



**HAL**  
open science

# Electroactive molecular layers produced by reduction of an aryldiazonium salt scrutinized by Tip Enhanced Raman Spectroscopy

Thomas Touzalin, Jessem Landoulsi, Laure Fillaud, Ivan T Lucas, Emmanuel Maisonhaute

## ► To cite this version:

Thomas Touzalin, Jessem Landoulsi, Laure Fillaud, Ivan T Lucas, Emmanuel Maisonhaute. Electroactive molecular layers produced by reduction of an aryldiazonium salt scrutinized by Tip Enhanced Raman Spectroscopy. *Optics Communications*, 2025, pp.132034. <10.1016/j.optcom.2025.132034>. <hal-05088386>

**HAL Id: hal-05088386**

**<https://hal.science/hal-05088386v1>**

Submitted on 28 May 2025

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

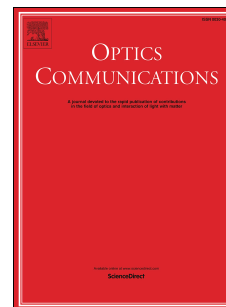


HAL Authorization

# Journal Pre-proof

Electroactive molecular layers produced by reduction of an aryldiazonium salt scrutinized by Tip Enhanced Raman Spectroscopy

Thomas Touzalin, Jessem Landoulsi, Laure Fillaud, Ivan T. Lucas, Emmanuel Maisonhaute



PII: S0030-4018(25)00562-0

DOI: <https://doi.org/10.1016/j.optcom.2025.132034>

Reference: OPTICS 132034

To appear in: *Optics Communications*

Received Date: 1 March 2025

Revised Date: 13 May 2025

Accepted Date: 26 May 2025

Please cite this article as: T. Touzalin, J. Landoulsi, L. Fillaud, I.T. Lucas, E. Maisonhaute, Electroactive molecular layers produced by reduction of an aryldiazonium salt scrutinized by Tip Enhanced Raman Spectroscopy, *Optics Communications*, <https://doi.org/10.1016/j.optcom.2025.132034>.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2025 Published by Elsevier B.V.

# Electroactive molecular layers produced by reduction of an aryldiazonium salt scrutinized by Tip Enhanced Raman Spectroscopy

Thomas Touzalin,<sup>1</sup> Jessem Landoulsi,<sup>2</sup> Laure Fillaud,<sup>1</sup> Ivan T. Lucas,<sup>3</sup> Emmanuel Maisonhaute\*<sup>4</sup>

<sup>1</sup>Sorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, LISE, F-75005 Paris, France

<sup>2</sup>Sorbonne Université, CNRS, Laboratoire de Réactivité de Surfaces, LRS, F-75005 Paris, France

<sup>3</sup>Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, Nantes 44320, France

<sup>4</sup>Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, F-75005 Paris, France

## Abstract

Surface modification methodologies are continuously refined, which in parallel necessitates accurate analytical methods to probe their chemical composition at the nanoscale. We describe here our electrochemical and Tip Enhanced Raman Spectroscopy results on surfaces modified through reduction of an electroactive aryldiazonium salt. Grafting may be first triggered electrochemically. In this case, thick and disorganized layers are produced, with important changes in spectral responses in comparison to the parent system. Conversely, spontaneous reduction of the salt also occurs during simple immersion in the diazonium solution, which leads to low surface coverages (*i.e.* thin layers) and preservation of the molecular backbone of the molecule. This study highlights the advantages of TERS to recover chemical information at the nanoscale even for complex surface modification processes.

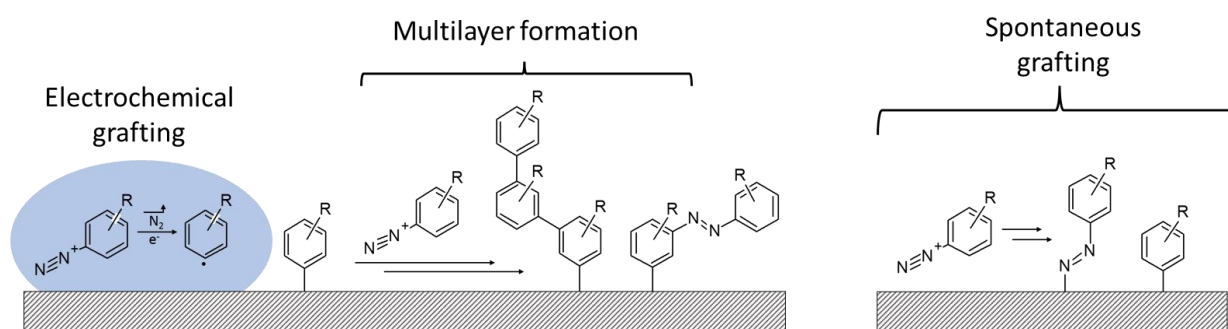
**Keywords:** Tip Enhanced Raman Spectroscopy, Electrochemistry, Operando spectroscopy, Diazonium, Molecular electronics

## 1) Introduction

Producing robust and well-defined modified surfaces is still a challenge. Self-assembled monolayers obtained from thiolated derivatives offer the possibility to get easily by wet

chemistry well-organized and tailored surfaces, but the gold-sulfur bond strength is however still very weak.[1, 2] In 1992, Pinson and collaborators found that electroreduction of aryldiazonium salts leads to covalent and robust grafting on many different materials such as carbon, silicon, gold or platinum.[3–5] These modified layers find interesting applications in many domains such as molecular electronics, plasmonics or (bio)sensing among others.[6–9] The process depicted in Scheme 1 involves reduction and breaking of the C-N bond so that a radical is produced and then grafted onto the surface. Nevertheless, given the intrinsic strong reactivity of radical species, subsequent overgrafting on the first layer currently occurs, so that inhomogeneous multilayers are very often observed. Cleavage of the C-N bond may also not happen, leading to azo bridge formation.[10–14] Less material may be deposited upon spontaneous grafting by simply immersing the surface in a solution of the diazonium salt without electrochemical activation. Otherwise, interesting various strategies have been proposed to avoid overgrafting,[15–19] but their efficiency needs to be assessed for each system, so that it is still of prime importance to analyze the produced layers regarding their thickness, homogeneity and ultimately composition. In this context, Tip Enhanced Raman Spectroscopy (TERS) approaches are appealing because they propose both chemical identification together with high spatial resolution. While TERS was already extensively used for surfaces modified by thiols [20–33] and more recently carbenes,[34–37] this paper represents to the best of our knowledge the first attempt to characterize layers obtained through diazonium reduction.

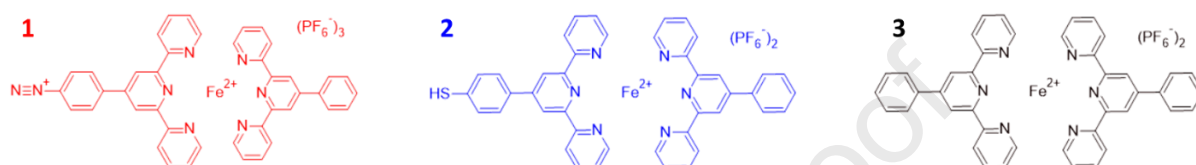
**Scheme1. Sketch of surface modification by aryldiazonium salts. The process may be triggered by electrochemical (left) or spontaneous (right) reduction.**



Below, we will propose the first Scanning Tunnelling Microscopy STM-TERS analysis of gold surfaces modified with the electroactive diazonium **1** shown in Scheme 2, either using electrochemical or spontaneous reduction. This family of systems has been shown to present an

interest in optical and molecular electronics, and particularly show memristor properties. [14, 38] We will also compare our results to those obtained for the parent thiol reference molecule **2** which forms conventional self-assembled monolayers.

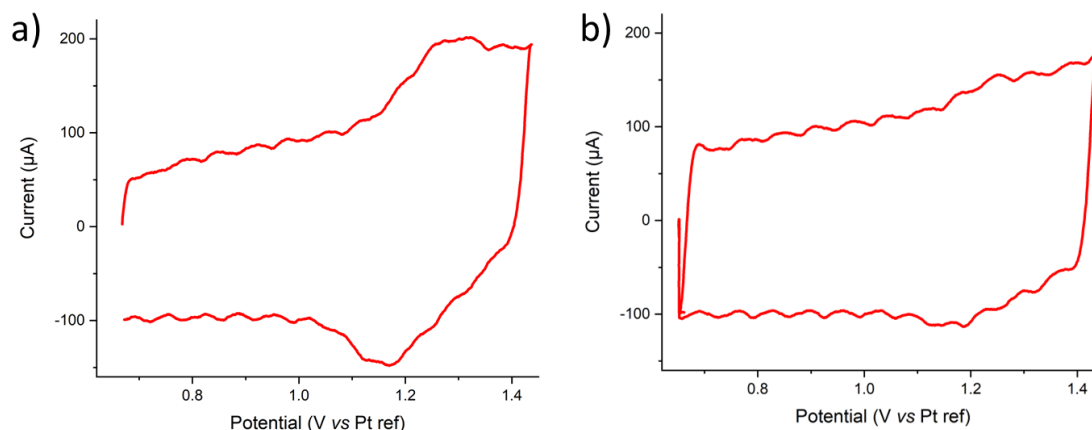
## Scheme 2. Organometallic complexes 1-3 used in this study.



### 2) Gold electrode functionalization

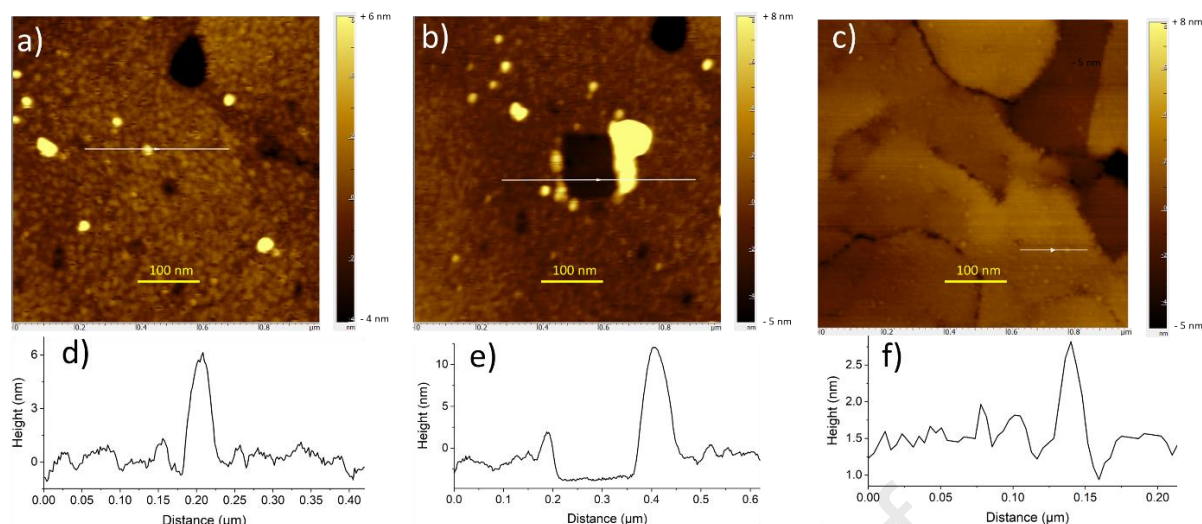
First, a gold ball electrode was immersed in a  $4 \times 10^{-5}$  M solution of **1** in acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. A first cyclic voltammogram (CV) was performed between 0.2 and -1.0 V / SCE at  $0.1 \text{ V.s}^{-1}$  to trigger electroreduction of **1**, as usually performed with such systems. Unfortunately, no clear reduction current wave could be observed because of the low concentration of the salt. The electrode was afterwards rinsed and immersed in the same electrolyte with the diazonium derivative. Figure 1a presents the CV obtained at  $3140 \text{ V.s}^{-1}$ . A clear bell-shape signal typical of adsorbed species is apparent near 1.2 V / Pt. Integration of the peak current gives an average surface coverage of  $\Gamma = 5.5 \pm 1 \times 10^{-8} \text{ mol.m}^{-2}$ . Such coverage is much lower than that obtained by chronoamperometry (typically performed during 1 to 5 min), in agreement with shorter times spent in the potential window where the diazonium bond is reduced. [14]

To assess the spontaneous grafting, the electrode was immersed for less than 10 s in a solution containing **1** at the same concentration without any electrochemical stimulation and then quickly rinsed. Here, the CV presented in Figure 1b clearly shows that much less electroactive material is adsorbed on the electrode, and accordingly  $\Gamma = 8.7 \pm 2 \times 10^{-9} \text{ mol.m}^{-2}$  is found.



**Figure 1. Cyclic voltammograms obtained for a gold ball electrode modified with molecule 1 performed at  $3140 \text{ V}\cdot\text{s}^{-1}$ . a) Electrochemical reduction performed in acetonitrile +  $0.1 \text{ M}$  tetrabutylammonium hexafluorophosphate + **1** at a concentration of  $4 \times 10^{-5} \text{ molL}^{-1}$ . b) Spontaneous adsorption obtained by immersing the electrode  $10 \text{ s}$  in a  $4 \times 10^{-5} \text{ molL}^{-1}$  solution of **1** in acetonitrile.**

Similar experiments were repeated on flat gold layers obtained by physical vapor deposition (sputtering) on mica in order to perform Atomic Force Microscopy (AFM) experiments. Figure 2a presents the AFM image of the gold substrate after electrochemical grafting. Here, the surface appears very inhomogeneous, with an important roughness. In addition, some islands of variable heights suggest that the electropolymerization process is not uniform on the surface. Scratching tests conducted with the AFM tip reveal (cf. Figure 2b and 2e) a height of *ca.* 2 to 3 nm, larger than the size of the radical molecular system (1.5 nm). Conversely, upon spontaneous grafting, the surface appears smoother in agreement with a sub-monolayer coverage, albeit still with some irregularities as shown in Figure 2c.

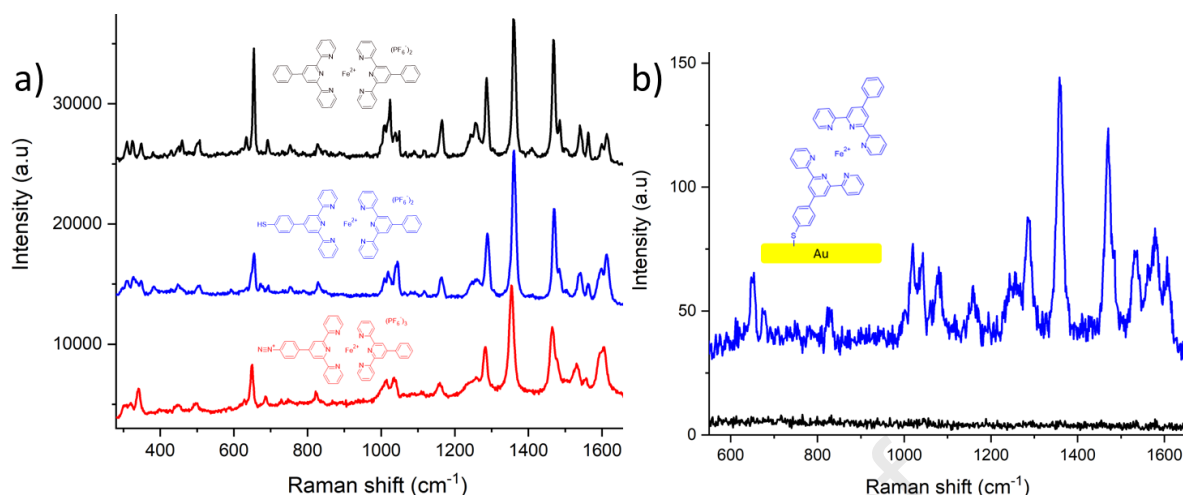


**Figure 2. AFM experiments.** a) AFM image obtained of a molecular layer formed by electrochemical reduction of the diazonium derivative **1**. b) AFM image obtained after scratching. c) AFM image of a molecular layer obtained upon spontaneous grafting of the diazonium derivative **1**. d, e, f) Corresponding profiles obtained at the position of the white lines in a, b and c respectively.

In summary, electrochemical and AFM tests provide consistent results: inhomogeneous molecular multilayers are formed upon electroreduction of **1**, while a submonolayer is produced after short immersion times without any electrochemical stimulation. However, no chemical information is available, which is the concern of the next section.

### 3) Tip-Enhanced Raman Spectroscopy

In order to investigate further the structure of the molecular layer grafted onto gold, STM-TERS measurements were performed *ex situ* (in air) on modified gold substrates. Conventional Raman measurements were also conducted on powders of molecules **1-3** as shown on Figure 3a. Prior investigating the target surfaces modified by electro- or spontaneous reduction of molecule **1**, we ran a preliminary STM-TERS study on a surface obtained after modification by system **2** used as a reference. Here, monolayers were formed after immersion in a 0.1 mM solution for one night (and rinsing) as is classically performed with thiol derivatives. STM-TERS spectra of **2** shown in Figure 3b are fully consistent with those obtained for the powder spectra of molecules **1** and **2**, and the parent complex **3** displayed in Figure 3a. The assignment of the main spectral features is provided in Table 1.[39] These measurements confirmed the ability of our STM-TERS setup to detect the molecule, and that even after 30 s irradiation, no degradation occurred.

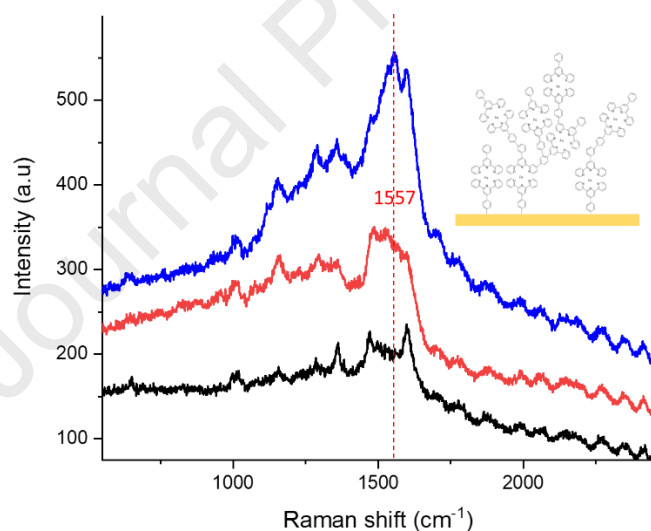


**Figure 3.** a) Reference powder Raman spectra obtained under 632.8 nm irradiation for complexes 1-3. b) Blue: STM TERS spectrum obtained on a surface immersed in a 0.1 mM of derivative 2 for one night. Laser power 10.8  $\mu$ W, acquisition time 30 s. Black: far-field spectrum. Bias voltage: 100 mV. Setpoint current: 200 pA.

**Table 1.** Main Raman and TERS bands found in spectra of 2 and their assignment.[39] The Raman shifts are in  $\text{cm}^{-1}$ ; the shift values marked with a star are found in only one spectrum. "bend.": bending; "str.": stretching.

Raman peak position ( $\text{cm}^{-1}$ )	TER peak position	Vibration mode
654	651	ring bend.
1009	997	ring str.
1024	1023	ring str.
-	1075	ring str. + C-H bend.
1166	1157	C-H bend.
1287	1285 (1294*)	ring str. + C-H bend.
1361	1362	C-H bend. + ring str.
1466	1470 (1485*)	ring str.
1563	1557*	ring str.
1612	1598	ring str.

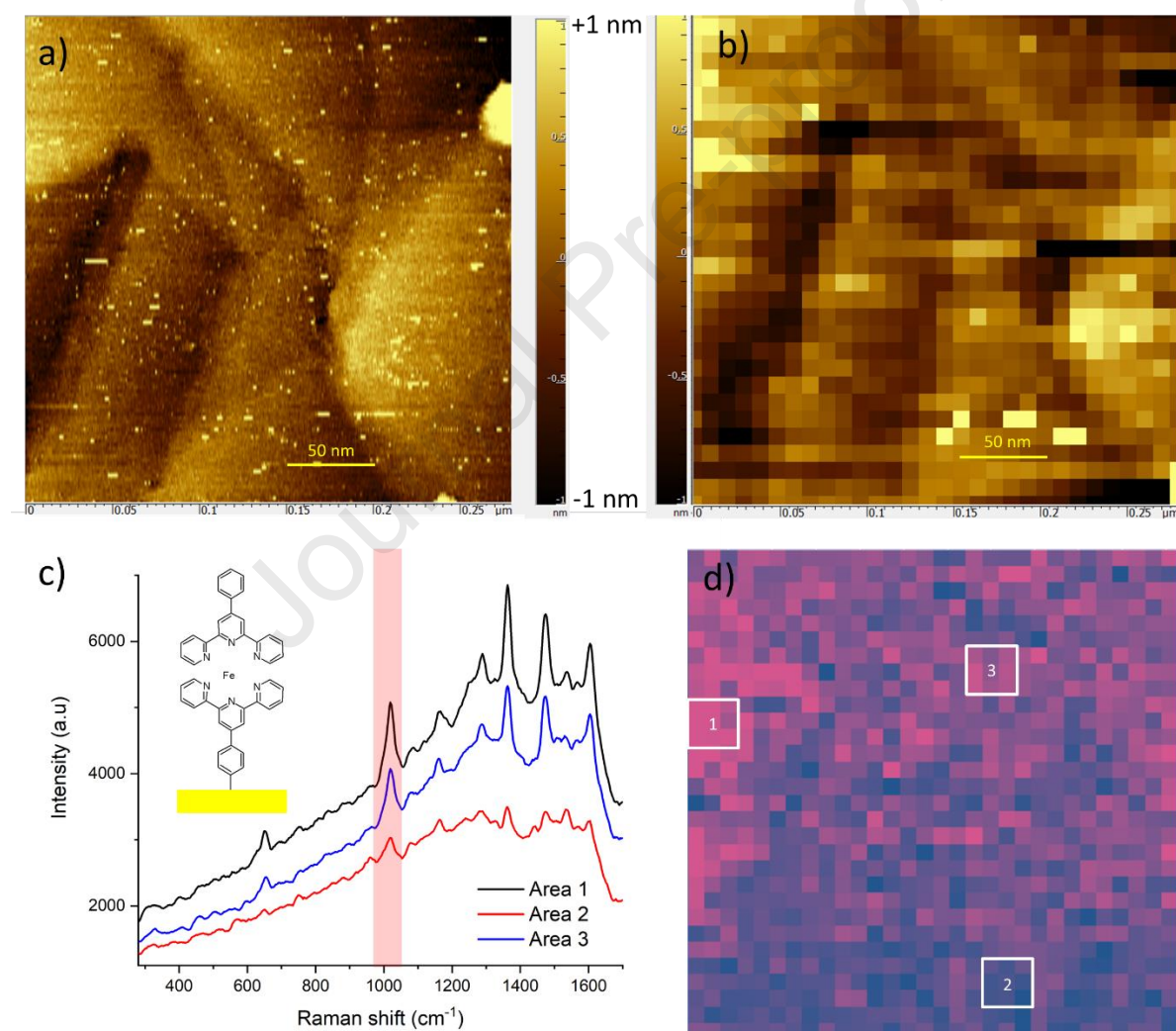
We then analysed a molecular layer obtained by electrochemical reduction of the diazonium derivative **1** corresponding to the AFM images of Figures **2a-b**. Here, no STM imaging was possible because of the important thickness of the sample, and likely penetration of the tip within the layer. We could however locally acquire the TERS spectra that are presented in Figure 4. They look indeed very different from those presented in Figure 3. The initial bands are still present but the spectra exhibit significant spectral changes both in intensities and spectral broadening width of the bands in agreement with a disordered layer. A new feature at  $1557\text{ cm}^{-1}$  appears in one spectrum. It was ascribed to the HNNH vibration by Tomasso *et al.* in an electrochemical Raman study of a thick film obtained from the same molecule but here deposited by chronoamperometry. [14] It is also noticeable that for the same sample the spectral features in Figure 4 look different, suggesting that at different positions of the tip the chemical nature of the layer is different. In this case, STM-TERS therefore does not seem to be the appropriate method to correlate topography and spectroscopy, and AFM-TERS or alternatively AFM-IR would probably be more indicated.[40–45]



**Figure 4. STM-TERS spectra obtained at different positions on a gold substrate modified by electrochemical reduction of molecule 1. Bias voltage: -0.100 V. Setpoint current: 200 pA.**

Then, a sample previously immersed for 30 min in a  $4 \times 10^{-5}\text{ molL}^{-1}$  acetonitrile solution of **1** was examined by STM in air (cf. Figure 4a). Similarly to what was observed by AFM, the underlying gold substrate with steps is clearly apparent in Figure 5a, albeit with some increased roughness compared to an unmodified surface. This suggests again the presence of molecular aggregates but those are here sparsely present and smaller. On the same area we acquired a

30×30 pixels<sup>2</sup> STM-TERS image with an acquisition time of 507 ms/pixel. The corresponding STM image displayed in Figure 5b is still representative of the topography albeit with a lower resolution. The intensity map of Figure 5d is constructed by integration of the band at 1021 cm<sup>-1</sup> corresponding to the ring stretching mode. Figure 5c presents 3 spectra (raw data) extracted at different positions on the sample. Those present all the same structure very similar to the one of **1-3**. This experiment demonstrates that upon grafting, the molecular structure of the complex is preserved, and also confirms that there is only very little overgrafting, though in that case the immersion time of the sample was longer than for electrochemical experiments. It is also interesting to discuss the obvious fluctuations in the TERS intensities that are evidenced in Figure 5d and seem somewhat correlated to topography.



**Figure 5.** a) Classical STM image obtained for a gold substrate modified with **1** by spontaneous adsorption. Bias voltage: 0.2 V. Setpoint current 200 pA. b) STM Topography obtained during TERS imaging. Bias voltage: 0.2 V. Setpoint current 200 pA. 30×30 pixels<sup>2</sup>. Pixel size 9.33 nm. Acquisition time: 507 ms/pixel. c) STM-TERS spectra obtained

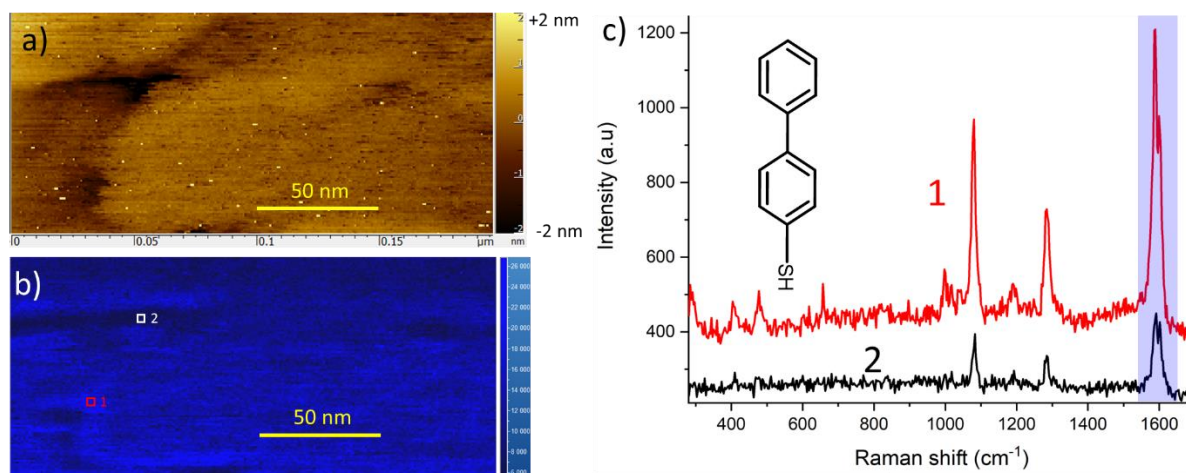
**at positions 1, 2 and 3 d). Each spectrum was obtained by averaging a 3×3 pixels<sup>2</sup> area. d) TERS cartography corresponding to b) obtained after integration of the 1021 cm<sup>-1</sup> band.**

Several reasons may be invoked to explain them:

- $\alpha$ ) Fluctuation of the tip-sample distance, then of the TERS enhancement. This hypothesis can be ruled out, as the STM feedback was very stable.
- $\beta$ ) Modification of the electromagnetic field amplification due to tip damage or morphological change. This hypothesis can also be ruled out here because this would involve a brutal intensity change between the bottom and top part of the image (scan was from bottom to top), not fluctuations related to topography.
- $\gamma$ ) Local variations in the electromagnetic amplification due to the nanostructuring of the substrate since our experiments are run in the so-called “gap-mode” configuration.
- $\delta$ ) Different local surface concentration of the molecule.

Point  $\gamma$ ) was explored by Zenobi and El Khoury among others. [46–48] Here, the precise morphology of the substrate is key, and thus we explored this issue for our gold substrates using a simple and standard Raman reporter, here bisphenyl thiol reported in Figure 6. Obvious fluctuations are observed, mostly near step edges albeit without a perfect correlation. The spatial extension of the signal amplifications seems to be about 5-20 nm, in agreement with what we observed in electrochemical conditions, and is similar to what is apparent in Figure 5d.[30] Our experimental conditions (substrate and tip) therefore produce similar results when compared to literature. Returning to the diazonium functionalized substrates, we suggest that further interpretation is delicate and beyond the scope of this paper, but clearly contribution from TERS amplification cannot be excluded.

More experiments would then be necessary to decipher and separate the contributions of point  $\delta$ ) versus  $\gamma$ ), and particularly imaging smaller areas with a better resolution, possibly on a single crystal surface.



**Figure 6. STM-TERS spectra obtained for a monolayer of bisphenyl thiol modified gold substrate. a) STM topography. b) TERS image obtained by integration of the double peak corresponding to the ring stretching mode of the benzene rings near  $1600\text{ cm}^{-1}$ . c) Spectra at positions 1 and 2 indicated in b) obtained by integration of an area of  $3\times 3\text{ pixels}^2$ . Bias voltage  $0.045\text{ V}$ . Setpoint current:  $1000\text{ pA}$ . Pixel size:  $0.8\text{ nm}$ . Acquisition time :  $9\text{ ms}$ .**

#### 4) Conclusion

A diazonium salt with a redox core was selected to modify gold substrates that were then studied by STM-TERS. Two grafting paths were investigated: the electrochemical reduction and the spontaneous grafting. Its anchoring onto the gold surface could be demonstrated by cyclic voltammetry and AFM. STM and TERS measurements revealed different molecular organizations depending on the grafting method. In electrochemical grafting, we concluded on the formation of a thick multilayer. TERS results corroborated this hypothesis by providing spectra that could be associated with a disorganized organic layer. Comparatively, the STM and TERS experiments conducted on a sample functionalized by spontaneous grafting suggested the anchoring of a less densely packed monolayer. The STM and TERS results were in this case complementary since STM images did not provide clear evidences of the grafting.

This is to the best of our knowledge the first set of TERS results provided on the grafting of diazonium salts. These preliminary results should be completed by deeper electrochemical and spectroscopic analysis, especially to measure the electron transfer rate in these redox layers and correlate them to the structure that can be investigated by STM and TERS. AFM-TERS investigations would also be very informative to study the thick layers for which STM imaging

is impossible. This work demonstrated that TERS can be a powerful tool for understanding the structure and mechanism of formation of complex layers, which are of major importance for many research and applied topics.

## 5) Experimental

### *Electrochemical measurements*

Electrochemical measurements were run using a three-electrode setup connected to an Autolab potentiostat for cyclic voltammetry measurements (below 1000V/s). Cyclic voltammograms with scan rates above 1000 V/s were recorded with a homemade potentiostat described elsewhere.[49-54] The acetonitrile solution contained 0.1 molL<sup>-1</sup> tetrabutylammonium tetrafluoroborate as supporting electrolyte. The reference electrode was either a standard calomel electrode (SCE) or a pseudo-reference platinum wire (Pt).

### *Surface modification*

Gold samples were produced by gold sputtering onto cleaved mica as published previously.[29] Spontaneous grafting. The samples were prepared by immersing flame-annealed gold surfaces in a 4×10<sup>-5</sup> molL<sup>-1</sup> solution of **1** in ACN for 30 min at 22°C. The surface was then thoroughly rinsed with ACN and ethanol to remove any physisorbed species from the surface and dried under a nitrogen flow.

Electrochemical grafting. The gold substrates were immersed in a solution containing **1** 4×10<sup>-5</sup> mM + tetrabutylammonium tetrafluoroborate 0.1 M. Then, CV was performed from 0.2 to -1.0 V vs SCE. We used either gold balls for CV experiments of Figure 1, or gold/mica samples. In this case the substrates were connected with a metallic tweezer. Copper sheets were introduced between the gold and the tweezer for a softer contact and avoid scratching the conductive gold layer, whose adhesion to mica is weak.

### *Atomic Force Microscopy and Tip Enhanced Raman Spectroscopy*

All Raman and TER spectra were acquired using a LabRam HR Evolution (Horiba) equipped with an EM-CCD camera (Newton 971, Andor), cooled to -70 °C. The spectrometer was calibrated prior to each new experiment with the 520.7 cm<sup>-1</sup> band of a silicon sample.

For TERS, STM or AFM measurements, an Omegascope (AIST) was used. TERS spectra were acquired using a side illumination of the tip. STM tips were made from gold wires using an electrochemical procedure.[55]

AFM experiments were performed in oscillating mode with commercial probes purchased from  $\mu$ mash and having a nominal spring constant near  $5 \text{ Nm}^{-1}$  and a resonant frequency near 160 kHz (NSC 14/Al BS).

### **Acknowledgements**

This work was funded by Sorbonne Université (Labex MiChem), the CNRS, the region Ile de France (C’Nano program) and the French National Research Agency (grant ANR-22-CE29-0027-04)

Journal Pre-proof

## References

1. Bürgi T (2015) Properties of the gold–sulphur interface: from self-assembled monolayers to clusters. *Nanoscale* 7:15553–15567. <https://doi.org/10.1039/C5NR03497C>
2. Lavrich DJ, Wetterer SM, Bernasek SL, Scoles G (1998) Physisorption and Chemisorption of Alkanethiols and Alkyl Sulfides on Au(111). *J Phys Chem B* 102:3456–3465. <https://doi.org/10.1021/jp980047v>
3. Pinson J, Podvorica F (2020) Surface modification of materials: Electrografting of organic films. *Curr Opin Electrochem* 24:44–48. <https://doi.org/10.1016/j.coelec.2020.05.016>
4. Bélanger D, Pinson J (2011) Electrografting: a powerful method for surface modification. *Chem Soc Rev* 40:3995–4048. <https://doi.org/10.1039/C0CS00149J>
5. Delamar M, Hitmi R, Pinson J, Saveant, JM J (1992) Covalent modifications of carbon surfaces by grafting of functionalized aryl radicals produced from electrochemical reduction of diazonium salts. *J Am Chem Soc* 114:5883–5884. <https://doi.org/10.1021/ja00040a074>
6. Yao X, Sun X, Lafalet F, Lacroix J (2020) Long-Range Charge Transport in Diazonium-Based Single-Molecule Junctions. *Nano Lett* 20:6899–6907. <https://doi.org/10.1021/acs.nanolett.0c03000>
7. Tijunelyte I, Kherbouche I, Gam-Derouich S, et al (2018) Multi-functionalization of lithographically designed gold nanodisks by plasmon-mediated reduction of aryl diazonium salts. *Nanoscale Horizons* 3:53–57. <https://doi.org/10.1039/c7nh00113d>
8. Hai L, Reisberg S, Chevillot-Biraud A, et al (2014) Simultaneous Electroreduction of Different Diazonium Salts for Direct Electrochemical DNA Biosensor Development. *Electrochimica Acta* 140:49–58. <https://doi.org/10.1016/j.electacta.2014.01.159>
9. Sayed SY, Bayat A, Kondratenko M, et al (2013) Bilayer Molecular Electronics: All-Carbon Electronic Junctions Containing Molecular Bilayers Made with “Click” Chemistry. *J Am Chem Soc* 135:12972–12975. <https://doi.org/10.1021/ja4065443>
10. Doppelt P, Hallais G, Pinson J, et al (2007) Surface modification of conducting substrates. Existence of azo bonds in the structure of organic layers obtained from diazonium salts. *Chem Mater* 19:4570–4575. <https://doi.org/10.1021/cm0700551>
11. Laforgue A, Addou T, Bélanger D (2005) Characterization of the deposition of organic molecules at the surface of gold by the electrochemical reduction of aryldiazonium cations. *Langmuir* 21:6855–6865. <https://doi.org/10.1021/la047369c>
12. Lyskawa J, Bélanger D (2006) Direct modification of a gold electrode with aminophenyl groups by electrochemical reduction of in situ generated aminophenyl monodiazonium cations. *Chem Mater* 18:4755–4763. <https://doi.org/10.1021/cm060752d>

13. Saby C, Ortiz B, Champagne G, Belanger D (1997) Electrochemical modification of glassy carbon electrode using aromatic diazonium salts .1. Blocking effect of 4-nitrophenyl and 4-carboxyphenyl groups. *Langmuir* 13:6805–6813. <https://doi.org/10.1021/la961033o>
14. Tomasso C, Petenzi T, Tidu A, et al (2025) Elucidation of Switching Mechanisms in Memristive Junctions Integrating a Iron(II)-Ter Pyridine Diazoted Complex. *Adv Electron Mater* 11:. <https://doi.org/10.1002/aelm.202400350>
15. Nielsen LT, Vase KH, Dong M, et al (2007) Electrochemical Approach for Constructing a Monolayer of Thiophenolates from Grafted Multilayers of Diaryl Disulfides. *J Am Chem Soc* 129:1888–1889. <https://doi.org/10.1021/ja0682430>
16. Peng Z, Holm A, Nielsen L, et al (2008) Covalent Sidewall Functionalization of Carbon Nanotubes by a “Formation-Degradation” Approach. *Chem Mater* 20:6068–6075. <https://doi.org/10.1021/cm800954t>
17. Leroux YR, Fei H, Noël J-M, et al (2010) Efficient Covalent Modification of a Carbon Surface: Use of a Silyl Protecting Group To Form an Active Monolayer. *J Am Chem Soc* 132:14039–14041. <https://doi.org/10.1021/ja106971x>
18. Menanteau T, Levillain E, Breton T (2013) Electrografting via Diazonium Chemistry: From Multilayer to Monolayer Using Radical Scavenger. *Chem Mater* 25:2905–2909. <https://doi.org/10.1021/cm401512c>
19. Pichereau L, Fillaud L, Kostopoulos N, et al (2022) Highly Reactive Diazenyl Radical Species Evidenced during Aryldiazonium Electroreduction. *J Phys Chem Lett* 13:11866–11871. <https://doi.org/10.1021/acs.jpcclett.2c03089>
20. Cai Z, Zheng L, Zhang Y, Zenobi R (2021) Molecular-Scale Chemical Imaging of the Orientation of an On-Surface Coordination Complex by Tip-Enhanced Raman Spectroscopy. *J Am Chem Soc* 143:12380–12386. <https://doi.org/10.1021/jacs.1c06366>
21. Lin W, Shao F, Stephanidis B, Zenobi R (2015) Tip-enhanced Raman spectroscopic imaging shows segregation within binary self-assembled thiol monolayers at ambient conditions. *Anal Bioanal Chem* 407:8197–8204. <https://doi.org/10.1007/s00216-015-8840-x>
22. Zheng L, Wang X, Shao F, et al (2018) Nanoscale Chemical Imaging of Reversible Photoisomerization of an Azobenzene-Thiol Self-Assembled Monolayer by Tip-Enhanced Raman Spectroscopy. *Angew Chem Int Ed* 57:1025–1029. <https://doi.org/10.1002/anie.201710443>
23. Sabanés NM, Elizabeth A, Pfisterer JHK, Domke KF (2017) The effect of STM parameters on tip-enhanced Raman spectra. *Faraday Discuss* 205:233–243. <https://doi.org/10.1039/C7FD00164A>
24. Wickramasinghe H, Chaigneau M, Yasukuni R, et al (2014) Billion-Fold Increase in Tip-Enhanced Raman Signal. *ACS Nano* 8:3421–3426. <https://doi.org/10.1021/nn406263m>

25. Zeng Z, Huang S, Wu D, et al (2015) Electrochemical Tip-Enhanced Raman Spectroscopy. *J Am Chem Soc* 137:11928–11931. <https://doi.org/10.1021/jacs.5b08143>
26. Pashae F, Hou R, Gobbo P, et al (2013) Tip-Enhanced Raman Spectroscopy of Self-Assembled Thiolated Monolayers on Flat Gold Nanoplates Using Gaussian-Transverse and Radially Polarized Excitations. *J Phys Chem C* 117:15639–15646. <https://doi.org/10.1021/jp403157v>
27. Touzalin T, Joiret S, Maisonhaute E, Lucas IT (2017) Complex Electron Transfer Pathway at a Microelectrode Captured by in Situ Nanospectroscopy. *Anal. Chem.* 89:8974–8980
28. Touzalin T, Joiret S, Maisonhaute E, Lucas IT (2017) Capturing electrochemical transformations by tip-enhanced Raman spectroscopy. *Curr Opin Electrochem* 6:46–52. <https://doi.org/10.1016/j.coelec.2017.10.016>
29. Touzalin T, Dauphin AL, Joiret S, et al (2016) Tip enhanced Raman spectroscopy imaging of opaque samples in organic liquid. *Phys Chem Chem Phys* 18:15510–15513. <https://doi.org/10.1039/c6cp02596j>
30. Touzalin T, Joiret S, Lucas IT, Maisonhaute E (2019) Electrochemical tip-enhanced Raman spectroscopy imaging with 8 nm lateral resolution. *Electrochem Commun* 108:. <https://doi.org/10.1016/j.elecom.2019.106557>
31. Fiocco A, Pavlic A, Kanoufi F, et al (2024) Electrochemical Tip-Enhanced Raman Spectroscopy for the Elucidation of Complex Electrochemical Reactions. *Anal. Chem.* 96:2791–2798. <https://doi.org/10.1021/acs.analchem.3c02601>
32. Steffenhagen M, Latus A, Trinh TMN, et al (2018) A Rotaxane Scaffold Bearing Multiple Redox Centers: Synthesis, Surface Modification and Electrochemical Properties. *Chem Eur J* 24:1701–1708. <https://doi.org/10.1002/chem.201705245>
33. van Schroyen Lantman E, Deckert-Gaudig T, Mank A, et al (2012) Catalytic processes monitored at the nanoscale with tip-enhanced Raman spectroscopy. *Nature Nanotech* 7:583–586. <https://doi.org/10.1038/NNANO.2012.131>
34. Li L, Mahapatra S, Schultz JF, et al (2024) Single-molecule spectroscopic probing of N-heterocyclic carbenes on a two-dimensional metal. *Chem.* <https://doi.org/10.1016/j.chempr.2024.08.013>
35. Li L, Mahapatra S, Schultz J, et al (2024) Chemically Interrogating N-Heterocyclic Carbenes at the Single-Molecule Level Using Tip-Enhanced Raman Spectroscopy. *ACS Nano* 18:32118–32125. <https://doi.org/10.1021/acsnano.4c10942>
36. Maisonhaute E, Sadek O, Rabah J, et al (2023) Tailored Functional Monolayers Made from Mesoionic Carbenes. *ChemRxiv*; doi:10.26434/chemrxiv-2023-dcwqr

37. Sadek O, Rabah J, Sowid S, et al (2024) Tailored functional monolayers made from mesoionic carbenes. *Electrochimica Acta* 507:145189  
<https://doi.org/10.1016/j.electacta.2024.145189>
38. Tefashe U, Nguyen Q, Lafalet F, et al (2017) Robust Bipolar Light Emission and Charge Transport in Symmetric Molecular Junctions. *J Am Chem Soc* 139:7436–7439.  
<https://doi.org/10.1021/jacs.7b02563>
39. Hansen PW, Jensen PW (1994) Vibrational studies on bis-terpyridine-ruthenium(II) complexes. *Spectrochimica Acta Part A: Molecular Spectroscopy* 50:169–183.  
[https://doi.org/10.1016/0584-8539\(94\)80125-8](https://doi.org/10.1016/0584-8539(94)80125-8)
40. Huang Y, Talaga D, Salinas G, et al (2025) Contactless manufacturing of TERS-active AFM tips by bipolar electrodeposition. *Nanoscale* 17:1411–1416.  
<https://doi.org/10.1039/d4nr03068k>
41. Kurouski D, Dazzi A, Zenobi R, Centrone A (2020) Infrared and Raman chemical imaging and spectroscopy at the nanoscale. *Chem Soc Rev* 49:3315–3347.  
<https://doi.org/10.1039/C8CS00916C>
42. Mishra N, Kumar G (2012) Near-Field Optical Analysis of Plasmonic Nano-Probes for Top-Illumination Tip-Enhanced Raman Scattering. *Plasmonics* 7:359–367.  
<https://doi.org/10.1007/s11468-011-9316-2>
43. Bao Y, Zhu M, Zhao X, et al (2024) Nanoscale chemical characterization of materials and interfaces by tip-enhanced Raman spectroscopy. *Chem Soc Rev* 53:10044–10079.  
<https://doi.org/10.1039/d4cs00588k>
44. Zhang K, Bao Y, Cao M, et al (2021) Low-Background Tip-Enhanced Raman Spectroscopy Enabled by a Plasmon Thin-Film Waveguide Probe. *Anal Chem* 93:7699–7706.  
<https://doi.org/10.1021/acs.analchem.1c00806>
45. Huang Y, Talaga D, Garrigue P, et al (2023) Nanostructured gold-coated AFM tips generated by potentiostatic electrodeposition for tip-enhanced Raman spectroscopy. *Chem Phys Lett* 832:140893. <https://doi.org/10.1016/j.cplett.2023.140893>
46. O’Callahan B, El-Khoury P (2022) A Closer Look at Tip-Enhanced Raman Chemical Reaction Nanoimages. *J Phys Chem Lett* 13:3886–3889.  
<https://doi.org/10.1021/acs.jpcclett.2c00574>
47. Wang C, Krayev A, El-Khoury P (2023) Subnanometer Visualization of Spatially Varying Local Field Resonances that Drive Tip-Enhanced Optical Spectroscopy. *Nano Lett* 23:9114–9118. <https://doi.org/10.1021/acs.nanolett.3c03028>
48. Zhang W, Cui X, Yeo B, et al (2007) Nanoscale roughness on metal surfaces can increase tip-enhanced Raman scattering by an order of magnitude. *Nano Lett* 7:1401–1405.  
<https://doi.org/10.1021/nl070616n>

49. Boitel-Aullen G, Fillaud L, Huet F, et al (2021) Electron Transfer Inside a Decaferrocenylated Rotaxane Analyzed by Fast Scan Cyclic Voltammetry and Impedance Spectroscopy. *ChemElectroChem* 8:3506–3511. <https://doi.org/10.1002/celec.202100738>
50. Steffenhagen M, Latus A, Trinh TMN, et al (2018) A Rotaxane Scaffold Bearing Multiple Redox Centers: Synthesis, Surface Modification and Electrochemical Properties. *Chem Eur J* 24:1701–1708. <https://doi.org/10.1002/chem.201705245>
51. Amatore C, Maisonhaute E, Schöllhorn B, Wadhawan J (2007) Ultrafast Voltammetry for Probing Interfacial Electron Transfer in Molecular Wires. *ChemPhysChem* 8:1321–1329. <https://doi.org/10.1002/cphc.200600774>
52. Zhou X-S, Mao B-W, Amatore C, et al (2016) Transient electrochemistry: beyond simply temporal resolution. *Chem Commun* 52:251–263. <https://doi.org/10.1039/C5CC07953E>
53. Zhou X, Liu L, Fortgang P, et al (2011) Do Molecular Conductances Correlate with Electrochemical Rate Constants? Experimental Insights. *J Am Chem Soc* 133:7509–7516. <https://doi.org/10.1021/ja201042h>
54. Fortgang P, Amatore C, Maisonhaute E, Schollhorn B (2010) Microchip for ultrafast voltammetry. *Electrochem Commun* 12:897–900. <https://doi.org/10.1016/j.elecom.2010.04.015>
55. Ren B, Picardi G, Pettinger B (2004) Preparation of gold tips suitable for tip-enhanced Raman spectroscopy and light emission by electrochemical etching. *Rev Sci Inst* 75:837–841. <https://doi.org/10.1063/1.1688442>

**Declaration of interest statement**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

On behalf of all authors

Emmanuel Maisonhaute

A handwritten signature in blue ink, appearing to read 'E. Maisonhaute', is written over a large, light gray diagonal watermark that says 'Journal Pre-proof'.