

# Ultra stable self-assembled monolayers of N-heterocyclic carbenes on gold

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**Since the first report of thiol-based self-assembled monolayers (SAMs) 30 years ago, these structures have been examined in a huge variety of applications. The oxidative and thermal instabilities of these systems are widely known, however, and are an impediment to their widespread commercial use. Here, we describe the generation of N-heterocyclic carbene (NHC)-based SAMs on gold that demonstrate considerably greater resistance to heat and chemical reagents than the thiol-based counterparts. This increased stability is related to the increased strength of the gold-carbon bond relative to that of a gold-sulfur bond, and to a different mode of bonding in the case of the carbene ligand. Once bound to gold, NHCs are not displaced by thiols or thioethers, and are stable to high temperatures, boiling water, organic solvents, pH extremes, electrochemical cycling above 0 V and 1% hydrogen peroxide. In particular, benzimidazole-derived carbenes provide films with the highest stabilities and evidence of short-range molecular ordering. Chemical derivatization can be employed to adjust the surface properties of NHC-based SAMs.**

Self-assembled monolayers (SAMs) on gold have significant applications in sensing, electrochemistry, drug delivery, surface protection, microelectronics and microelectromechanical systems<sup>1–5</sup>. Remarkably, since the ground-breaking report of sulfur-based SAMs on gold 30 years ago<sup>1</sup>, no truly general alternatives for these ligands have been found<sup>6–8</sup>, even though the oxidative and thermal instability of thiol-based SAMs on gold are significant impediments to their widespread commercial use<sup>9–17</sup>. Although thiol-based SAMs are stable when stored in an ultra high vacuum in the absence of light<sup>13</sup>, degradation has been observed after as little as 1–2 weeks at room temperature in air<sup>11,12,14–17</sup> and over 70% of surface thiols are lost by simple immersion in pure THF at room temperature for 24 hours<sup>17</sup>. Thus, according to Salvarezza and co-workers, ‘the chemical stability of thiolate and dithiolate SAMs is one of the most serious problems for their applications in ambient and aqueous environments’<sup>9</sup>. Although improvements in stability have been made by changes to the nature of the gold surface<sup>14</sup>, the use of longer-chain thiols<sup>18</sup>, the application of additives<sup>19</sup> or the use of multidentate sulfur-based ligands<sup>20</sup>, the development of ligands that bind by a fundamentally different mode might be expected to yield more dramatic improvements in stability. As an example, films prepared from diazo compounds provide much-enhanced stability, but without good control over monolayer versus multilayer deposition<sup>21</sup>.

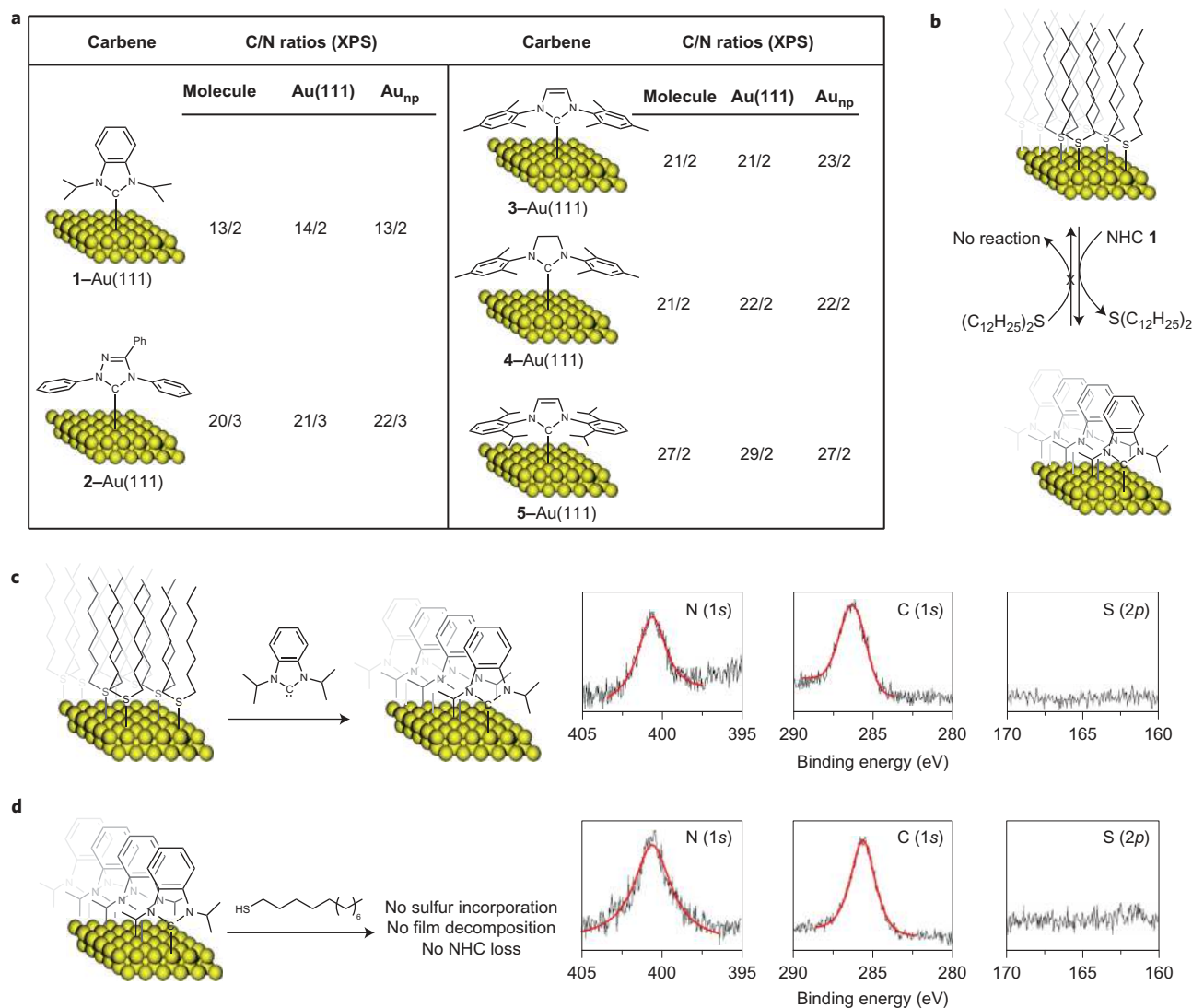
In the field of molecular complexes of transition metals, carbon-based ligands known as N-heterocyclic carbenes (NHCs) have played a significant role over the past two decades<sup>22–25</sup>. These ligands are integral parts of such game-changing catalysts as the Grubbs second-generation metathesis catalyst<sup>26</sup> and NHC-based cross-coupling catalysts<sup>27</sup>. Unlike typical carbenes, which are highly reactive and have very limited stability, NHCs usually have two heteroatoms adjacent to the carbene carbon<sup>28,29</sup>, which increases their

stability to the extent that NHCs can be prepared on the gram scale<sup>30</sup>, crystallized<sup>29</sup>, distilled<sup>30</sup> and stored for long periods of time, making them readily and even commercially available reagents. NHCs are also easily derivatizable<sup>22–30</sup>, and several NHCs are commercially available in the carbene form.

Considering that the Au–NHC bond is estimated to be on the order of 90 kJ mol<sup>−1</sup> stronger than the corresponding Au–phosphine bond and double that of metal sulfide bonds in molecular complexes<sup>31</sup>, NHCs promise to be highly valuable ligands for the protection and functionalization of gold and other metal surfaces. However, as noted in the seminal review by Mercs and Albrecht<sup>32</sup>, applications of these carbenes to materials science and other fields outside homogeneous catalysis are still limited.

McBreen<sup>33</sup> and Nuckolls<sup>34</sup> and their co-workers have described the formation of alkylidene-terminated surfaces, which represent examples of reactive surface-bound carbenes, in contrast to NHC–metal interactions, which are predicted to be stabilizing and unreactive and so potentially general alternatives to thiols. Although there are a handful of reports of NHC-modified nanoparticles, these particles are generally of limited stability<sup>35–40</sup> and, to our knowledge, there are only two reports of the reaction between NHCs and flat gold surfaces<sup>41,42</sup>. Johnson and co-workers described the immobilization of an NHC that contained an ancillary reactive metal alkylidene on a Au surface and employed this species to initiate polymerization reactions from the surface<sup>41</sup>. In this case, the formation of a stable monolayer was not the goal, and only 20–60% monolayer coverage was observed<sup>41</sup>. In the only other report, Weidner *et al.* described an NHC film in which order was inferred from NEXAFS (near-edge X-ray absorption fine structure) C K-edge spectroscopy, but the stability of the monolayer was not assessed and the films lacked the potential for derivatization<sup>42</sup>.

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**Figure 1 | Reaction of NHCs with bare and sulfide-protected Au surfaces, and reaction of thiols and sulfides with 1-protected Au(111) surfaces.**

**a**, Reactions of NHCs 1–5 with Au(111) surfaces and Au nanoparticles resulted in clean transfer of the carbene to the surface, as evidenced by the C/N ratios determined by XPS. **b**, Reaction of NHC 1 with dodecyl-sulfide-protected Au(111) surfaces resulted in complete displacement of sulfide, and, once formed, NHC-protected surfaces showed no back reaction on treatment with dodecyl sulfide (C-7 chains are shown for ease of illustration). **c**, XPS evidence for the complete loss of dodecyl sulfide on treatment with 1 as demonstrated by the lack of an S (2p) signal (C-7 chains are shown for ease of illustration). **d**, XPS analysis of the treatment of 1-protected Au(111) surfaces with dodecanethiol shows no incorporation of sulfur. Au<sub>np</sub>, gold nanoparticle.

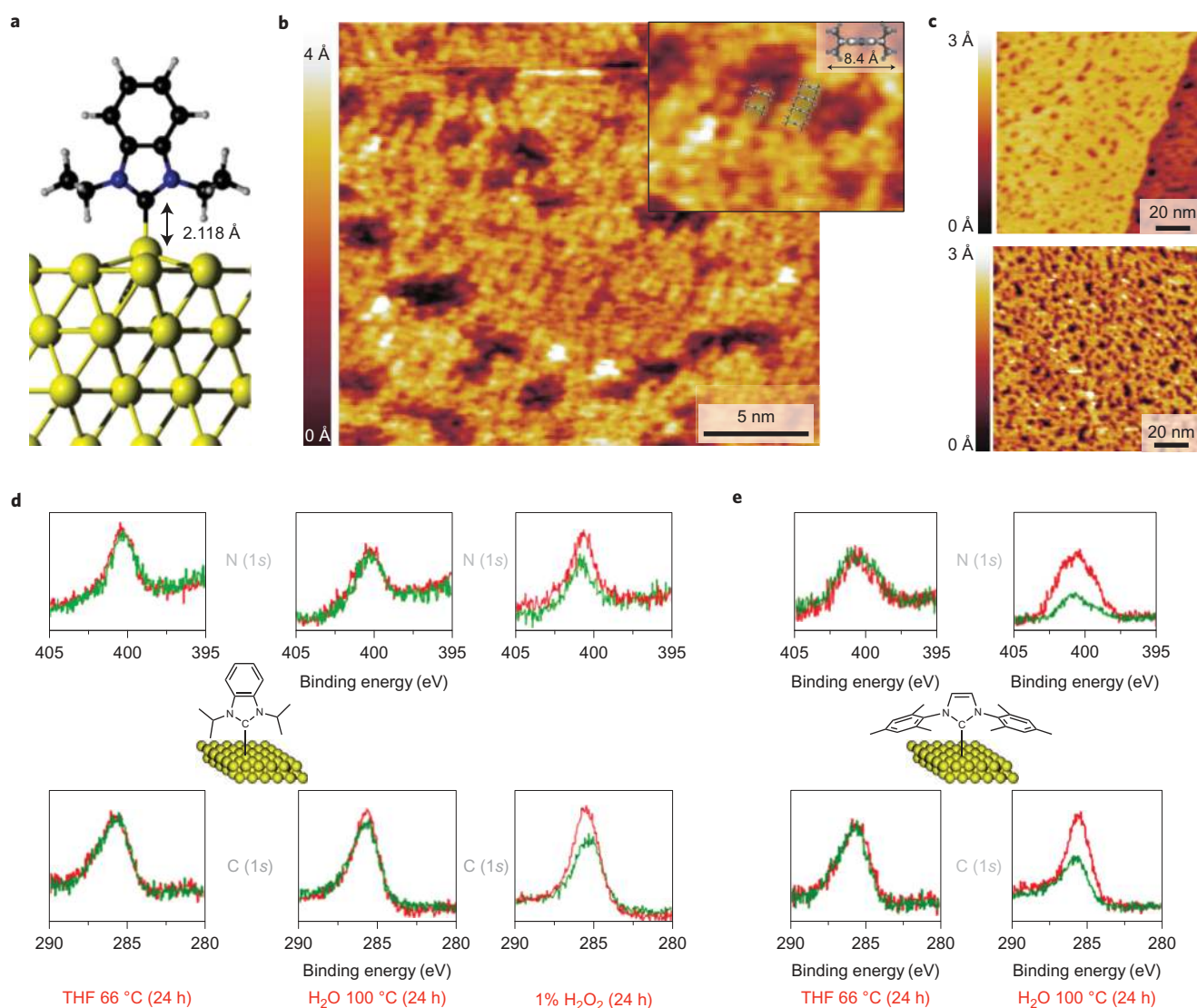
Herein, we demonstrate that by tuning the structure of the NHC, monolayers on Au(111) surfaces can be formed that are exceptionally stable, showing no reaction with thiols, sulfides, refluxing organic solvent, refluxing water, high-temperature acid and base, and only slight decomposition with hydrogen peroxide. Thus, the use of NHCs on gold promises to increase dramatically the stability and lifetime of SAMs and significantly expand the reaction chemistry that can be explored on gold surfaces. We found that NHC-based monolayers prepared on gold electrodes demonstrated exceptionally high electrochemical stability relative to related thiol monolayers, which illustrates the increased stability.

## Results and discussion

As an initial test of the ability of NHCs to form stable monolayers on gold surfaces, thioether-protected gold nanoparticles and Au(111) films on mica were treated with representative NHCs. NHCs 1–5 (Fig. 1a) were all found to react with Au surfaces after simple immersion of Au(111) or Au nanoparticles in a solution of the carbene in organic solvents at room temperature. Despite the

considerable variety in NHC structure, the C/N ratios for the films and nanoparticles, as determined by X-ray photoelectron spectroscopy (XPS), were in agreement with the NHC precursors (within experimental error), which indicates clean reactions with the surface (Fig. 1a). Scanning tunnelling microscopy (STM) was also used to analyse selected films (vide infra).

In addition to the demonstration by the C/N ratios of an effective transfer of the NHC to the surface, XPS data also show the complete removal of dodecyl sulfide from the surface of the gold nanoparticles or Au(111) surfaces on treatment with a 1 mM solution of the NHC in toluene at room temperature for 24 hours (Fig. 1b,c). Figure 1c shows XPS spectra obtained after the reaction of 1 with Au(111) surfaces protected by dodecyl sulfide. No S (2p) signal was observed, which indicates the complete displacement of dodecyl sulfide by 1 within the limits of detection. Remarkably, treating 1-protected Au(111) surfaces with a 1 mM solution of dodecyl sulfide or dodecanethiol for 24 hours at room temperature resulted in no incorporation of sulfur, as determined by XPS, and no loss of carbene from the surface (Fig. 1d and



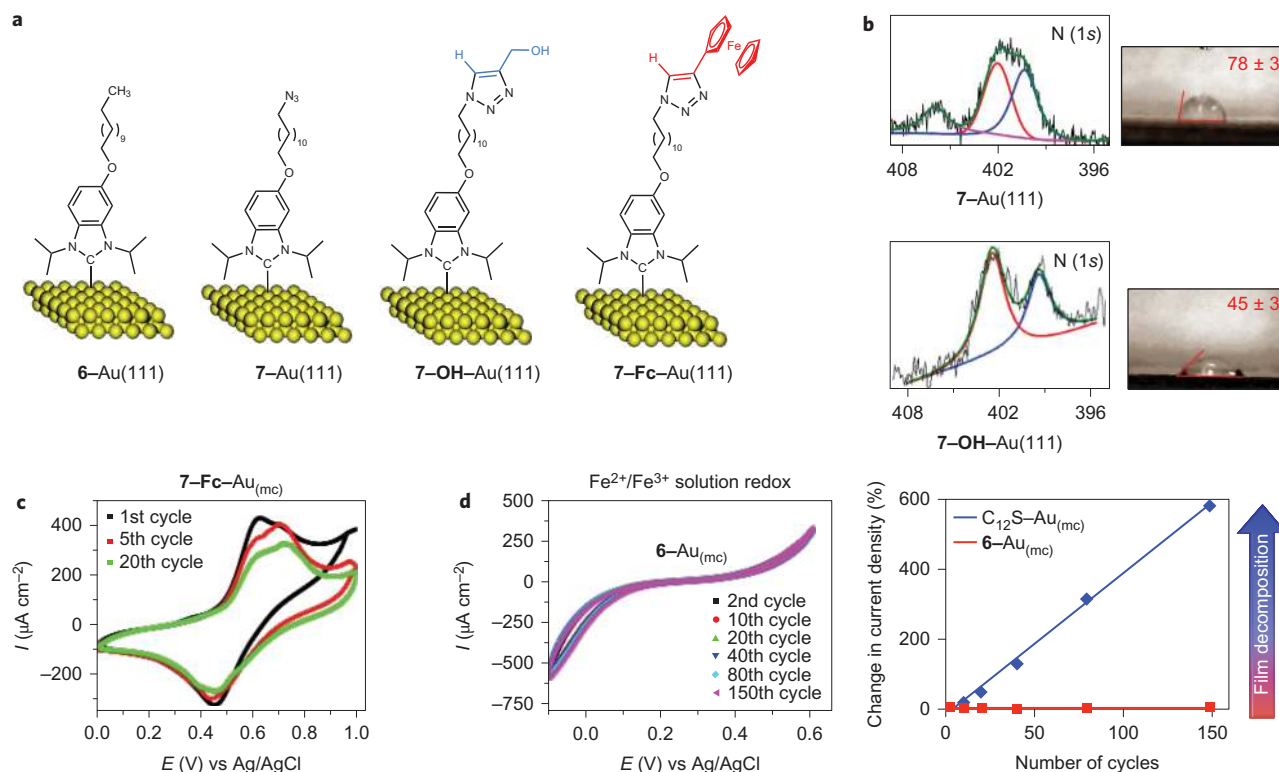
**Figure 2 | Molecular-scale ordering and high stability of NHC-Au(111) surfaces.** **a**, Bonding geometry of **1** on Au(111) as determined from DFT calculations. **b**, An STM image of **1** on Au(111) shows the local order that comprises 5–10 stacked units of **1** on the surface. Inset, schematic representations of individual molecules overlaid to scale. **c**, Lower magnification images of **1**-Au(111) (top) and **3**-Au(111) illustrate the different levels of pitting for the two surfaces. **d**, N (1s) and C (1s) XPS data demonstrate the chemical stability of **1** to treatment with boiling organic and aqueous solutions (left and centre), and 1%  $\text{H}_2\text{O}_2$  for 24 hours (right). Red, before; green, after. **e**, N (1s) and C (1s) XPS data show stability of **3**-Au(111) films in boiling THF (left) and decomposition in boiling water (right). Red, before; green, after.

Supplementary Fig. 1). These observations imply that: (1) the gold–carbene bond is at least as strong as the gold–thiol bond, and (2) once formed, the NHC surface coverage is dense enough to prevent even dodecanethiol from penetrating and binding to sites not covered by the NHC. Analyses of STM images and electrochemistry data corroborate that the **1**-Au(111) surface is densely packed (vide infra).

Although dodecyl sulfide is completely removed from the Au(111) surface by NHC **1**, for dodecanethiol-stabilized surfaces only 55–60% of the thiol is removed from the surface on similar treatment (Supplementary Fig. 2a,b). This is consistent with literature reports that show, even in displacement reactions where one thiol replaces another, up to 40% of the surface thiolate is non-exchangeable, except on immersion in neat thiol at elevated temperature<sup>17</sup>. However, interestingly, NHC **1** is able to remove benzenethiol completely from a PhSH-protected Au(111) surface (Supplementary Fig. 3a) and even the bidentate thiols benzene-1,2-dithiol and propane-1,3-dithiol were largely or completely

removed on treatment with **1** (Supplementary Fig. 3b,c). The bulkier NHC **3** was only partially effective or completely ineffective at replacing thiols in these films (Supplementary Fig. 4a–c), which highlights the unique character of NHC **1**.

The strength and nature of the interactions of NHC **1** with an Au(111) film on mica were simulated by density functional theory (DFT) methods (Fig. 2). In the case of thiol-modified gold surfaces, typically thiols are expected to bind to gold via tetrahedral sites such that each thiol binds to three gold atoms<sup>43</sup>, with a binding energy of approximately  $125 \text{ kJ mol}^{-1}$  (refs 44,45). Note that the Au–S bond energy quoted as  $30 \text{ kcal mol}^{-1}$  is based on the experimental work of Scoles and co-workers<sup>44</sup>. An earlier report by Nuzzo *et al.*<sup>45</sup> in which the same value is estimated at  $40 \text{ kcal mol}^{-1}$  is often cited in the literature, even though Nuzzo *et al.* emphasized that this value was only approximate. However, for NHC–Au(111) surfaces, DFT calculations indicate that the most-stable binding mode is one in which the NHC binds at ‘atop’ sites via a single gold–carbon bond (Fig. 2a)<sup>40</sup>. The calculated bond strength of this bonding mode is



**Figure 3 | Chemical derivatization of Au(111) surfaces and film stability under repeated electrochemical cycling.** **a**, Au(111) surfaces modified by derivatives of NHC **1** that contain either a C-12 alkyl chain (**6**), an azide (**7**) or derivatives of the azide film prepared by Huisgen cycloaddition between **7**-Au(111) and propargyl alcohol (**7-OH**) or ethynyl ferrocene (**7-Fc**). **b**, XPS and contact-angle measurements on the azide-terminated and alcohol-terminated NHC surfaces. **c**, Electrochemical cycling experiments of the ferrocene-terminated film **7-Fc-Au**<sub>(mc)</sub>. **d**, Left: cyclic voltammogram of **6** on an Au<sub>(mc)</sub>-modified electrode that shows repeated cycles for the reduction and oxidation of Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> in solution. Right: change in current density as related to the number of redox cycles for Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> in solution that employ dodecanethiol-terminated films (blue) and NHC **6** films (red) on Au<sub>(mc)</sub> electrodes. Au<sub>(mc)</sub> = microcrystalline Au on Si.

150 kJ mol<sup>-1</sup>, approximately 25 kJ mol<sup>-1</sup> stronger than the thiolate-Au bond on Au(111)<sup>44,45</sup> (Supplementary Fig. 5). The Au-C bond length is calculated to be 2.118 Å, which is fully consistent with molecular gold-NHC species<sup>46</sup>.

As shown in Fig. 2b,c (top), STM images of **1**-Au(111) films are characterized by local ordering throughout the film and a low void density. Individual molecules are found to form one-dimensional arrays and the array alignment is independent of the STM scan direction. The dominant features in the STM images are approximately 4.8 Å × 3.4 Å in size (Fig. 2b), consistent with the benzimidazole portion of the carbene sitting upright on the surface in stacked arrays with neighbouring molecules. Scaled representations of molecule **1** are overlaid on the image (Fig. 2b, inset) to illustrate the probable stacked arrangement of the molecules on the surface.

The STM images also show the presence of darker regions, one Au layer in depth, which are not present on the unreacted Au(111) film and indicate restructuring of the Au surface analogous to the 'etch pits' commonly seen on alkanethiol-Au(111) SAMs<sup>9,47</sup>. Also in analogy with thiol results, these etch pits are not predicted to be defects in the SAM itself, which would be expected to provide ample sites for incorporation of thiol in previous experiments (Fig. 1d), but rather areas of relocation of gold atoms<sup>9,47</sup>. However, the density of the darker regions is significantly greater for films prepared from **3** (Fig. 2c, bottom) compared with those from **1** (Fig. 2c, top). The high density of step edges may be necessary to accommodate the bulky mesityl side groups of the NHC and, at this level of disorder, may indicate an overall lower stability of the film. Films of **3** on Au(111) do not show local ordering on the surface at any level of analysis (Supplementary Fig. 6). The bulky mesityl side groups of

NHC **3** probably contribute, so a less-organized and more loosely packed SAM is expected at the Au(111) surface.

As stability in thiol-based SAMs is closely related to ordering<sup>9,18</sup>, and **1**-based films display local order, we set out to explore the stability of these surfaces. To begin, NHC-modified nanoparticles were analysed by solid-state <sup>13</sup>C CP/MAS (cross-polarization magic angle spinning) NMR spectroscopy, which showed a signal in a region appropriate for a Au-C bond (Supplementary Fig. 7). Chemical stabilities of the NHC-Au(111) films were then assessed. In terms of chemical stability, SAMs formed from NHC **1** showed no change by XPS after heating in boiling THF for 24 hours (Fig. 2d, left), which is remarkable considering that SAMs prepared from octadecanethiol are reported to lose 70% of the thiol after 24 hours in THF at room temperature<sup>17</sup>. SAMs of **1** also showed no discernible change on heating in 100 °C water or decalin for 24 hours, which demonstrates high thermal stability (Fig. 2d centre and Supplementary Fig. 8a). A large fraction of the surface remains even on treatment with 1% H<sub>2</sub>O<sub>2</sub> for 24 hours (Fig. 2d, right). That 80 ± 5% of the film survives treatment with 1% H<sub>2</sub>O<sub>2</sub> for 24 hours is remarkable by comparison with the oxidative sensitivity of thiol-based SAMs<sup>12</sup>. Films of **1** were also completely stable in aqueous solutions that ranged from pH 2 to pH 12 for 24 hours at 100 °C (Supplementary Fig. 8b,c), and no decomposition was observed after storage in water for one month (Supplementary Fig. 8d).

SAMs generated from the bulkier carbene **3** were also stable in boiling THF (Fig. 2e, left); however, more than 50% of the film was lost after 24 hours in boiling water (Fig. 2e, right), and lower stability under other conditions was also observed (Supplementary Fig. 9a-c). These observations are consistent with the higher ordering and denser packing of **1** on Au(111) compared to that of **3**.

Similar to regular alkylthiol-based SAMs, in which stability is provided by both gold thiolate bonds and van der Waals interactions between the alkyl groups<sup>1–5,18</sup>, the ability to stack on the surface probably provides enhanced stability for benzimidazole-based SAMs that employ NHC **1**. In addition, the smaller size of the isopropyl wing-tip substituents of **1** compared to the mesityl substituents of **3** is probably important for bonding to a flat surface.

To prepare functional, derivatizable films, simple aromatic substitution and S<sub>N</sub>2 chemistry were employed to prepare analogues of NHC **1**, including NHC **6** (in which a long alkyl chain is appended off the backbone) and NHC **7** (in which a terminal azide group is present) (Fig. 3a). In the case of **7**, the azide-terminated Au(111) surfaces were reacted with the hydrophilic alkyne propargyl alcohol in the presence of Cu catalyst, and the expected Huisgen cycloaddition (click reaction)<sup>48</sup> formed a chemically modified SAM (**7-OH**, Fig. 3a). The success of this reaction was monitored by XPS and contact-angle measurements (Fig. 3b). The latter technique confirmed that the azide-terminated surface with a contact angle of 78 ± 3° was transformed into an alcohol-terminated surface with the expected contact angle of 45 ± 3°. Treatment of the same surface in the absence of either Cu or the alkyne resulted in no discernible change in the contact angle. Importantly, in the N (1s) region of the XP spectrum of **7-Au(111)**, the diagnostic signal for the central nitrogen of the azide (Fig. 3b, top) was lost after exposure of the surface to propargyl alcohol and Cu catalyst (Fig. 3b, bottom). Ethynyl ferrocene was also reacted with **7-Au(111)** and XPS analysis demonstrated that functionalization of the film was successful and that non-selective adsorption of ethynyl ferrocene did not occur (Supplementary Fig. 10a,b).

With these films in hand, the next step was to determine whether the chemical stability demonstrated by **1-Au(111)** would extend to a functional application, namely the use of NHC-Au monolayers in electrochemistry. In the case of thiol-based SAMs, instability of the film under repeated electrochemical cycling is a limitation for their application in some electrochemical detection schemes. Beginning with films functionalized with the electroactive ferrocene group **7-Fc**, 20 redox cycles were carried out, cycling at 1 V sec<sup>-1</sup> (Fig. 3c, Supplementary Fig. 11a) which resulted in a 16% reduction in peak intensity of the cyclic voltammogram over these 20 cycles. These losses are consistent with those commonly observed in ferrocene-terminated thiol-based films, and are attributed to nucleophilic attack on the ferricenium group rather than to film decomposition<sup>49</sup>, but they do allow for an estimation of current density and electron-transfer rate of the films (Supplementary Fig. 11b). The charge transferred at the second cycle is 3.5 ± 0.5 electrons nm<sup>-2</sup>, from which we are able to infer a surface density of 3.5 ± 0.5 **7-Fc** molecules nm<sup>-2</sup>. This value is completely consistent with the density of features observed on the STM images of **1-Au** films. Computational methods predict that a completely packed surface will have a density of 3.5 molecules nm<sup>-2</sup>, which provides further evidence for the high density of the NHC films on gold prepared as described herein.

To assess fully the film stability under electrochemical conditions, the reduction and oxidation cycles of Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> were examined in solution using simple C-12 alkylated **6-Au**(<sub>mc</sub>) films and dodecanethiol films on Au(<sub>mc</sub>). (Au(<sub>mc</sub>) = microcrystalline gold on Si). Au electrodes functionalized with dodecanethiol showed a significant increase (by 600%) in current density over 150 cycles, which is related to the appearance of defects in the film that permit an increased charge transfer between the naked gold surface and the solution electroactive species<sup>50</sup>. By comparison, the NHC films prepared from **6** on Au showed no detectable change in current density over the same 150 cycles (Fig. 3d and Supplementary Fig. 12). This demonstrates a remarkable increase in film stability in an important application in which the instability of thiol-based SAMs affects performance. The same experiment was

repeated at a more negative voltage to assess the stability of the film to reductive stripping. Interestingly, in this regard the thiol film outperformed the NHC film because the thiol was removed at a voltage of -1.1 V versus Ag/AgCl, consistent with that expected for electrochemical desorption of the thiol<sup>50</sup>. However, for the NHC film, the desorption peak appeared at -0.4 V versus Ag/AgCl, which indicates a lower stability under strongly reducing conditions (Supplementary Fig. 13).

## Conclusions

The high thermal, hydrolytic, chemical, oxidative and electrochemical (above 0 V versus Ag/AgCl) stabilities that characterize NHC-derived SAMs make these species exceptionally valuable alternatives to sulfur-based ligands. The ultra high stability observed is attributed to a different mode of bonding for carbon-based NHCs and increased ligand-metal bond strengths for NHCs relative to the sulfur ligands more commonly used. Tuning the chemical structure of the NHC employed proved important to obtain the maximum stability of the resultant films and permitted the demonstration of molecular ordering on the surface. As ligands, NHCs can be bottled and stored for extended periods of time, or they can be generated in one simple step from imidazolium or benzimidazolium precursors, which are indefinitely stable in air at room temperature. The NHCs employed present opportunities for chemical derivatization, as we demonstrate in the preparation of 'clickable' surfaces (which allow for the modification of surface properties in a controllable, potentially printable manner) in the same way that thiol monolayers can be treated. These various features promise to increase dramatically the range of applications in which SAMs can be employed and to improve the performance in others, which are under active investigation in our labs, along with the translation of these properties to nanoparticles.

## Methods

Detailed information on materials and methods is available in the Supplementary Information. NHCs were prepared by literature methods, and compounds **6** and **7** were prepared by typical aromatic chemistry and S<sub>N</sub>2 displacement reactions. SAMs were prepared by immersion of the gold substrates in a 1 mM solution of the corresponding carbene in anhydrous toluene for four hours at room temperature in a glove box. Then, substrates were rinsed in anhydrous THF (5 × 2 ml) and dried under a nitrogen-gas stream.

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### Author contributions

C.M.C. conceived the concept, and J.H.H. and C.M.C. equally designed the experiments and prepared the manuscript using feedback from the other authors. Synthetic studies were carried out in C.M.C.'s lab, and surface studies in J.H.H.'s lab. A.B.M. and B.D. carried out STM studies, G.W. carried out solid-state MAS NMR studies, N.J.M. carried out computational studies, I.L.E., E.C.K. and T.S. worked on the syntheses of NHCs 6 and 7. O.V.Z., J.D.L. and A.R.-W. worked on the synthesis and adsorption of carbenes 1–5 on surfaces. O.V.Z. and I.L.E. carried out the stability studies. I.L.E. carried out surface characterizations. Z.S. and H.B.K. carried out electrochemical measurements.

### Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at [www.nature.com/reprints](http://www.nature.com/reprints). Correspondence and requests for materials should be addressed to C.M.C. and J.H.H.

### Competing financial interests

The authors declare no competing financial interests.

## ERRATUM

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In the version of this Article originally published, J. Hugh Horton should also have been denoted a corresponding author, with the e-mail address: [jhh@queensu.ca](mailto:jhh@queensu.ca). This error has now been corrected in the online versions of the Article.

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