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Thiolate Chemistry: A Powerful and Versatile Synthetic Tool for Immobilization/Functionalization of Oligothiophenes on a Gold Surface

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Dedicated to Professor Jan Becher

Abstract: The synthesis and characterization of a series of quaterthiophenes (4Ts) with thiolate groups protected with 2-cyanoethyl (CNE), 2-trimethylsilylethyl (TMSE), and acetyl (Ac) groups are described. Sequential cleavage of these different protecting groups allows for the preparation of 4Ts derivatized with ferrocene and/or alkanethiol chains. The electrochemical behavior of these compounds has been analyzed in solution by cyclic voltammetry (CV). A ferrocene-derivatized dithiol 4T **14** and a dithiol 4T **15** with two TMSE-protected thiolate groups have been immobilized on a gold surface as monolayers that have been characterized by CV, ellipsometry, contact-angle measurement, and X-ray photoelectron spectroscopy (XPS). The results show that molecules **14** and **15** are doubly grafted with a horizontal orientation of the conjugated system relative to the surface. Furthermore, application of the deprotection/alkylation sequence of the remaining protected thiolate groups on a monolayer of **15** allows for efficient post-functionalization.

Keywords: conjugation · cyclic voltammetry · molecular electronics · monolayers · thiophene

Introduction

Self-assembled monolayers (SAMs) based on electroactive π-conjugated systems are the subject of high interest on account of their applications in the fields of molecular electronics,[1–4] organic electronics,[5] photovoltaic conversion,[6–9] sensors[10,11] and surfaces with magnetic properties.[12] These SAMs are generally formed by chemisorption on a semiconducting or metallic surface of a π-conjugated molecule that bears a fixation group such as thiol, sulfide, thiocyanate, carboxylic/phosphonic acids, or silane directly grafted on the π-conjugated system or through an alkyl linker.[13,14] Interactions between π-conjugated chains reinforced by lipophilic interactions between alkyl spacers contribute to ensure the cohesion of the SAMs and the quasivertical orientation of the conjugated chains on the surface of the substrate.

Compared to the extensively investigated surface-chemistry of nonconjugated SAMs,[13,15] the functionalization of SAMs based on π-conjugated systems is much less developed. For instance, the extension of π-conjugated systems grafted onto metal surfaces has been achieved by imine condensations.[16] More recently, integration of molecules between two gold electrodes has been realized by stepwise synthesis of molecular bridges by using click chemistry.[17] Click chemistry was also used for covalent grafting of ferrocene onto monolayers of phenylethynyl.[18] Gold nanoparticles have been covalently attached on the top of SAMs of thiophene diblock oligomers.[3c] Donor–acceptor thiophene-based conjugated systems immobilized on a diamond surface

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201003687. It includes the synthesis of 3-methylsulfanylthiophene and **10**, details on analytical techniques, ^{1}H NMR spectra of 3-methylsulfanylthiophene and compounds **2**–**11** and **13**–**15**, and potentiodynamic electrooxidation of dithiol **15**.

have been prepared by covalent grafting of an iodo intermediate followed by a Suzuki coupling,[19a] whereas ferrocene redox probes have been introduced on biphenyl derivatives adsorbed onto glassy carbon by electrochemical activation.[19b]

As reviewed recently,[20] SAMs that involve oligothiophenes have been widely investigated[3c,d,21–31] and used for applications in molecular junctions,[25] diodes,[3c,d,f] switches,[26] field-effect transistors,[5d,e] mass spectrometry,[27] chemosensors,[28] or photovoltaic devices.[6c,d,9a]

Whereas most of this work has concerned monolayers of singly attached conjugated molecules in a quasivertical orientation on the surface, few approaches have been devoted to the elaboration of SAMs with oligothiophenes horizontally oriented with respect to the surface.[23,32–34] In particular, the double fixation of a π-conjugated system with a controlled horizontal orientation can be of both fundamental and technical interest.[34,35] Besides an improved stability related to multiple anchoring sites,[5f,9a,34] such horizontal orientation is considerably more efficient for absorption of incident light.[6d] On the other hand, the possibility to achieve a direct through-space charge transfer between the conjugated system and the metal electrode instead of the through-bond transfer associated with the usual vertical fixation can help to enrich the toolbox for the design of molecular-electronic devices.

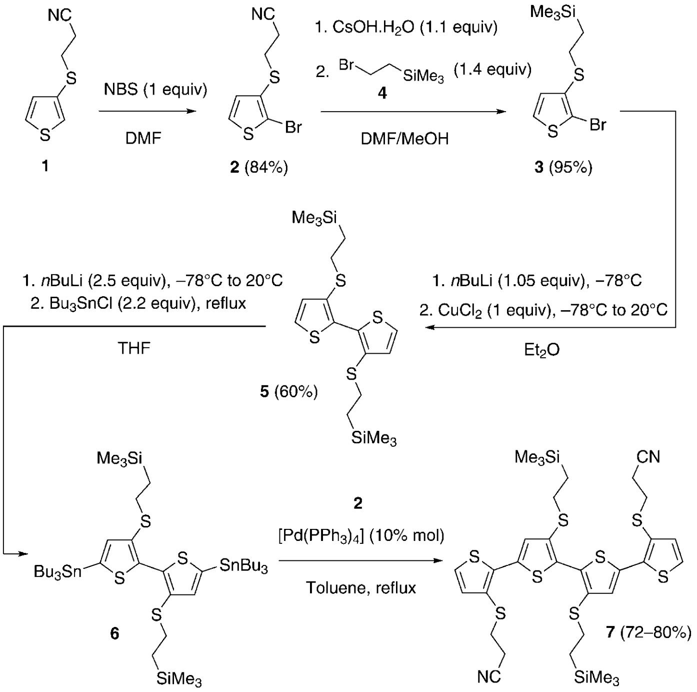
We have recently shown that substitution of a π-conjugated 4T by two alkylthiol chains introduced at the internal β positions of the two terminal thiophene rings allows for the efficient horizontal double fixation onto a gold surface.[36] As a further step, we present here a versatile synthetic strategy for the preparation of functionalized surfaces based on doubly fixed oligothiophenes. To this end, a series of 4Ts functionalized with thiolate groups protected with 2-cyanoethyl (CNE), 2-trimethylsilylethyl (TMSE), and acetyl (Ac) groups has been synthesized. Sequential cleavage of these different protecting groups leads to the stepwise preparation of 4Ts functionalized with ferrocene units and/or two alkanethiol chains.

The electrochemical properties of these compounds have been analyzed in solution, and their immobilization as monolayers on gold has been investigated. The structure and the properties of the monolayers are discussed on the basis of results of cyclic voltammetry, ellipsometry, contact-angle measurement, and X-ray photoelectron spectroscopy (XPS). Furthermore, surface chemistry on chemically active monolayers has been tested by means of thiolate deprotection and subsequent S-alkylation by using a ferrocene probe.

Results and Discussion

Synthesis: The key to our strategy relies on the preparation of 4T **7** in which each thiophene ring bears a masked thiolate group at the 3- or 4-position. Two types of thiolate protecting groups have been used: 1) a 2-cyanoethyl (CNE) group that can be deprotected in basic conditions (e.g., hydroxide ions, *n*-butyllithium),[37–39] and 2) a 2-trimethylsilylethyl (TMSE) group that is stable under the previous conditions but that can be cleaved in the presence of fluoride anions.[3c,40]

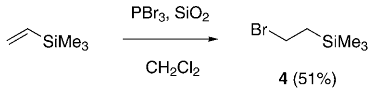
The synthesis of **7** is depicted in Scheme 1. Regioselective bromination at the 2-position of 3-(2-cyanoethylsulfanyl)thiophene (**1**)[38] by *N*-bromosuccinimide (NBS; 1 equiv) in dimethylformamide (DMF)[41] led to compound **2**. The CNE protecting group of **2** was then replaced by a TMSE group. Thus deprotection of the thiolate group of **2** with CsOH (1 equiv) and subsequent reaction with (2-bromoethyl)trimethylsilane **4** gave compound **3** in almost quantitative yield. Symmetrical 2,2′-bithiophene **5** was prepared in 60% yield from compound **3** after lithium–bromine exchange with *n*BuLi (1 equiv) at low temperature and further oxidative coupling of the resulting anion in the presence of $CuCl_2$.[42] Treatment of **5** with 2.5 equiv of *n*BuLi and subsequent addition of Bu_3SnCl afforded the 5,5′-distannyl derivative **6**, which was engaged in the following Stille reaction without purification. Heating at reflux a mixture of **6** and bromo derivative **2** (2.5 equiv based on **5**) in the presence of catalytic amount of tetrakis(triphenylphosphine)palladium(0) in toluene led to the target 4T **7** in 72–80% yields based on compound **5**.



Scheme 1. Synthesis of compound **7**.

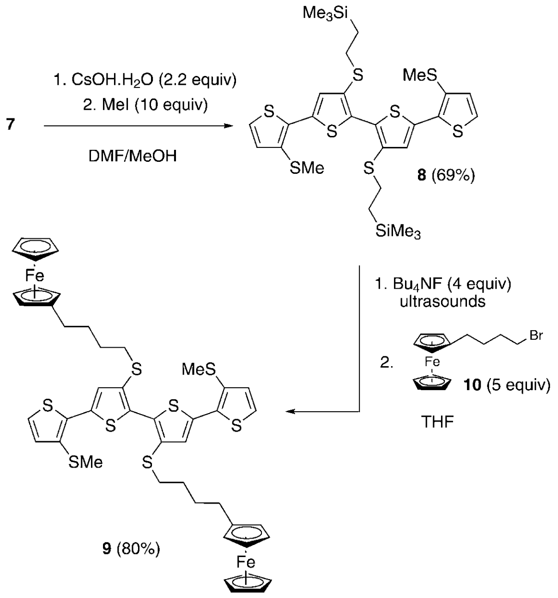
Compound **4** was readily synthesized according to an anti-Markovnikov addition of HBr on vinyltrimethylsilane (Scheme 2). Compared to previous synthetic procedures of **4**,[43–45] HBr was generated in situ by reaction of PBr_3 and silica gel in CH_2Cl_2.[46]

The deprotection conditions of the two different types of masked thiolate group of compound **7** have been investigat-



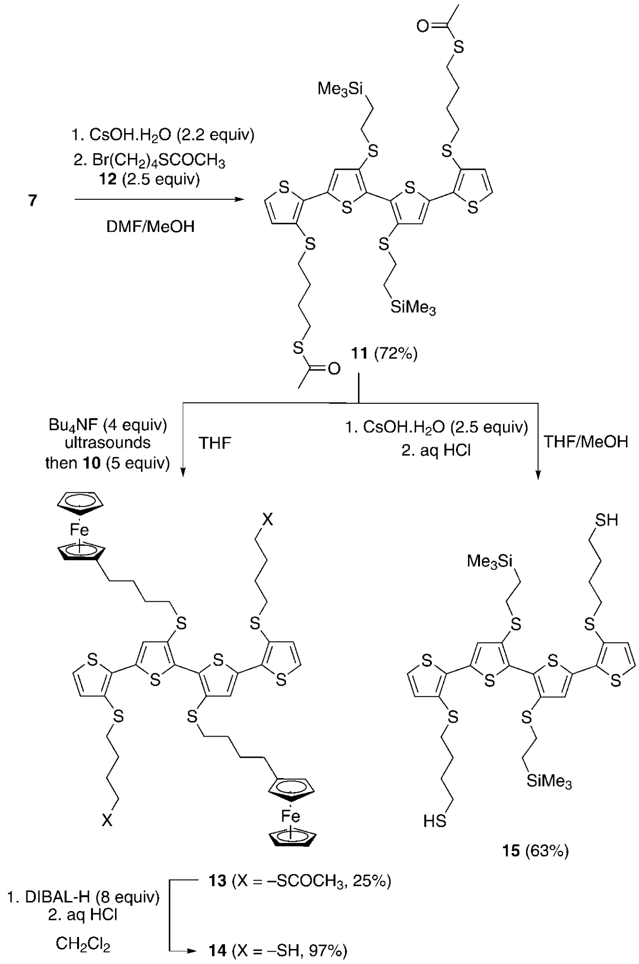
Scheme 2. Synthesis of (2-bromoethyl)trimethylsilane (**4**).

ed. As reported previously,[3c] fluoride anions can cleave the CNE groups of **7** due to their basicity. In fact, treatment of **1** with Bu_4NF in tetrahydrofuran (THF) followed by addition of CH_3I gave 3-methylsulfanylthiophene in 60 % yield (see the Supporting Information). The sequential deprotection of the thiolate groups of **7** was tested as shown in Scheme 3. Treatment of compound **7** with CsOH (2.2 equiv) in methanol and reaction with an excess amount of CH_3I afforded compound **8** in 69 % yield. Treatment of **8** with Bu_4NF in THF[40a,b] led to a dithiolate compound, which, upon addition of 4-bromobutylferrocene **10**, gave the ferrocenyl-functionalized 4T **9** in 80 % yield.



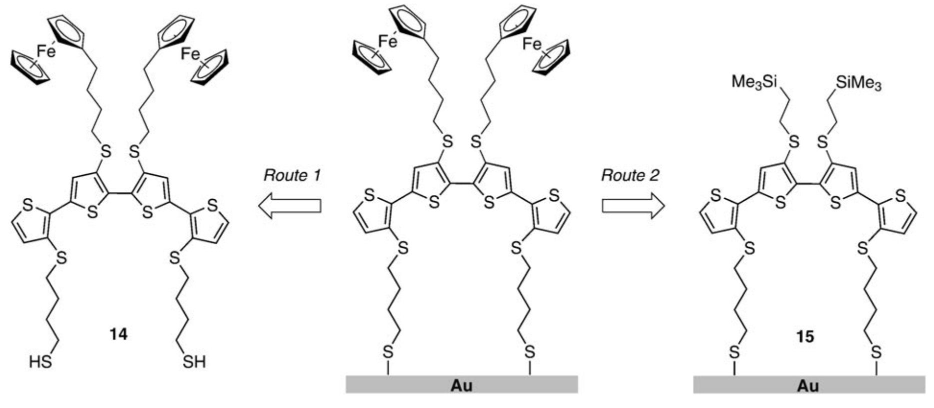
Scheme 3. Functionalization of **7**.

The synthesis of dithiol compounds **14** and **15** is described in Scheme 5. Two alkylsulfanyl chains with terminal acetyl-protected thiol were first introduced in compound **11**. Selective cleavage of the CNE groups of **7** with CsOH (2 equiv) and subsequent reaction of the resulting dithiolate salts with an excess amount of *S*-4-bromobutyl ethanethioate **12** led to **11** in 72 % yield. Thiol ester **12** was prepared in 63 % yield



Scheme 5. Synthesis of dithiols **14** and **15**.

Reagent **10** was prepared using a known procedure (see the Supporting Information).[47] To confirm the versatility of the proposed synthetic approach, monolayers of doubly attached functionalized 4Ts were prepared by two distinct routes, (Scheme 4) namely, immobilization of the ferrocenyl-functionalized dithiol **14** (route 1) and the post-functionalization of a monolayer of dithiol **15** by using the remaining TMSE-protected thiolate groups (route 2).



Scheme 4. Different routes to ferrocenyl-functionalized 4T fixed on gold.

by treating potassium thioacetate with 1,4-dibromobutane (1.5 equiv) as previously reported.[36,48]

Dithiol **14** was prepared in high yield from compound **13** after reduction of the thioester groups by using diisobutylaluminum hydride (DIBAl-H) in anhydrous CH_2Cl_2 followed by addition of HCl. Compound **13** was obtained after treatment of **11** with Bu_4NF in THF and subsequent alkylation reaction with an excess amount of ferrocenyl derivative **10**. Although the yield remains modest (25 %), the access to dithioester **13** from **11** shows that it is possible to selectively cleave the two TMSE groups of **11** in the presence of fluoride anions while preserving the thioacetyl ester groups.[40a,49] Dithiol **15** was synthesized by saponification of dithioester **11** in the presence of CsOH.

Electrochemical and optical properties in solution: The electrochemical and optical properties of the 4Ts have been analyzed by cyclic voltammetry and UV/Vis spectroscopy. The anodic peak potentials (E_{pa}) and absorption maxima are listed in Table 1.

Table 1. Absorption maxima (in CH_2Cl_2) and oxidation peak potentials of 4Ts (1 mM in 0.10 M Bu_4NPF_6 and CH_3CN/CH_2Cl_2 (1:1 v/v), scan rate 100 mV s^{-1}, Pt working electrode and SCE reference electrode).

Compound	λ_{max} [nm]	E_{pa}^{Fc} [V]	E_{pa}^{SH} [V]	E_{pa}^{1} [V]	E_{pa}^{2} [V]
7	275, 392	–	–	0.85	1.04
8	276, 388	–	–	0.72	0.91
9	299 (sh), 385	0.41	–	0.84	0.96
11	297, 390	–	–	0.74	0.91
13	295 (sh), 390	0.37	–	0.82	0.93
14	295 (sh), 389	0.45	–	0.91	1.02
15	298, 391	–	0.67	0.78	0.98

The CV results of all 4T derivatives exhibit two one-electron reversible oxidation waves at E_{pa}^{1} and E_{pa}^{2}, which correspond to the successive formation of the radical cation and dication (Table 1). Replacement of the CNE groups of **7** by methyl (**8**) produces a 130 mV negative shift of E_{pa}^{1} and E_{pa}^{2} due to the suppression of the electron-withdrawing effect of the cyano groups.

The presence of the ferrocenyl (Fc) groups in 4T **9** is confirmed by the intense reversible oxidation wave of the Fc/Fc^{+} couple at 0.41 V (Figure 1). The occurrence of a single well-resolved oxidation peak for the two Fc units suggests an absence of interaction between them. Replacement of the TMSE groups of **8** by two Fc units (**9**) leads to 120 and 50 mV positive shifts of E_{pa}^{1} and E_{pa}^{2}, respectively, probably due to the suppression of the electron-donating effect of the TMSE moiety.

Compounds **8** and **11** show close E_{pa}^{1} and E_{pa}^{2} values that are in agreement with their similar structures. As for **9**, the CV of compound **13** exhibits the typical signature of the Fc units ($E_{pa}^{Fc} = 0.37$ V) and 4T core ($E_{pa}^{1} = 0.82$ V and $E_{pa}^{2} = 0.93$ V). Integration of the peaks of the deconvoluted CV of **13** gives results consistent with a ratio of two Fc units per 4T (Figure 2). Comparison of the CV results of dithiol **14** with that of **13** reveals a slight broadening of the electrochemical response in the 0.70–1.20 V region, which can be attributed to the oxidation of the thiol groups of **14**.

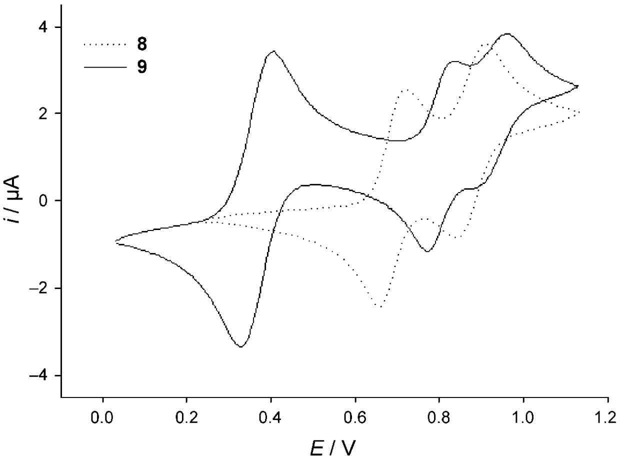


Figure 1. Cyclic voltammograms of compounds **8** and **9** (1 mM in 0.10 M Bu_4NPF_6 and CH_2Cl_2/CH_3CN (1:1), scan rate 0.1 V s^{-1}, Pt working electrode, saturated calomel electrode (SCE) reference electrode).

In fact, application of recurrent potential scans between −0.10 and 1.40 V to a solution of dithiol **14** leads to the progressive development of a broad redox system between 0.60 and 1.20 V with a sharp redox peak at around 0.45 V due to Fc units (Figure 3). This behavior is indicative of the electrodeposition of a polydisulfide material that results from the oxidation of thiol groups, as previously observed.[36] Examination of the first CV traces of **14** (Figure 3, top) clearly shows that in addition to the redox waves associated with the 4T and Fc units, a new redox system appears around 0.75 V. This suggests that besides polydisulfide formation, some coupling of the 4T radical cation that leads to more extended conjugated chains also occurs. This result contrasts with the behavior of dithioesters **11** and **13** for which the stability of the cation radical is confirmed by the reversibility of the oxidation process. A possible explanation for this different behavior could involve a more favored coupling of the 4T radical cation of **14** in the confined environment of the polydisulfide film.

The CV of the polymer recorded in a monomer-free medium (Figure 3, middle), shows a good stability upon cycling between 0.2 and 1.2 V/SCE. In addition to the intense oxidation peak at 0.47 V related to the Fc units and the broad wave centered at 0.90 V due to the two oxidation steps of the 4T backbone, the persistence of a redox system at around 0.75 V confirms the presence of a more extended conjugated system.

For dithiol **15**, the CV shows an irreversible oxidation peak that corresponds to the oxidation of the thiol groups at $E_{pa}^{SH} = 0.67$ V (Figure 4). The oxidation of the 4T system in radical cation and in dication occurs at $E_{pa}^{1} = 0.78$ V and $E_{pa}^{2} = 0.98$ V, respectively. Interestingly, the passage from dithioester **11** to dithiol **15** leads to a 40 mV and a 70 mV positive shift of E_{pa}^{1} and E_{pa}^{2}, respectively. These positive shifts

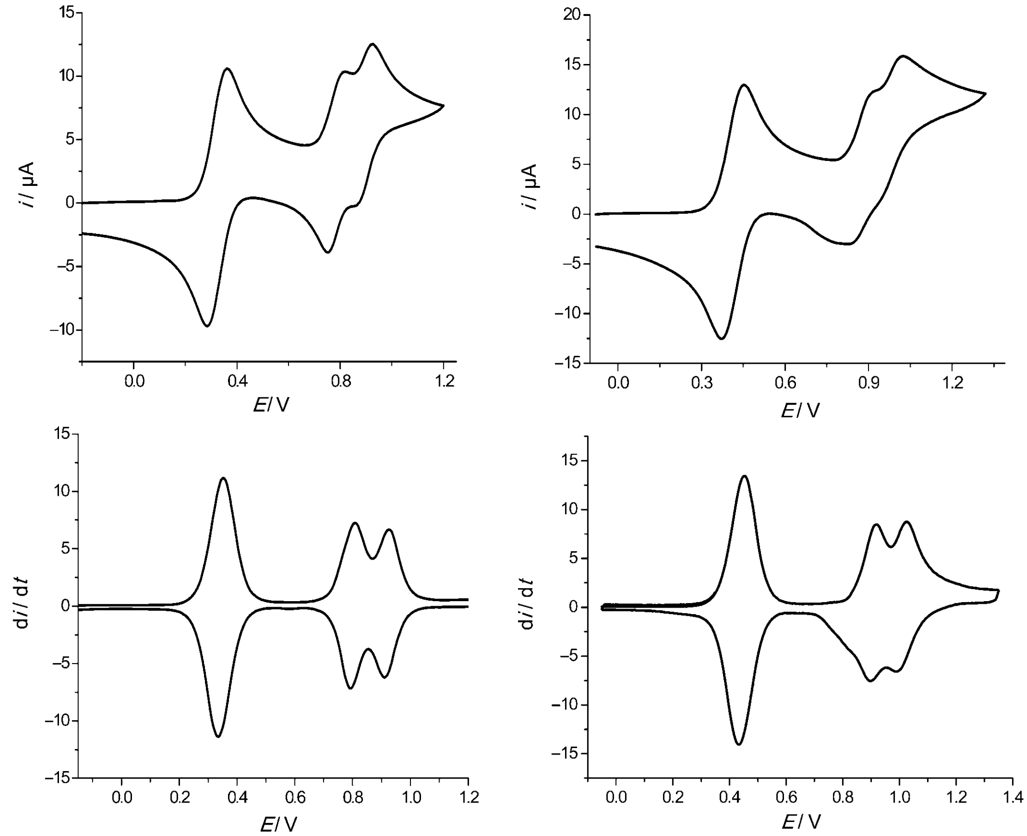


Figure 2. Cyclic voltammograms (top) and deconvoluted cyclic voltammograms (bottom) of dithioester **13** (left) and dithiol **14** (right) (1 mM in 0.10 M Bu_4NPF_6 and CH_2Cl_2/CH_3CN (1:1), scan rate 0.1 $V s^{-1}$, Pt working electrode, SCE reference electrode).

are even more pronounced when comparing the CV results of dithioester **13** and dithiol **14** (Table 1). This phenomenon may arise from the rapid modification of the electrode surface by electrodeposition of polydisulfide (vide supra) or by chemical adsorption of thiols **14** and **15** on Pt during CV measurement. In fact, application of recurrent potential scans between −0.10 and 1.40 V/SCE to solutions of dithiol **15** leads to the electrodeposition of a polydisulfide material as in the case of dithiol **14** (see Figure S16 in the Supporting Information).

Preparation and cyclic voltammetry of monolayers of 4Ts 14 and 15: Dithiols **14** and **15** were subjected to chromatography before monolayer preparation to avoid disulfide formation.[36,50,51] Monolayers were prepared under an argon atmosphere by immersion of cleaned gold-bead electrodes in a millimolar solution of compound **14** or **15** in CH_2Cl_2 for a period of 2 or 3 days. The resulting electrodes were then rinsed with pure CH_2Cl_2 and CH_3CN before immersion in CH_2Cl_2 for 4 h to eliminate physisorbed molecules.

The CV results of monolayer of **14** shows a reversible sharp oxidation peak at 0.45 V that corresponds to the oxidation of the Fc units (Figure 5). A broad reversible wave centered at 1.12 V is associated to the oxidation of the 4T backbone. Thus, immobilization of **14** leads to a coalescence of the two distinct one-electron oxidation waves observed in solution. The sharp and symmetrical electrochemical response of the Fc units shows that they do not interact strongly after immobilization.[13e] The similarity of the surface area of the two waves is consistent with two-electron processes that correspond to Fc units on one hand, and the radical cation and dication of 4T on the other. The linear variation of the peak current versus scan rate confirms that molecules **14** are immobilized on the electrode surface.

The surface coverage (Γ) of molecules **14** has been determined by integration of the voltammetric peak of the ferrocene or that of the 4T signal after correction for double layer charge.[52] Values of $\Gamma = 2\times10^{-10}\,mol\,cm^{-2}$ (1.2×10^{14} molecules cm^{-2} or 83.4 Å^2 per molecule) and $\Gamma = 2.5\times10^{-10}\,mol\,cm^{-2}$ (1.5×10^{14} molecules cm^{-2} or 66.7 Å^2 per molecule) were obtained. These results are in close agreement with previous results for doubly fixed 4T[36] and consistent with the horizontal orientation of the 4T chain expected for a double grafting. The CV results of the monolayer of **14** remained unchanged after 400 cycles between −0.10 and 1.40 V, thus confirming its good stability.

The CV of the monolayer of **15** (Figure 6) exhibits a broad reversible oxidation wave centered at 1.07 V; as for monolayer of **14**, this wave can be attributed to the two oxidation processes of the 4T backbone. Again, the linear scan-rate dependence of the peak current versus scan rate confirms the surface immobilization of the molecules, whereas

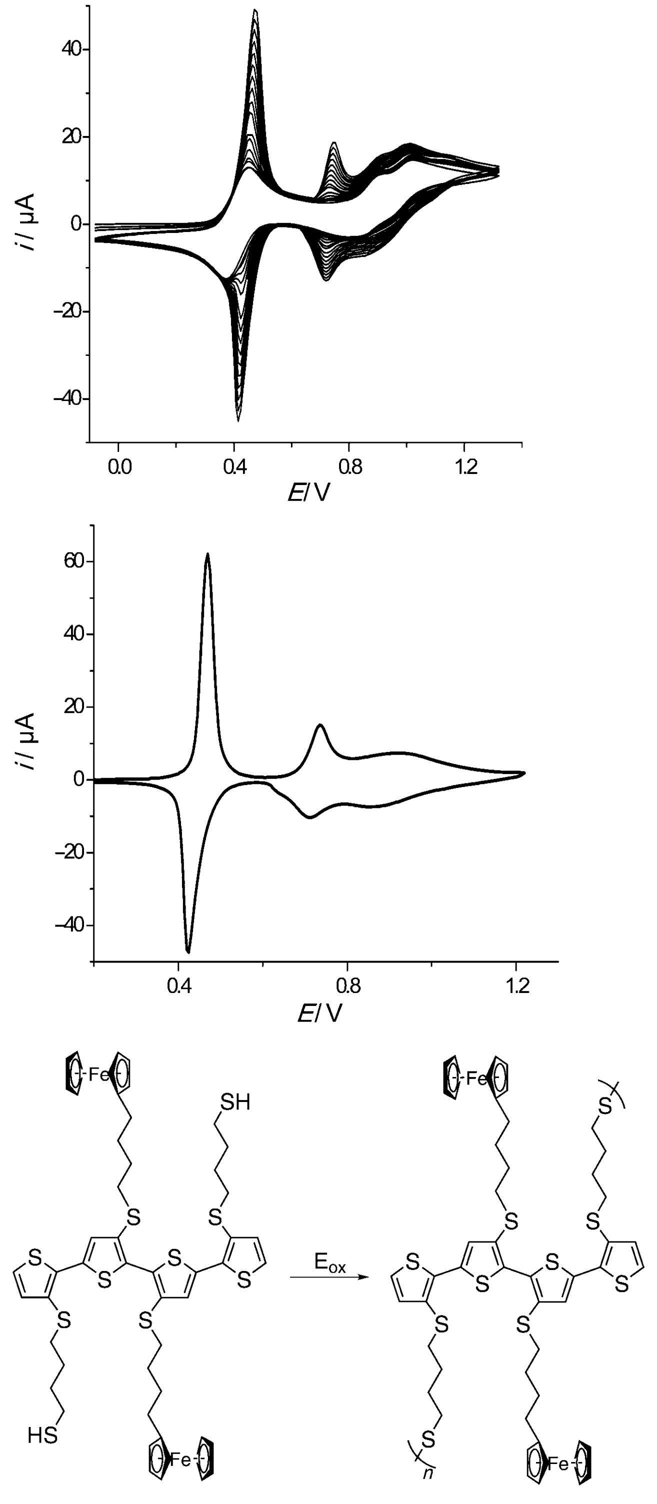


Figure 3. Potentiodynamic electrooxidation of a 2 mM solution of dithiol **14** in 0.10 M Bu_4NPF_6/CH_2Cl_2 (top) and a cyclic voltammogram of the resulting material deposited on a Pt working electrode in 0.10 M Bu_4NPF_6/CH_3CN, scan rate 0.1 $V s^{-1}$ (middle), SCE reference electrode.

the absence of modification of the CV after 200 scans between −0.20 and 1.20 V indicates the good stability of the monolayer. The estimated Γ value of 1.5×10^{-10} mol cm^{-2} is consistent with the formation of a monolayer.[53–55]

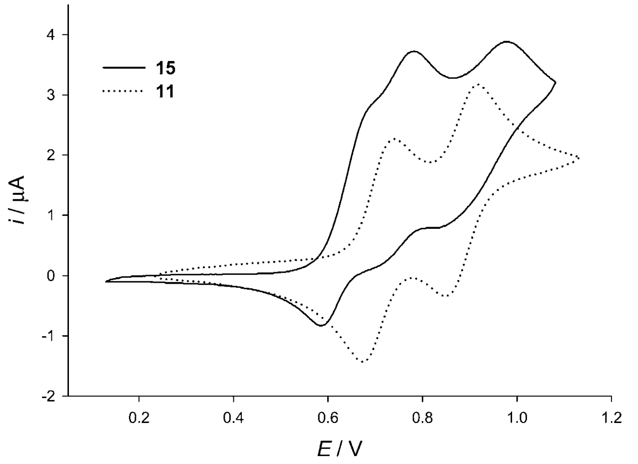


Figure 4. Cyclic voltammograms of dithioester **11** and dithiol **15** (1 mM in 0.10 M Bu_4NPF_6 and CH_2Cl_2/CH_3CN (1:1), scan rate 0.1 $V s^{-1}$, Pt working electrode, SCE reference electrode).

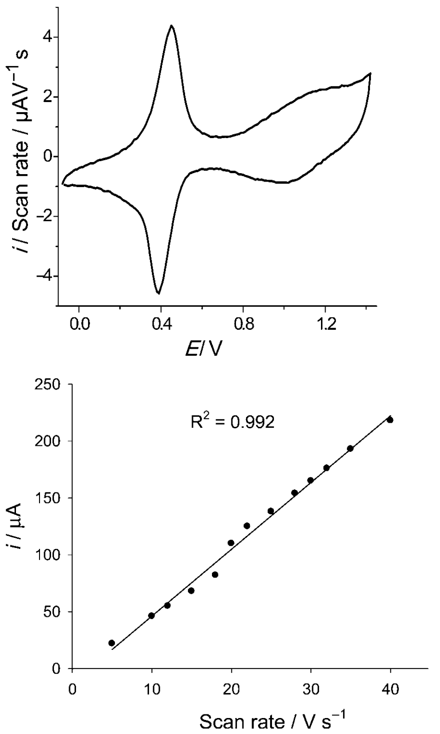


Figure 5. Top: cyclic voltammogram of the monolayer of **14** in 0.10 M Bu_4NPF_6/CH_3CN, scan rate = 20 $V s^{-1}$, SCE reference electrode. Bottom: variation of the peak intensity related to the oxidation of ferrocene versus scan rate.

Structural characterization of monolayers of 14 and 15: Monolayers of **14** and **15** were prepared on an evaporated gold layer (200 nm) on silicon wafers recovered by a 10 nm layer of titanium. The thickness of the monolayers was determined by ellipsometry, which gave values of (19 ± 2) Å and (16 ± 2) Å, respectively for **14** and **15**. These values are in good agreement with a monolayer formation and with the calculated 21–22 and 18–19 Å height for molecules **14** and

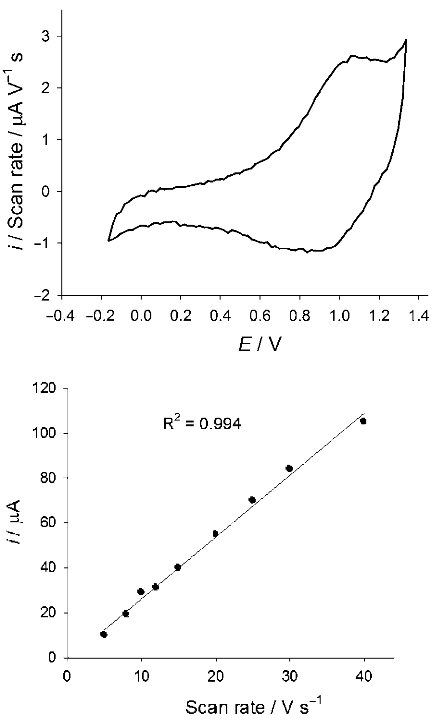


Figure 6. Top: cyclic voltammogram of the monolayer of **15** in 0.10 M Bu_4NPF_6/CH_3CN, scan rate = 20 V s^{-1}, SCE reference electrode. Bottom: variation of the intensity of the oxidation peak versus scan rate.

Table 2. XPS binding energies (BE), full width at half-maximum (FWHM), and assignment of emission peaks measured from high-resolution XPS of monolayers of **14** and **15** adsorbed on gold.

XPS signal	BE [eV]	FWHM [eV]	Corrected area[a] [A.U.]	Assignment
monolayer of **14**				
C 1s	284.6	1.20	*19610*	C 1s
S 2s	227.6	2.59	*3440*	
S 2p[b]			*3416*	
band 1	163.4	1.24	1656	S 2p$_{3/2}$–C
band 2	164.6	1.24	828	S 2p$_{1/2}$–C
band 3	161.9	1.24	463	S 2p$_{3/2}$–Au
band 4	163.1	1.24	232	S 2p$_{1/2}$–Au
Fe 2p				
band 1	720.5	1.20	186	Fe 2p$_{1/2}$
band 2	707.7	1.20	530	Fe 2p$_{3/2}$
monolayer of **15**				
C 1s	284.7	1.37	*27057*	C 1s
S 2s	227.8	2.50	*6202*	
S 2p[b]			*5665*	
band 1	163.6	1.12	3126	S 2p$_{3/2}$–C
band 2	164.8	1.12	1563	S 2p$_{1/2}$–C
band 3	161.9	1.12	898	S 2p$_{3/2}$–Au
band 4	163.0	1.12	449	S 2p$_{1/2}$–Au

[a] The corrected areas were calculated using empirically derived sensibility factors (C 1s: 0.3; S 2s: 0.4; S 2p: 0.57; Fe 2p: 2.7). Each measured peak area was divided by this factor to obtain the corrected area. The total corrected areas of each peak are in italics. [b] The ratio S 2p$_{1/2}$/S 2p$_{3/2}$ for the related shifts in binding energy were fixed to 0.52 and 1.17 eV, respectively.[58]

15, respectively, in the conformation expected for double fixation (Figure 7). These latter values have been estimated with the MOPAC 3D software and assuming a S–Au distance of about 2 Å.[56]

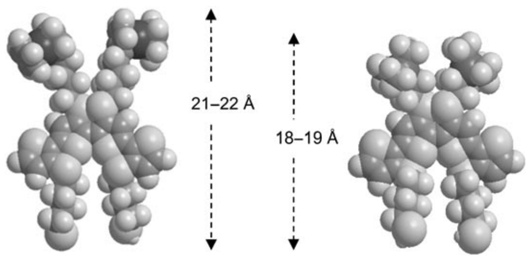


Figure 7. Molecular structures of dithiols **14** (left) and **15** (right) drawn from ellipsometry data in a conformation that leads to a double fixation on gold (from MOPAC-ChemDraw 3D optimization).

The relatively high values of water contact angle for monolayers of **14** (θ_{H_2O} = (87 ± 2)°) and **15** (θ_{H_2O} = (91 ± 2)°) show that these surfaces present an hydrophobic character that can be explained by the presence of the aromatic ferrocenyl groups or the lipohilic TMSE groups on the top of the surface.[3d,53]

Monolayers of **14** and **15** have been analyzed by XPS. The binding energies (BE) of C 1s, S 2s, S 2p, and Fe 2p signals are reported in Table 2, whereas the high-resolution XPS spectra of the S 2p region of monolayers of **14** and **15** are given in Figure 8.

Comparison of the peak area of the S 2s or S 2p signals to that of the C 1s signal provides an estimation of the S/C ratio in the monolayer. In the case of monolayer of **14**, the S 2p/C and S 2s/C ratios of 0.18 is very close to the theoretical value of S/C = 10:52 = 0.19. As expected, the spectrum shows the presence of iron atoms with a Fe/C ratio of 0.037 for a theoretical value of Fe/C = 2:52 = 0.038. The Fe 2p binding energies observed for the iron doublet Fe 2p$_{1/2}$ and Fe 2p$_{1/2}$ at 720.5 and 707.7 eV, respectively, are in good agreement with literature values.[57] For monolayer of **15**, the S 2p/C and S 2s/C ratios of 0.21 and 0.22, respectively, deviate slightly from the theoretical value (S/C = 10:34 = 0.29). Thus the chemical composition determined by XPS for each monolayer confirms the immobilization of **14** and **15** on the gold surface.

The high-resolution XPS spectra of the S 2p region (Figure 8) are decomposed in individual contributions. The curve-fitted high-resolution XPS spectra for the S 2p region of monolayers of **14** and **15** show two doublets. Each doublet results from spin–orbit splitting of the S 2p level and consists of a high-intensity S 2p$_{3/2}$ peak at lower energy and a low-intensity S 2p$_{1/2}$ peak at higher energy separated by 1.2 eV with an intensity ratio of 2:1.[58] The value of the S 2p$_{3/2}$ peak at around 161.9 eV for monolayers of **14** and **15** is in excellent agreement with the binding energy for bound alkanethiolate on gold (161.9–162.0 eV).[53,59] Thus, peaks at 161.9 and 163.1 eV of the lower-energy doublet S 2p$_{3/2,1/2}$ of

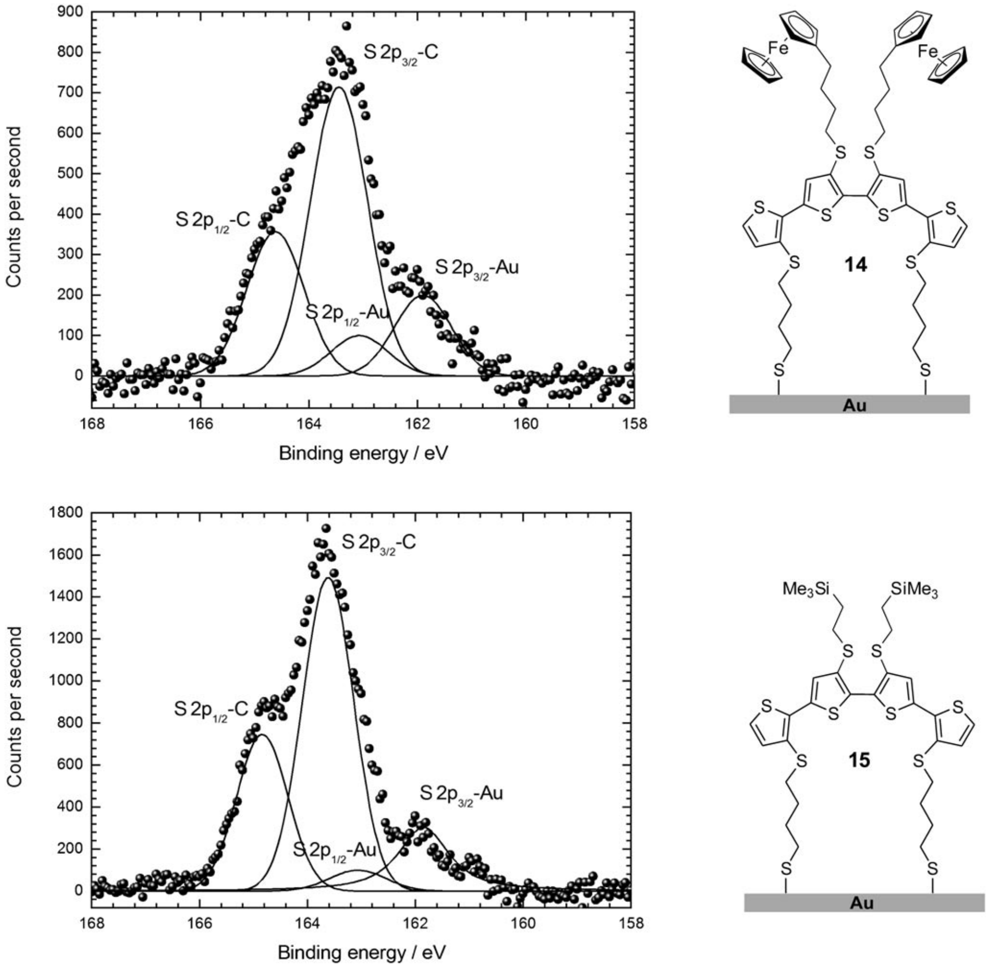


Figure 8. Curve-fitted, high-resolution XPS spectra for the S 2p region of molecules **14** (top) and **15** (bottom) adsorbed on gold.

monolayers of **14** (161.9 and 163.0 eV for **15**) may be assigned to the thiol chemisorbed on the Au surface.[58–60]

The other doublet S 2p$_{3/2,1/2}$ at 163.4 and 164.6 eV for **14** (163.6 and 164.8 eV for **15**) corresponds to the other sulfur atoms of compound **14** (or **15**). Comparison of the areas of these two doublet signals leads to an estimated S−C/S−Au ratio of $\gamma = 3.6 \pm 1$, which is in agreement with the expected value (S−C/S−Au = 4) for a double fixation of molecule **14** on gold by formation of two S−Au bonds. For molecule **15**, a S−C/S−Au ratio of 3.5 ± 1 has been obtained also relatively close to the theoretical value expected for a double fixation (S−C/S−Au = 4). The grafting of molecules **14** or **15** by a single S−Au bond would lead to a theoretical ratio of $\gamma = 9$, which is quite far from experimental values. Thus, XPS results and ellipsometry measurements confirm that the majority of molecules **14** and **15** are doubly fixed on the gold surface as shown in Figure 7.

Post-functionalization of monolayer of 15: In a glovebox (argon atmosphere), a monolayer of **15** on gold beads has been immersed in a 1 M solution of Bu_4NF in anhydrous THF for 20 min, then rapidly rinsed with THF, immediately immersed in a 10 mM solution of ferrocenyl derivative **10** in THF for 0.5 h, and finally washed thoroughly with THF. The post-functionalization process has been followed by CV analysis (Figure 9). The CV results of monolayer of **15** after treatments show a broad oxidation wave centered at approximately 1.10 V/SCE, which is associated to the radical cation and the dication of the 4T system. More importantly, a new intense and reversible oxidation peak at around 0.40 V/SCE, which corresponds to the oxidation of Fc units, is also observed. The estimated 1:1 ratio between the areas of these two oxidation waves suggests an efficient post-functionalization process (Scheme 6). In a control experiment, monolayers of **15** were treated with ferrocenyl derivative **10** in THF and thoroughly washed with THF. In this case, the absence of electrochemical signature of ferrocene indicates that molecules **10** do not physisorb on the monolayer, thus confirming that the functionalization of monolayer of **15** by Fc units results from a nucleophilic substitution of molecules **10** by thiolate groups generated from **15** on the surface.

Finally, the similarity of the CV of the 4T system in the monolayer of **15** and that observed after covalent grafting of ferrocene in Figure 9 suggests that the surface coverage of molecules is practically unaffected by the post-immobilization functionalization. On the other hand, the calculated

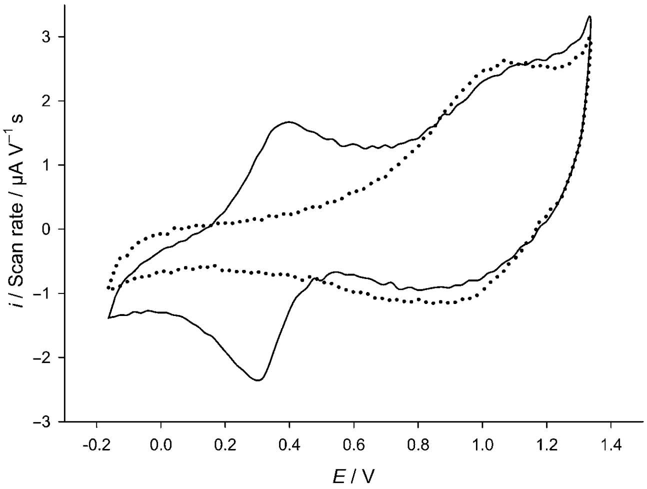
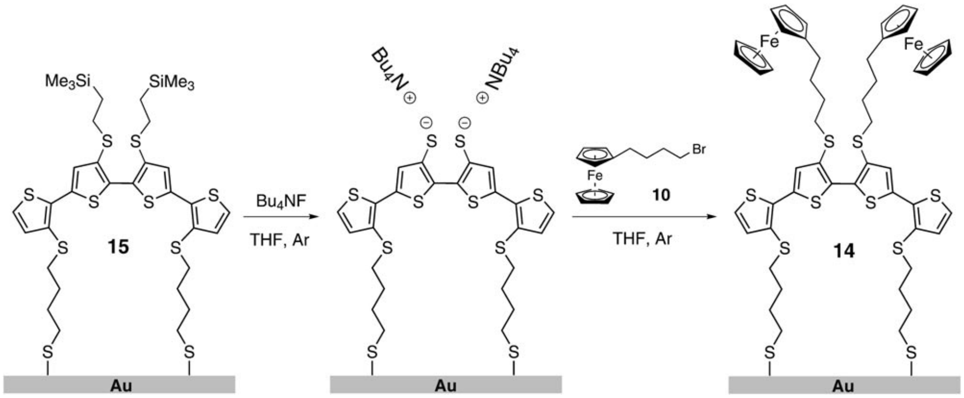


Figure 9. Cyclic voltammograms of the monolayer of **15** before (dotted line) and after treatment with Bu_4NF and then compound **10** (solid line). Cyclic voltammograms were recorded in 0.10 M Bu_4NPF_6/CH_3CN, scan rate = 20 V s^{-1}, SCE reference electrode.



Scheme 6. Formation of monolayer of **14** by means of post-functionalization of the monolayer of **15**.

value of Γ ($\approx 1.5\times10^{-10}$ mol cm^{-2}), which is slightly lower than that observed for the monolayer of **14** (Γ = 2–2.5 × 10^{-10} mol cm^{-2}) and the broadening of the electrochemical response of post-functionalized monolayer of **15** compared to that of the monolayer of **14** can be related to a weaker organization of the native monolayer of **15**.

Conclusion

We have described a versatile synthetic approach that allows for multiple functionalizations of oligothiophene derivatives. Our strategy is based on the concomitant use of different thiolate protecting groups. The different conditions of deprotection of these groups allow for a sequential functionalization of the 4T skeleton. To illustrate the potentialities of this approach, stable monolayers of 4T derivatives functionalized with Fc units have been prepared either by direct grafting of Fc-containing molecules or by post-functionalization of monolayer of **15** by cleavage and S-alkylation of the remaining protected thiolates.

Characterization of the monolayers by cyclic voltammetry, ellipsometry, water contact-angle measurements, and XPS provide coherent results that indicate that the molecules are doubly attached on the surface with a horizontal orientation of the main axis of the 4T system. These results that illustrate the rich potentialities of the versatile thiolate chemistry can open interesting perspectives for future developments in sensors and molecular electronics.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded at 500.13 and 125.7 MHz, respectively; chemical shifts (δ) are given in ppm relative to TMS, and coupling constants (J) are in Hz. IR spectra were recorded by using samples embedded in KBr disks or thin films between NaCl plates. Melting points are uncorrected. The synthesis of bromobutylferrocene is described in the Supporting Information following a known procedure.[47]

2-Bromo-3-(2-cyanoethylsulfanyl)thiophene (2): A solution of *N*-bromosuccinimide (2.91 g, 17.7 mmol) in DMF (15 mL) was added dropwise to a solution of compound **1** (3.0 g, 17.7 mmol) in DMF (20 mL) under N_2 at 0 °C in the absence of light. The mixture was stirred 4 h at 20 °C, concentrated in vacuo, and the residue was diluted with CH_2Cl_2 (200 mL). The organic phase was washed with water, dried over Na_2SO_4, evaporated in vacuo, and subjected to chromatography on silica gel (1:1 CH_2Cl_2/petroleum ether (PE)) to give a white solid (3.69 g, 84 % yield). M.p. 40–41 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.57 (t, ^3J = 7.5 Hz, 2 H), 3.05 (t, ^3J = 7.5 Hz, 2 H), 7.00 (d, ^3J = 5.7 Hz, 1 H), 7.32 ppm (d, ^3J = 5.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.6, 30.8, 117.8, 118.5, 126.8, 129.6, 131.5 ppm; IR (KBr): $\tilde{\nu}$ = 2246 cm^{-1} (CN); elemental analysis calcd (%) for $C_7H_6BrNS_2$: C 33.88, H 2.44, S 25.84, N 5.64; found: C, 33.88, H, 2.38, S, 25.54, N, 5.62.

2-Bromo-3-(2-trimethylsilylethylsulfanyl)thiophene (3): Under an N_2 atmosphere, a solution of $CsOH.H_2O$ (5.36 g, 31.9 mmol) in N_2-degassed MeOH (15 mL) was added dropwise to a solution of **2** (7.20 g, 29.0 mmol) in degassed DMF (50 mL). The reaction mixture was stirred for 1 h at 20 °C before addition of a solution of bromo derivative **4** (7.36 g, 40.6 mmol) in degassed DMF (15 mL). After 4 h of additional stirring at 20 °C and evaporation of the solvents, the residue was dissolved in CH_2Cl_2 and the organic phase was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (9:1 PE/CH_2Cl_2 as eluent) gave compound **3** as yellow oil (8.10 g, 95 % yield). Note that **3** slowly decomposes when stored at +4 °C, hence it is preferable to use it quite rapidly after synthesis. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (d, ^3J = 5.4 Hz, 1 H; H^5_{thio}), 6.92 (d, ^3J = 5.4 Hz, 1 H; H^4_{thio}), 2.92–2.88 (m, 2 H; CH_2–S), 0.90–0.86 (m, 2 H; CH_2–Si), 0.02 ppm (s, 9 H; CH_3–Si); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 133.2, 130.1, 125.8, 113.5, 31.0, 17.5, −1.8 ppm; MS (70 eV): m/z (%): 296 (100) and 294 (100) $[M^{+\bullet}]$, 268 (18) and 266 (18), 253 (46) and 251 (46); elemental analysis calcd (%) for $C_9H_{15}BrS_2Si$: C 36.74, H 5.14; found: C 37.55, H 5.13.

(2-Bromoethyl)trimethylsilane (4): Under an N_2 atmosphere, a solution of phosphorus tribromide (4.10 mL, 22.5 mmol) in anhydrous CH_2Cl_2 was added dropwise to a mixture of vinyltrimethylsilane (10 mL, 67.8 mmol) and silica gel (30 g) in anhydrous CH_2Cl_2 cooled to −10 °C. After 10 min of stirring at −10 °C, the reaction mixture was allowed to warm to 20 °C over a period of 0.5 h, after which silica gel was separated by filtration. The filtrated solution was washed with a saturated aqueous solution of Na_2CO_3, dried over Na_2SO_4, and concentrated to dryness to give pure **4** as slightly yellow oil (6.30 g, 51 % yield). Note that **4** slowly decomposes at room temperature or when stored at +4 °C, hence it is preferable to use it quite rapidly after synthesis. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=3.59$–3.55 (m, 2H; CH_2–Br), 1.39–1.36 (m, 2H; CH_2–Si), 0.04 ppm (s, 9H; CH_3–Si).

3,3′-Bis(2-trimethylsilylethylsulfanyl)-2,2′-bithiophene (5): Under an N_2 atmosphere, a solution of *n*BuLi 1.6 M in hexanes (13.2 mL, 21.1 mmol) was added dropwise to a solution of **3** (5.95 g, 20.1 mmol) in anhydrous Et_2O (100 mL) cooled to −78 °C. After 0.5 h of additional stirring at −78 °C, copper(II) chloride 99.995 % (2.8 g, 20.8 mmol, Aldrich) was added in one portion to the reaction mixture. The latter was further stirred at −78 °C for 15 min, warmed to 20 °C, and stirred at 20 °C overnight. After dilution with Et_2O (150 mL), the organic phase was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (8:2 PE/CH_2Cl_2 as eluent) gave compound **5** as a yellow oil (2.59 g, 60 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.37$ (d, $^3J=5.3$ Hz, 2H; H_{thio}), 7.07 (d, $^3J=5.3$ Hz, 2H; H_{thio}), 2.85–2.82 (m, 4H; CH_2–S), 0.84–0.82 (m, 4H; CH_2–Si), −0.02 ppm (s, 18H; CH_3–Si); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=132.2$, 132.1, 130.5, 125.9, 31.7, 17.4, −1.8 ppm; UV/Vis (CH_2Cl_2): $\lambda=279$ nm; MS (MALDI): *m*/*z*: 447 [$M^{+\cdot}$+17], 430 [$M^{+\cdot}$]; elemental analysis calcd (%) for $C_{18}H_{30}S_4Si_2$: C 50.22, H 7.03; found: C 49.98, H 6.99.

Compound 6: Under an N_2 atmosphere, a solution of *n*BuLi 1.6 M in hexanes (6.7 mL, 10.75 mmol) was added dropwise to a solution of **5** (1.85 g, 4.3 mmol) in anhydrous THF (50 mL) cooled to −78 °C. The reaction mixture was allowed to warm to 20 °C and stirred at this temperature for 1 h before addition of tributyltin chloride (2.6 mL, 9.5 mmol). The mixture was heated to reflux for 1 h. At 20 °C, petroleum ether (150 mL) was added, and the organic phase was washed with a saturated aqueous solution of NH_4Cl and then with water. The organic phase was dried over $MgSO_4$ and concentrated to dryness to afford **6** as yellow oil (4.35 g), which was engaged in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.06$ (s, 2H; H_{thio}), 2.82 (m, 4H; CH_2–S), 1.64–1.56 (m, 12H), 1.38–1.28 (m, 12H), 1.11 (m, 12H), 0.93–0.85 (m, 18H), 0.85 (m, 4H; CH_2–Si), −0.04 ppm (s, 18H; CH_3–Si).

Compound 7: Under an N_2 atmosphere, [Pd(PPh_3)$_4$] (0.50 g, 0.43 mmol) was added in one portion to an N_2-degassed solution of **6** (4.34 g) and compound **2** (2.70 g, 10.88 mmol) in toluene (50 mL). The reaction mixture was heated to reflux overnight. After evaporation of the solvent and addition of CH_2Cl_2 (200 mL), the organic phase was washed with water (2×75 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (9:1 CH_2Cl_2/PE as eluent) led to compound **7** as orange oil, which slowly crystallized (2.37–2.63 g, 72–80 % yield based on **5**). M.p. 74–76 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.36$ (s, 2H; H_{thio}), 7.27 (d, $^3J=5.3$ Hz, 2H; H_{thio}), 7.09 (d, $^3J=5.3$ Hz, 2H; H_{thio}), 3.05 (t, $^3J=7.4$ Hz, 4H; S–CH_2–CH_2–CN), 2.95–2.91 (m, 4H; S–CH_2–CH_2–Si), 2.58 (t, $^3J=7.4$ Hz, 4H; CH_2–CN), 0.94–0.90 (m, 4H; CH_2–Si), 0.01 ppm (s, 18H; CH_3–Si); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=138.8$, 134.7, 133.4, 132.9, 132.2, 129.7, 124.5, 124.3, 117.9, 32.1, 31.6, 18.5, 17.5, −1.7 ppm; IR (KBr): $\tilde{\nu}=2251$ cm^{-1} (CN); UV/Vis (CH_2Cl_2): λ (logε)=275 (4.53), 392 nm (4.23); MS (70 eV): *m*/*z* (%): 764 (30) [$M^{+\cdot}$], 711 (16), 422 (15), 390 (22), 126 (100); MS (MALDI): *m*/*z*: 781 [$M^{+\cdot}$+17]; elemental analysis calcd (%) for $C_{32}H_{40}N_2S_8Si_2$: C 50.26, H 5.28; found: C 49.96, H 5.39.

Compound 8: Under an N_2 atmosphere, a solution of $CsOH.H_2O$ (0.22 g, 1.3 mmol) in N_2-degassed MeOH (7 mL) was added dropwise to a solution of **7** (0.45 g, 0.6 mmol) in degassed DMF (15 mL). The reaction mixture was stirred for 1 h at 20 °C before the addition of a solution of iodomethane (0.37 mL, 5.9 mmol). After 4 h of additional stirring at 20 °C and evaporation of the solvents, the residue was dissolved in CH_2Cl_2. The organic phase was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (6:4 PE/CH_2Cl_2 as eluent) gave compound **8** as yellow oil (0.28 g, 69 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.32$ (s, 2H; H_{thio}), 7.23 (d, $^3J=5.3$ Hz, 2H; H_{thio}), 7.05 (d, $^3J=5.3$ Hz, 2H; H_{thio}), 2.93–2.90 (m, 4H; CH_2–S), 2.49 (s, 6H; CH_3–S), 0.94–0.90 (m, 4H; CH_2–Si), 0.00 ppm (s, 18H; CH_3–Si); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=135.4$, 132.9, 132.6, 131.9, 130.5, 130.2, 129.2, 123.9, 32.1, 18.8, 17.5, −1.7 ppm; UV/Vis (CH_2Cl_2): λ (logε)=276 (4.63), 388 nm (4.23); MS (MALDI): *m*/*z*: 686 [$M^{+\cdot}$].

Compound 9: Under an N_2 atmosphere, a solution of tetrabutylammonium fluoride (1 M) in THF (1.40 mL, 1.40 mmol) was added dropwise to a solution of **8** (0.24 g, 0.35 mmol) in anhydrous THF (4 mL). The solution turned rapidly from yellow to violet. The reaction mixture was stirred under ultrasound for 1.5 h before the addition of compound **10** (0.56 g, 1.75 mmol) dissolved in anhydrous THF (5 mL) to afford an orange color to the reaction mixture, which was left under stirring overnight. After evaporation of the solvent and the subsequent addition of CH_2Cl_2, the solution was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (from an 8:2 to a 1:1 mixture of PE/CH_2Cl_2 as eluent) led to compound **9** as brown oil (0.27 g, 80 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.34$ (s, 2H; H_{thio}), 7.24 (d, $^3J=5.2$ Hz, 2H; H_{thio}), 7.05 (d, $^3J=5.2$ Hz, 2H; H_{thio}), 4.13 (s, 10H; H_{Fc}), 4.09 (s, 4H; H_{Fc}), 4.07 (s, 4H; H_{Fc}), 2.85 (t, $^3J=7.0$ Hz, 4H; CH_2–S), 2.49 (s, 6H; CH_3–S), 2.24 (br t, $^3J=6.6$ Hz, 4H; CH_2–Fc), 1.63 (m, 4H; CH_2), 1.55 ppm (m, 4H; CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=135.6$, 132.9, 132.7, 131.7, 130.5, 130.3, 129.3, 124.0, 88.9, 68.4, 68.0, 67.0, 36.1, 30.1, 29.4, 29.1, 18.8 ppm; UV/Vis (CH_2Cl_2): λ (logε)=299 (sh), 385 nm (4.25); MS (MALDI): *m*/*z*: 966 [$M^{+\cdot}$].

Compound 11: Under a N_2 atmosphere, a solution of $CsOH.H_2O$ (0.96 g, 5.76 mmol) in N_2-degassed MeOH (5 mL) was added dropwise to a solution of **7** (2 g, 2.62 mmol) in degassed DMF (25 mL). The reaction mixture was stirred for 1 h at 20 °C before addition of a solution of bromo derivative **12** (1.40 g, 6.55 mmol) in degassed DMF (10 mL) . After 4 h of additional stirring at 20 °C and evaporation of the solvents, the residue was dissolved in CH_2Cl_2 and the organic phase was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (1:2 PE/CH_2Cl_2 as eluent) gave compound **11** as orange oil (1.73 g, 72 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.34$ (s, 2H; H_{thio}), 7.20 (d, $^3J=5.2$ Hz, 2H; H_{thio}), 7.04 (d, $^3J=5.2$ Hz, 2H; H_{thio}), 2.94–2.91 (m, 4H; S–CH_2–CH_2–Si), 2.88–2.84 (m, 8H; SCH_2), 2.29 (s, 6H; CH_3–CO), 1.71–1.69 (m, 8H), 0.96–0.93 (m, 4H; CH_2–Si), 0.02 ppm (s, 18H; CH_3–Si); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=195.8$, 135.6, 135.4, 132.7, 132.3, 131.7, 129.2, 127.9, 123.6, 35.5, 32.1, 30.6, 28.6, 28.5, 17.5, −1.7 ppm; IR (NaCl): $\tilde{\nu}=1690$ cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ (logε)=297 (3.61), 390 nm (4.18); MS (MALDI): *m*/*z*: 918 [$M^{+\cdot}$]; elemental analysis calcd (%) for $C_{38}H_{54}O_2S_{10}Si_2$: C 49.67, H 5.93; found: C 49.56, H 6.02.

Compound 13: Under an N_2 atmosphere, a solution of tetrabutylammonium fluoride (1 M) in THF (1.75 mL, 1.75 mmol) was added dropwise to a solution of **11** (0.40 g, 0.44 mmol) in anhydrous THF (6 mL). The reaction mixture was stirred under ultrasound for 1.5 h before addition of compound **10** (0.70 g, 2.18 mmol) in anhydrous THF (5 mL). The reaction mixture was stirred for 2 h at 20 °C. After concentration and the addition of CH_2Cl_2, the solution was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (6:4 PE/Et_2O as eluent) led to compound **13** as yellow oil (0.13 g, 25 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.37$ (s, 2H; H_{thio}), 7.22 (d, $^3J=5.6$ Hz, 2H; H_{thio}), 7.05 (d, $^3J=5.6$ Hz, 2H; H_{thio}), 4.11 (s, 10H; H_{Fc}), 4.06 (s, 8H; H_{Fc}), 2.88–2.83 (m, 12H; CH_2–S), 2.30 (s, 6H; CH_3–CO), 2.25 (t, $^3J=7.7$ Hz, 4H; CH_2–Fc), 1.69–1.61 (m, 12H), 1.60–1.52 ppm (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=195.8$, 135.5, 133.1, 132.4, 131.5, 129.5, 128.0, 123.7, 69.0, 68.5, 67.5, 36.1, 35.6, 30.7, 30.0, 29.3, 29.1, 28.58, 28.54, 28.50 ppm; IR (NaCl): $\tilde{\nu}=1690$ cm^{-1} (C=O); UV/Vis (CH_2Cl_2): $\lambda=295$ (sh), 390 nm; HRMS (ESI): *m*/*z*: calcd for $C_{56}H_{62}Fe_2O_2S_{10}$: 1198.0656; found: 1198.0687; MS (MALDI): *m*/*z*: 1197 [$M^{+\cdot}$−1].

Compound 14: Under an N_2 atmosphere, a solution of DIBAL-H (1 M) in CH_2Cl_2 (0.7 mL, 0.7 mmol) was added dropwise to a solution of **13** (0.10 g, 0.08 mmol) in anhydrous CH_2Cl_2 (5 mL) cooled to 0 °C. After 2 h of stirring at 0 °C, an aqueous solution (3 M) of HCl (3 mL) was added to the reaction mixture, which was further stirred at 20 °C for 0.5 h. The mixture was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (1:1 PE/CH_2Cl_2 as eluent) led to compound **14** as orange oil (0.09 g, 97 % yield). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.37$ (s, 2H; H_{thio}), 7.22 (d, $^3J = 5.6$ Hz, 2H; H_{thio}), 7.05 (d, $^3J = 5.6$ Hz, 2H; H_{thio}), 4.07 (s, 10H; H_{Fc}), 4.02 (s, 8H; H_{Fc}), 2.88–2.85 (m, 8H; $CH_2{-}S$), 2.52–2.47 (m, 4H; $CH_2{-}SH$), 2.28 (t, $^3J = 7.7$ Hz, 4H; $CH_2{-}Fc$), 1.73–1.70 (m, 8H), 1.68–1.55 (m, 8H), 1.31 ppm (t, $^3J = 7.9$ Hz, 2H; SH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 135.5, 133.1, 132.4, 131.5, 129.5, 128, 123.7, 69.6, 68.2, 67.2, 36.1, 35.7, 32.8, 30.1, 29.4, 29.1, 28.2, 24.2 ppm; UV/Vis (CH_2Cl_2): $\lambda = 295$ (sh), 389 nm; MS (MALDI): m/z: 1114 [$M^{+\cdot}$].

Compound 15: A solution of $CsOH{\cdot}H_2O$ (0.16 g, 0.95 mmol) in N_2-degassed MeOH (5 mL) was added dropwise to a solution of compound **11** (0.35 g, 0.38 mmol) in N_2-degassed THF (15 mL). The reaction mixture was stirred for 2 h before addition of an aqueous solution of HCl (1 M, 1 mL, 1 mmol). After 2 h of additional stirring, the reaction mixture was concentrated and diluted with CH_2Cl_2 (100 mL). The organic phase was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (1:1 CH_2Cl_2/PE as eluent) gave compound **15** as yellow oil (0.20 g, 63 % yield). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.34$ (s, 2H; H_{thio}), 7.21 (d, $^3J = 5.2$ Hz, 2H; H_{thio}), 7.05 (d, $^3J = 5.2$ Hz, 2H; H_{thio}), 2.94–2.90 (m, 4H; $S{-}CH_2{-}CH_2{-}Si$), 2.87 (t, $^3J = 6.7$ Hz, 4H; $S{-}CH_2{-}(CH_2)_3{-}SH$), 2.50 (q, $^3J = 7.7$ Hz, 4H; $CH_2{-}SH$), 1.73–1.71 (m, 8H; $CH_2{-}(CH_2)_2{-}CH_2$), 1.31 (t, $^3J = 7.9$ Hz, 2H; SH), 0.94–0.91 (m, 4H; $CH_2{-}Si$), 0.01 ppm (s, 18H; $CH_3{-}Si$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 135.6$, 135.4, 132.7, 132.3, 131.8, 129.3, 128.0, 123.7, 35.7, 32.8, 32.1, 28.2, 24.2, 17.5, −1.7 ppm; IR (NaCl): $\tilde{\nu} = 2563\ cm^{-1}$ (S−H); UV/Vis (CH_2Cl_2): λ ($\log\varepsilon$) = 298 (4.17), 391 nm (4.23); MS (MALDI): m/z: 834 [$M^{+\cdot}$].

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