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Tailored Functional Monolayers Made from Mesoionic Carbenes

Omar Sadek,+[b] Jad Rabah,+[a] Dimitri Mercier,[d] Philippe Marcus,[d] Clément Chauvier,[b] François Ribot,*[c] Louis Fensterbank,*[b] Emmanuel Maisonhaute*[a]

[a] Dr. J. Rabah, Pr. E. Maisonhaute
Sorbonne Université, CNRS
Laboratoire Interfaces et Systèmes Electrochimiques
4 place Jussieu, F75252 Paris Cedex 05, France
E-mail: emmanuel.maisonhaute@sorbonne-universite.fr

[b] Dr. O. Sadek, Dr. C. Chauvier, Pr. L. Fensterbank
Sorbonne Université, CNRS
Institut Parisien de Chimie Moléculaire (IPCM)
4 place Jussieu, F75252 Paris Cedex 05, France
E-mail: louis.fensterbank@sorbonne-universite.fr

[c] Dr. F. Ribot
Sorbonne Université, CNRS
Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP)
4 place Jussieu, 75252 Paris Cedex 05, France
E-mail: francois.ribot@sorbonne-universite.fr

[d] Dr. D. Mercier, Pr. P. Marcus
Institut de Recherche de Chimie Paris (IRCP), Physical Chemistry of Surfaces Research Group
PSL Research University, CNRS - Chimie ParisTech
11 rue Pierre et Marie Curie, 75005 Paris, France

Supporting information for this article is given via a link at the end of the document.

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Abstract: Significant progress has been made over the last decades in surface functionalization of coinage metals using thiols and more recently N-heterocyclic carbenes. As shown in this work, mesoionic carbenes (MICs) provide straightforward access to a novel class of surface ligands and thus materials. Importantly, MICs are easily accessed from triazolium salts (TS) onto which functional groups may be attached with little synthetic effort. Here, we present a library of TS that were further converted into MICs, *in situ*, and grafted to gold surfaces. The modified surfaces were thoroughly characterized by advanced spectroscopic methods and electrochemistry for MICs bearing electroactive moieties. We also prepared mixed MIC/thiol self-assembled monolayers, which opens the route to multifunctional surfaces.

Tuning surface properties is crucial to many domains such as molecular electronics, (bio)sensing or energy harvesting among others.[1] In the 1980s, the discovery of self-assembled monolayers (SAMs) provided a facile method for the attachment of thiol ligands to gold or silver surfaces allowing greater structural control compared to electropolymerization.[2,3] This discovery paved the way to a wealth of applications while also stimulating alternative surface modification strategies for the development of well-defined and robust interfaces on various substrates.

An alternative and interesting possibility is offered by grafting aryl diazonium or iodonium salts.[4,5] Here, aryl radicals, generated under negative potentials, illumination or spontaneously, may react and bind to the surface. However, controlling surface organization remains quite difficult despite the proposition of interesting yet elaborated strategies.[6–8] Often, these various protocols lead to non-homogeneous multilayers. Alternatively, hydrosilylation can be used to produce monolayers on silicon, but the approach is restricted to this substrate and requires rather harsh preparation conditions.[9] Hence, there is a demand for proposing novel, reproducible and robust synthetic routes towards SAMs.

For slightly more than a decade, (benz)imidazolium-based N-heterocyclic carbenes (NHCs), well-known ligands in organometallic chemistry, have appeared as promising surface anchors in material science.[10–14] Initially used to stabilize metallic nanoparticles,[15–26] they were soon after studied on flat surfaces where they exhibit strong anchoring and simultaneously provide monolayers.[27–33] Cyclic (alkyl)(amino)carbenes have also been deposited on metallic surfaces.[34] However, a significant drawback of these NHCs emerges when non-symmetric, backbone-modified or functional analogues are required. Access is often difficult as it requires multiple synthetic steps or post-modification on a pre-functionalized surface which represents an equally complicated strategy.[26,27]

Herein, we describe a new approach that relies on the use of 1,2,3-triazole-based mesoionic carbenes (MICs) as surface-capping ligands.[35,36] From a synthetic point of view, MICs are easily generated by deprotonation of their parent triazolium salts. These salts are readily obtained via the modular copper-catalyzed alkyne-azide cycloaddition (CuAAC) click reaction, followed by quaternization of the γ-nitrogen (N^3). This highlights a major advantage of MICs over NHCs in the simplicity of backbone modification through alkylation at the N^3 position. Moreover, the carbanionic character of the coordinating site makes MICs more σ-donating than classical NHCs, *a priori* resulting in a stronger metal-carbene interaction when grafted on surfaces. This has already been exploited for the synthesis of gold or silver nanoparticles but has never been described for surface functionalization.[37–40]

Herein, we demonstrate for the first time that various easily-prepared MICs can be tightly anchored to gold surfaces and provide careful characterization of the latter through X-ray photoelectron (XPS), infrared (IR) and Tip Enhanced Raman (TERS) spectroscopies. Electrochemical studies are also presented to monitor the monolayer formation and determine the molecular coverages as a function of time. Finally, we also demonstrate that mixed MIC/thiol monolayers may be formed, opening an avenue to multivalent surfaces.

At the outset of this study, we prepared the functionalized triazolium salts (**TS 1**-**5**) in two steps from the two common triazole precursors **6a-b** (Scheme 1a). Briefly, the latter heterocycles were readily obtained by a CuAAC click reaction and subsequently engaged in an alkylation step with an alkyl bromide (R^2–Br), some of them bearing specific functional groups such as a ferrocenyl moiety (**TS 1** and **TS 2**) or substituted arenes (**TS 3** and **TS 4**). This pool of reagents not only allows us to investigate the generality of the gold surface functionalization event, but also conveys a specific purpose in that **TS 1**, **TS 2** and **TS 3** are electroactive and **TS 4** bears a biphenyl entity with a characteristic Raman spectroscopic signature. Triazolium **TS 5** was also studied as reference to our former work on nanoparticles.[40] Detailed syntheses are provided in the Supporting Information (SI).

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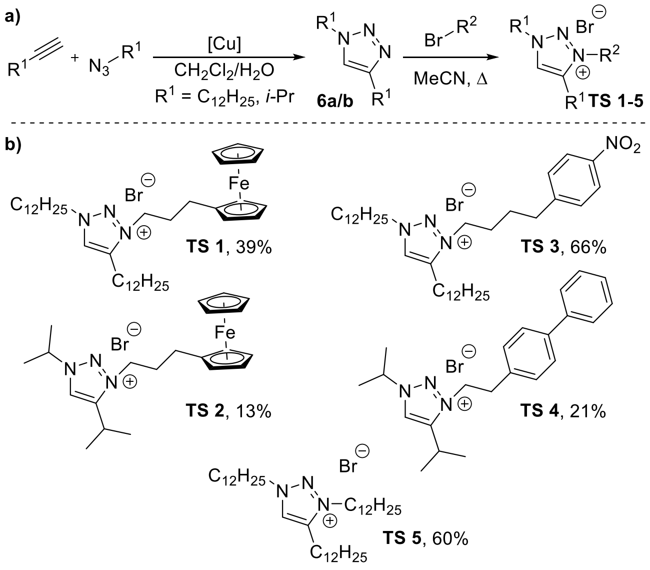
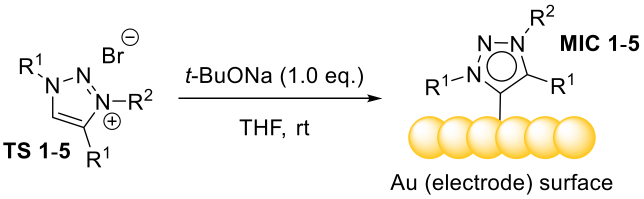


Scheme 1. a) General synthetic route to functionalized triazolium salts **TS**. b) Systems **TS 1-5** investigated in this study; yields are calculated over two synthetic steps.

To assess the potential of the MICs derived from the triazolium salts **TS 1-5** to functionalize gold surfaces or gold electrodes, we set out to prepare the free mesoionic carbenes **MIC 1-5** by deprotonation of **TS 1-5** prior to exposing them to a gold surface. To that end, we prepared 1 mM THF solutions of the triazolium precursors into which we added, under argon, 1 equivalent of *t*-BuONa as base (Scheme 2). Gold surfaces were subsequently introduced in the reactor or in the electrochemical cell and left in the carbene solution for times from 5 minutes to 3 hours. After thorough rinsing to remove any physisorbed molecule (see the SI for details), in depth surface analytical methods were used to characterize the new material and to assess the extent of surface coverage.



Scheme 2. Gold surface or electrode functionalization with **MICs 1-5**.

First, characterization of a gold surface functionalized with **MIC 5** was performed by XPS. As expected, peaks attributed to carbon (C1s ~ 285 eV) and nitrogen (N1s ~ 400 eV) are observed, in addition to those of gold, confirming the immobilization of the MIC at the surface (see Figure S1). A fine analysis of the C1s and N1s peaks (presented in the SI) confirms the presence of the MIC without degradation (N/C = 0.053 compared to the theoretical ratio N/C = 0.079). The slightly lower observed N/C ratio can be explained by a stronger attenuation of the N signal, which comes from atoms screened by the alkyl chains, in agreement with a coordination geometry as depicted on Scheme 2.

The N1s peak can be split into two components at 401.5 and 400.0 eV with a 2:1 ratio corresponding to the different chemical environments of the nitrogen atoms.[40] Compared to the binding energy of the triazolium salt, a shift of 1.8 eV is observed toward lower binding energy. This shift already described previously on gold NPs confirms the covalent bond between the MIC and gold substrate.[23,24,40] We did not detect any Br, which indirectly confirms covalent grafting and the absence of physisorbed triazolium salt precursor. A layer thickness of 1.6 nm and a surface density of $2.8 \cdot 10^{-6}$ mol·m^{-2} could be roughly estimated by solving the set of equations given in the SI.

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Attenuated total reflectance (ATR) infrared measurements onto SAMs made from **MIC 1**-**3** and **MIC 5** on flat gold surfaces were also performed to verify that the molecular integrity of the surface ligands was preserved upon grafting. The recorded spectra and their analysis are provided in Figures S2-5 and Table S1. All the assemblies showed characteristic bands corresponding to the specific pendent functional groups.

As an alternative spectroscopic approach, Surface Enhanced Raman Spectroscopy (SERS) has been formerly used to analyze the ligand shell around nanoparticles and assess their stability.[41,42] For our macroscopic surfaces, we resorted here to Tip Enhanced Raman Spectroscopy (TERS) that allows to observe, at the nanometer scale, whether molecules are uniformly distributed or not. TERS advantageously combines scanning probe microscopy (here scanning tunneling microscopy) with SERS.[43–51] It requires the use of a tip for which the localized plasmon resonance can be stimulated using a laser of adapted wavelength so as to considerably amplify the electromagnetic field below the tip. In this study, we used a gold STM tip to image the surface and record Raman spectra for **MIC 4** adsorbed on a flat gold substrate over 180 minutes as presented in Figure 1.

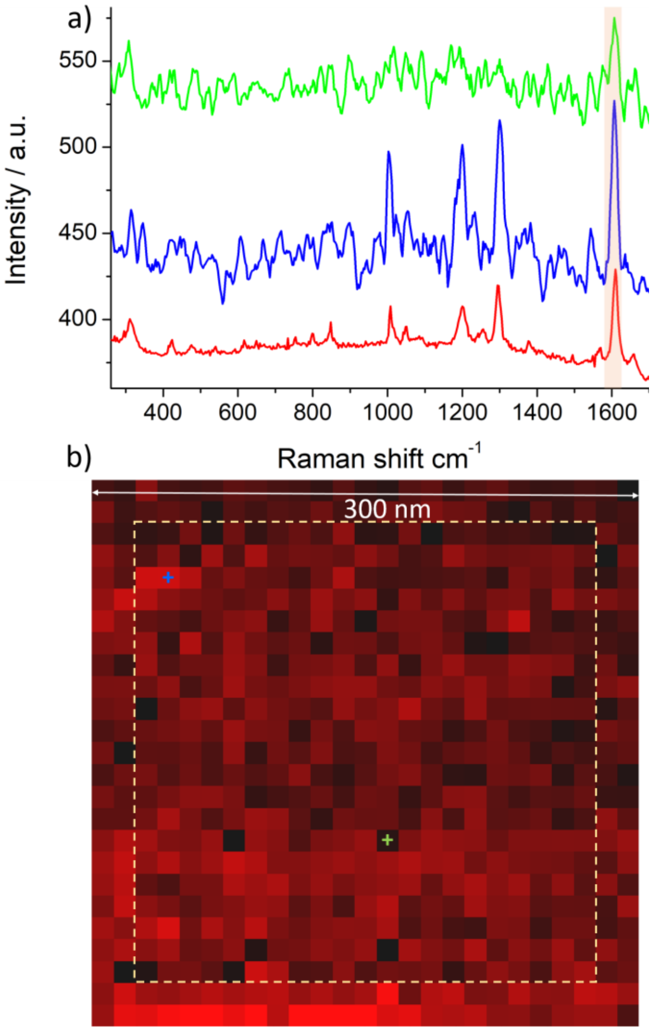

Figure 1. a) Average Raman spectrum of **MIC 4** over the area delimited by a square in Figure 1b (red). Spectra at a bright pixel (blue) and at a dark pixel (green) at positions indicated on b). b) TERS intensity map of **MIC4** obtained by integration of the band highlighted in Figure 1a between 1582 and 1643 cm^{-1}; black pixels are less intense than red pixels.

At each pixel, we recorded a Raman spectrum, with a spatial resolution of a few nanometers as described in the SI. The average signal over the area is provided by the red trace in Figure 1a. The characteristic features of the phenyl moieties' vibrations are apparent, with a clear similarity to 4-biphenylthiol signals, and in agreement with theoretical calculations reported in

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the SI (table S2).[52,53] This allowed us to construct the intensity map presented in Figure 1b by integration of the phenyl rings breathing mode vibrations at 1609 cm^{-1} over an area of 12×12 nm^2 (an average of four 6x6 nm^2 pixels in our acquisition procedure). The two traces in Figure 1a corresponding to one rather intense (blue trace, red pixel in Figure 1b) and one less intense (green trace, black pixel in Figure 1b) pixel show that in fact there is little intensity fluctuation. It is however difficult to ascertain if the observed variations are due to different local concentrations, orientation of the molecules or electromagnetic amplification. Overall, we can conclude that the whole surface was covered by **MIC 4**, with little concentration variations, and that there were no large areas without molecules. A TERS signal was also recorded with **MIC 3**, which presents an intense band at 1325 cm^{-1} ascribed to the symmetric NO_2 stretching mode.[54] Spectroscopic and electrochemical data for this system are presented in Figures S6-7.

This spectroscopic evidence confirms that MICs were efficiently grafted onto gold surfaces. In order to more accurately quantify the molecules present on the surface and assess the grafting kinetics, we used **MIC 2** that bears a redox tag. The molecular coverage was estimated by cyclic voltammetry (CV). In this approach, the number of redox entities grafted on an electrode as a function of immersion time could be easily followed by simple integration of the faradaic current peak. Indeed, when performing CV on a SAM, the faradaic charge that flows through the electrode is directly proportional to the number of adsorbed redox systems.[55] Experimentally, we resorted to gold balls that were flame annealed prior to immersion in **MIC 2** solutions for different times.[56,57] After rinsing, the electrodes were immersed in a 0.1 M tetrabutylammonium hexafluorophosphate solution (dichloromethane) as supporting electrolyte. A scan rate of 100 V·s^{-1} was chosen to prevent any degradation of the molecule while in its oxidized state.[33]

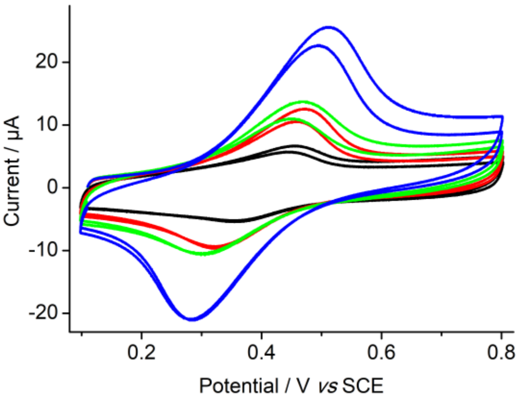

Figure 2. Cyclic voltammograms obtained in 0.1 M tetrabutylammonium hexafluorophosphate (dichloromethane) for a gold electrode modified with **MIC 2** during 5 (black), 15 (red), 60 (green) and 180 (blue) minutes. Two consecutive cycles were recorded.

The recorded voltammograms in Figure 2 displayed well-resolved peaks with a bell-shape behavior corresponding to the reversible oxidation of the ferrocene entities with apparent standard potentials at +389 ± 10 mV *vs* SCE. The corresponding surface coverages quickly increased during the first 30 minutes to finally reach $\Gamma = 1.2\times10^{-6}$ mol·m^{-2} after 3 hours, therefore quite close to the compact packing of the molecules estimated considering hexagonal pavement with a molecular diameter of 0.9 nm (2.3×10^{-6} mol·m^{-2}) and in qualitative agreement with XPS estimations of **MIC 5** and typical values obtained for other NHCs on gold.[58,59] Longer immersion times occasionally resulted in reproducibility issues regarding surface coverage. This may be due to a competition between adsorption and organization in the monolayer with partial degradation of the layer possibly leading to detachment of the electroactive entity. At this present stage, further investigations are necessary to explain such variations.

Notably, the time necessary for significant surface coverage with MICs is larger than that with thiols, indicating an activation limited process. While the stability of NHCs coatings on NPs or surfaces is usually addressed by replacement experiments,[19,21,26,38,40] we realized that such

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stability tests may be fruitfully exploited in the fabrication of partial or mixed SAMs. This would pave the way towards alternative strategies for adjusting molecular coverage, and importantly for producing multifunctional surfaces. We thus proceeded to examine the reversibility of thiol incorporation in MIC monolayers or vice versa. Using the same protocol developed for **MIC 2**, we coated an electrode with **MIC 1** over 18 hours ($\Gamma = 8.3\times10^{-7}$ mol·m^{-2}). Following immersion of the electrode into a 1 mM dodecanethiol solution (THF), we observed a gradual decrease of molecular coverage leading to almost complete loss of all redox entities after 3 hours as shown in Figure 3. However, when the same electrode was once again immersed in a solution of **MIC 1** for 3 hours, 75% of the initial **MIC 1** coverage was recovered evidencing effective **MIC 1** incorporation. It is nevertheless very likely that thiols were still present on the electrode surface as suggested by the larger standard potential (528 *vs* 464 mV) most likely resulting from an increased hydrophobic environment near the redox centers.[60] We suggest that in the MIC partial pavement vacancies of the electrode surface, there is still room for some smaller dodecanethiol molecules that are then not removed. These experiments may seem surprising considering the supposedly stronger Au-C bond in comparison to the Au-S one.[33] However, for NHC-capped gold NPs, stability tests show very different results depending on the ligands, solvents and ionic concentrations involved, with only a few systems presenting good resistance to thiol exchange.[19,21,26,38,40] For surfaces, a single benzimidazole-derived NHC reported in 2014 by Crudden *et al.* was shown to be stable to dodecanethiol displacement.[33] Our assumption is that the SAM stability does not only depend on the Au-C bond strength but also on many other factors such as Van der Waals interactions within the layer to exclude or conversely incorporate another ligand, the surface preparation procedure or the solvent used. The mobility of coordinated gold atoms on a surface is also an important parameter,[29] as revealed by single molecule experiments.[61–64] Indeed, when a dithiol is trapped between a STM tip and the surface, rupture occurs between two gold atoms but not between the Au and S ones. As a final proof of the complexity for interpreting these replacement experiments, we performed similar experiments with **MIC 2** as shown in Figure S8. In this case, we could not significantly displace dodecanethiol while both MIC structures (**1** and **2**) are similar and hence probably their Au-C bond strengths.

Therefore, this work introduces a novel route beyond the traditional Au-S affinity to provide complex and multifunctional SAMs. Importantly, it is also shown that mixed MIC/thiol SAMs with controlled composition may be created. The ease of preparation of functional MICs in comparison with NHCs will pave the way for future applications. Further studies will aim at understanding and controlling the grafting mechanism and organization, and to extend the methodology to other substrates.

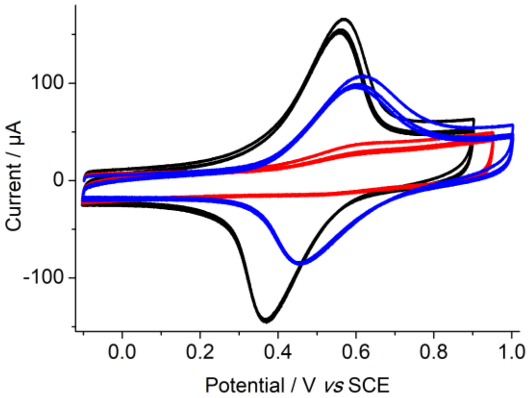

Figure 3. Initial signal obtained after immersion of a gold electrode in 1 mM **MIC 1** for 18 hours ($\Gamma = 8.3\times10^{-11}$ mol·cm^{-2}, black), then 3 hours in 1 mM dodecanethiol (red), then again in 1 mM **MIC 1** for 3 hours ($\Gamma = 6.2\times10^{-11}$ mol·cm^{-2}, blue).

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Supporting Information

SI describes synthetic and experimental procedures, XPS, ATR and additional Raman, TERS and electrochemical experiments together with NMR spectra of the compounds used in this paper. The authors have cited additional references within the Supporting Information.[65–74]

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Keywords: mesoionic carbenes • surface functionalization • self-assembled monolayers • cyclic voltammetry • tip enhanced Raman spectroscopy

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