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ARTICLE TYPE

Spontaneous assembly of silylethane-thiol derivatives on Au(111): a chemically robust thiol protecting group as precursor for the direct formation of aromatic gold thiolate monolayers

Claude Niebel,^a François Calard,^a Thibaut Jarrosson,^a Jean-Pierre Lère-Porte, Tony Breton^{*b} and Françoise Serein-Spirau^{*a}

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Self-assembled monolayers (SAMs) on gold were obtained from the direct absorption of a fully conjugated phenylenethienylene derivative (4) presenting robust silylethane-thiol protecting groups as anchoring agents. The thiol deprotection and SAM formation have been evidenced by quartz crystal microbalance measurements (QCM) and X-ray photoelectron spectroscopy (XPS), and have been compared to the SAM obtained from its thioacetate analog (5). The chemically robust silylethane-thiol protecting group appeared as a surprisingly effective anchoring agent for the elaboration of aromatic SAMs on Au(111), suitable for a subsequent post-functionalization.

The formation of organic Self-Assembled Monolayers (SAMs) on a substrate has been extensively studied in the last decade due to its major interest in surface science.^{1,2,3,4} Among the variety of organic self-assemblies, SAMs formed by organic thiols on gold are of particular interest with a potential application ranging from nanopatterning to molecular electronics.^{2,3,5} Thiols are known to form well-ordered and reproducible SAMs, while tolerating a wide variety of functional groups.^{2,3} Thiol precursors can however be easily oxidized into disulfide and other oxidized species during storage or SAMs formation,⁶ hence leading to SAMs of different quality.⁷ To overcome this problem, different thiol protecting groups have been used as alternative thiol-like anchoring agents. Organic thiosulfates, for instance, have been described to generate chemisorbed thiolate SAMs on gold, but they evidenced a low surface coverage and many defects compared to their analog thiol SAMs.⁸ On the contrary, thioacetate group is well known to allow the formation of chemisorbed and densely packed gold thiolate SAMs. Indeed, thioacetate is by far the most employed thiol protecting group to form gold thiolate SAMs, whether by direct chemisorption on gold surface,^{6a,7,9} or by an *in situ* acidic or base-mediated deprotection.^{6,10,11} Despite its extensive use as thiolate SAMs precursor, the thioacetate function still presents a major drawback lying in its chemical sensitivity to moisture and nucleophiles. For this reason, the thioacetate group is usually introduced at the end of a SAMs precursor synthesis, which limits the scope of its use. In addition, thiocyanate have also been used as an efficient alternative precursor for the direct chemisorption of alkyl or

aromatic thiols on Au(111).¹² Thiocyanate function exhibits many advantages such as its chemical stability to air and moisture. As far as π -conjugated systems are concerned, the thiocyanate function may induce a loss of chemoselectivity during palladium(0) mediated cross-couplings, and remains reactive towards nucleophiles. By analogy to the thioacetate group, the thiocyanate function is added to an aromatic core as the last step,^{12a,12e} which again drastically restricts its use to less sophisticated π -conjugated SAMs precursors. More recently, gold thiolate aromatic SAMs have also been made from sulfenyl chloride derivatives.¹³ Nevertheless, sulfenyl chlorides reactivity versus nucleophiles or palladium (0) cross-couplings remains similar to thiocyanate one. Conversely, silylethane function represents another relevant thiol protecting group: up to now it is mostly known for its chemical robustness, and is therefore widely used by organic chemists for the synthesis of functionalized π -conjugated systems.^{14,15} Indeed, its capability as an anchoring agent for the elaboration of aromatic SAMs remains poorly documented. Aromatic silylethane thiol derivatives were once used to generate potential assisted assemblies on a premodified silver adlayer gold surface.¹⁶ More recently, Yu¹⁷ and Tao¹⁸ used silylethane thiols as anchoring precursors and chemically deprotected the silicon entity before the chemisorption of the conjugated segments on gold.

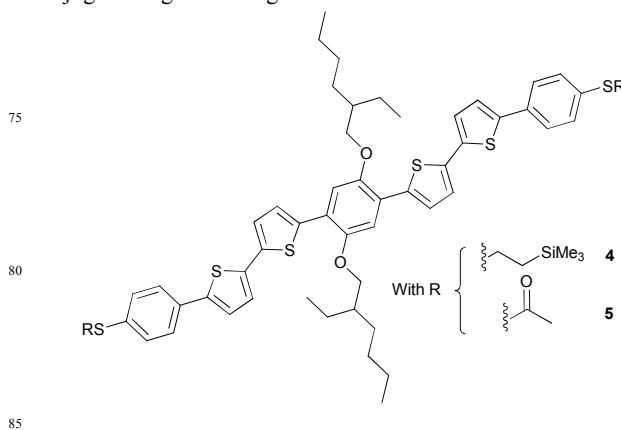
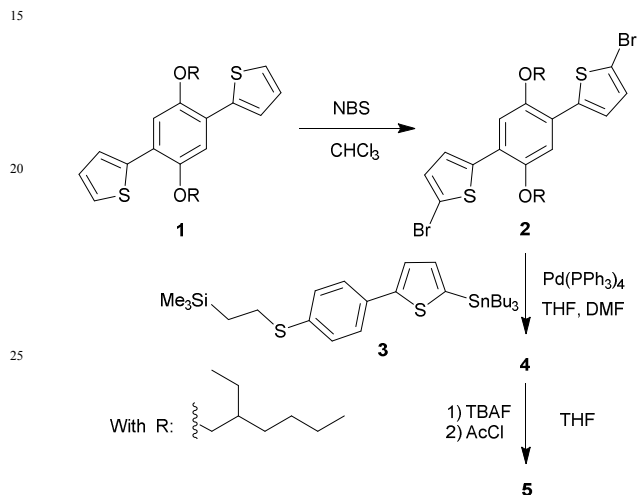


Fig.1 Structure of the studied phenylenethienylene derivatives 4 and 5

Moreover, Kaifer and Ren have also observed the formation of

gold nanoparticles dimers and chains, linked by metallayne spacers presenting the initial silylethane thiol function.¹⁹ However, the usefulness of this chemically robust thiol protecting group, as an efficient anchoring agent for the direct self-assembly of aromatic monolayers on gold, without prior deprotection, needs to be evidenced.

Herein we report on the synthesis and adsorption of two π -conjugated SAMs precursors (**4** and **5**) bearing respectively silylethane thiol and thioacetate functions as anchoring groups. The core of these molecules is made up of a 1,4-bis(2-thienyl)-2,5-dialkoxyphenylene unit which is a very promising group for organic electronics due to its extended conjugation.²⁰ The SAMs obtained by the direct chemisorption of the two fully conjugated precursors on gold surfaces were compared using QCM and XPS.



Scheme 1 Synthesis of the phenylenethienylene derivatives **4** and **5**

The phenylenethienylene derivative **4** was efficiently prepared in only two steps from the corresponding phenylenethienylene moiety **1**^{21,22} (Scheme 1). The synthesis started with the dibromination of **1**, affording **2** in a good yield. **4** was then obtained by a Stille palladium (0) cross coupling between **2** and the stannylated anchoring precursor **3** (see the Supporting Information). Silylethane-thiol protecting groups of **4** could then be converted in more conventional thioacetate anchoring agents by a fluoride-mediated deprotection, directly followed by an acylation using acetyl chloride. The dithioacetate **5** was thus obtained in 67% yield starting from **4**.

Self-assembled monolayers on gold were prepared from millimolar solutions of **4** and **5** in CH_2Cl_2 . Quartz crystal microbalance appears to be a powerful method to quantify the surface coverage of the monolayers and to compare the deposition kinetics of the two phenylenethienylene derivatives. Figure 2 shows the frequency-time curves recorded on gold coated quartz during the adsorption of **4** and **5**.

As previously reported for SAMs formation,²³ the deposition process is characterized by a fast mass increase at the initial stage, followed by a slower increase before stabilization. Initial deposition rates were recorded and valued to 8.8×10^{-10} and $9.3 \times 10^{-10} \text{ mol.s}^{-1}$ for **4** and **5** respectively. Those very close values indicate a similar adsorption rate of the phenylenethienylene moieties regardless of the anchoring group. In contrast, the steady state values reached after stabilization are

not the same. Deposited masses of 215 ng.cm^{-2} for **4** and 310 ng.cm^{-2} for **5** were measured, corresponding to surface coverage of 2.0×10^{-10} and $3.2 \times 10^{-10} \text{ mol.cm}^{-2}$ respectively. Those values are close to those previously reported for SAMs prepared from unsubstituted conjugated structures such as tetrathiafulvalene²⁴ or bithiophene.²⁵ Such a relatively high density for **4** and **5** SAMs was unexpected because of the steric hindrance involved by the bulky lateral alkyl chains (i.e. 2-ethylhexyloxy groups). The significant difference of surface coverage observed between SAMs prepared from **4** and **5** remains difficult to explain at this stage and will be discussed from XPS results.

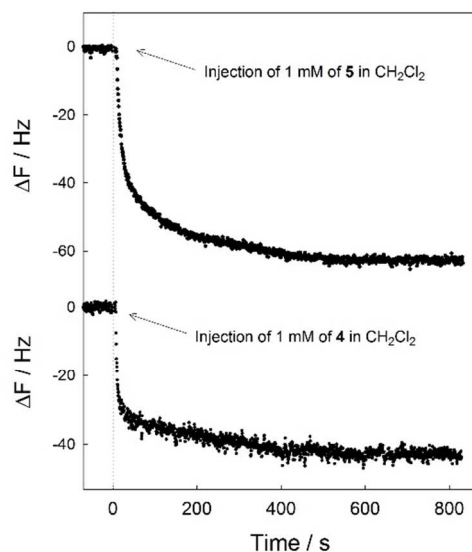


Fig. 2 Frequency-time curves recorded on a gold coated quartz during the adsorption of **4** and **5** dissolved in CH_2Cl_2 .

Both SAMs were analysed by X-ray photoelectron spectroscopy to obtain informations on the layer atomic composition. Au 4f, C 1s, S 2p and Si 2p signals were examined and the relative concentration of each element was determined by integration of the signals. The results are depicted in Table 1.

Table 1 Calculated atomic ratios of the elements of the SAM from integration of the XPS core level spectra signals

	Au ^a	S ^a	C ^a	Si ^a	S _{Au} ^b	S _{org} /S _{Au} ^b
SAM of 4	46.2	3.3	44.6	0.64	0.48	5.9
SAM of 5	41.1	4.9	52.6	-	0.57	7.6

^aHigh resolution spectra were carried out with a 0.1 eV step size and a 20 eV pass energy. S_{Au}^b corresponds to chemisorbed sulfur atoms and S_{org} corresponds to unbonded sulfur atoms (see the text). O 1s integrations are not included.

Figure 3 presents the sulfur core level spectra recorded for the SAMs obtained from **4** and **5**. Two main series were identified at 162.1/163.3 eV and 163.7/164.9 eV, corresponding to two different sulfur species. The first series is consistent with sulfur atoms bounded to the surface as thiolate species (S_{Au}).²⁶ The second one is commonly assigned to unbounded S state (S_{org}).²⁷

Considering the Au/S_{Au} ratios, it can be calculated that SAM

prepared from **5** contains 1.3 times more adsorbed molecules than SAM prepared from **4**. This ratio is slightly lower than the one provided by QCM data ($\Delta F_{\text{SAM } 5}/\Delta F_{\text{SAM } 4}=1.6$) but confirms that the use of **5** leads to the formation of a somewhat more compact monolayer. Au/C ratios follow the same trend (i.e. $(\text{Au}/\text{C})_4/(\text{Au}/\text{C})_5=1.32$).

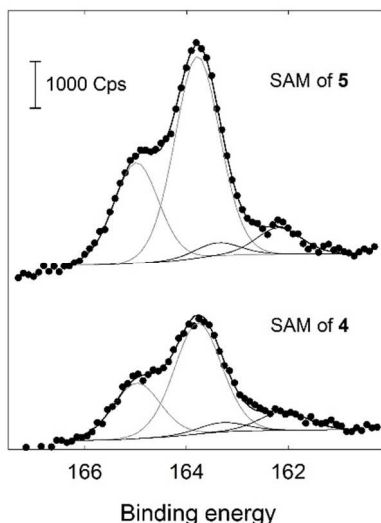


Fig. 3 S 2p core level spectra for SAMs prepared with **4** and **5** respectively. The two spectra were fitted with a combination of two pseudo-Voigt peaks (S 2p_{3/2}/ S 2p_{1/2}) with a fixed intensity ratio of 0.5, an energy splitting of 1.2 eV and a fwhm of 1.1 eV. No oxidized sulfur species (S 2p > 166 eV) were detected in any sample.

The unbounded /bounded sulfur ratio was valued to 5.9 for the SAM prepared from **4**. This result is in good agreement with the theoretical one expected for a single sulfur adsorption of the molecule (i.e. 5). With respect to the SAM elaborated from **5**, the unbounded /bounded sulphur ratio reaches 7.6, which is too high to correspond to a pure chemisorbed self-assembled monolayer. At this stage, the presence of physisorbed thioacetate derivatives within the layer cannot be excluded and could also explain the overestimation of the $\Delta F_{\text{SAM } 5}/\Delta F_{\text{SAM } 4}$ ratio calculated from QCM measurements compared to XPS results.

Integration of S_{Au} and Si XPS signals of the SAM prepared from **4** leads to comparable atomic percentages (i.e. 0.48 and 0.64 % respectively, see the supporting information for Si 2p core level spectrum). Those rather close values are consistent with the presence of one silicon atom per chemisorbed molecule. The adsorption mechanism of the silylethane thiol derivative was not investigated further but these first results seem to indicate a loss of only one of the two protecting group during the adsorption process. The second remaining silylethane thiol functions are therefore available for a post-functionalisation of the SAM prepared from **4**.

Conclusions

In conclusion, we have elaborated aromatic gold thiolate monolayers directly from chemically robust silylethane thiol protecting groups. The spontaneous formation of aromatic thiolate monolayers on gold were evidenced by quartz crystal microbalance measurements and XPS. Integration of specific XPS signals also shows that only one silylethane thiol function of

4 is deprotected during the adsorption process, leading to a SAM suitable for a relevant post-functionalisation. Silylethane thiol-mediated monolayers were slightly less dense than the self-assemblies obtained from its thioacetate analogs, but both adsorption kinetics were equivalent. The chemically robust silylethane-thiol protecting group appeared as a surprisingly effective anchoring agent for the elaboration of chemisorbed aromatic SAMs on Au(111). This easily introduced thiol protecting group therefore represents a powerful tool for the direct formation of aromatic gold thiolate SAMs. The investigations of the promising electronic properties of gold-mediated molecular junctions based on **4** are currently underway.

Notes and references

- ^a Equipe Architectures Moléculaires et Matériaux Nanostructurés, UMR CNRS 5253, Institut Charles Gerhardt, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'École Normale, 34293 Montpellier Cedex, France. Fax: (+33)4 6714 4322; Tel: (+33)4 6714 7222; E-mail: francoise.spirau@enscm.fr
- ^b Equipe Electrochimie, Réactivité, Dynamique et Structuration des Surfaces, UMR CNRS 6200, Laboratoire MOLTECH-Anjou, Université d'Angers, 2 boulevard Lavoisier, 49045 Angers, France. Fax: (+33)2 4173 5405; Tel: (+33)2 4173 5376; E-mail: tony.breton@univ-angers.fr
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