1.41$ V, that is, very near to the peak potential (E^3_{pa}).

In the case of the crown-TTF derivative **3b**, electropolymerization could not be observed below an applied potential of 1.8 V, presumably because of the steric hindrance induced by the crown-ether part. The formation of poly(**3a**) and poly(**3b**) could also be observed by recurrent potential scans, for which the progressive increase of the peaks intensity denotes the growing of the films (Figure 1a). Also, the

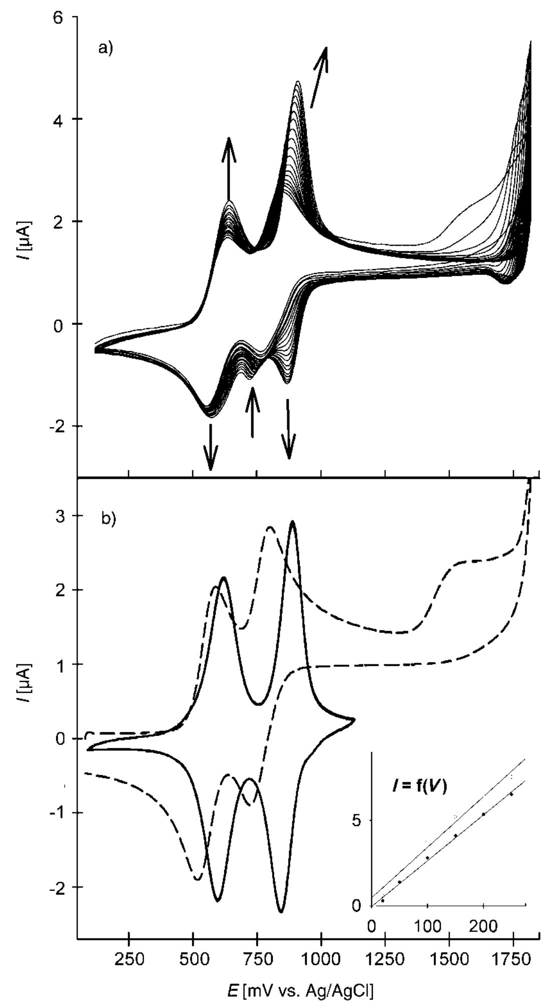


Figure 1. a) Electropolymerization of **3b** (1 mM), in 0.10 M Bu_4NPF_6/CH_3CN, 20 cycles at $100\,mV\,s^{-1}$, Pt∅ = 1 mm. b) CV of monomer **3b** (– – –) and of poly(**3b**) (——), $\Gamma = 4.5{\cdot}10^{-9}\,mol\,TTF\,cm^{-2}$, in 0.10 M Bu_4NPF_6/CH_3CN, Pt∅ = 1 mm; Insert: plot of the peak intensity versus scan rate, for both TTF redox systems.

redox peaks appear thinner upon increasing, as expected when changing from a diffusion-controlled to a surface-confined redox process. This behaviour is illustrated by the CV of the polymers recorded in a monomer-free electrolytic solution (Figure 1b). Two well-defined reversible oxidation peaks are observed ($E^1_{pa} = 0.62$ V, $E^2_{pa} = 0.90$ V), which are characteristic of surface confined redox couples, with the expected linear relationship of both peak currents (i_{pa1} and i_{pa2}) with the scan rate v (Figure 1b, insert). To confirm this, the additional usual criteria for characterizing a surface reaction consists of controlling the anodic/cathodic peaks separation (ΔE_p), which should ideally tends to 0 V. This is the case here for each redox systems of poly(**3a**) and poly(**3b**), the very small differences observed indicating that the redox processes of the TTF system are partially limited by charge and/or mass transport in the polymer film.

Additionally, whereas E^1_{pa} are similar for the monomer and the corresponding polymer, a significant positive shift of the second redox system of TTF ($\Delta E^2_{pa} = 75$ mV) is observed (Figure 1a and b). This observation can be assigned to the electronic effect of the positively charged PP backbone on the electroactivity of the grafted TTF system.

Noteworthy, the electrochemical signature of the PP backbone does not appear clearly on the CV response of poly(**3a**) or poly(**3b**) (Figure 1b). This one is expected at about 0.45 V for N-alkyl PP.[20] Therefore, the redox signature of the PP skeleton is partially masked by the first oxidation process of TTF. Additionally, the PP backbone is certainly oxidized at a higher potential than for usual N-alkyl derivatives due to torsions in the polymeric chain which are generated by the bulky TTF groups. This torsion leads to a loss of the conjugation, and therefore to an increase of the oxidation potential of the PP chain [poly(N-methylpyrrole) is oxidized at ca. +300 mV relative to naked PP],[21] as well as to a weaker doping level. Therefore the charge contribution of the PP backbone part is certainly very low in comparison to that of the two 1e redox waves of TTF.

The film deposition efficiency could be evaluated in the case of poly(**3a**). It has been calculated from the ratio between the charge corresponding to the deposited material (determined by integration of the anodic current in the CV response after transfer of the modified electrode in a pure electrolyte), and the charge consumed during the electrolysis, and using a value of 4.33 for the number of electrons transferred/monomer during the deposition process.[18,22,23] On this basis, polymerization yields of 80–90 % were found, for charges values of $19\text{–}25\,mC\,cm^{-2}$ which, in the latter case, corresponds to a coverage ratio of $\Gamma = 8.8\;10^{-9}\,mol\,cm^{-2}$ in TTF units.

3-Substituted pyrroles 4a, b: Polypyrrole substituted in the 3-position generally present higher conductivities than their N-substituted analogues as well as a better stability.[24] The CV of pyrrole-TTF assemblies **4a**, **4b** exhibit three redox processes, respectively, assigned to the two one-electron reversible oxidations of TTF ($E^1_{1/2} = 0.55$ V, $E^2_{1/2} = 0.76$ V), and to the irreversible oxidation of the pyrrole moiety ($E^3_{pa} = 1.06$ V for **4a** and 1.33 V for **4b**). The fact that only the irreversible process is affected between **4a** and **4b** is assigned to significantly different diffusion coefficients between both monomers.

These values (E^3_{pa}) are much lower than for their N-pyrrole analogues (**3a**, **b**), in accordance with literature data.[20] As shown by recent ab initio calculations,[25] this results from a higher electron-donating inductive effect of the alkyl chain at the 3-position compared with N-substitution.

Different attempts of electropolymerization were carried out for millimolar solutions of **4a** and **4b** in acetonitrile, that is, by application of recurrent potential scans, or under potentiostatic conditions. The best results were obtained with an applied potential of 1.06 V for **4a**, and 1.35 V for **4b**. The electrochemical behaviour of the corresponding modified electrode in a monomer-free solution, is similar for poly(**4a**) and poly(**4b**) (Figure 2). Analogous observations are made as for poly(**3a**) and poly(**3b**), with the characteristic CV shape of surface confined redox processes ($E^1_{pa} = 0.60$ V; $E^2_{pa} = 0.84$ V). Contrary to their N-substituted analogues, a slow but progressive decreasing of the signal intensity for poly(**4a**) and poly(**4b**) upon cycling the potentials

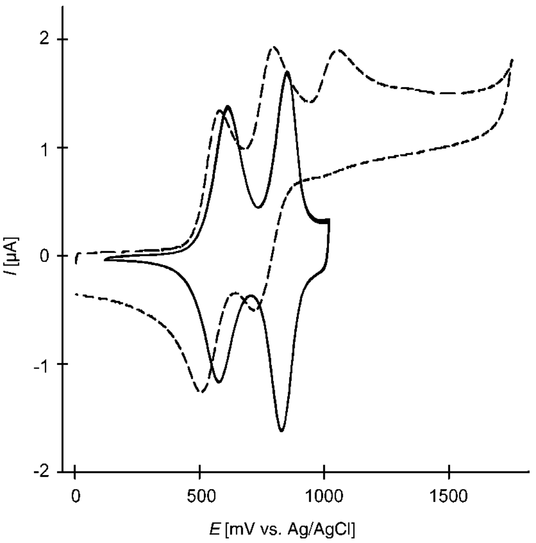


Figure 2. Electrochemical response of monomer **4a** (---) and of poly(**4a**) (——), $\Gamma=5.4\cdot10^{-9}$ mol TTF cm^{-2}, CH$_3$CN, 100 mV s^{-1}, Bu$_4$NPF$_6$ (0.1 M), Ag/AgCl, Pt∅ = 1 mm.

was observed. This instability is somewhat surprising when considering the fact that 3-substituted polypyrrole are precisely known to be more stable than their N-substituted analogues. No convincing explanation can be given to this observation, except unfavourable steric factors. In order to statistically dilute the functionalized pyrrole units among naked pyrrole moieties along the PP chain, and therefore decrease the steric demand, we also attempted copolymerization experiments in the presence of pyrrole (1–5 %). Unfortunately, the electropolymerization only furnished unsubstituted PP.

EDOT derivatives 5a, b: Poly(3,4-ethylenedioxythiophene) (PEDOT) has been extensively studied over the last decade due to its remarkable optical, electrochemical and electrical properties,[26] with notably a broad window of electroactivity which makes it a suitable matrix for preparing modified electrodes.

The CV of monomers **5a** and **5b** exhibits the successive two-steps reversible oxidation of TTF (**5a**: $E^1_{1/2}=0.57$ V, $E^2_{1/2}=0.83$ V; **5b**: $E^1_{1/2}=0.54$ V, $E^2_{1/2}=0.75$ V), and the irreversible oxidation of the EDOT moiety ($E^3_{pa}=1.62$ V for both monomers). This latter value, close to that of the starting hydroxymethyl-EDOT **16**,[17] illustrates the absence of electronic interaction between the substituent and the EDOT moiety. Electropolymerization of monomers **5a** and **5b** was carried out under similar conditions except that a higher concentration in monomer was required in the latter case (5 mM). Formation of poly(**5a**) and poly(**5b**) was realized either under potentiostatic ($E_{appl}=1.51$ V) or potentiodynamic conditions (0 to 1.51 V) (Figure 3), giving rise to stable films.

Figure 3b shows a typical electrochemical response for the resulting polymer, illustrating the two-steps oxidation process of the TTF moiety (poly(**5a**): $E^1_{pa}=0.62$ V ; $E^2_{pa}=0.90$ V; poly(**5b**): $E^1_{1/2}=0.59$ V ; $E^2_{1/2}=0.84$ V). As for the different poly(TTF) studied in the present work, the first redox system appears broader than the second one. This behaviour reflects the existing interactions between TTF species when reaching the radical-cation state as already observed in oligo- and poly-(TTF) systems.[8c,27] Contrary to PP derivatives described above, an electrochemical signature appears from about 0 V till the first TTF system, which corresponds to the doping/dedoping process of the poly(EDOT) backbone.

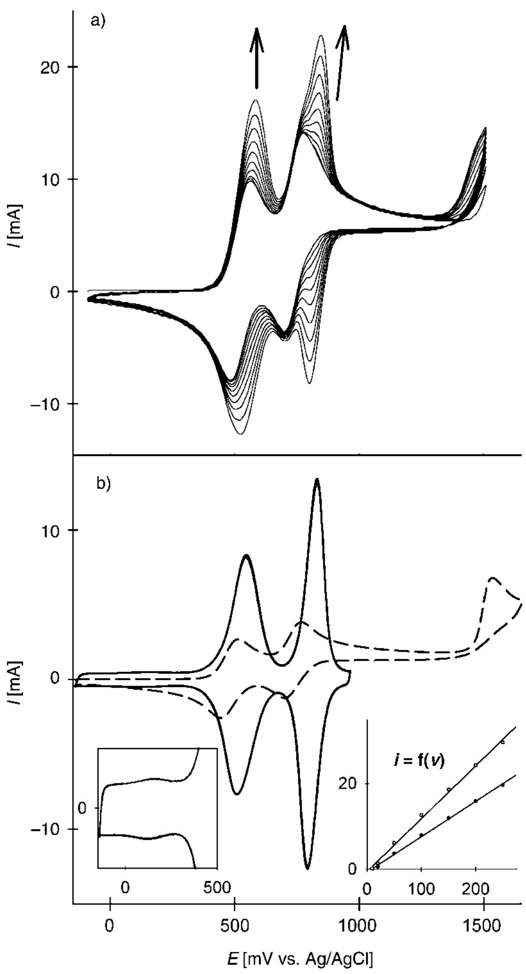
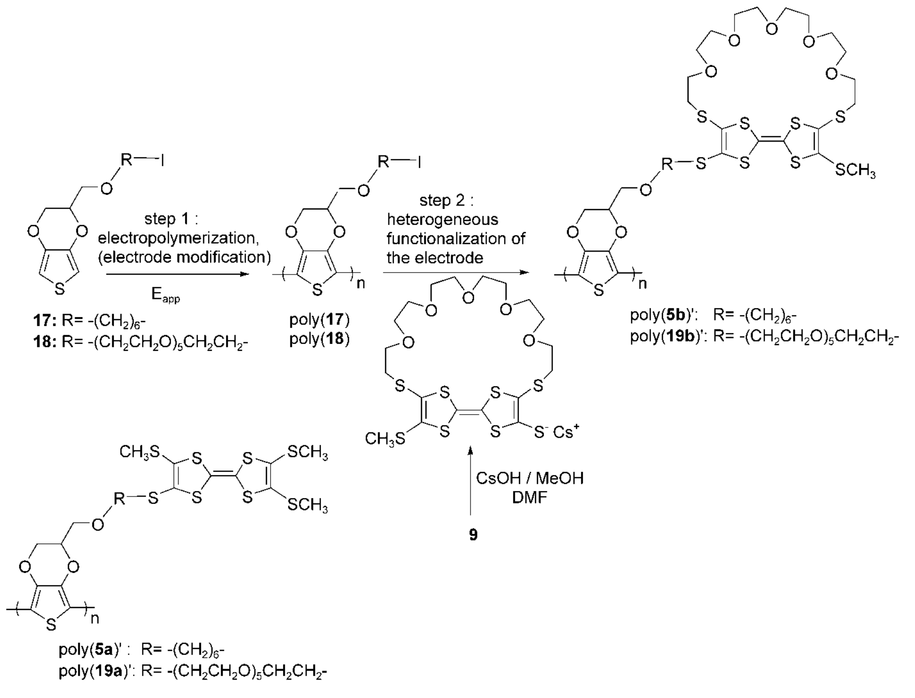


Figure 3. a) Electropolymerization of **5b** (5 mM), CH$_3$CN, 100 mV s^{-1}, Bu$_4$NPF$_6$ (0.1 M), 10 cycles, Pt∅ = 1 mm; b) Electrochemical response of **5b** (---) and of poly(**5b**) (——) $\Gamma=1.8\cdot10^{-8}$ mol TTF cm^{-2}, CH$_3$CN, 100 mV s^{-1}, Bu$_4$NPF$_6$ (0.1 M), Pt∅ = 1 mm; Insert: left) zoom of the PEDOT skeleton contribution; right) plot of the peak intensity as a function of the scan rate, for both TTF redox systems.

Coulometric measurements show that the ratio between the charges exchanged during the oxidation of the PEDOT backbone and one TTF oxidation on the other hand is close to 0.2. This value would lead to a doping level of 0.2 as generally observed for polythiophene derivatives.[28] The polymerisation yields appear approximately constant (ca. 90 %) for both species for applied charges ranging from 13 to 26 mC cm^{-2}. Peaks intensity varies linearly with scan rate for both TTF redox systems (Figure 3b) which, associated to the small anodic–cathodic potentials peaks separation is characteristic of surface-confined redox systems.

As for PP films, we observe a significant anodic shift of the potentials associated to TTF in the film compared to starting monomer (Figure 3b), notably for the $TTF^{\bullet+}/TTF^{2+}$ process ($\Delta E^2_{1/2} = +90$ mV). This can be attributed to repulsive electrostatic interactions between the TTF system and the doped poly(EDOT) backbone. This hypothesis is confirmed by the fact that this observation is the same whatever the film thickness, which excludes a problem of mobility of the species within the film. Another possible explanation results from the conducting character of the PEDOT backbone as a function of the applied potential. Indeed, it has been established that the conductivity of PEDOT reaches a plateau and then decreases for higher potentials (bipolaronic state). Then, the different behaviors observed for the two redox processes of TTF, could also be explained by a lower PEDOT conductivity at the second redox potential. This could be the reason why in the plotting of the peak currents (i_{pa1}) and (i_{pa2}) with the scan rate v (Figure 3b, insert), the slope of the second is significantly lower than the first one. Finally, these modified electrodes show a very good stability when stored in atmosphere or upon repeated cycling, as shown by the very good reproducibility of the electrochemical response.

Post-polymerization functionalization: We have recently reported an alternative method of derivatization of poly(EDOT) involving a post-polymerization functionalization of a preformed polymer.[11] Hereby, we depict a similar methodology applied to the specific case of electrodes incorporating crown-TTF systems (Scheme 5). The modified electrodes reached by this methodology lead to active films poly(**5b**)′, whose molecular formula is expected to be similar to poly(**5b**) obtained from the corresponding monomer. Then, a comparison of the films properties, according to their preparation method will be possible.



Scheme 5. Pt surface modification by the post-polymerization functionalization strategy.

Also, modified electrodes poly(**19a**)′ and poly(**19b**)′, incorporating a polyether linker between the EDOT and TTF units, have been prepared.

Modified electrodes bearing pendant TTF active species, were prepared in two steps (Scheme 5): i) electropolymerization of the EDOT monomer (**17** or **18**) bearing an ω-iodinated chain; ii) derivatization, in heterogeneous conditions, of the PEDOT film with the thiolatoTTF ($TTFS^-$) intermediate obtained from basic treatment of **9** (or **2**).

Step 1: As expected, iodinated compounds **17** and **18** present a similar irreversible oxidation potential ($E^3_{pa} = 1.60$ V) as for EDOT itself or for monomers **5a**, **5b**. They could be electropolymerized either in potentiostatic ((**17**) $E_{app} =$ 1.50 V; (**18**) $E_{app} = 1.55$ V) or potentiodynamic conditions. The CV response in a monomer-free electrolytic medium, exhibits a very broad redox system characteristic of poly(EDOT) in the −0.3 to +0.50 V region (Figure 4a).

Step 2: The polymer-coated electrode thus obtained (poly(**17**) or poly(**18**)) is then immersed, under inert atmosphere (glove box), in a DMF solution containing the thiolato derivative previously generated from crown-TTF **9** (or model TTF **2**) ($C = 1\times10^{-2}$ M) and a stoichiometric amount of cesium hydroxide (Scheme 5). In order to check the application range of this methodology, poly(**17**) films of different thicknesses were tested (ca. 0.05 to 1.50 μm).[11,29] Although the reaction is carried out in heterogeneous conditions, the nucleophilic displacement of terminal iodine by the thiolate group is surprisingly rapid (less than 20 minutes) whatever the film thickness, which can be monitored by recording the CV of the resulting electrode (Figure 4a, b). The electrode is thoroughly rinsed with DMF, acetonitrile, and immersed in a fresh electrolytic medium. Figure 4b shows the CV response of a functionalized electrode poly(**5b**)′ obtained from reaction between **9** and a film of poly(**17**) grown potentiostatically with 16 mC cm^{-2}. The CV clearly exhibits a first redox system extending from −0.30 to +0.40 V corresponding the doping/undoping process of the substituted PEDOT backbone (Figure 4b, insert), followed by two more intense reversible oxidation processes ($E^1_{pa} = 0.59$ V; $E^2_{pa} = 0.84$ V), associated to the TTF moiety. An analogous electrochemical behavior is observed for the other crown-TTF functionalized film poly(**19b**)′, obtained by reaction between poly(**18**) and thiolate obtained from **9**, but also for the films incorporating the model–STTF(SMe)$_3$ system[11] (poly(**5a**)′ and poly(**19a**)′,

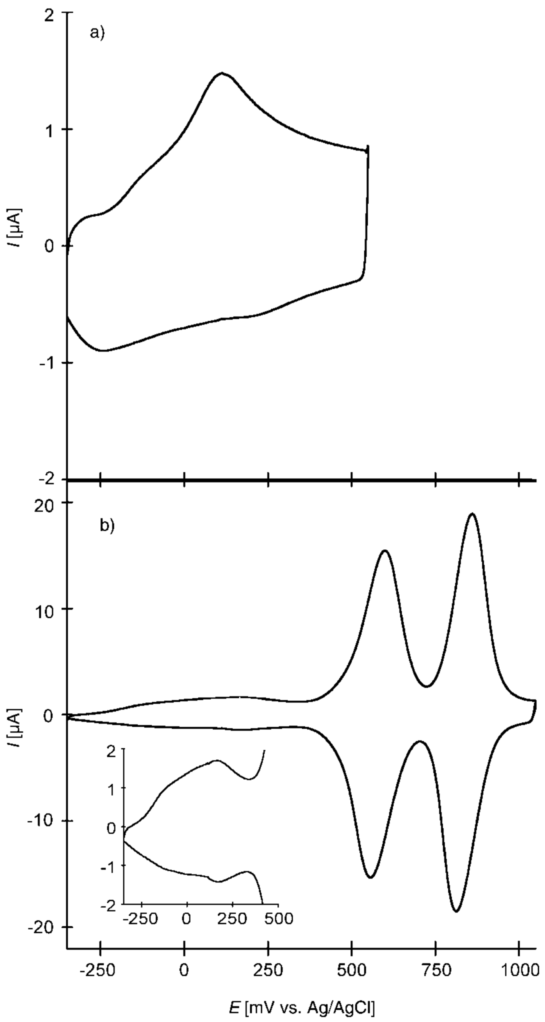


Figure 4. a) CV response of poly(**17**) (before derivatization) and b) corresponding poly(**5b**)′ after treatment of poly(**17**) for 20 min with **9**/CsOH/DMF; $\Gamma = 3.2 \cdot 10^{-8}$ mol TTF cm^{-2}; CH_3CN, Bu_4NPF_6 (0.1 M), 100 mV s^{-1}, Pt∅ = 1 mm. Insert: zoom on the response of the poly(EDOT) backbone part.

respectively, obtained from the reaction between poly(**17**) and thiolate prepared from **2**, and from poly(**18**) and **2**).

At this stage we have in our hand a unique opportunity to compare the electrochemical behaviours of two modified surfaces, namely poly(**5b**) and poly(**5b**)′, built from the same synthons, but according to two different strategies. As seen by comparing Figures 3b and 4b, the CVs of poly(**5b**) and poly(**5b**)′ are very similar. TTF redox systems (E^1_{pa}, E^2_{pa}) are very close (less than 20 mV difference between the two films), and the contribution of the poly(EDOT) backbone appears at the same level in both cases. Indeed, coulometric measurements for poly(**5b**), poly(**5b**)′, poly(**19a**)′ and poly(**19b**)′ show similar values for the ratio of the charge contribution of the PEDOT backbone and that of TTF. This observation, already made in the case of poly(**5a**)′ films[11] indicates that in the range of investigated thickness, the derivatization, though carried out in a heterogeneous medium, is rapid, quantitative and involves the integrity of the polymer. This result is supported by the study of the films morphology, shown by scanning electron microscopy (Figure 5). The films of poly(**17**), poly(**5a**)′ and poly(**19b**)′, exhibit a similar porous morphology, associated to an important specific surface and allowing a high degrees of derivatization, even for thick films. This is further confirmed by the very small amount of residual iodine atom detected by X-ray energy dispersion spectrometry[30] (<5%) for poly(**5a**)′ (Γ = 4.0.10^{-7} mol TTF cm^{-2}).

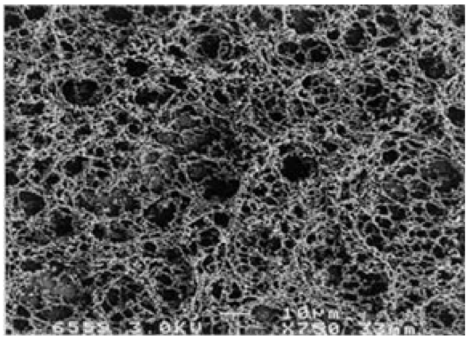


Figure 5. Scanning electron micrograph of poly(**5a**)′ on a Pt electrode ($\Gamma = 4.0 \cdot 10^{-7}$ mol TTF cm^{-2}), ×750.

In order to prevent possible steric interactions along the polymeric chain, a solution is to operate a dilution of the number of active sites, by copolymerization of **17** and EDOT. The copolymer was prepared under potentiostatic conditions from a 50:50 mixture of **17** and EDOT. The resulting film was then subjected to the above described post-polymerization fonctionalisation with crown-TTF **2** under basic conditions, and afforded poly(**5b**)″. The CV of poly(**5b**)″ (Figure 6) is similar to that of poly(**5b**)′ ($E^1_{½}$ = 0.57 V, $E^2_{½}$ = 0.84 V) but shows as expected, a larger charge contribution of the PEDOT backbone (−200 to +400 mV).

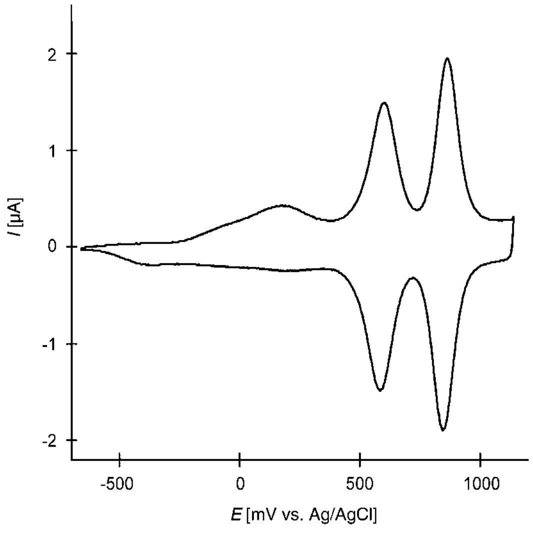


Figure 6. CV response of a modified electrode from poly(**5b**)″, Γ = 1.5·10^{-9} mol TTF cm^{-2}, CH_3CN, Bu_4NPF_6 (0.1 M), Ag/AgCl, 100 mV s^{-1}, Pt∅ = 1 mm.

Finally, it has to be pointed out that all of these electrodes obtained by heterogeneous fonctionalization of precoated poly-EDOT films (poly(**5b**)′, poly(**5b**)″, poly(**19a**)′ and poly(**19b**)′), exhibit a remarkable stability, since no loss of the electrochemical signature has been observed upon repeated cycling, or after standing for days in solution.

Modified electrodes—Recognition properties: The crown-TTF unit is structurally derived from compound **1**, for which the recognition properties for Ba^{2+} in solution have already been described.[3a,b]

We first checked that the grafting of a polymerizable unit (i.e., a pyrrole heterocycle) on the periphery of the crown-TTF ligand does not alter the recognition properties. Increasing amounts of Ba^{2+} are progressively introduced in a millimolar solution of monomer **3b** in acetonitrile, and CV are sequentially recorded (Figure 7).

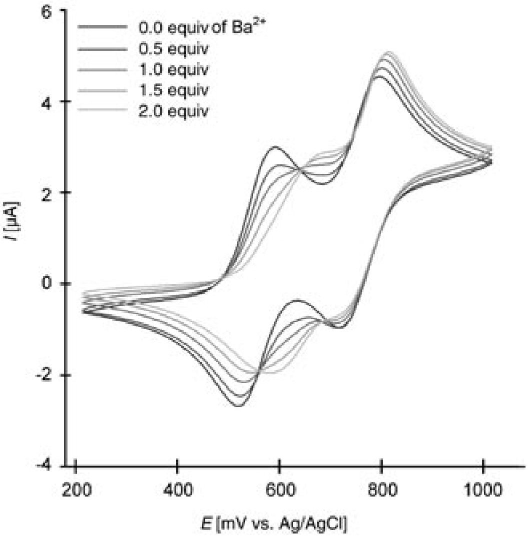


Figure 7. CV titration study of **3b** in presence of increasing concentrations of Ba^{2+}, CH_3CN, 100 mV s^{-1}, Bu_4NPF_6 (0.1 M)/Ag/AgCl.

Figure 7 shows that the first redox system of TTF in **3b** ($E^1_{½} = 0.57$ V), progressively disappears to the benefit of a new one located at a higher potential (0.66 V), whereas the potential value of the second system remains approximately constant. Furthermore, no additional potential shift is observed for an excess of added cation.

These observations have already been made with ligand **1**, and have been associated to the progressive 1:1 complexation of Ba^{2+} in the polyether cavity.[3a,b] The TTF partner in the barium complex is more difficult to oxidize ($\Delta(E^1) = +90$ mV) because of the effect of the positive charge of the metal onto the TTF core. The invariance of the second potential is a manifestation of the expulsion of Ba^{2+} outside the cavity by repulsive electrostatic interactions between the cation and TTF^{2+}. The binding constants for the three oxidation states of the TTF part in **3b** (TTF^0, TTF^+, TTF^{2+}) have been evaluated by the simulation program DIGISIM 2.1 de BAS,[3,31] ($\log K^0 = 3.5$, $\log K^+ = 2.1$, $K^{2+} = 0$, in acetonitrile). These values are slightly lower than those observed for **1** ($\log K^o = 4.3$, $\log K^+ = 2.4$, $K^{2+} = 0$, acetonitrile/dichloromethane 1/1),[3a,b] a difference which can be attributed to the use of a more dissociating medium (acetonitrile) in the case of **3b**. This titration experiment clearly shows that the introduction of a monomer unit on the ligand does not alter its recognition properties.

The electrochemical behaviour of the various families of modified electrodes has been investigated in the presence of Ba^{2+} cation (Table 1). All polymers incorporating the crown-TTF ligand exhibit a positive shift of $E^1_{½}$ in the presence of Ba^{2+} The magnitude of the shift appears strongly dependent on the coverage ratio (Γ) and hence on the film thickness; thinner films ($\Gamma = 10^{-8}$–10^{-9} mol TTF cm^{-2}) show the largest response.

Table 1. Ba^{2+} electrochemical response of different modified electrodes.

Polymer	$E^1_{½}$ shift ($\Delta E^1_{½}$) [V]	[Ba^{2+}] saturation [mM]	TTF coverage (Γ) [mol cm^{-2}]
poly(**3b**)	+20	1.0	$8.8 \cdot 10^{-9}$
poly(**4b**)	+15	2.0	$1.9 \cdot 10^{-9}$
poly(**5b**)	+60	4.0	$1.4 \cdot 10^{-9}$
poly(**19b**)′	+30	4.0	$9.0 \cdot 10^{-9}$

Figure 8 shows as an illustrative example the electrochemical response of a film of poly(**19b**)′ in the presence of Ba^{2+}.

A decrease of the peaks intensity is observed, notably for the lowest Ba^{2+} concentrations.[32] This presumably reflects either structural reorganizations in the film, or a shielding effect of the anion, for which the mobility in the film is lowered upon Ba^{2+} complexation. Noteworthy, the initial CV is restored (peaks intensity and peak potentials) by cycling the

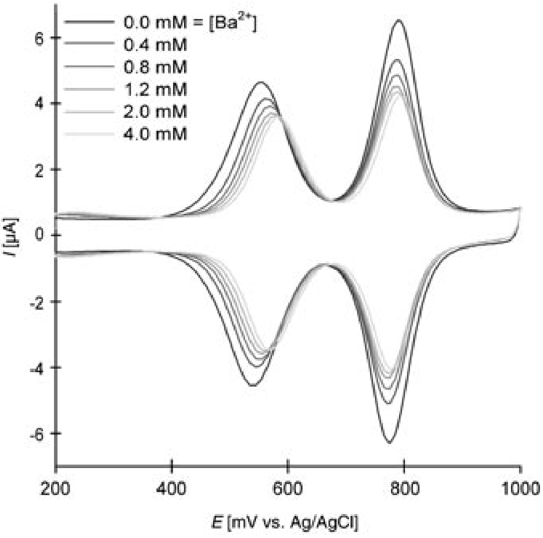


Figure 8. CV response of poly(**19b**)′ upon progressive addition of $Ba(ClO_4)_2$, $\Gamma = 9.0 \cdot 10^{-9}$ mol TTF cm^{-2} in 0.10 M Bu_4NPF_6/CH_3CN, 100 mV s^{-1}, Pt∅ = 1 mm.

modified electrode into a barium free electrolyte, which illustrates the reversibility of the process. The drop of electroactivity is stabilized with a Ba^{2+} concentration of ≈ 1 millimolar. A progressive positive shift of $E^{1}_{1/2}$ observed in presence of increasing concentrations in Ba^{2+}, even though moderate (+30 mV), clearly illustrates the complexation of the metal by the crown-TTF ligand. Conversely, the second redox system ($E^{2}_{1/2}$) remains constant which is consistent with an expulsion of the metal from the cavity at this potential. The smaller value of the potential shift ($\Delta E^{1}_{1/2}$) compared to homogeneous media, is presumably due to the steric and the constraints on the species mobility in the film. No more variation of $E^{1}_{1/2}$ is observed for Ba^{2+} concentrations higher than 4 mM, which indicates a saturation of the film. Analogous results were observed with the other electrodes tested, with the most significant results in each case being presented in Table 1.

Modified electrodes—Electroactivity in water: Very few examples of TTF derivatives are soluble in water and, and very few has been done to describe the electroactivity of TTF in water.[33] In the cases of the polymers associating a crown-TTF part to a PEDOT backbone (i.e., poly(**5b**), poly(**5b**)′, poly(**5b**)″ and poly(**19b**)′), a reversible electroactivity was observed in water. However, due to competitive strong solvating effect of water, no complexation of Ba^{2+} in aqueous media could be characterized. A slight decrease in the intensity of the peaks is observed upon repeated potentials cycles above the second TTF redox step, traducing a lack of stability of the film in water when reaching the dicationic TTF^{2+} stage. An analogous observation was made by Graetzel et al. for free TTF in an aqueous micellar solution.[33] A higher stability was observed for poly(**19b**)′, for which the CV shows the two well defined TTF redox systems and the PEDOT signature under the TTF peaks (Figure 9). This well defined electrochemical behavior is probably related to the hydrophilic character of both the (PEDOT) backbone and the polyether linker.[34]

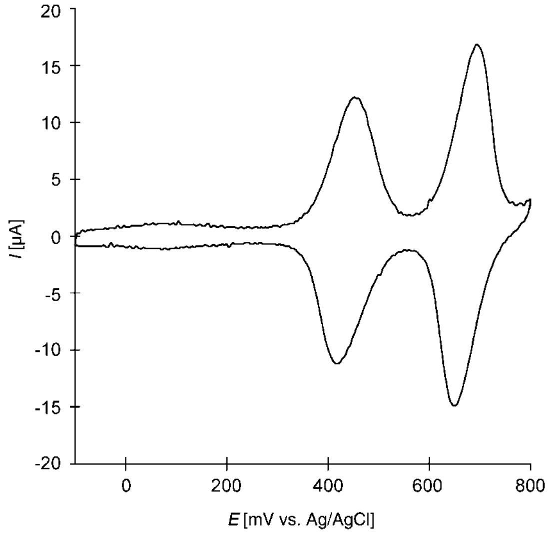


Figure 9. CV response of poly(**19b**)′ in H_2O; $LiClO_4$ (0.1 M), Ag/AgCl, 100 mV s^{-1}, Pt∅ = 1 mm.

Conclusion

We have described the synthesis and the electrochemical properties of various electropolymerizable monomers incorporating a ligating crown-TTF unit, including the first examples of covalent association between pyrrole and TTF. A good electropolymerization ability was observed for N-pyrrole (**3a**, **b**) and EDOT (**5a**, **b**) derivatives, whereas 3-substituted pyrroles (**4a**, **b**) polymerized with difficulty. An alternative method of electrode modification involved the functionalization of pre-formed poly(EDOT) films by the crown-TTF active group. The efficiency of the covalent grafting within the film, though carried out in heterogeneous medium, is demonstrated by the analogy between the electrochemical response and stability of modified electrodes obtained by this method and a *classical* electropolymerization of a substituted EDOT monomer.

The electrochemical recognition properties of these modified electrodes have been tested with Ba^{2+}, and analogous trends as for the free ligand in solution were found, though of lesser magnitude. Such an electrochemical effect is the first observed for an electropolymerized film incorporating a TTF-based redox probe. Regeneration capability of these electrodes has also been investigated, as well as their electroactivity in water. Extension of these results to the preparation of TTF-based modified surfaces able to control the binding/expulsion process of metal cations has been published very recently.[35]

Experimental Section

General methods: ^{1}H NMR (500.13 MHz) and ^{13}C NMR (125.75 MHz) spectra have been recorded on a Bruker Avance DRX 500 spectrometer. Chemical shifts (δ are expressed in ppm related to the tetramethylsilane (TMS) signal. ^{1}H NMR assignments are given as follows: δ (multiplicity, coupling constant, number of protons involved, assignment). Mass spectra (MS) using electronic impact (EI) and fast atom bombardment (FAB-LSIMS) have been achieved either on a VG-Autospec EBE (VG analytical) spectrometer or on a JEOL JMS 700 B/ES spectrometer. Cyclic voltammetry experiments have been carried out on a potentiostat-galvanostat EG&G PARK models 273 or 273A, with solvents and electrolytes of electrochemical grades. When specified, electrochemical experiments have been performed in a Jacomex glove-box (usual O_2 and H_2O contents: 5 ppm). For syntheses, anhydrous solvents have been obtained by distillation on the appropriate drying agent (sodium/benzophenone for THF, sodium for toluene, P_2O_5 for dichloromethane, CaH_2 for acetonitrile). The other solvents are used as purchased (DMF, chloroform).

Electrochemical set and Ba^{2+} titration: The substrate solution is placed in an electrolysis cell including three electrodes: a working electrode (platinum disk) on which takes place the electropolymerization (diameter: 1 mm, surface: 7.85×10^{-3} cm^{2}), an auxiliary electrode (platinum wire), and a reference electrode (Ag/AgCl) (or a silver wire whose potential was determined versus Ag/AgCl, for Ba^{2+} titration experiments[36]). For electrochemical titration of Ba^{2+}, microvolumes of a barium perchlorate solution (0.2 M) in acetonitrile were added, followed by a vigorous stirring for two minutes before recording the resulting CV.

Synthetic procedures

2-(6′-Pyrrol-1-ylhexylsulfanyl)-3,6,7-trimethylsulfanyltetrathiafulvalene (3a): Cesium hydroxide monohydrate (336 mg, 2 equiv, 2 mmol) in dry methanol (10 mL) was added under N_2 to tetrathiafulvalene derivative **2** (427 mg, 1 equiv, 1 mmol) in dry DMF (50 mL). After 15 min of stirring at room temperature, 1-(6-iodohexyl)pyrrole (**12**; 415.5 mg, 1.5 equiv, 1.5 mmol) in solution in dry DMF (10 mL) was added. The reaction mixture was stirred overnight and the solvent was removed in vacuo. The brownish residue was dissolved in dichloromethane, washed with water, dried over sodium sulfate. The organic phase was concentrated in vacuo and the oil was purified by chromatography on a silica gel column (dichloromethane/ethyl acetate 9:1) to yield an orange oil (483 mg, 94 %). ^{1}H NMR (CDCl$_3$): δ = 1.27–1.81 (m, 8H, CH_2), 2.43 (3s, 9H, CH_3S), 2.80 (t, J = 7.1 Hz, 2H, SCH_2), 3.88 (t, J = 7.1 Hz, 2H, CH_2N), 6.14 (t, J = 2.1 Hz, 2H, CHCHN), 6.65 (t, J = 2.1 Hz, 2H, CHCHN); ^{13}C NMR (CDCl$_3$): δ = 19.2 and 19.3 (CH$_3$S), 26.2, 29.5, 29.7 and 31.9 (CH$_2$), 35.9 (SCH$_2$), 49.5 (NCH$_2$), 107.9 (CHCHN), 110.9 and 111.2 (central C=C), 120.4 (CHCHN), 125.4, 127.5 and 129.8 (lateral C=C).

(*Z*,*E*)-6(7)-Methylsulfanyl-3-(6′-(*N*-pyrryl)hexylsulfanyl)-2,7(6)-(4,7,10,13,16-pentaoxa-1,19-dithianonadecane-1,19-diyl)tetrathiafulvalene (3b): Cesium hydroxide monohydrate (110 mg, 2 equiv, 1.82 mmol) in dry methanol (10 mL) was added under N$_2$ to tetrathiafulvalene derivative **9** (331.5 mg, 1 equiv, 1 mmol) in dry DMF (80 mL). After 15 min of stirring at room temperature, 1-(6-iodohexyl)pyrrole (**12**; 124 mg, 1.2 equiv, 0.45 mmol) in solution in dry DMF (10 mL) was added. The reaction mixture was stirred overnight and the solvent was removed in vacuo. The brownish residue was dissolved in dichloromethane, washed with water, dried over sodium sulfate. The organic phase was concentrated in vacuo and the oil was purified by chromatography on a silica gel column (dichloromethane) to yield an orange oil (181.3 mg, 68 %); *Z*/*E* 55:45 (^{1}H NMR). ^{1}H NMR (CDCl$_3$): δ = 1.31 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 1.64 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 2.43 (s, 3H, CH_3S, 50 %), 2.46 (s, 3H, CH_3S, 50 %), 2.82 (t, 2H, SCH_2), 2.98 (m, 4H, SCH_2CH$_2$O), 3.68 (m, 20H, CH_2O), 3.88 (t, 2H, CH_2N), 6.13 (t, 2H, CHCHN), 6.65 (t, 2H, CHCHN); ^{13}C NMR (CDCl$_3$): δ = 19.2 and 19.3 (CH$_3$S), 26.2 and 28.0 (CH$_2$), 29.5, 29.7 and 31.9 (CH$_2$), 34.9 and 35.0 (SCH$_2$), 36.2 and 36.2 (SCH$_2$), 49.5 (NCH$_2$), 70.2, 70.5, 70.6, 70.6, 70.7, 70.7, 70.8, 70.8, 70.9 and 70.9 (OCH$_2$), 107.9 (CHCHN), 110.5, 111.0, 111.0 and 111.4 (central C=C), 120.5 (CHCHN), 124.2, 124.8, 126.2, 126.8, 128.7, 129.9, 130.5 and 131.7 (lateral C=C); HRMS-EI(+): m/z: calcd for C$_{29}$H$_{43}$NO$_5$S$_8$: 741.0907; found: 741.0872 [M]$^+$; elemental analysis calcd (%) for: C 46.13, H 5.67, S 34.55, N 1.89; found: C 47.17, H 5.88, S 34.65, N 1.84.

2-(6′-(Pyrrol-3-yl)hexylsulfanyl)-3,6,7-trimethylsulfanyl tetrathiafulvalene (4a): Cesium hydroxide monohydrate (118 mg, 2.8 equiv, 0.70 mmol) in dry methanol (3 mL) was added under N$_2$ to tetrathiafulvalene derivative **2** (150 mg, 1.4 equiv, 0.35 mmol) in dry DMF (20 mL). After the reaction mixture was stirred for 15 min at room temperature, a degassed solution of 3-(6-iodohexyl)-1-(triisopropylsilyl)pyrrole (**15**) (104 mg, 0.24 mmol) in dry DMF (10 mL) was added. After 3 h of stirring, the solvent was removed in vacuo. The residue was dissolved in dichloromethane, washed with water, dried over sodium sulfate and the organic phase was concentrated in vacuo. The resulting oil was purified by chromatography on a silica gel column (petroleum ether/dichloromethane 8:2) to yield an orange oil (91.3 mg, 83 %). ^{1}H NMR (CDCl$_3$): δ = 1.37–1.41 (m, 4H, CH_2), 1.57–1.65 (m, 4H, CH_2), 2.42 and 2.43 (2 s, 9H, CH_3S), 2.49 (t, J = 7.1 Hz, 2H, CH_{pyrrole}), 2.82 (t, J = 7.0 Hz, 2H, CH_2S), 6.10 (s, 1H, CHCHN), 6.58 (s, 1H, CHCHN), 6.73 (s, 1H, CHN), 8.21 (large s, 1H, NH); ^{13}C NMR (CDCl$_3$): δ = 19.2 and 19.3 (CH$_3$S), 26.8, 28.2, 30.8 and 30.9 (CH$_2$), 36.2 (SCH$_2$), 108.3 (CHCHN), 110.8 and 111.0 (central C=C), 114.8 (CHN), 117.5 (CHN), 124.5, 126.4, 129.0 and 129.8 (lateral C=C).

(*Z*,*E*)-6(7)-Methylsulfanyl-3-(6′-(pyrrol-3-yl)hexylsulfanyl)-2,7(6)-(4,7,10,13,16-pentaoxa-1,19-dithianonadecane-1,19-diyl)tetrathiafulvalene (4b): Cesium hydroxide monohydrate (50 mg, 2 equiv, 0.32 mmol) in dry methanol (3 mL) was added under N$_2$ to tetrathiafulvalene derivative **9** (98.8 mg, 1 equiv, 0.16 mmol) in dry DMF (10 mL). After 20 min of stirring at room temperature, a degassed solution of 3-(6-iodohexyl)-1-(triisopropylsilyl)pyrrole (**15**; 130 mg (purity 70 %), 1.3 equiv, 0.21 mmol) in dry DMF (10 mL) was added. The reaction mixture was stirred overnight and the solvent was removed in vacuo. The brown residue was dissolved in dichloromethane, washed with water, dried over sodium sulfate and the organic phase was concentrated in vacuo. The resulting oil was purified by chromatography on a silica gel column (dichloromethane and dichloromethane/ethyl acetate 9:1) to yield an orange oil (86.2 mg, 73 %); *Z*/*E* 50:50 (^{1}H NMR). ^{1}H NMR (CDCl$_3$): δ = 1.37–1.45 (m, 4H, CH_2), 1.57–1.65 (m, 4H, CH_2), 2.43 (Z) and 2.44 (E) (2s, 3H, CH_3S), 2.49 (t, J = 7.1 Hz, 2H, C$H_{2\,\text{pyrrole}}$), 2.83 (quin, J = 7.4 Hz, 2H, CH_2S), 2.95–2.99 (m, 4H, SCH_2CH$_2$O), 3.61–3.71 (m, 20H, CH_2O), 6.06 (s, 1H, CHCHN), 6.57 (s, 1H, CHCHN), 6.71 (s, 1H, CHN), 8.21 (brs, 1H, NH); ^{13}C NMR (CDCl$_3$): δ = 19.1 and 19.1 (CH$_3$S), 26.6, 26.7, 28.2, 28.3, 28.6, 28.6, 29.6 and 29.6 (CH$_2$), 30.8 and 30.9 (CH$_2$), 34.8, 34.8, 35.0 and 35.1 (SCH$_2$), 36.2 and 36.3 (SCH$_2$), 70.1, 70.1, 70.4, 70.4, 70.5, 70.5, 70.6, 70.6, 70.6, 70.7, 70.7, 70.8 and 70.8 (OCH$_2$), 108.3 (CHCHN), 110.3, 110.9, 111.0 and 111.4 (central C=C), 114.8 (CHN), 117.5 (CHN), 124.0, 124.5, 125.5, 126.4, 129.0, 130.3, 130.5 and 131.6 (lateral C=C); EI-MS: m/z (%): calcd for C$_{29}$H$_{43}$NO$_5$S$_8$: 741.0907; found: 741 (100) [M]$^+$, 606 (7), 80 (73); HR-EI(+) MS: m/z: found: 741.0941 [M]$^+$.

2-(8-EDOT-7-oxaoctylsulfanyl)-3,6,7-trimethylsulfanyl)tetrathiafulvalene (5a): Cesium hydroxide monohydrate (336 mg, 2 equiv, 2 mmol) in solution in methanol (5 mL), was added under N$_2$, to tetrathiafulvalene derivative **2** (427 mg, 1 equiv, 1 mmol) in dichloromethane (60 mL). After 15 min of stirring, iodo compound **17** (382 mg, 1 equiv, 1 mmol) dissolved in dichloromethane (10 mL) was added. The reaction was stirred overnight. The organic phase was washed with water, dried over sodium sulfate and concentrated in vacuo. The resulting oil was purified by chromatography on a silica gel column (petroleum ether/dichloromethane 7:3) to yield an orange oil (324 mg, 52 %). ^{1}H NMR (CDCl$_3$): δ = 1.37–1.42 (m, 4H, CH_2), 1.53–1.65 (m, 4H, CH_2), 2.43 (s, 9H, CH_3S), 2.82 (t, J = 7.1 Hz, 2H, SCH_2), 3.50 (t, J = 6.5 Hz, 1H, CH_2O), 3.64 (ddd, J = 5.8, 10.3, 15.1 Hz, 2H, CH_2O), 4.06 (dd, J = 7.5, 11.7 Hz, 1H, CH_2O), 4.23–4.30 (m, 2H, CH_2O, CHO), 6.48 (s, 2H, CH); ^{13}C NMR (CDCl$_3$): δ = 19.2 and 19.3 (CH$_3$S), 25.5, 28.2, 29.9 and 30.6 (CH$_2$), 36.1 (SCH$_2$), 66.1 (OCH$_2$), 99.5 and 99.6 (SCH), 110.8 and 111.3 (central C=C), 124.4, 126.2, 129.8, and 130.3 (lateral C=C), 141.5 and 141.6 (O−C=C); ESI-MS: m/z: calcd for C$_{22}$H$_{28}$O$_3$S$_9$: 627.9; found: 627.9 [M]$^+$, 650.9 [M+Na]$^+$, HRMS-EI(+) MS: m/z: calcd for: 650.9423; found: 650.9430 [M+Na]$^+$.

(*Z*,*E*)-6(7)-Methylsulfanyl-3-(8-EDOT-7-oxaoctylsulfanyl)-2,7(6)-(4,7,10,13,16-pentaoxa-1,19-dithianonadecane-1,19-diyl)tetrathiafulvalene (5b): Cesium hydroxide monohydrate (100 mg, 2 equiv, 0.62 mmol) in dry methanol (5 mL) was added under N$_2$, to tetrathiafulvalene derivative **9** (200 mg, 1 equiv, 0.31 mmol) in dry and degassed DMF (80 mL). After the reaction mixture was stirred for 15 min, iodo derivative **17** (135 mg, 1.2 equiv, 0.37 mmol) in dry DMF (20 mL) was added. The reaction mixture was stirred overnight and the solvent was removed in vacuo. The brown residue was dissolved in dichloromethane, washed with water and dried over sodium sulfate. After evaporation, the oil was purified by chromatography on a silica gel column (petroleum ether/dichloromethane 1:1 and then dichloromethane/ethyl acetate 9:1) to yield an orange oil (123 mg, 48 %). *Z*/*E* 60:40 (^{1}H NMR); ^{1}H NMR (CDCl$_3$): δ = 1.35–1.44 (m, 4H, CH_2), 1.57–1.66 (m, 4H, CH_2), 2.42 (Z) and 2.45 (E) (2s, 3H, CH_3S), 2.80–2.86 (m, 2H, SCH_2), 2.95–2.98 (m, 4H, SCH_2), 3.48 (dd, J = 6.4, 6.4 Hz, 2H, CHO), 3.57–3.70 (m, 22H, CH_2, CH_2), 4.04 (dd, J = 4.1, 7.5 Hz, 1H, CH_2O), 4.23 (d, J = 11.6 Hz, 1H, CH_2O), 4.28 (dd, J = 5.9, 12.0 Hz, 1H, CHO), 6.32 (dd, J = 3.7, 6.7 Hz, 2H, CH); ^{13}C NMR (CDCl$_3$): δ = 19.1 (CH$_3$S), 25.5 and 28.2 (CH$_2$), 29.3 and 29.6 (CH$_2$), 35.0 and 35.1 (SCH$_2$), 36.2 and 36.2 6 (SCH$_2$), 66.1 (OCH$_2$), 69.1, 70.1, 70.5, 70.6, 70.6, 70.7, 70.8, 70.9, 70.9, 71.6 and 71.8 (OCH$_2$), 99.5 and 99.6 (SCH), 110.3, 110.8, 110.9 and 111.3 (central C=C), 124.4, 124.8, 126.2, 126.7, 128.7, 129.8, 130.3 and 131.5 (lateral C=C), 141.5 and 141.5 (C_2); FAB(+) MS: m/z: calcd for C$_{32}$H$_{46}$O$_8$S$_9$: 846.1; 846.1 [M]$^+$; HR-FAB(+): m/z: calcd for: 846.06797; found: 846.0678 [M]$^+$.

1,17-Diodo-3,6,9,12,15-pentaoxaheptadecane (7b): A large excess of sodium iodide (10 equiv) was added to 3,6,9,12,15-pentaoxa-1,17-heptadecyl di-*p*-toluenesulfonate (**7a**)[13] (17.7 mmol, 7.76 g) dissolved in acetone (200 mL), and the mixture was heated under reflux overnight. The solvent was removed in vacuo and the residue was washed with a solution of sodium thiosulfate, and then with water. After drying over magnesium sulfate, the solution was concentrated in vacuo and the oil was purified by chromatography on a silica gel column (dichloromethane) to yield a yellow pale oil (7.4 g, 78 %). ^{1}H NMR (CDCl$_3$): δ = 3.15 (t, 4H, CH_2I); 3.50–3.70 (m, 20H, CH_2O); EI-MS: m/z: calcd for C$_{12}$H$_{24}$I$_2$O$_5$: 502.0; found: 502.0 [M]$^+$.

(*Z*,*E*)-3,6(7)-Bis(2-cyanoethylsulfanyl)-2,7(6)-(4,7,10,13,16-pentaoxa-1,19-dithianonadecane-1,19-diyl)tetrathiafulvalene (8): Cesium hydroxide monohydrate (672 mg, 2 equiv, 4 mmol) in methanol (10 mL) was added to 2,3,6,7-tetrakis(2-cyanoethylsulfanyl)tetrathiafulvalene (**6**; 1.09 g, 2 mmol) in dry DMF (50 mL). The mixture was stirred for 15 min. This solution and 1,17-diodo-3,6,9,12,15-pentaoxaheptadecane (**7b**; 1.04 g, 1 equiv, 2 mmol) in dry DMF (60 mL) was simultaneously added to dry degassed DMF (300 mL) over 20 h (3 mL h^{-1}) with a perfursor pump.

The mixture was then allowed to stir for another 2 h before the solvents were removed in vacuo. The brown residue was dissolved in dichloromethane, washed with water, dried over sodium sulfate and concentrated in vacuo. The residue was purified by chromatography on a silica gel column (dichloromethane/ethyl acetate 8:2) and recrystallised in dichloromethane/methanol to yield an orange powder (753 mg, 55 %). *Z*/*E* 70:30; *Z* isomer: ^{1}H NMR ($CDCl_3$): $\delta=2.72$ (t, 4H, CH_2CN), 3.05 (m, 8H, SCH_2), 3.59–3.74 (m, 20H, CH_2O); ^{13}C NMR ($CDCl_3$): $\delta=18.8$ (CH$_2$CN), 31.4 (SCH$_2$CH$_2$CN), 35.2 (SCH$_2$CH$_2$O), 70.0, 70.1, 70.4, 70.4, 70.5, 70.5, 70.6, 70.7, 70.7, 70.8, 70.8 and 70.9 (CH$_2$O), 111.7 (central C=C), 117.6 (CN), 123.4 and 132.5 (lateral C=C). *E* isomer: ^{1}H NMR ($CDCl_3$): $\delta=2.77$ (t, 4H, CH_2CN), 3.03 (m, 8H, SCH_2), 3.59–3.74 (m, 20H, CH_2O); ^{13}C NMR ($CDCl_3$): $\delta=18.7$ (CH$_2$CN), 31.5 (SCH$_2$CH$_2$CN), 35.5 (SCH$_2$CH$_2$O), 70.0, 70.1, 70.4, 70.4, 70.5, 70.5, 70.6, 70.7, 70.7, 70.8, 70.8 and 70.9 (CH$_2$O), 111.6 (*central C*=*C*), 117.9 (CN), 123.9 and 132.9 (lateral C=C); EI-HR MS: *m*/*z*: calcd for $C_{24}H_{32}N_2O_5S_8$: 684.0077; found: 684.0075 $[M]^+$:; elemental analysis calcd (%) for: C 42.14, H 4.71, O 11.69, S 37.50, N 4.09; found: C 42.32, H 4.70, O 12.23, S 36.57, N 4.27.

(*Z*,*E*)-6(7)-Methylsulfanyl-3-(2-cyanoethylsulfanyl)-2,7(6)-(4,7,10,13,16-pentaoxa-1,19-dithianonadecane-1,19-diyl)tetrathiafulvalene (9): Cesium hydroxide monohydrate (168 mg, 1 equiv, 1 mmol) in dry methanol (10 mL) was added to a solution of tetrathiafulvalene derivative **8** (684 mg, 1 mmol) in dry and degassed DMF (40 mL), cooled to 0 °C with an ice bath. After 15 minutes of stirring, a large excess of iodomethane (1 mL) was poured. After 5 h at room temperature, the reaction mixture was concentrated in vacuo and the brown residue was dissolved in dichloromethane, washed with water and dried over sodium sulfate. The solvent was removed in vacuo and the resulting oil was purified by chromatography on a silica gel column (dichloromethane/ethyl acetate 9:1) and recrystallised from dichloromethane/methanol to yield an orange powder (467 mg, 72 %); *Z*/*E* 60:40; ^{1}H NMR ($CDCl_3$): $\delta=2.44$ (s, 3H, SCH_3, *Z*), 2.45 (s, 3H, SCH_3, *E*), 2.73 (t, 2H, CH_2CN, *Z*), 2.78 (t, 2H, CH_2CN), 2,98 (m, 6H, SCH_2), 3.05 (m, 6H, SCH_2, *Z*), 3.66 (m, 20H, CH_2O, *Z*+*E*); ^{13}C NMR ($CDCl_3$): $\delta=18.7$ (CH$_2$CN), 19.2 and 19.3 (SCH$_3$), 31.4 and 31.5 (SCH$_2$CH$_2$CN), 35.1 and 35.3 (SCH$_2$CH$_2$O), 70.0, 70.1, 70.4, 70.4, 70.5, 70.5, 70.6, 70.7, 70.7, 70.8, 70.8 and 70.9 (CH$_2$O), 109.5, 109.7, 112.5 and 113.0 (central C=C), 117.6 and 117.9 (CN), 123.3, 124.6, 131.2 and 132.5 (lateral C=C); $C_{22}H_{31}NO_5S_8$: EI-HR MS: *m*/*z*: calcd for: 644.9968; found: 644.9960.

1-(6-Chlorohexyl)pyrrole (11): Potassium pyrryl **10**[5] (1.41 g, 1 equiv, 13.4 mmol) dissolved in DMSO (20 mL) was added dropwise to 1-bromo-6-chlorohexane (2.0 mL, 1 equiv, 13.4 mmol) in dry THF (50 mL). The reaction mixture was stirred for 12 h. The solvents were removed in vacuo and the residue dissolved in dichloromethane. The organic phase was washed with water, dried over magnesium sulfate and concentrated in vacuo. The compound was purified by chromatography on a silica gel column (petroleum ether). A mixture of chloro and bromo compounds (90:10, ^{1}H NMR) was obtained as a pale yellow oil (1.8 g, 72 %); ^{1}H NMR ($CDCl_3$): $\delta=1.31$ (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 1.77 (m, 4H, CH_2), 3.42 (t, 2H, CH_2Br, 10 %), 3.52 (t, 2H, CH_2Cl, 90 %), 3.88 (t, 2H, CH_2N), 6.14 (t, 2H, CHCHN), 6.65 (t, 2H, CHCHN).

1-(6-Iodohexyl)pyrrole (12): The Cl/Br mixture of the 1-(6-halogenohexyl)pyrrole (**11**; 1.0 g, ≈ 54 mmol) was dissolved in acetone (80 mL) whereupon sodium iodide (9.0 g, 11 equiv, 540 mmol) was added. The mixture was heated under reflux overnight. The solvent was removed in vacuo and the residue dissolved in dichloromethane. The organic phase was washed with water, dried over magnesium sulfate and concentrated in vacuo. The compound was purified by chromatography on a silica gel column (petroleum ether/dichloromethane 9:1) to yield a pale yellow oil (760 mg, 51 %). ^{1}H NMR ($CDCl_3$): $\delta=1.31$ (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 1.78 (m, 4H, CH_2), 3.17 (t, 2H, CH_2I), 3.88 (t, 2H, CH_2N), 6.14 (t, 2H, CHCHN), 6.65 (t, 2H, CHCHN), ^{13}C NMR ($CDCl_3$): $\delta = 6.4$ (CH$_2$I), 25.6, 30.0, 31.3 and 33.3 (CH$_2$), 49.4 (CH$_2$N), 107.9 (CHCHN), 120.4 (CHCHN); EI MS: calcd for $C_{10}H_{16}IN$: *m*/*z*: 277; found: 277 $[M]^+$.

3-Bromo-1-(triisopropylsilyl)pyrrole (14): *N*-Bromosuccinimide (0.80 g, 1 equiv, 4.5 mmol) dissolved in distilled THF (5 mL) was added to 1-(triisopropylsilyl)pyrrole (**13**;[16] 1.00 g, 1 equiv, 4.5 mmol) in distilled THF (10 mL) cooled to −80 °C. The reaction mixture was stirred 1 h at −80 °C and then, allowed to warm to room temperature in 1 h. The mixture was milky white. Pyridine (0.15 mL) in hexane (5 mL) was added and the solution which became yellow was stirred for an additional 1 h. The solvent was removed in vacuo, and then the residue was dissolved in dichloromethane, washed with water and dried over sodium sulfate. The solution was concentrated in vacuo and afterwards, purified by chromatography on a silica gel column (petroleum ether). The compound was obtained accompanied by 5 % of 2-bromo-1-(triisopropylsilyl)pyrrole. Colorless oil (1.15 g, 86 %); ^{1}H NMR ($CDCl_3$): $\delta=1.11$ (d, $J = 7.5$ Hz, 18H, CH_3), 1.47 (m, $J = 7.5$ Hz, 3H, CH), 6.30 (dd, $J = 1.4$, 2.8 Hz, 1H, CHCHN), 6.67 (dd, $J = 2.8$, 2.8 Hz, 1H, CHCHN), 6.73 (dd, $J = 1.4$, 2.8 Hz, 1H, CHN), ^{13}C NMR ($CDCl_3$): $\delta=11.4$ (SiCH), 17.5 and 17.6 (CH$_3$), 97.8 (CBr), 112.9 (CHCHN), 123.2 (CBrCHN), 124.6 (CHCHN); EI(+) MS: *m*/*z*: calcd for $C_{13}H_{24}BrNSi$: 301.1; found: 303 $[M]^+$.

3-(6-Iodohexyl)-1-(triisopropylsilyl)pyrrole (15): Under nitrogen atmosphere, 3-bromo-1-(triisopropylsilyl)pyrrole (**14**; 0.50 g, 1 equiv, 2.25 mmol) in distilled THF (120 mL) was cooled to −78 °C. *tert*-Butyllithium (2.65 g, 2 equiv, 4.5 mmol) was added and the reaction mixture which immediately turned yellow was stirred for 30 min at −78 °C. Then, 1,6-diiodohexane (0.76 g, 1 equiv, 2.25 mmol) in distilled THF (10 mL) was added and the mixture became immediately colorless. Temperature was allowed to rise to RT, and the solvent was removed in vacuo. The residue was dissolved in dichloromethane, washed with water, dried over sodium sulfate and concentrated in vacuo. The resulting oil was purified by chromatography on a silica gel column (cyclohexane) to yield a colorless oil (180 mg, 23 %); ^{1}H NMR ($CDCl_3$): $\delta=1.11$ (m, 18H, CH_3), 1.35–1.46 (m, 7H, CH and 2×CH_2), 1.60 (quint, $J = 7.3$ Hz, 2H, CH_2CH$_{2\,\mathrm{pyrrole}}$), 1.83 (quint, $J = 7.0$ Hz, 2H, CH_2CH$_2$I), 2.49 (t, $J = 7.3$ Hz, 2H, C$H_{2\,\mathrm{pyrrole}}$), 3.18 (t, $J = 7.0$ Hz, 2H, CH_2I), 6.14 (s, 1H, CHCHN), 6.52 (s, 1H, CHCHN), 6.69 (s, 1H, CHN); EI(+) MS: calcd for $C_{19}H_{36}INSi$: 433.2; found: 433 $[M]^+$, 390 $[M-i\mathrm{Pr}]^+$, 306 $[M-\mathrm{I}]^+$.

2-(8-Iodo-2-oxaoctyl)-2,3-dihydrothieno[3,4-*b*]-1,4-dioxine (17): A solution of sodium hydride (washed with pentane) (1.54 g, 20 equiv, 19 mmol) in distilled THF (40 mL) was cooled to 0 °C under N_2. A solution of hydroxymethyl-EDOT **16**[17] (164 mg, 1 equiv, 0.953 mmol) and [18]crown-6 (5 %) in distilled THF (10 mL) was added dropwise. The alkoxide was carefully transferred by a cannula to another three-necked flask containing a solution of 1,6-bromochlorohexane (3.8 g, 2 equiv, 1.9 mmol) in dry and distilled THF. After the temperature has raised (RT), the reaction mixture was heated under reflux overnight. Water was poured and the solvent was removed in vacuo. The residue was dissolved in dichloromethane, washed with water and dried over sodium sulfate. The chlorinated intermediate was purified by chromatography on a silica gel column (petroleum ether/dichloromethane) to produce a yellow pale oil (274 mg, 99 %). The same experiment was carried out several times, and the resulting chlorinated product put together. An excess of sodium iodide was added to the chloro compound (1.42 g, 1 equiv, 4.9 mmol) in acetone (50 mL). The mixture was heated under reflux for 1 d. After temperature has cooled to RT, it was filtered and then concentrated. The residue was dissolved in dichloromethane, washed with a sodium thiosulfate saturated solution, with water and dried over sodium sulfate. After concentration in vacuo, the iodo compound **17** was purified by chromatography on a silica gel column (dichloromethane) to yield a pale yellow oil (1.68 g, 90 %). ^{1}H NMR ($CDCl_3$): $\delta=1.37$ (m, 4H, CH_2), 1.60 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 3.19 (t, $^3J=6.5$ Hz, 2H, CH_2I), 3.50 (t, $^3J = 6.3$ Hz, 2H, CH$_2$CH_2O), 3.59 (dd, $^{gem}J=10.4$, $J=5.9$ Hz, 1Hb, OCH_2CH), 3.68 (dd, $^{gem}J=10.4$, $J=5.0$ Hz, 1Ha, OCH_2CH), 4.06 (dd, $^{gem}J=11.6$, $^{trans}J=7.5$ Hz, 1Hb, =C(C)OCH_2), 4.24 (dd, $^{gem}J=11.6$, $^{cis}J=2.2$ Hz, 1Ha,=C(C)OCH_2), 4.30 (m, 1H, CHCH$_2$OCH$_2$), 6.33 (s, 2H, C$H_{\mathrm{thiophene}}$); ^{13}C NMR ($CDCl_3$): $\delta=6.9$ (CH$_2$I), 25.0, 29.3, 30.2 and 33.4 (CH$_2$), 66.2, 69.2, 71.9 and 72.7 (CH$_2$O), 99.6 and 99.7 (2×SCH); 141.6 and141.6 (2×CO); FAB MS: *m*/*z*: calcd for $C_{13}H_{19}IO_3S$: 382.0; found: 382.0 $[M]^+$; HRMS FAB: *m*/*z*: calcd for 382.0100; found: 382.0104 $[M]^+$.

2-(19-Iodo-2,5,8,11,14,17-hexaoxa-1-nonadecyl)-2,3-dihydrothieno[3,4-*b*]-1,4-dioxine (18): A solution of sodium hydride (1.6 g at 60 % in oil, 4.2 equiv) (washed with pentane) in distilled THF (150 mL) was cooled to 0 °C with an ice bath. Hydroxymethyl-EDOT **16**[17] (1.67 g, 1.05 equiv, 9.7 mmol) and [18]crown-6 (5 %) in THF (10 mL) was added slowly. The resulting mixture was transferred by a cannula to another three-necked flask containing a solution of 3,6,9,12,15-pentaoxa-1,17-heptadecyl di-*p*-toluenesulfonate (**7a**)[13] (4.13 g, 1.0 equiv, 9.7 mmol). The reaction mixture was heated under reflux for 24 h. Water was slowly added and the solvent was removed in vacuo. The residue was dissolved in dichloromethane and washed with water, dried over sodium sulfate and concentrated in vacuo. The tosylate intermediate was purified by chromatography on a silica gel column (dichloromethane/ethyl acetate 6:4) to produce a pale yellow oil (2.66 g, 46 %). A large excess of sodium iodide was added to the resulting tosylate (2.66 g, 4.5 mmol) in acetone and the mixture was heated under reflux for 24 h. After the reaction mixture was allowed to cool to room temperature, the solvent was removed in vacuo and the residue was dissolved in dichloromethane. This solution was washed with sodium thiosulfate and then with water, dried over sodium sulfate and concentrated in vacuo. The iodo compound **19** was purified by chromatography on a silica gel column (dichloromethane/ethyl acetate 6:4) to yield a pale yellow oil (1.84 g, 75 %). ^{1}H NMR ($CDCl_3$): δ = 3.26 (t, ^3J = 7.0 Hz, 2H, CH_2I), 3.65 (m, 23H, OCH_2), 3.76 (m, 1Ha, OCH_2CH), 4.06 (dd, $^{trans}J$ = 7.5 and ^{gem}J = 11.7 Hz, 1Hb, =C(C)OCH_2), 4.25 (dd, ^{cis}J = 2.2 and ^{gem}J = 11.7 Hz, 1Ha, =C(C)OCH_2), 4.32 (m, 1H, CHCH$_2$O), 6.32 (d, 1H, ^4J = 3.7 Hz, C$H_{\text{thiophene}}$), 6.33 (d, ^4J = 3.7 Hz, 1H, C$H_{\text{thiophene}}$); ^{13}C NMR ($CDCl_3$): δ = 2.9 (CH_2I); 66.1, 69.6, 70.2, 70.6, 70.7, 71.2, 72.0 and 72.6 (CH_2O), 99.6 and 99.7(2 × SCH), 141.5 and 141.6 (2 × CO); EI(+) MS: m/z: calcd for $C_{19}H_{31}O_8IS$: 546.8; found: 546.1 $[M]^+$; HRMS FAB: calcd for: 546.0756; found: 546.0798 $[M]^+$.

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