

Structural Control of the Horizontal Double Fixation of Oligothiophenes on Gold

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Abstract: Quaterthiophenes bearing one (**1**) or two (**2**) alkanethiol chains attached at the internal β -position of the outermost thiophene ring through a sulfide linkage have been synthesized. Cyclic voltammetric analysis of their electrochemical behavior in solution suggests that electrooxidation of the doubly substituted oligomer **2** leads to electrodeposition of a poly(disulfide) on the anode surface. Monolayers of **1**

or **2** on gold surfaces have been investigated and characterized by cyclic voltammetry, ellipsometry, contact angle measurement, and X-ray photoelectron spectroscopy. The results of these investigations indicate that introduction of two thiol groups in the structure

leads to double fixation of the oligothiophene chain with the main axis of the conjugated system oriented parallel to the surface. The effects of single versus double fixation of the quaterthiophene chain on the electrochemical properties and stability of the corresponding monolayers are discussed.

Keywords: conjugation • dithiols • gold • monolayers • self-assembly

Introduction

Self-assembled monolayers (SAMs) based on the adsorption of electroactive π -conjugated systems on metal or semiconductor surfaces are of growing interest owing to their potential applications in the fields of molecular electronics,^[1,2] photovoltaic conversion,^[3,4,5] and sensors.^[6]

These SAMs are generally formed by chemical adsorption of a conjugated molecule bearing one fixation group such as a thiol, sulfide, disulfide, thiocyanate, or silane, often linked


to the conjugated system by a flexible linear alkyl chain. Interactions between the π -conjugated chains reinforced by lipophilic interactions between alkyl spacers contribute to ensure the cohesion of the SAMs and the quasi-vertical orientation of the conjugated chains on the surface of the substrate.^[7]

Taking advantage of this quasi-vertical orientation, Tour and co-workers have investigated the conductance of single conjugated molecules by scanning tunneling microscopy (STM).^[1d,f] Metzger and co-workers have used a similar arrangement to analyze the rectifying properties of Langmuir–Blodgett-based monomolecular junctions,^[8] whereas SAMs have also been developed for this purpose.^[9] In another approach, monolayers of vertically oriented, stacked, conjugated systems have recently been used to realize organic field-effect transistors in which the thickness of the channel corresponds to the length of the active conjugated molecule.^[10]

Monolayers of linear oligothiophenes with a vertical or quasi-vertical orientation immobilized through a single attachment on a surface have been described by several groups^[9c,d,11–18] and investigated as molecular junctions,^[13] diodes,^[9c,d,f] switches,^[14] and field-effect transistors,^[10] and for the development of a matrix-assisted laser desorption/ionization technique.^[15] Otsubo and co-workers have reported SAMs of oligothiophenes vertically immobilized on gold by means of a tripodal anchoring group and their use as charge injection layers in organic light-emitting diodes.^[16] Hirayama

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 Supporting information (¹H NMR spectra of compounds **1**, **2**, and **6–8**, an illustration of the electrothermic properties of the polysulfide film and its proposed structure, and cyclic voltammograms of **8**) for this article is available on the WWW under <http://www.chemeurj.org/> or from the author.

et al. have prepared monolayers consisting of C₆₀-substituted quater- and octithiophene linked to a gold surface with a disulfide anchoring group, and have analyzed their photo-electrochemical behavior.^[3a] Improved photocurrent generation was subsequently obtained when surface fixation was achieved by a tripod anchoring group that ensured a denser surface coverage than the single-point attachment.^[3c]

More recently, Jen and co-workers have synthesized SAMs based on a dithienylpyrrole disubstituted by C₆₀ groups with an anchoring aryl thiol attached at the nitrogen atom of the median pyrrole unit.^[3d] The greater photocurrent generation than in previous systems was attributed to a better absorption of the incident light thanks to the horizontal orientation of the conjugated system.

The literature contains very few other examples of monolayers in which extended linear π -conjugated systems are fixed horizontally on a surface.^[11,19,20] Berlin, Zotti, and co-workers have investigated the influence of molecular geometry on the electrochemical coupling of bi- and terthiophene adsorbed on indium tin oxide (ITO). They have shown that SAMs of cyclopentabithiophenes, in which the conjugated system is fixed parallel to the surface by a single attachment, can be trimerized electrochemically.^[11b]

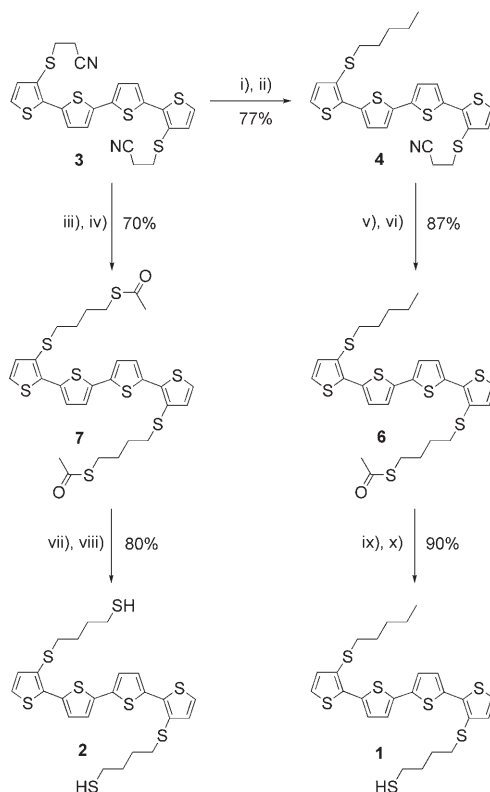
The horizontal immobilization of linear π -conjugated systems on a substrate^[3d,20] can contribute to the toolbox for the fabrication of molecular electronic devices or electrochemical sensors. In this context, a possible approach to imposing a horizontal orientation on the conjugated system can be to introduce two anchoring groups at two sufficiently remote points of an extended π -conjugated system. Double fixation of a dithiol molecule on gold was previously reported by Gokel, Kaifer, and co-workers for a catenane-like structure.^[21] More recently, Kern and Sauvage have described the double fixation on a gold surface of a disulfide incorporating copper(I) catenane,^[22] and Raymo has reported that of a copper(I) complex based on 4,4'-bipyridinium arms terminated by a thiol group.^[23] Echegoyen and co-workers have reported the formation of a pseudo crown-ether loop on a surface by double fixation of an acyclic bis-podant thiol, owing to the template effect of K⁺ ions during monolayer formation.^[24] Although α,ω -alkanedithiols have been shown to adopt an upright alignment of their hydrocarbon chains on the gold surface,^[25] formation of a looped configuration was also reported in several examples^[26] and it was found recently that the orientation of alkanedithiol molecules in monolayers has a strong impact on the electrical transport in molecular junctions.^[26c]

In this context, we report here on the synthesis of two quaterthiophenes **1** and **2** bearing respectively one and two alkanethiol chains attached at the internal β -position of the outermost thiophene ring by a sulfide linkage. The electrochemical properties of these compounds in solution have been analyzed and their immobilization as monolayers on gold electrodes has been investigated. The influence of the presence of one versus two thiol group(s) on the formation, structure, and properties of the monolayers is discussed on the basis of their characterization by cyclic voltammetry,

ellipsometry, contact angle measurement, and X-ray photoelectron spectroscopy (XPS).

Results and Discussion

Synthesis: Our approach to the synthesis of the target compounds **1** and **2** (Scheme 1) is based on the chemistry of thiolate derivatives protected by a 2-cyanoethyl group.^[27–29] Selective deprotection of one thiolate group of 3,3'''-bis(2-cyanoethylsulfanyl)-2,2':5',2'':5'',2'''-quaterthiophene **3**^[29a] with cesium hydroxide (1 equiv) and subsequent reaction with an excess of 1-iodopentane in DMF gave **4** in 77% yield. Similarly, further treatment of **4** with cesium hydroxide (1 equiv) and S-alkylation with an excess of S-4-bromobutyl ethanethioate **5** led to **6** in 87% yield. Thiol ester **5** was prepared in 63% yield by reaction of potassium thioacetate with 1,4-dibromobutane (1.5 equiv). Reduction of the thioester group of **6** by diisobutylaluminum hydride (DIBAL-H) in anhydrous CH₂Cl₂ followed by addition of hydrochloric acid led to the target 3-(4-mercaptobutylsulfanyl)-3'''-pentylsulfanyl-2,2':5',2'':5'',2'''-quaterthiophene **1** in 90% yield. Similarly, dithiol **2** was obtained by reduction of the two thioester groups of **7** with DIBAL-H. Dithioester **7** was prepared by double deprotection of the two thiolate groups of **3** with



Scheme 1. Synthesis of monothiol **1** and dithiol **2**. i) CsOH·H₂O (1.1 eq), ii) IC₅H₁₁ (4.4 eq); iii) CsOH·H₂O (2.2 eq), iv) Br(CH₂)₄SCOCH₃ (**5**); v) CsOH·H₂O (1.2 eq), vi) Br(CH₂)₄SCOCH₃ (**5**); vii) DIBAL-H, 0 °C, viii) aq. HCl; ix) DIBAL-H, 0 °C, x) aq. HCl.

a slight excess of cesium hydroxide followed by addition of an excess of **5**.

Cyclic voltammetry (CV) in solution:

The electrochemical properties of quaterthiophene (4T) mono- and dithiols **1** and **2** as well as their precursors **3**, **6**, and **7** have been analyzed by CV in the presence of Bu_4NPF_6 : **3**, **6**, and **7** exhibit two one-electron reversible oxidation waves corresponding to the successive formation of the radical cation and dication of the 4T backbone (Figure 1 and Table 1). As already observed for parent 4T systems,^[29b,c,e] the stability of these 4T radical cations can be explained by the localization of the sulfide group at the inner β -position of the terminal thiophene rings; in contrast, when introduced at the outer β -positions such electron donor groups enhance the reactivity of the radical cation, thus favoring polymerization.^[30]

All compounds show a first oxidation potential (E_{pa}^1) around 0.80 V except for **3**, in which the electron-withdrawing effect of the cyano groups induces a 140 mV positive shift of E_{pa}^1 .

The CV of the mono- and dithiols **1** and **2** also exhibits two successive oxidation peaks at $E_{\text{pa}}^1=0.80$ V and $E_{\text{pa}}^2=1.00$ – 1.05 V/SCE (Figure 2). However, comparison with the CV of compounds **6** (see the Supporting Information, Figure S7) and **7** (Figure 1), respectively, reveals a broadening of the first wave for **1** and an intensification of the same wave for **2**. Integration and comparison of the oxidation waves of the deconvoluted CVs show that the first oxidation peak of **1** corresponds to a two-electron process, whereas that of **2** involves a three-electron process. These results indicate that the first oxidation peak corresponds to the superimposition of two processes, namely the reversible oxidation of the 4T chain into its radical-cation and the irreversible one-electron oxidation of the thiol groups into disulfide or polydisulfides.

The oxidation of the thiol group of **1** is clearly evident when the platinum working electrode is replaced by gold. Whereas E_{pa}^1 and E_{pa}^2 values are nearly identical to those observed on Pt, the anodic peak associated with the oxidation of the thiol group is shifted

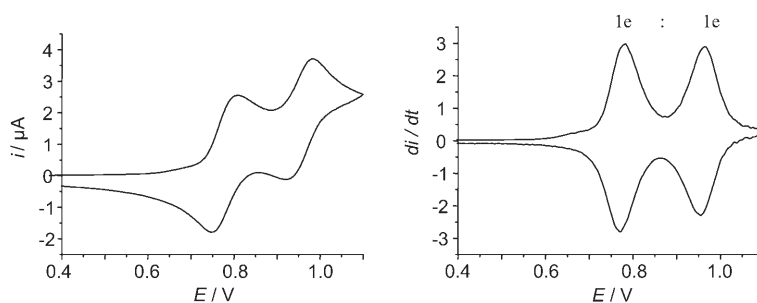


Figure 1. CV (left) and deconvoluted CV (right) of dithioester **7** (1 mM) in 0.10 M $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ (1:1, v/v), scan rate 0.1 V s^{-1} , Pt working electrode, SCE reference electrode.

Table 1. Absorption maxima (in CH_2Cl_2) and oxidation peak potentials of quaterthiophenes (1 mM) in 0.10 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN-CH}_2\text{Cl}_2$ (1:1, v/v), scan rate 100 mV s^{-1} , Pt working electrode).

| Compd | λ_{max} [nm] | $E_{\text{pa}}^1/\text{SCE}$ [V] | $E_{\text{pa}}^2/\text{SCE}$ [V] |
|----------|-----------------------------|----------------------------------|----------------------------------|
| 1 | 407 | 0.80 | 1.05 |
| 2 | 408 | 0.80 | 1.00 |
| 3 | 403 | 0.94 | 1.10 |
| 6 | 406 | 0.85 | 1.05 |
| 7 | 405 | 0.81 | 0.98 |
| 8 | 407 | 0.79 | 1.11 |

toward more positive potentials ($E_{\text{pa}}^{\text{SH}}=0.96$ V) (Figure 3). The irreversibility of this electrochemical process may be related to the rapid formation of a disulfide in the vicinity of the electrode.

This hypothesis was confirmed by the analysis of the CV of the disulfide **8** obtained by chemical oxidation of the thiol group of **1** using FeCl_3 (see the Supporting Information, Figure S8).

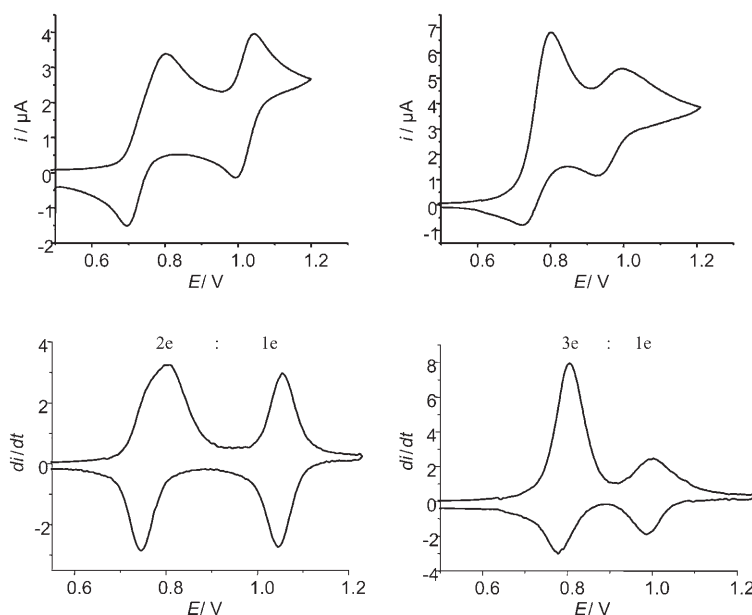


Figure 2. CVs (top) and deconvoluted CVs (bottom) of monothiol **1** (left) and dithiol **2** (right) (all 1 mM) in 0.10 M $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ (1:1, v/v), scan rate 0.1 V s^{-1} , Pt working electrode, SCE reference electrode.

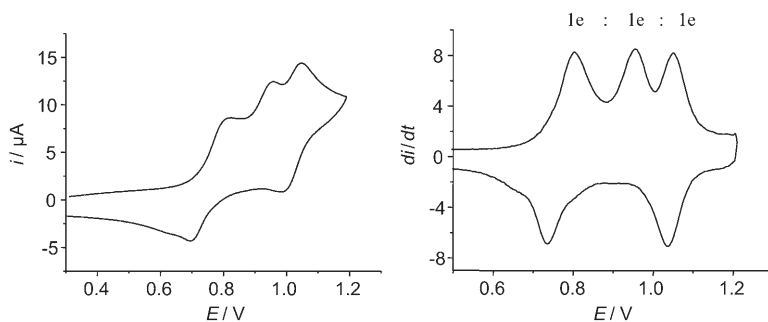
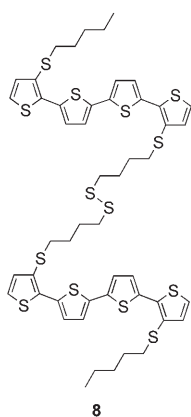


Figure 3. CV (left) and deconvoluted CV (right) of monothiol **1** (2 mM) in 0.10 M Bu₄NPF₆/CH₂Cl₂-CH₃CN (1:1, v/v), scan rate 0.1 V s⁻¹, Au working electrode, SCE reference electrode.



Recurrent potential scans between 0.20 and 1.20 V/SCE were then performed on solutions of **1** and of **2**. A stable CV was observed in the case of **1**, whereas the same procedure for compound **2** leads to the progressive development of a broad redox system indicative of the electrodeposition of an electroactive material (Figure 4). In addition to the two redox systems associated with the 4T radical cation and dication, a first system of weak intensity appears around 0.60 V. This indicates the coupling of the 4T radical cation into more extended conjugated chains during the initial steps of the overall electrooxidation process, besides the electrochemical generation of a polydisulfide. This result, which contrasts with the stability the radical cation in solution (Figure 1), suggests that the coupling of the 4T radical cation of **2** could be favored in the confined environment of the polydisulfide film deposited at the electrode. Further work is needed to clarify this point.

The CV of the polymer recorded in a monomer-free medium shows an intense oxidation peak at approximately 0.90 V/SCE. The absence of an oxidation signal below

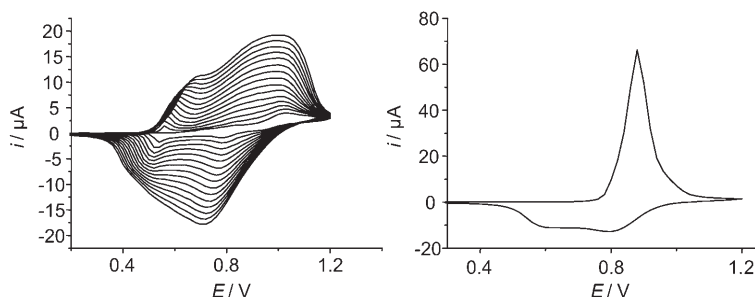


Figure 4. Potentiodynamic electro-oxidation of a solution of dithiol **2** (1 mM) in 0.10 M Bu₄NPF₆/CH₂Cl₂ (left) and CV of the resulting material in 0.10 M Bu₄NPF₆/CH₃CN (right), scan rate 0.1 V s⁻¹, Au working electrode, SCE reference electrode.

0.80 V suggests that the effective conjugation length of the deposited material is probably limited to a 4T chain. This hypothesis is further supported by the UV/Vis spectrum of a polymer film on ITO which shows a $\lambda_{\text{max}} = 430$ nm. These results are consistent with a polydisulfide material containing 4T chains; the red shift compared with the solution spectrum of compound **2** ($\lambda = 408$ nm) can be attributed to π interactions between the conjugated chains in the solid state.

Preparation and cyclic voltammetry of monolayers of **1** and **2**:

Monolayers of **1** and **2** were prepared under a controlled argon atmosphere by immersion of cleaned gold bead electrodes in a millimolar solution of **1** or **2** in CH₂Cl₂. The resulting electrodes were then rinsed with pure CH₂Cl₂ and CH₃CN before immersion in CH₂Cl₂ for 4 h to eliminate physisorbed molecules. Compounds **1** and **2** were stored under a nitrogen atmosphere at +4 °C. However, reproducible monolayers of dithiol **2** were obtained only if **2** was freshly generated from dithioester **7** and purified by chromatography before monolayer preparation. Otherwise, as already reported, multilayers of disulfide compounds were obtained.^[23,31]

Formation of a monolayer of **2** is relatively fast since a CV characteristic of an immobilized molecule is obtained after 3 h of immersion. In contrast, at least 24 h of immersion in a solution of **1** are required to obtain a CV typical of a monolayer. Another striking difference is that the reproducibility of monolayer formation is only 30% for **1**, but it is close to 100% for **2**.

The cyclovoltammetry of monolayers of each of **1** and **2** (Figure 5) exhibits two reversible oxidation peaks characteristic of the 4T radical cation and dication respectively, at $E_{\text{pa}}^1 = 0.83$ V and $E_{\text{pa}}^2 = 1.15$ V for monolayers of **1** and at $E_{\text{pa}}^1 = 0.84$ V and $E_{\text{pa}}^2 = 1.08$ V for monolayers of **2**, values close to those recorded in solution. The linear variation of the peak current versus scan rate confirms that **1** and **2** are immobilized on the electrode surface.

The surface coverage Γ has been determined by integration of the voltammetric peaks after correction for double layer charge.^[32] A value of $\Gamma = 4 \times 10^{-10}$ mol cm⁻² ($\Gamma = 2.4 \times 10^{14}$ molecules cm⁻² or 41.7 Å² per molecule) was obtained for monolayers of **1**; this value is somewhat smaller than is typi-

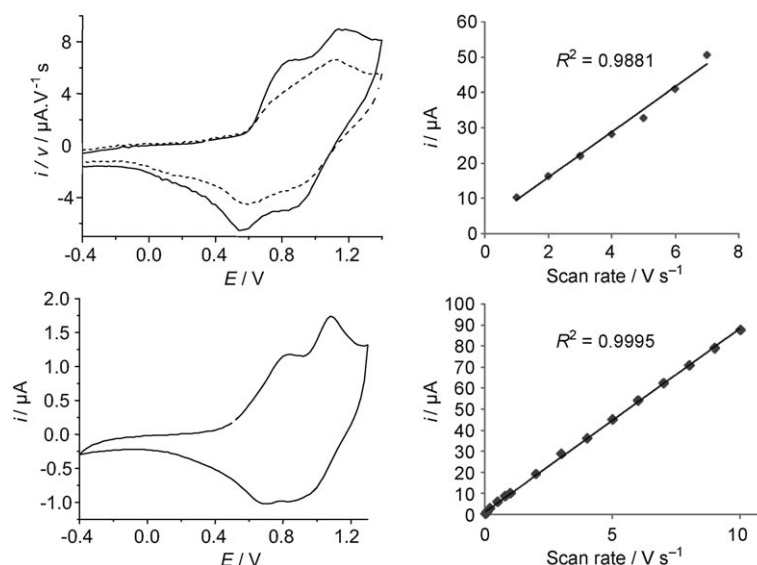


Figure 5. Left: CV of monolayers of **1** (top, scan rate = 6 V s⁻¹) $t_0 + 24$ h (-----), t_0 (—); and **2** (bottom, scan rate = 0.1 V s⁻¹) in 0.10 M Bu₄NPF₆/CH₃CN, SCE reference electrode. Right: variation of the intensity of the second oxidation peak versus scan rate.

cal for close-packed monolayers of alkanethiol ($\Gamma = 4.7 \times 10^{14}$ molecules cm⁻²)^[33a,34,35] or ω -(3-thienyl)alkanethiol ($\Gamma = 6.5$ – 7.0×10^{14} molecules cm⁻²) on gold.^[33c] However, the stability of the monolayer of **1** is limited since the intensity of the CV waves decreases significantly after 24 h of storage in atmospheric conditions or after sonication for 1 min (Figure 5).

For monolayers of **2** the estimated surface coverage of $\Gamma = 2 \times 10^{-10}$ mol cm⁻² (1.2×10^{14} molecules cm⁻² or 83.3 Å² per molecule), half that obtained for **1**, is consistent with the larger area occupied by the 4T molecule when doubly fixed in a horizontal orientation.

Monolayers of **2** are considerably more stable than those of **1**. Thus, the CV remained unaltered after application of 400 recurrent potential scans between -0.40 and 1.20 V/SCE at a scan rate of 0.5 V s⁻¹ or after sonication for 1 min in acetonitrile. No change in the CV was observed after storage for one week in ambient conditions. This markedly improved stability of monolayers of **2** can be related to the double fixation of the 4T molecules to the gold surface.

To confirm the absence of free thiol groups in monolayers of **2**, a monolayer was immersed in a solution of cesium hydroxide (0.10 M) in MeOH/DMF for 15 min (to generate thiolate from hypothetical remaining thiol groups) and then immersed in a solution of 4-bromobutylferrocene (10 mM)^[36] in DMF for 1 h to fix ferrocene groups on these hypothetical thiolates. The absence of the typical signature of ferrocene in the CV of the resulting modified electrodes provides indirect support for the absence of free thiol groups in monolayers of **2** as expected for a double fixation of **2**.

Structural characterization of the monolayers: Monolayers of **1** and **2** for surface characterization were prepared by immersion of substrates consisting of an evaporated gold layer

on silicon wafers in millimolar solutions of freshly purified compounds **1** and **2** for a period of 72 h and 3 h, respectively.

The thickness of the monolayers of **2** determined on two different samples by ellipsometry gave values ranging from 11.8 to 14.0 Å, which are in good agreement with formation of a monolayer and with the calculated 13–14 Å height of molecule **2** in the expected conformation for double fixation (Figure 6). These latter values have been estimated with the MOPAC 3D software and assuming an S–Au distance of about 2 Å.^[37] In this case, although the main axis of the 4T



Figure 6. Molecular structure of dithiol **2** drawn from ellipsometry data in a conformation favorable to double fixation on gold (from MOPAC-ChemDraw 3D optimization).

segment is almost parallel to the surface, molecules of **2** stand up on the surface thus allowing π -stacking interactions and the formation of densely packed domains, in agreement with the relatively high value of Γ determined by CV. Assuming that molecule **2** adopts the conformation shown in Figure 6, the molecular area estimated with MOPAC 3D would correspond to a 4.4 Å × 15.6 Å rectangle of 68.6 Å² per molecule. Comparison with the 83.3 Å² per molecule obtained by CV shows that the experimental result represents approximately 80% of the maximum theoretical coverage.

The water contact angle of monolayers of **2** ($\theta_{\text{H}_2\text{O}} = 83.5 \pm 1^\circ$) is characteristic of a surface constituted by aromatic systems such as thiophene.^[9d,33]

The thickness of monolayers of **1** varies from 9.3 to 11.7 Å. These values are much lower than expected for a vertical orientation of the molecule relative to the surface. The water contact angle ($\theta_{\text{H}_2\text{O}} = 89 \pm 1^\circ$) is higher than that of monolayers of **2**, suggesting a more lipophilic surface, in agreement with the presence of the pentyl chain of **1**. However, this value is much lower than the 105° expected for a molecular conformation in which a pentyl chain points out of the surface.^[38] These results may be due to the fact that molecules **1** do not stand upright in a stretched conforma-

tion but adopt a rather disordered arrangement on the gold surface.

Monolayers derived from **1** and **2** have been analyzed by XPS. A first examination of the spectrum did not show any contamination from residual CH₂Cl₂ solvent and CH₂Cl₂/CH₃CN rinsing solution. The high-resolution XPS spectra of the S2p region (Figure 7) are decomposed in individual con-

tributions whose binding energies (*BE*) are reported in Table 2. Comparison of the peak area of the S2s or S2p signals with that of the C1s signal allows us to estimate the experimental S/C ratio in the monolayer. For a monolayer of **1**, the S2p/C and S2s/C ratio of 0.29 for both is very close to the theoretical value of $S/C = \frac{7}{25} = 0.28$. For monolayer of **2**, the S2p/C and S2s/C ratios of 0.27 and 0.24 respectively deviate slightly from the theoretical value ($S/C = \frac{8}{24} = 0.33$) related to the chemical structure of **2**. The curve-fitted high-resolution XPS spectra for the S2p region of a monolayer of each of **1** and **2** show two doublets (Figure 7). Each doublet results from spin-orbit splitting of the S2p level and consists of a high-intensity S2p_{3/2} peak at lower energy and a low-intensity S2p_{1/2} peak at higher energy separated by 1.2 eV with an intensity ratio of 2:1.^[39] The value of the S2p_{3/2} peak at 161.9 eV for monolayers of **1** and **2** is in excellent agreement with the binding energy for bound alkanethiolate on gold (161.9–162.0 eV).^[25,34] Thus, peaks at 161.9 and 163.1 eV of the lower-energy doublet S2p_{3/2,1/2} of monolayers of **1** and **2** may be assigned to the thiol chemisorbed on the Au surface.^[25,39,40] The other doublet, S2p_{3/2,1/2}, at 163.5 and 164.7 eV for **1** and 163.6 and 164.7 eV for **2**, corresponds to

the other sulfur atoms of compound **1** and **2**, respectively. Comparison of the areas of these two doublet signals leads to an estimated S–C/S–Au ratio of $\gamma = 6.0 \pm 0.5$ which is in full agreement with the expected value (S–C/S–Au=6) for a single fixation of molecule **1** to the gold surface via formation of an S–Au bond. In the case of molecule **2**, the experimentally determined S–C/S–Au ratio of 3.7 ± 0.5 is relatively close to the theoretical value expected for a double fixation (S–C/S–Au=3). That the experimental ratio is higher than the theoretical one may be a result of the attenuation of the signal of the sulfur at the Au/monolayer interface by the overlying organic layer.

A single fixation of molecule **2** to the surface would leave one free S–H group. In fact, the S2p_{3/2,1/2} signals of a sulfur atom exclusively linked to carbon atoms (S–C) and that of a free alkanethiol (S–H) are very close in energy (for example, the energy of the S2p_{3/2,1/2} signal of S–H was reported to be 163.5/164.8 eV).^[39,40] Thus, in this energy range, the integration of the S2p_{3/2,1/2} signal corresponds to the different contributions of the sulfur atom exclusively linked to carbon atoms (S–C) and that of a free alkanethiol (S–H). A theoretical

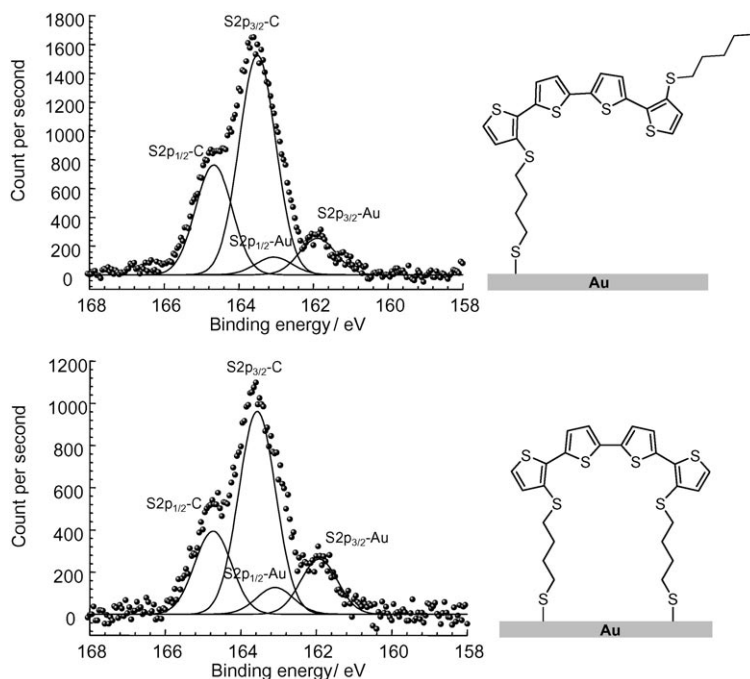


Figure 7. Curve-fitted high-resolution XPS spectra for the S2p region of molecules **1** (top) and **2** (bottom) adsorbed on gold.

tributions whose binding energies (*BE*) are reported in Table 2.

Comparison of the peak area of the S2s or S2p signals with that of the C1s signal allows us to estimate the experimental S/C ratio in the monolayer. For a monolayer of **1**, the S2p/C and S2s/C ratio of 0.29 for both is very close to the theoretical value of $S/C = \frac{7}{25} = 0.28$. For monolayer of **2**, the S2p/C and S2s/C ratios of 0.27 and 0.24 respectively deviate slightly from the theoretical value ($S/C = \frac{8}{24} = 0.33$) related to the chemical structure of **2**. The curve-fitted high-resolution XPS spectra for the S2p region of a monolayer of each of **1** and **2** show two doublets (Figure 7). Each doublet results from spin-orbit splitting of the S2p level and consists of a high-intensity S2p_{3/2} peak at lower energy and a low-intensity S2p_{1/2} peak at higher energy separated by 1.2 eV with an intensity ratio of 2:1.^[39] The value of the S2p_{3/2} peak at 161.9 eV for monolayers of **1** and **2** is in excellent agreement with the binding energy for bound alkanethiolate on gold (161.9–162.0 eV).^[25,34] Thus, peaks at 161.9 and 163.1 eV of the lower-energy doublet S2p_{3/2,1/2} of monolayers of **1** and **2** may be assigned to the thiol chemisorbed on the Au surface.^[25,39,40] The other doublet, S2p_{3/2,1/2}, at 163.5 and 164.7 eV for **1** and 163.6 and 164.7 eV for **2**, corresponds to

Table 2. XPS Binding energies (*BE*), full-width half-maximum (FWHM) and assignment of emission peaks measured from high-resolution XPS of monolayers of **1** and **2** adsorbed on gold.

| XPS signal | <i>BE</i> [eV] | FWHM [eV] | Corrected area ^[a] [A.U.] | Assignment |
|-----------------------|----------------|-----------|--------------------------------------|------------------------|
| <i>Monolayer of 1</i> | | | | |
| C1s | 284.5 | 1.38 | 20437 | C1s-C; C1s-S |
| S2s | 227.7 | 2.39 | 5927 | |
| S2p | | | 5914 | |
| band 1 | 163.5 | 1.15 | 3281 | S2p _{3/2} -C |
| band 2 | 164.7 | 1.15 | 1640 | S2p _{1/2} -C |
| band 3 | 161.9 | 1.15 | 547 | S2p _{3/2} -Au |
| band 4 | 163.1 | 1.15 | 274 | S2p _{1/2} -Au |
| <i>Monolayer of 2</i> | | | | |
| C1s | 284.6 | 1.30 | 17687 | C1s-C; C1s-S |
| S2s | 227.6 | 2.64 | 4785 | |
| S2p | | | 4279 | |
| band 1 | 163.6 | 1.15 | 2068 | S2p _{3/2} -C |
| band 2 | 164.7 | 1.15 | 1033 | S2p _{1/2} -C |
| band 3 | 161.9 | 1.15 | 563 | S2p _{3/2} -Au |
| band 4 | 163.1 | 1.15 | 281 | S2p _{1/2} -Au |

[a] The corrected areas were calculated empirically using the sensitivity factor (C1s 0.3; S2s 0.4; S2p 0.57). Each measured peak area was divided by this factor to obtain the corrected area. The total corrected areas of each peak are in italics. A.U.: arbitrary units.

cal (S–C+S–H)/S–Au ratio of 7:1 is expected if all molecules **2** are singly fixed. By using a simple linear combination of the two extreme states where all molecules **2** are either singly or doubly fixed on the surface, the experimental ratio $\gamma = (\text{S–C+S–H})/\text{S–Au}$ can be expressed as Equation (1), where α represents the fraction of doubly fixed molecules **2**.

$$\gamma = 3\alpha + 7(1-\alpha) \quad (1)$$

From our XPS result for a monolayer of **2** ($\gamma = 3.7 \pm 0.5$), we can deduce that around (83 ± 12)% of molecules **2** are chemisorbed on the surface through two S–Au fixation sites. Although it remains difficult to fit accurately the experimental curves of the XPS spectra of the S2p region with deconvoluted curves, and considering that the presence of different types of sulfur atoms in the monolayer makes the XPS analysis more complicated, our XPS study shows that most of the molecules **2** are doubly fixed on the surface, although it is likely that only a few singly fixed molecules of **2** subsist inside the monolayer.

Conclusion

We have described a selective and straightforward synthesis of oligothiophenes functionalized by one and two thiol groups using 2-cyanoethyl as a thiolate protecting group. Analysis of the electrochemical properties of these compounds by cyclic voltammetry has shown that electrooxidation of the quaterthiophene bearing two thiol groups leads to the electrodeposition of an electroactive poly(disulfide) on the electrode surface. Monolayers of **1** and **2** have been prepared by chemisorption on a gold surface. Cyclic voltammetric results have shown that the doubly functionalized quaterthiophene leads to faster and more reproducible formation of a monolayer than the singly substituted system. Characterization by CV, ellipsometry, and XPS of the monolayers obtained provided coherent results indicating that in the monolayers derived from the doubly functionalized oligomer, most of the conjugated molecules are doubly attached on the surface with a horizontal orientation of the conjugated system. This result, combined with the enhanced stability of the doubly fixed monolayers, opens interesting perspectives for the development of functional electroactive monolayers for application in sensors and molecular electronics. Work in this direction is now under way and will be reported in future publications.

Experimental Section

Syntheses

3-(2-Cyanoethylsulfanyl)-3''-pentylsulfanyl-2,2':5',2'':5'',2'''-quaterthiophene (4): Under a N₂ atmosphere, a solution of CsOH·H₂O (0.18 g, 1.1 mmol) in N₂-degassed MeOH (10 mL) was added dropwise to a solution of **3** (0.5 g, 1 mmol) in degassed DMF (50 mL). The reaction mixture

was stirred for 1 h at 20°C before addition of a solution of 1-iodopentane (0.79 g, 4 mmol) in degassed DMF (5 mL). After 4 h of additional stirring at 20°C and evaporation of the solvents, the residue was dissolved in CH₂Cl₂ and the organic phase was washed with water, dried over MgSO₄, and concentrated. Purification by chromatography on silica gel (CH₂Cl₂ as eluent) gave compound **4** as orange crystals (0.40 g, 77% yield). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.32$ (d, 1H, ³J = 3.9 Hz, H_{thio}), 7.30 (d, 1H, ³J = 3.9 Hz, H_{thio}), 7.23 (d, 1H, ³J = 5.3 Hz, H_{thio}), 7.19 (d, 1H, ³J = 5.3 Hz, H_{thio}), 7.16 (d, 1H, ³J = 3.9 Hz, H_{thio}), 7.15 (d, 1H, ³J = 3.9 Hz, H_{thio}), 7.08 (d, 1H, ³J = 5.2 Hz, H_{thio}), 7.04 (d, 1H, ³J = 5.2 Hz, H_{thio}), 3.04 (t, 2H, ³J = 7.3 Hz, CH₂–S), 2.87 (t, 2H, ³J = 7.4 Hz, CH₂–S), 2.56 (t, 2H, ³J = 7.3 Hz, CH₂–CN), 1.62 (m, 2H, ³J = 7.4 Hz), 1.40–1.34 (m, 2H), 1.32–1.27 (m, 2H), 0.87 ppm (t, 3H, ³J = 7.3 Hz, CH₃); ¹³C NMR (125 MHz, CDCl₃): $\delta = 139.6, 138.4, 137.0, 135.6, 135.1, 133.5, 132.2, 128.3, 127.7, 126.9, 123.8$ (2C), 123.5, 123.3, 117.8, 36.2, 31.7, 30.9, 29.3, 22.2, 18.5, 13.9 ppm; IR (KBr): $\tilde{\nu} = 2246$ cm⁻¹ (CN); UV/Vis (CH₂Cl₂): λ_{max} (log $\epsilon = 403$ nm (4.30); MALDI MS: 517 [M⁺] ($M = 517.02$ for C₂₄H₂₃NS₆); elemental analysis calcd (%) for C₂₄H₂₃NS₆: C 55.67, H 4.48; found: C 55.62, H 4.65.

S-4-Bromobutyl ethanethioate (5): Under a N₂ atmosphere, a solution of potassium thioacetate (5.28 g, 46.3 mmol) in EtOH was added dropwise to a solution of 1,4-dibromobutane (15 g, 70 mmol) in CH₂Cl₂ at 20°C. A white precipitate was formed and the reaction mixture was stirred for 15 h at 20°C. After evaporation of the solvents, the residue was dissolved in CH₂Cl₂ and the organic phase was washed with water, dried over MgSO₄, and concentrated. Purification by chromatography on silica gel (CH₂Cl₂/petroleum ether, 4:6, v/v) gave compound **5** as a slightly yellow oil (6.13 g, 63% yield). ¹H NMR (500 MHz, CDCl₃): $\delta = 3.40$ (t, 2H, ³J = 6.5 Hz, CH₂–Br), 2.89 (t, 2H, ³J = 7.2 Hz, CH₂–S), 2.32 (s, 3H, CH₃–CO), 1.92 (m, 2H, CH₂–CH₂Br), 1.73 (m, 2H); IR (film): $\tilde{\nu} = 1680$ cm⁻¹ (C=O).

3-(6-Oxo-5-thiaheptylsulfanyl)-3'''-pentylsulfanyl-2,2':5',2'':5'',2'''-quaterthiophene (6): Under a N₂ atmosphere, a solution of CsOH·H₂O (0.14 g, 0.84 mmol) in N₂-degassed MeOH (5 mL) was added dropwise to a solution of **4** (0.36 g, 0.70 mmol) in degassed DMF (25 mL). The reaction mixture was stirred for 1 h at 20°C before addition of a solution of **5** (0.61 g, 2.8 mmol) in degassed DMF (5 mL) and 4 h of additional stirring at 20°C. After evaporation of the solvents, the residue was dissolved in CH₂Cl₂ and the resulting organic phase was washed with water, dried over MgSO₄, and concentrated. Purification by chromatography on silica gel (CH₂Cl₂/petroleum ether, 1:1, v/v, as eluent) gave compound **6** as a yellow oil (0.36 g, 87% yield). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.28$ (2d, 2H, ³J = 3.8 Hz, H_{thio}), 7.18 (m, 2H, H_{thio}), 7.15 (m, 2H, H_{thio}), 7.04 (d, 1H, ³J = 5.3 Hz, H_{thio}), 7.03 (d, 1H, ³J = 5.3 Hz, H_{thio}), 2.85 (m, 6H, CH₂–S), 2.30 (s, 3H, CH₃–CO), 1.66 (m, 4H), 1.63 (m, 2H), 1.40 (m, 2H), 1.38 (m, 2H), 0.87 ppm (t, 3H, ³J = 7.3 Hz, CH₃); ¹³C NMR (125 MHz, CDCl₃): $\delta = 195.8, 137.5, 137.3, 136.4, 135.7, 134.7, 134.4, 132.5, 132.2, 127.9, 127.2, 126.9, 126.8, 123.5, 123.4, 123.2, 123.1, 36.1, 35.6, 30.8, 30.6, 29.2, 28.5, 28.4, 22.2, 14.0$ ppm; IR (film): $\tilde{\nu} = 1690$ cm⁻¹ (C=O); UV/Vis (CH₂Cl₂): $\lambda_{\text{max}} = 406$ nm; MALDI MS: 594 [M⁺] ($M = 594.03$ for C₂₇H₃₀OS₅).

3-(4-Mercaptobutylsulfanyl)-3'''-pentylsulfanyl-2,2':5',2'':5'',2'''-quaterthiophene (1): Under a N₂ atmosphere, a solution (1M) of DIBAL-H in CH₂Cl₂ (2.1 mL, 2.1 mmol) was added dropwise to a solution of compound **6** (0.31 g, 0.53 mmol) in anhydrous CH₂Cl₂ (15 mL) cooled to 0°C. The reaction mixture was stirred for 2 h at 0°C before addition of an aqueous solution of HCl (3M, 2 mL). After 0.5 h of additional stirring at 20°C, the reaction mixture was washed with water, dried over MgSO₄, and concentrated to dryness. Purification by chromatography on silica gel (CH₂Cl₂/petroleum ether, 1:1, v/v, as eluent) gave compound **1** as an orange oil (0.26 g, 90% yield). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.29$ (d, 2H, ³J = 3.9 Hz, H_{thio}), 7.19 (d, 1H, ³J = 5.3 Hz, H_{thio}), 7.18 (d, 1H, ³J = 5.2 Hz, H_{thio}), 7.15 (d, 1H, ³J = 3.8 Hz, H_{thio}), 7.15 (d, 1H, ³J = 3.8 Hz, H_{thio}), 7.04 (d, 1H, ³J = 5.2 Hz, H_{thio}), 7.03 (d, 1H, ³J = 5.2 Hz, H_{thio}), 2.86 (t, 4H, ³J = 7.2 Hz, CH₂–S), 2.50 (m, 2H, CH₂–SH), 1.70 (m, 4H), 1.63 (m, 2H), 1.38 (m, 2H), 1.28 (m, 3H, CH₂+SH), 0.87 ppm (t, 3H, CH₃); IR (KBr): $\tilde{\nu} = 2563$ cm⁻¹ (S–H); UV/Vis (CH₂Cl₂): $\lambda_{\text{max}} = 407$ nm (log $\epsilon = 4.68$); MALDI MS: 552 [M⁺] ($M = 552.02$ for C₂₅H₂₈S₅).

3,3''-Bis(6-oxo-5-thiaheptylsulfanyl)-2,2':5':2'':5'':2'''-quaterthiophene (**7**): Under a N₂ atmosphere, a solution of CsOH·H₂O (0.74 g, 4.40 mmol) in N₂-degassed MeOH (5 mL) was added dropwise to a solution of **3** (1 g, 2 mmol) in degassed DMF (25 mL). The reaction mixture was stirred for 1 h at 20 °C before addition of a solution of **5** (1.10 g, 5 mmol) in degassed DMF (5 mL) and 4 h of additional stirring at 20 °C. After evaporation of the solvents, the residue was dissolved in CH₂Cl₂ and the organic phase was washed with water, dried over MgSO₄ and concentrated to dryness. Purification by chromatography on silica gel (CH₂Cl₂ as eluent) gave compound **7** as an orange oil (0.90 g, 70% yield). ¹H NMR (500 MHz, CDCl₃): δ = 7.29 (d, 2H, ³J = 3.9 Hz, H_{thio}), 7.19 (d, 2H, ³J = 5.3 Hz, H_{thio}), 7.15 (d, 2H, ³J = 3.9 Hz, H_{thio}), 7.03 (d, 2H, ³J = 5.3 Hz, H_{thio}), 2.86 (t, 4H, ³J = 6.9 Hz, CH₂-S), 2.84 (t, 4H, ³J = 6.9 Hz, CH₂-S), 2.30 (s, 6H, CH₃-CO), 1.69–1.66 ppm (m, 8H, CH₂-CH₂); ¹³C NMR (125 MHz, CDCl₃): δ = 195.8, 137.5, 136.5, 134.5, 132.5, 127.2, 127.0, 123.5, 123.3, 35.6, 30.6, 28.53, 28.52, 28.48 ppm; IR (film): ν̄ = 1690 cm⁻¹ (C=O); UV/Vis (CH₂Cl₂): λ_{max} = 405 nm; MALDI MS: 654 [M⁺] (M = 654.00 for C₂₈H₃₀O₂S₈); elemental analysis calcd (%) for C₂₈H₃₀O₂S₈: C 51.34, H 4.62; found: C 51.25, H 4.71.

3,3''-Bis(4-mercaptobutylsulfanyl)-2,2':5':2'':5'':2'''-quaterthiophene (**2**): Under a N₂ atmosphere, a 1 M solution of DIBAL-H in CH₂Cl₂ (7 mL, 7 mmol) was added dropwise to a solution of compound **7** (0.57 g, 0.87 mmol) in anhydrous CH₂Cl₂ (15 mL) cooled to 0 °C. The reaction mixture was stirred for 2 h at 0 °C before addition of an aqueous solution of HCl (3 M, 3 mL). After 0.5 h of additional stirring at 20 °C, the reaction mixture was washed with water, dried over MgSO₄, and concentrated to dryness. Purification by chromatography on silica gel (CH₂Cl₂/petroleum ether, 1:1, v/v, as eluent) gave compound **2** as an orange oil (0.40 g, 80% yield). ¹H NMR (500 MHz, CDCl₃): δ = 7.29 (d, 2H, ³J = 3.9 Hz, H_{thio}), 7.19 (d, 2H, ³J = 5.3 Hz, H_{thio}), 7.15 (d, 2H, ³J = 3.9 Hz, H_{thio}), 7.04 (d, 2H, ³J = 5.3 Hz, H_{thio}), 2.86 (t, 4H, ³J = 6.6 Hz, CH₂-S), 2.50 (m, 4H, CH₂-SH), 1.75–1.70 (m, 8H, CH₂-CH₂), 1.30 ppm (t, 2H, ³J = 7.9 Hz, SH); ¹³C NMR (125 MHz, CDCl₃): δ = 137.5, 136.5, 134.5, 132.5, 127.3, 127.0, 123.5, 123.3, 35.6, 32.8, 28.1, 24.2 ppm; UV/Vis (CH₂Cl₂): λ_{max} = 408 nm; MALDI MS: 570 [M⁺] (M = 569.98 for C₂₄H₂₆S₈).

Disulfide of 3-(4-mercaptobutylsulfanyl)-3''-pentylsulfanyl-2,2':5':2'':5'':2'''-quaterthiophene (**8**): A suspension of ferric chloride (40 mg, 0.25 mmol) in anhydrous CH₂Cl₂ (3 mL) was added slowly to a solution of monothiol **1** (70 mg, 0.13 mmol) in anhydrous CH₂Cl₂ (10 mL). The reaction mixture was stirred overnight at 20 °C. After addition of water and extraction with CH₂Cl₂, the organic phase was concentrated. The residue was purified by chromatography on silica gel (CH₂Cl₂/petroleum ether, 3:7, v/v, as eluent) to give disulfide **8** as a green oil (23 mg, 33% yield); ¹H NMR (500 MHz, CDCl₃): δ = 7.29 (d, 4H, ³J = 4.0 Hz, H_{thio}), 7.17 (d, 2H, ³J = 5.4 Hz, H_{thio}), 7.16 (d, 2H, ³J = 5.8 Hz, H_{thio}), 7.14 (d, 2H, ³J = 4.0 Hz, H_{thio}), 7.13 (d, 2H, ³J = 4.0 Hz, H_{thio}), 7.03 (d, 2H, ³J = 5.6 Hz, H_{thio}), 7.02 (d, 2H, ³J = 5.6 Hz, H_{thio}), 2.86 (t, 4H, ³J = 7.1 Hz, CH₂-S), 2.84 (t, 4H, ³J = 7.1 Hz, CH₂-S), 2.60 (t, 4H, ³J = 7.1 Hz, CH₂-S-S), 1.76 (m, 4H), 1.68 (m, 4H), 1.64 (m, 4H), 1.38 (m, 4H), 1.28 (m, 4H), 0.87 ppm (t, 6H, ³J = 7.1 Hz, CH₃); UV/Vis (CH₂Cl₂): λ_{max} = 407 nm (log ε = 4.78); MALDI MS: 1102 [M⁺]; 551 [(M/2)⁺] (M = 1102.03 for C₃₀H₃₄S₁₄).

Cyclic voltammetry and preparation of gold electrodes: Electrochemical experiments were carried out by using a PAR 273 potentiostat–galvanostat in a three-electrode single-compartment cell equipped with a platinum or gold disk, diameter 2 mm, and modified gold beads as working electrodes, a platinum wire counter electrode, and a silver wire as a pseudo-reference electrode. The ferricinium/ferrocenium couple Fc⁺/Fc was used as an internal reference (E°(Fc⁺/Fc) = 0.405 V/SCE in 0.1 M Bu₄NPF₆/CH₃CN or CH₂Cl₂). Potentials were then expressed relative to a saturated calomel reference electrode (SCE).

Gold monolayers of mono- and dithiols **1** and **2** have been obtained by using different substrates: gold bead electrodes for cyclic voltammetry experiments and evaporated gold on silicon for structural analysis. Substrates were cleaned thoroughly by previously reported methods.^[41,42] The gold beads were prepared according to the literature.^[41] They were subjected to repetitive potential scans between 0 and 1.6 V/SCE in an aqueous H₂SO₄ solution (0.5 M) until a sharp reduction peak was formed associated with the reduction of oxidized gold species to gold. The gold beads

were then rinsed successively with deionized water, acetonitrile, and dichloromethane before immersion in the freshly prepared thiol solution. The geometric area of the working gold bead electrodes was estimated from the slope of the linear plots of the CV cathodic peak current intensity versus the square root of scan rate, for the diffusion-controlled reduction of Fe(CN)₆³⁻ (10⁻² M in 0.50 M NaCl at 25 °C). Comparative experiments with gold disk electrodes of known surface area (2 mm diameter from Radiometer Analytical SA) led to typical surfaces ranging from 0.02 to 0.04 cm² for gold bead electrodes.

Ellipsometry, contact angle measurements, and XPS analyses were performed on SAMs prepared from gold films 200 nm thick, evaporated onto silicon wafers covered by a titanium or chromium sublayer (10 nm) deposited under ultrahigh vacuum. After gold deposition, annealing,^[43] and cleaning in an 37% HCl/65% HNO₃/deionized water (3:1:16, v/v/v) mixture for 5 min led to atomically flat gold terraces. Silicon and gold were purchased from Siltronix and Goodfellow respectively.

Contact angle measurements: Contact angles were measured, in a clean room (class about 1000) at a well controlled relative humidity (40%) and temperature (20 °C), with a remote-computer controlled goniometer system (Digidrop; GBX, France). A drop (in the range 1–10 μL) of deionized water (18 mΩ cm⁻¹) was deposited on the surface and the projected image was acquired and stored by the remote computer. Contact angles were then extracted by contrast contour image analysis software. These angles were determined around 2 s after application of the drop. The precision of these measurements was ± 2°.

Spectroscopic ellipsometry: Spectroscopic ellipsometry data in the visible range were obtained by using a UVISEL Jobin Yvon Horiba Spectroscopic Ellipsometer equipped with DeltaPsi 2 data analysis software. The system acquired a spectrum ranging from 2 to 4.5 eV (corresponding to 300–750 nm) with 0.05 eV (or 7.5 nm) intervals (angle of incidence 70°; the compensator was set at 45.0°). Data were fitted by regression analysis to a film-on-substrate model as described by their thickness and their complex refractive indices. Two spectra, before and after monolayer deposition, were obtained to determine the thickness. In the software, we used a two-layer model: layer 1 is gold, layer 2 the organic monolayer. To determine the monolayer thickness, we used the spectrum measured on the sample before the monolayer deposition for layer 1, and we fixed the refractive index at 1.50 for layer 2. Usual values in the literature are in the range 1.45–1.50;^[44] a change from 1.50 to 1.55 would result in less than 1 Å error for a thickness less than 30 Å. To determine the thickness, the software compared the measured data with the simulated data. The estimated accuracy of the SAM thickness measurements was ± 2 Å.

X-ray photoelectron spectroscopy: The chemical composition of the SAMs was analyzed and any contaminant that had not been removed was detected by XPS by using a Physical Electronics 5600 spectrometer fitted in a UHV chamber with a residual pressure of 2 × 10⁻¹⁰ torr. High-resolution spectra were obtained with a monochromatic Al_{Kα} X-ray source (hν = 1486.6 eV), a detection angle of 45° referenced to the sample surface, an analyzer entrance slit width of 400 μm and an analyzer pass energy of 12 eV. In these conditions, the overall resolution measured from the FWHM of the Ag 3d_{5/2} line was 0.55 eV. Semiquantitative analysis was completed after standard background subtraction according to Shirley's method.^[45] Peaks were decomposed by using Voigt functions and a least-squares minimization procedure and by keeping constant the Gaussian and Lorentzian broadenings for each component of a given peak.

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- [1] a) L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* **1996**, *271*, 1705–1707; b) J. M. Tour, *Chem. Rev.* **1996**, *96*, 537–553; c) M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **1997**, *278*, 252–254; d) J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791–804; e) Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price Jr., A. M. Rawlett, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* **2001**, *292*, 2303–2307; f) D. K. James, J. M. Tour, *Chem. Mater.* **2004**, *16*, 4423–4435.
- [2] For recent reviews see: a) R. L. Carroll, C. B. Gorman, *Angew. Chem.* **2002**, *114*, 4556–4579; *Angew. Chem. Int. Ed.* **2002**, *41*, 4378–4400; b) S. M. Lindsay, M. A. Ratner, *Adv. Mater.* **2007**, *19*, 23–31; c) N. Weibel, S. Grunder, M. Mayor, *Org. Biomol. Chem.* **2007**, *5*, 2343–2353.
- [3] a) D. Hirayama, T. Yamashiro, K. Takimiya, Y. Aso, T. Otsubo, H. Norieda, H. Imahori, Y. Sakata, *Chem. Lett.* **2000**, 570–571; b) S.-G. Liu, C. Martineau, J.-M. Raimundo, J. Roncali, L. Echegoyen, *Chem. Commun.* **2001**, 913–914; c) D. Hirayama, K. Takimiya, Y. Aso, T. Otsubo, T. Hasobe, H. Yamada, H. Imahori, S. Fukuzumi, Y. Sakata, *J. Am. Chem. Soc.* **2002**, *124*, 532–533; d) K.-S. Kim, M.-S. Kang, H. Ma, A. K.-Y. Jen, *Chem. Mater.* **2004**, *16*, 5058–5062; e) C.-H. Huang, N. D. McClenaghan, A. Kuhn, G. Bravic, D. M. Bassani, *Tetrahedron* **2006**, *62*, 2050–2059.
- [4] a) H. Imahori, H. Norieda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 100–110; b) T. Konishi, A. Ikeda, S. Shinkai, *Tetrahedron* **2005**, *61*, 4881–4889; c) Y.-J. Cho, T. K. Ahn, H. Song, K. S. Kim, C. Y. Lee, W. S. Seo, K. Lee, S. K. Kim, J. D. Kim, T. Park, *J. Am. Chem. Soc.* **2005**, *127*, 2380–2381; d) S. Saha, E. Johansson, A. H. Flood, H.-R. Tseng, J. I. Zink, J. F. Stoddart, *Chem. Eur. J.* **2005**, *11*, 6846–6858; e) Y. Shirai, L. Cheng, B. Chen, J. M. Tour, *J. Am. Chem. Soc.* **2006**, *128*, 13479–13489.
- [5] For a review on SAMs based on C₆₀ see: D. Bonifazi, O. Enger, F. Diederich, *Chem. Soc. Rev.* **2007**, *36*, 390–414.
- [6] a) L. M. Goldenberg, M. R. Bryce, M. C. Petty, *J. Mater. Chem.* **1999**, *9*, 1957–1974; b) S. Flink, F. C. J. M. van Veggel, D. Reinholdt, *Adv. Mater.* **2000**, *12*, 1315–1328; c) S. Zhang, C. M. Cardona, L. Echegoyen, *Chem. Commun.* **2006**, 4461–4473.
- [7] For exhaustive reviews see: a) A. Ulman, *Chem. Rev.* **1996**, *96*, 1533–1554; b) F. Schreiber, *Prog. Surf. Sci.* **2000**, *65*, 151–256; c) F. Schreiber, *J. Phys. Condens. Matter* **2004**, *16*, R881–R900; d) R. K. Smith, P. A. Lewis, P. S. Weiss, *Prog. Surf. Sci.* **2004**, *75*, 1–68; e) J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103–1169.
- [8] a) R. M. Metzger, B. Chen, U. Höpfner, M. V. Lakshminantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hugues, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer, G. J. Ashwell, *J. Am. Chem. Soc.* **1997**, *119*, 10455–10466; b) R. M. Metzger, *Chem. Rev.* **2003**, *103*, 3803–3834.
- [9] For examples see: a) M. L. Chabinye, X. Chen, R. E. Holmlin, H. Jacobs, H. Skulason, C. D. Frisbie, V. Mujica, M. A. Ratner, M. A. Rampi, G. M. Whitesides, *J. Am. Chem. Soc.* **2002**, *124*, 11730–11736; b) G. J. Ashwell, W. D. Tyrrell, A. J. Whittam, *J. Am. Chem. Soc.* **2004**, *126*, 7102–7110; c) P. Jiang, G. M. Morales, W. You, L. Yu, *Angew. Chem.* **2004**, *116*, 4571–4575; *Angew. Chem. Int. Ed.* **2004**, *43*, 4471–4475; d) S. Lenfant, D. Guérin, F. Tran Van, C. Cheverrot, S. Palacin, J.-P. Bourgoïn, O. Bouloussa, F. Rondelez, D. Vuillaume, *J. Phys. Chem. B* **2006**, *110*, 13947–13958; e) G. J. Ashwell, W. D. Tyrrell, B. Urasinska, C. Wang, M. R. Bryce, *Chem. Commun.* **2006**, 1640–1642; f) S. Lenfant, C. Krzeminski, C. Delerue, G. Allan, D. Vuillaume, *Nano Lett.* **2003**, *3*, 741–746.
- [10] M. Mottaghi, P. Lang, F. Rodriguez, A. Rumyantseva, A. Yassar, G. Horowitz, S. Lenfant, D. Tondelier, D. Vuillaume, *Adv. Funct. Mater.* **2007**, *17*, 597–604.
- [11] a) A. Berlin, G. Zotti, G. Schiavon, S. Zecchin, *J. Am. Chem. Soc.* **1998**, *120*, 13453–13460; b) A. Berlin, G. Zotti, *Macromol. Rapid Commun.* **2000**, *21*, 301–318.
- [12] a) B. Liedberg, Z. Yang, I. Engquist, M. Wirde, U. Gelius, G. Götz, P. Bäuerle, R.-M. Rummel, Ch. Ziegler, W. Göpel, *J. Phys. Chem. B* **1997**, *101*, 5951–5962; b) R. Michalitsch, A. El-Kasmi, P. Lang, A. Yassar, F. Garnier, *J. Electroanal. Chem.* **1998**, *457*, 129–139; c) E. Mishina, Y. Miyakita, Q.-K. Yu, S. Nakabayashi, H. Sakaguchi, *J. Chem. Phys.* **2002**, *117*, 4016–4021; d) C. Nogués, P. Lang, M. Rei Vilar, B. Desbat, T. Buffeteau, A. El-Kasmi, F. Garnier, *Colloids and Surfaces A* **2002**, *198–200*, 577–591; e) B. de Boer, H. Meng, D. F. Perepichka, J. Zheng, M. M. Franck, Y. J. Chabal, Z. Bao, *Langmuir* **2003**, *19*, 4272–4284; f) M. Rei Vilar, P. Lang, G. Horowitz, C. Nogués, Y. Jugnet, O. Pellegrino, A. M. Botelho do Rego, *Langmuir* **2003**, *19*, 2649–2657; g) G. Zotti, S. Zecchin, B. Vercelli, A. Berlin, S. Grimaldi, L. Groenendaal, R. Bertonecello, M. Natali, *Chem. Mater.* **2005**, *17*, 3681–3694.
- [13] a) C. Kergueris, J.-P. Bourgoïn, S. Palacin, D. Esteve, C. Urbina, M. Magoga, C. Joachim, *Phys. Rev. B* **1999**, *59*, 12505–12513; b) N. B. Zhitenev, H. Meng, Z. Bao, *Phys. Rev. Lett.* **2002**, *88*, 226801; c) N. B. Zhitenev, A. Erbe, Z. Bao, *Phys. Rev. Lett.* **2004**, *92*, 186805/1–4; d) W. Huang, G. Masuda, S. Maeda, H. Tanaka, T. Ogawa, *Chem. Eur. J.* **2006**, *12*, 607–619; e) S. Yasuda, S. Yoshida, J. Sasaki, Y. Okutsu, T. Nakamura, A. Taninaka, O. Takeuchi, H. Shigekawa, *J. Am. Chem. Soc.* **2006**, *128*, 7746–7747.
- [14] a) N. Katsonis, T. Kudernac, M. Walko, S. J. van der Molen, B. J. van Wees, B. L. Feringa, *Adv. Mater.* **2006**, *18*, 1397–1400; b) R. Baron, A. Onopriyenko, E. Katz, O. Lioubashevski, I. Willner, S. Wang, H. Tian, *Chem. Commun.* **2006**, 2147–2149; c) J. Areephong W. R. Browne, N. Katsonis, B. L. Feringa, *Chem. Commun.* **2006**, 3930–3932; d) M. Taniguchi, Y. Nojima, K. Yokota, J. Terao, K. Sato, N. Kambe, T. Kawai, *J. Am. Chem. Soc.* **2006**, *128*, 15062–15063; e) A. Staykov, D. Nozaki, K. Yoshizawa, *J. Phys. Chem. C* **2007**, *111*, 3517–3521.
- [15] L. Sanguinet, O. Alévêque, P. Blanchard, M. Dias, E. Levillain, D. Rondeau, *J. Mass Spectrom.* **2006**, *41*, 830–833.
- [16] a) L. Zhu, H. Tang, Y. Harima, K. Yamashita, D. Hirayama, Y. Aso, T. Otsubo, *Chem. Commun.* **2001**, 1830–1831; b) L. Zhu, H. Tang, Y. Harima, K. Yamashita, D. Hirayama, Y. Aso, T. Otsubo, *J. Mater. Chem.* **2002**, *12*, 2250–2254.
- [17] J. Chen, I. Ratera, A. Murphy, D. F. Ogletree, J. M. J. Fréchet, M. Salmeron, *Surf. Sci.* **2006**, *600*, 4008–4012.
- [18] D. Bong, I. Tam, R. Breslow, *J. Am. Chem. Soc.* **2004**, *126*, 11796–11797.
- [19] a) S.-C. Ng, P. Miao, Z. Chen, H. S. O. Chan, *Adv. Mater.* **1998**, *10*, 782–786; b) Z. Mekhalif, A. Larzarescu, L. Hevesi, J.-J. Pireaux, J. Delhalle, *J. Mater. Chem.* **1998**, *8*, 545–551; c) S. Inaoka, D. M. Collard, *Langmuir* **1999**, *15*, 3752–3758; d) R. Michalitsch, C. Nogués, A. Najari, A. El Kasmi, A. Yassar, P. Lang, F. Garnier, *Synth. Met.* **1999**, *101*, 5–6; e) U. Harm, R. Bürgler, W. Fürbeth, K.-M. Mangold, K. Jüttner, *Macromol. Symp.* **2002**, *187*, 65–75.
- [20] For molecular rotors mounted on an Au(111) surface see: X. Zheng, M. E. Mulcahy, D. Horinek, F. Galeotti, T. F. Magnera, J. Michl, *J. Am. Chem. Soc.* **2004**, *126*, 4540–4542.
- [21] T. Lu, L. Zhang, G. W. Gokel, A. E. Kaifer, *J. Am. Chem. Soc.* **1993**, *115*, 2542–2543.
- [22] L. Raehm, J.-M. Kern, J.-P. Sauvage, C. Hamann, S. Palacin, J.-P. Bourgoïn, *Chem. Eur. J.* **2002**, *8*, 2153–2162.
- [23] I. Yildiz, J. Mukherjee, M. Tomasulo, F. M. Raymo, *Adv. Funct. Mater.* **2007**, *17*, 814–820.
- [24] K. Bandyopadhyay, L. Shu, H. Liu, L. Echegoyen, *Langmuir* **2000**, *16*, 2706–2714.
- [25] H. Rieley, G. K. Kendall, F. W. Zemical, T. L. Smith, S. Yang, *Langmuir* **1998**, *14*, 5147–5153.
- [26] a) K. Kobayashi, J. Umamura, T. Horiuchi, H. Yamada, K. Matsushige, *Jpn. J. Appl. Phys.* **1998**, *37*, L297–L299; b) T. Y. B. Leung, M. C. Gerstenberg, D. J. Lavrich, G. Scoles, F. Schreiber, G. E. Poirier, *Langmuir* **2000**, *16*, 549–561; c) H. B. Akkerman, A. J. Krone-meijer, P. A. van Hal, D. M. de Leeuw, P. W. M. Blom, B. de Boer, *Small* **2008**, *4*, 100–104.
- [27] N. Svenstrup, K. M. Rasmussen, T. K. Hanssen, J. Becher, *Synthesis* **1994**, 809–812.

- [28] P. Blanchard, B. Joussetme, P. Frère, J. Roncali, *J. Org. Chem.* **2002**, 67, 3961–3964.
- [29] a) P. A. van Hal, E. H. A. Beckers, S. C. J. Meskers, R. A. J. Janssen, B. Joussetme, P. Blanchard, J. Roncali, *Chem. Eur. J.* **2002**, 8, 5415–5429; b) B. Joussetme, P. Blanchard, E. Levillain, J. Delaunay, M. Allain, P. Richomme, D. Rondeau, N. Gallego-Planas, J. Roncali, *J. Am. Chem. Soc.* **2003**, 125, 1363–1370; c) B. Joussetme, P. Blanchard, N. Gallego-Planas, J. Delaunay, M. Allain, P. Richomme, E. Levillain, J. Roncali, *J. Am. Chem. Soc.* **2003**, 125, 2888–2889; d) B. Joussetme, P. Blanchard, E. Levillain, J. Roncali, *Macromolecules* **2003**, 36, 3020–3025; e) B. Joussetme, P. Blanchard, N. Gallego-Planas, J. Delaunay, M. Allain, P. Richomme, E. Levillain, J. Roncali, *Chem. Eur. J.* **2003**, 9, 5297–5306; f) B. Joussetme, P. Blanchard, M. Oçafrain, M. Allain, E. Levillain, J. Roncali, *J. Mater. Chem.* **2004**, 14, 421–427; g) B. Joussetme, P. Blanchard, M. Dias, E. Levillain, J. Roncali, *J. Phys. Chem. A* **2006**, 110, 3488–3494.
- [30] A. Smie, A. Synowczyk, J. Heinze, R. Alle, P. Tschunky, G. Götz, P. Bäuerle, *J. Electroanal. Chem.* **1998**, 452, 87–95.
- [31] S. Sortino, S. Conoci, I. Yildiz, M. Tomasulo, F. M. Raymo, *J. Mater. Chem.* **2006**, 16, 3171–3173.
- [32] H. O. Finklea, *Electroanal. Chem.* **1996**, 19, 109–335.
- [33] a) C. A. Widrig, C. Chung, M. D. Porter, *J. Electroanal. Chem.* **1991**, 310, 335–359; b) J. T. Sullivan, K. E. Harrison, J. P. Mizzell III, S. M. Kilbey II, *Langmuir* **2000**, 16, 9797–9803; c) H. Ahn, M. Kim, D. J. Sandman, J. E. Whitten, *Langmuir* **2003**, 19, 5303–5310.
- [34] P. E. Laibinis, G. Whitesides, D. L. Allara, Y.-T. Tao, A. N. Parikh, R. G. Nuzzo, *J. Am. Chem. Soc.* **1991**, 113, 7152–7167.
- [35] G. E. Poirier, *Chem. Rev.* **1997**, 97, 1117–1127.
- [36] C. J. Yu, H. Wang, Y. Wan, H. Yowanto, J. C. Kim, L. H. Donilton, C. Tao, M. Strong, Y. Chong, *J. Org. Chem.* **2001**, 66, 2937–2942.
- [37] H. Sellers, A. Ulman, Y. Shnidman, J. E. Eilers, *J. Am. Chem. Soc.* **1993**, 115, 9389–9401.
- [38] a) Y. Fadeev, J. McCarthy, *Langmuir* **2000**, 16, 7268–7274; b) R. Etchenique, V. L. Brudny, *Langmuir* **2000**, 16, 5064–5071; c) H. H. J. Persson, W. R. Caseri, U. W. Suter, *Langmuir* **2001**, 17, 3643–3650; d) P. E. Laibinis, G. M. Whitesides, *J. Am. Chem. Soc.* **1992**, 114, 1990–1995.
- [39] A. L. Vance, T. M. Willey, A. J. Nelson, T. van Buuren, C. Bostedt, L. J. Terminello, J. A. Fox, *Langmuir* **2002**, 18, 8123–8128.
- [40] D. G. Castner, K. Hinds, D. W. Grainger, *Langmuir* **1996**, 12, 5083–5086.
- [41] S. Liu, H. Liu, K. Bandyopadhyay, Z. Gao, L. Echegoyen, *J. Org. Chem.* **2000**, 65, 3292–3298.
- [42] D. Stamou, D. Gourdon, M. Liley, N. A. Burnham, A. Kulik, H. Vogel, C. Duschl, *Langmuir* **1997**, 13, 2425–2427.
- [43] M. D. Mowery, H. Menzel, M. Cai, C. E. Evans, *Langmuir* **1998**, 14, 5594–5602.
- [44] a) A. N. Parikh, D. L. Allara, I. Ben Azouz, F. Rondelez, *J. Phys. Chem.* **1994**, 98, 7577–7577; b) A. Ulman, *An Introduction to Ultrathin Organic Films : From Langmuir–Blodgett to Self-Assembly*, Academic Press, San Diego, **1991**.
- [45] D. A. Shirley, *Phys. Rev. B* **1972**, 5, 4709–4714.

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