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COMMUNICATION

No more compromise: a facile route towards functionalized surfaces with stable monolayers

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The results reported in this study clearly show that it is possible to easily control the formation of a functional monolayer by spontaneous reduction of an aryldiazonium salt on gold in a single step, mimicking the SAM technique.

The immobilization of functional organic molecules is a commonly adopted strategy to tailor surface chemistry and produce new specific properties.[1–3] The choice of the used method depends both on the scientific background of the authors and on the goal (or application) sought. In any case, it is necessary to compromise either on the stability of the layers obtained, the control of their growth, their ease of implementation or sometimes even on the choice of the functional derivative considered.

Self-assembled monolayers (SAMs) can be obtained easily and spontaneously, and their preparation is recognized to be compatible with the immobilization of a wide variety of functional molecules in a single step. By this route, electroactive molecules derived from (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO),[4] ferrocene,[5–9] tetrathiafulvalene,[10–12] thienylene vinylene,[13] anthraquinone,[14] perylene diimide,[15,16] or metal complexes[17] for example, could be immobilized on gold surfaces. Likewise, organosulfide modified biological material such as DNA[18–21] or proteins[22,23] has also been used to effectively decorate gold substrates. However, the major drawback inherent in the use of SAMs is their moderate stability,[24] which limits the application scope, especially as platforms for sensing.[25]

Methods giving rise to more robust functional surfaces, such as the reduction of diazonium salts, make it possible to propose alternatives.[26] Unfortunately, the formation of thick and uncontrolled disorganized layers linked to the strong reactivity of the radicals produced during diazonium reduction remains an obstacle to the generalization of the method towards the development of optimized and controlled functional devices.[27] In addition, the electrochemical methods generally required to reduce the precursors undeniably add complexity to the implementation, compared to spontaneous methods. Indeed, in addition to a need to adjust various experimental variables (static or dynamic technique, potential, scan rate), the electro-grafting of fragile entities often requires the implementation of a two-step methodology involving first of all the electro-generation of a reactive film and then the chemical post-functionalization of the platform formed, by the species of interest, under the appropriate conditions. [28,29]

With the objective of eliminating compromise between control, stability and ease of implementation, the work presented in this article shows that it is possible to spontaneously form monolayers on gold exploiting the diazonium chemistry. Following the model of the SAM precursors, composed of an anchoring head, a spacer and a functional group, we synthesized a molecule comprising the following key elements: an aryldiazonium group (anchoring head), a 12-carbon alkyl chain (spacer) and an electroactive group (ferrocene, Fc) (Figure 1, **$DC_{12}Fc$**) and investigated its adsorption on gold. The presence of a long alkyl chain is essential since it is expected that it could suppress the electron tunneling through the first grafted organic layer, thus stopping the film growth to produce compact monolayers.[30] To validate our approach and justify the hypothesis stated above, a second Fc derivative having a shorter 2-carbon chain was synthesized (Figure 1, **DC_2Fc**) and immobilized on gold.

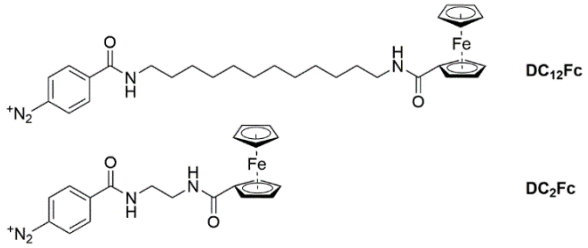

Figure 1. $DC_{12}Fc$ and DC_2Fc derivatives.

[a]. Univ Angers, CNRS, MOLTECH-Anjou, SFR MATRIX, F-49000 Angers, France.

Electronic Supplementary Information (ESI) available: Experimental procedures, synthesis of AC_2Fc compound, comparative voltammetric study of bare Fc and $DC_{12}Fc$, multiple scan rate CV experiments, XPS analyses, AFM analyses of C_2Fc layers. See DOI: 10.1039/x0xx00000x

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$DC_{12}Fc$ and DC_2Fc were obtained from the corresponding aniline derivatives ($AC_{12}Fc$ and AC_2Fc, respectively). The aniline derivative $AC_{12}Fc$ was synthesized according to a procedure already described in ref[30] and AC_2Fc was synthesized according to a protocol detailed in Supplementary Information.

Gold electrodes obtained by physical vapor deposition (PVD)[31] were immersed for various times in a solution containing the diazonium salt $DC_{12}Fc$, formed in-situ from the corresponding aniline ($AC_{12}Fc$). It is now understood that organic layers obtained by the latter method, conventionally used in many studies, have the same properties as those obtained from isolated diazonium cations.[32,33] Figure 2 represents the cyclic voltammograms (CVs) recorded on the $C_{12}Fc$ surfaces obtained by immersion of PVD gold electrodes (S = 0.2 cm^{-2}) in a solution containing 1 mM of $AC_{12}Fc$ and 5 equivalents of *tert*-butyl nitrite (tBuONO) as nitrosating reagent, in dichloromethane.

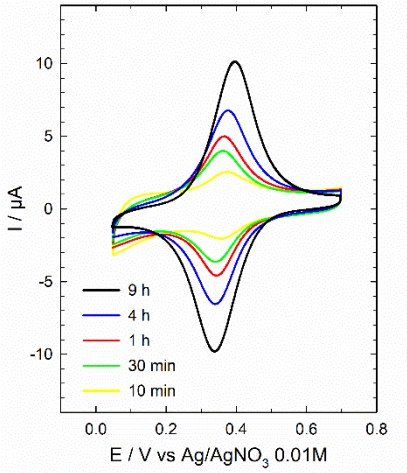

Figure 2. CVs recorded in 0.1 M nBu_4NPF_6 in dichloromethane on layers spontaneously elaborated by immersion during different times in $DC_{12}Fc$ (formed in-situ from 1 mM $AC_{12}Fc$ + 5 mM tBuONO) in dichloromethane. Scan rate: 100 $mV.s^{-1}$.

All the CVs recorded on Fc-based films obtained after different immersion times show the characteristic reversible one-electron oxidation of ferrocene. The signal intensity increases as the functionalization time increases. Integration of the anodic peaks leads to surface coverages ranging from $7.5 \pm 0.2 \times 10^{-11}$ to $5.5 \pm 0.3 \times 10^{-10}$ $mol.cm^{-2}$ for immersion times between 10 min and 9 h. It should be noted that longer functionalization times (overnight) do not lead to higher surface coverages. Interestingly, the threshold value of 5.5×10^{-10} $mol.cm^{-2}$ matches that previously obtained during a study carried out on Fc-based SAMs on gold,[34] which suggests the formation of very thin layers.

To ensure that this value is representative of the entire layer and not linked to incomplete electroactivity of a thick layer, atomic force microscopy (AFM) scratching measurements were performed to determine the thickness of the obtained layers.[35] The obtained scratch profile is exploited to extract the layer thickness from the whole scratched area to have an optimal statistic. All experiments were performed under ambient conditions on modified Pyrolyzed Photoresist Films (PPF) characterized by low surface roughness (< 0.5 nm) in comparison with gold substrates (≈ 1 nm). Surface coverages values obtained on PPF substrates were lower than those obtained on PVD gold substrates (3.9 10^{-10} $mol.cm^{-2}$ instead of 5.5 10^{-10} $mol.cm^{-2}$), which is attributed to the lower surface roughness of PPF. Figure 3 shows the topographic image of a scratch on $C_{12}Fc$ layers obtained after a 9 h immersion in the grafting solution (A) and the corresponding depth profile (B).

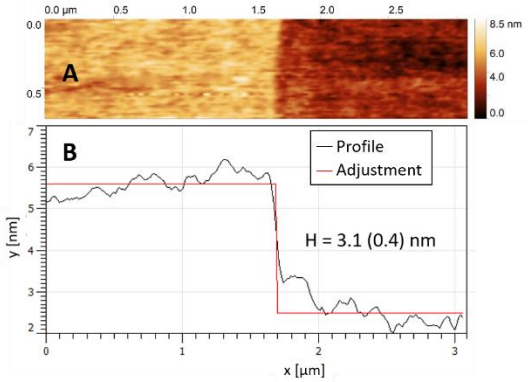

Figure 3. A. AFM image of a $C_{12}Fc$ layer obtained by a 9 h immersion of a PPF substrate, after scratching. B. Depth profile of the scratched area.

An average film thickness of 3.1 ± 0.4 nm was estimated from the measurements. Such a value is consistent with the calculated height of a $C_{12}Fc$ group (2.8 nm, calculated by molecular mechanics (MM2) calculations), confirming that the film growth is restricted to an ultrathin layer. Taken together, voltammetric and AFM experiments on $C_{12}Fc$ layers formed from $DC_{12}Fc$ leave no doubt that thin films were obtained.

As reported by Tanaka et al,[30] the obtaining of such thin layers can be justified by the following hypothesis: when a first layer of organic $C_{12}Fc$ molecules completely covers the electrode, the tunneling through the formed layer is no longer possible due to the presence of the long alkyl chains. Thus, the reduction of the diazonium cations located at the substrate-solution interface no longer takes place. As no radicals are produced, the film no longer grows and stops at the monolayer stage. To prove this hypothesis, a reducing agent was added to the grafting solution after the formation of a monolayer to confirm that further grafting can occur on the layer via chemical reduction of the diazonium derivative in solution. To this end, bare ferrocene (Fc) was chosen as reducing agent to produce reactive radicals from diazonium cations. Although the $DC_{12}Fc$ layer precursor already contains a Fc entity, the latter cannot act itself as a reducing agent because its cyclopentadiene ring substitution by an amide withdrawing function increases the Fc oxidation potential. Indeed, a difference of 160 mV was measured between the redox potential of bare Fc and that of Fc carried by the $DC_{12}Fc$ molecule, preventing the reduction of the diazonium function (see Figure SI-2).

A monolayer was first formed by a 24 hour-immersion in a solution containing $DC_{12}Fc$ in-situ generated from $AC_{12}Fc$ and tBuONO. This $C_{12}Fc$-functionalized gold electrode was then immersed in a second solution containing, in addition to $AC_{12}Fc$ and tBuONO, bare Fc as a reducing agent (Figure 4).

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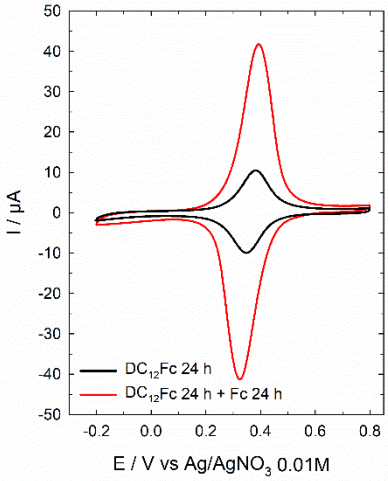

Figure 4. CVs recorded in 0.1 M nBu_4NPF_6 in dichloromethane on $C_{12}Fc$ layers spontaneously elaborated by 24 h-immersion in $DC_{12}Fc$ (formed in-situ from 1 mM $AC_{12}Fc$ + 5 mM tBuONO) in dichloromethane (black line) and by subsequent 24h-immersion in a second solution containing $DC_{12}Fc$ (formed in situ from 1 mM $AC_{12}Fc$ + 5 mM tBuONO) and 1 mM bare Fc in dichloromethane (red line). Scan rate: 100 mV.s^{-1}.

The CV recorded on a $C_{12}Fc$ layer spontaneously obtained from $DC_{12}Fc$ after a 24 h-immersion (I_{peak} = 11 µA) is similar to the one recorded after a 9 h-immersion (Figure 2, I_{peak} = 11 µA). After a subsequent 24 h-immersion in a grafting solution containing bare Fc, the surface coverage had increased 5-fold. The addition of a reducing agent in the presence of the in-situ formed diazonium cation therefore allowed the additional grafting of a large quantity of aryl entities.

This observation proves on the one hand that the reduction of the diazonium function is possible under the experimental conditions used and, on the other hand, that the radicals formed during this reduction are able to react with the monolayer already formed. This experiment thus validates the initial hypothesis, which is based on the inhibition of the diazoniums reduction by the surface when the latter is covered with a layer composed of $C_{12}Fc$ entities. The addition of a reducing agent is necessary for this reduction to occur again.

A second experiment was carried out to highlight the role of the 12-carbon chain in suppressing the tunnel effect through an already grafted $C_{12}Fc$ monolayer: the spontaneous grafting of a Fc-functional diazonium incorporating a shorter alkyl chain. CVs presented in Figure 5 show the comparative study of $C_{12}Fc$ and C_2Fc layers obtained by immersion of the electrode in solutions containing $DC_{12}Fc$ or DC_2Fc, respectively.

Both voltammograms show the characteristic redox process of the ferrocene but a much larger amount of immobilized species is obtained for the C_2Fc layer (threshold values at least three times greater). This observation remains valid for all immersion times tested (Figure 5B). The measured value for a 7 h-immersion (i.e. 18×10^{-10} mol.cm^{-2}) is typical of a multilayer formation and thus demonstrates the possible grafting of aryl radicals on an already grafted monolayer. Multiple-scan rate cyclic voltammetry experiments were carried out on $C_{12}Fc$ and C_2Fc layers in order to evaluate the evolution of the electroactivity of the immobilized species as a function of the scan rate. For the $C_{12}Fc$ layer, the graph representing log(I_{peak}) vs log(scan rate) shows a slope close to 1, in agreement with the formation of a monolayer within which all of the immobilized species remain electroactive, even at high scan rate. On the opposite, data recorded on C_2Fc layers show a lower slope (0.68) owing to the formation of multilayered species (Figure SI-3)

These results show that the reduction of aryldiazonium salts in solution (by electron transfer from the surface through the organic layer) becomes possible when immobilized molecules carry an alkyl chain of only 2 carbons.

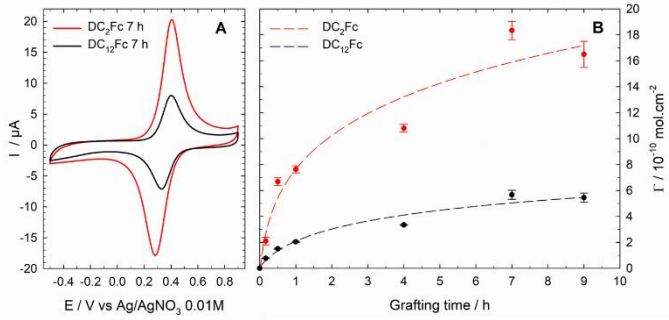

Figure 5. A. CVs recorded in 0.1 M nBu_4NPF_6 in dichloromethane on layers spontaneously elaborated from $DC_{12}Fc$ (black line) or from DC_2Fc (red line), by 7 h-immersion in 1 mM aniline derivative + 5 mM tBuONO in dichloromethane. Scan rate: 100 mV.s^{-1}. B. Evolution of the Fc surface coverage as a function of grafting time, the dotted curves are not trend curves but visual references.

X-ray Photoelectron Spectroscopy (XPS) measurements undertaken on $C_{12}Fc$ and C_2Fc layers confirm the results obtained by cyclic voltammetry. Indeed, the higher intensity of the Fe2p signal corresponding to the Fc entities, recorded on C_2Fc layer, highlighted a larger amount of immobilized species, as demonstrated by electrochemical studies (see Figure SI-4A). Moreover, considering the depth of the sample probed (about 10 nm), the signal related to the substrate (Au4f) is all the more intense as the film is thin. This is the reason why the Au4f signal recorded on $C_{12}Fc$ film is higher than the one recorded on C_2Fc film, which is thicker (see Figure SI-4B).

AFM analyses performed on C_2Fc films did not allow determination of the layer thickness since the heterogeneity of the obtained films led to very disparate values (see Figure SI-5).

A comparative stability study was then carried out on SAMs elaborated from the thiol derivative SH-C_{15}-Fc (structure drawn on Figure 6B and synthesis described in ref[34]) and layers obtained from $DC_{12}Fc$ diazonium. Both monolayers were synthesized under the same conditions, by a 7 h-immersion of a gold electrode in a solution containing 1 mM of precursor (ie. $DC_{12}Fc$ formed in-situ or SH-C_{15}-Fc). After rinsing with dichloromethane, the modified electrodes were studied by

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repetitive cyclic voltammetry in the same potential range (0 V - 0.8 V vs Ag/$AgNO_3$ 0.01 M, Figure 6A).

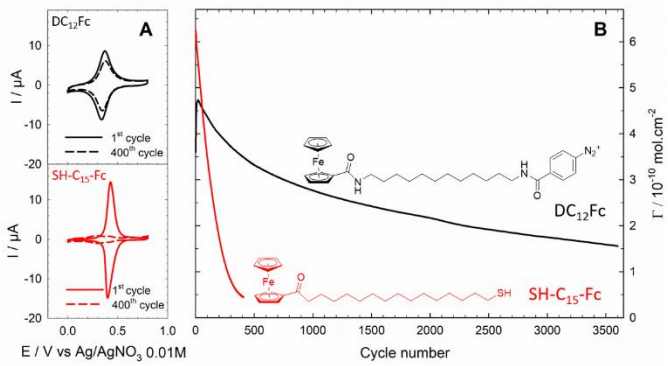

Figure 6. A. Top. CVs (20th cycle: solid line and 400th cycle: dashed line) recorded in 0.1 M nBu_4NPF_6 in dichloromethane on layers spontaneously elaborated by 7 h-immersion in 1 mM $DC_{12}Fc$ formed in-situ (black). Bottom. CVs (20th cycle: solid line and 400th cycle: dashed line) recorded in 0.1 M nBu_4NPF_6 in dichloromethane on layers spontaneously elaborated by 7 h-immersion in 1 mM SH-C_{15}-Fc (red). Scan rate: 100 mV.s^{-1}. B. Evolution of the Fc surface coverage vs cycle numbers.

Both CVs presented in Figure 6A show the characteristic ferrocene signal, located around 0.4 V but significant differences have to be noted. First, the weaker full width at half maximum (FWHM) for the voltammetric peak recorded on the SAM (75 mV versus 120mV for the $C_{12}Fc$ layer) shows that the structures of the two layers are not strictly identical. Second, the surface coverage, which goes from 5.6×10^{-10} mol.cm^{-2} to a null value for the SAM between the 20th and the 400th cycle, shows the total disappearance of the signal after this electrochemical bias. On the contrary, the $C_{12}Fc$ layer unambiguously shows a drastic stability increase since calculated surface coverages corresponding to 74% and 33% of the value recorded for the 20th cycle are found after 400 and 3600 cycles respectively (Figure 6B).

These series of experiments clearly demonstrate the advantage provided by the surface modification from diazonium salts in terms of sustainability. The most likely explanation lies in the lability of the sulfur-gold bond which results in an equilibrium between the immobilized species and the SAM storage medium, thus promoting desorption of the species. The higher robustness of the carbon-gold bond explains the lower signal loss recorded on the layer obtained from $DC_{12}Fc$ and the charge decrease observed during the potential scans can be related to an electrochemical deactivation of the immobilized species or corrosion of gold substrate.

To expand the application range of surfaces modified by organic molecules, it is essential to move towards methods that are both simple to implement and give rise to stable and controlled devices. The methodology proposed here appears to meet these criteria. Indeed, the incorporation of a long alkyl chain between the aryl diazonium and the functional moiety allows growth to be terminated at the monolayer stage while taking advantage of the stability brought by diazonium grafting.

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

There are no conflicts to declare.

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