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Using Surface-Enhanced Raman Spectroscopy to Unravel the Wingtip-Dependent Orientation of N-Heterocyclic Carbenes on Gold Nanoparticles

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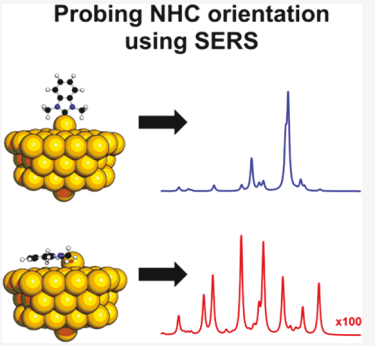
ABSTRACT: N-Heterocyclic carbenes (NHCs) are an attractive alternative to thiol ligands when forming self-assembled monolayers on noble-metal surfaces; however, relative to the well-studied thiol monolayers, comparatively little is known about the binding, orientation, and packing of NHC monolayers. Herein, we combine surface-enhanced Raman spectroscopy (SERS) and first-principles theory to investigate how the alkyl "wingtip" groups, i.e., those attached to the nitrogens of N-heterocyclic carbenes, affect the NHC orientation on gold nanoparticles. Consistent with previous literature, smaller wingtip groups lead to stable flat configurations; surprisingly, bulkier wingtips also have stable flat configurations likely due to the presence of an adatom. Comparison of experimental SERS results with the theoretically calculated spectra for flat and vertical configurations shows that we are simultaneously detecting both NHC configurations. In addition to providing information on the adsorbate geometry, this study highlights the extreme SERS enhancement of vibrational modes perpendicular to the surface.



Dense, ordered, self-assembled monolayers (SAMs) on noble-metal surfaces are a prerequisite for many applications in sensing,[1−3] catalysis,[4−6] and electronics.[7,8] While thiols have been the ligand of choice for many decades now, N-heterocyclic carbenes (NHCs) recently emerged as an attractive alternative as they form strong σ-bonds to transition metals and well-ordered SAMs on metal surfaces.[9−11] When compared to thiol-SAMs, NHC-SAMs deliver superior performance in a range of thermal, chemical, and biological conditions;[12−15] however, the formation and stability of NHC monolayers are highly dependent on the NHC structure.[16] For example, the NHC wingtip groups, i.e., the groups attached to the NHC nitrogens, provide steric interactions that can modify the surface packing and orientation.[17] Meanwhile, appending R groups to the NHC backbone enables postsynthetic modifications and modulates the electronics of the NHC structure.[17]

The binding geometries of NHCs to flat gold surfaces are well documented (Figure 1); however, much less is known about NHC binding to roughened surfaces and nanoparticles. Crudden and co-workers[18,19] first demonstrated the wingtip-dependent orientation of NHCs on Au(111): NHCs with sterically bulky wingtips (i.e., ^{i}Pr) display a tendency to form upright configurations while ones with smaller wingtip groups (i.e., Me) primarily form flat-laying species. Fuchs, Glorius, and co-workers[20,21] also investigated the effects of wingtip size on the binding motif of the NHC on Au(111). More recently, it was found that NHCs with smaller wingtips can additionally form dimer structures that attach to the surface via an adatom.[18,20,22−25] To date, the orientation of NHCs on gold surfaces has been determined mainly using high-resolution electron-energy loss spectroscopy (HREELS),[18] scanning tunneling microscopy (STM),[18,20] and near-edge X-ray absorption fine-structure spectroscopy (NEXAFS).[26] Unfortunately, these techniques are not easily applied to nanoparticles in aqueous solutions.

Surface-enhanced Raman spectroscopy (SERS) can determine the orientation of adsorbed molecules and is often utilized in the study of nanoparticle systems.[27] Furthermore, SERS is uniquely positioned to answer questions related to molecular orientation as the intensity of spectral bands are dictated by surface selection rules, in which vibrational modes normal to the surface experience the largest enhancement.[28−31] This preferential enhancement could enable detection of small populations of molecules that have vertical configurations. SERS, combined with calculations and isotope labeling, has previously been used to investigate the binding of imidazolium

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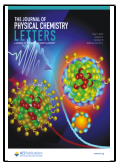

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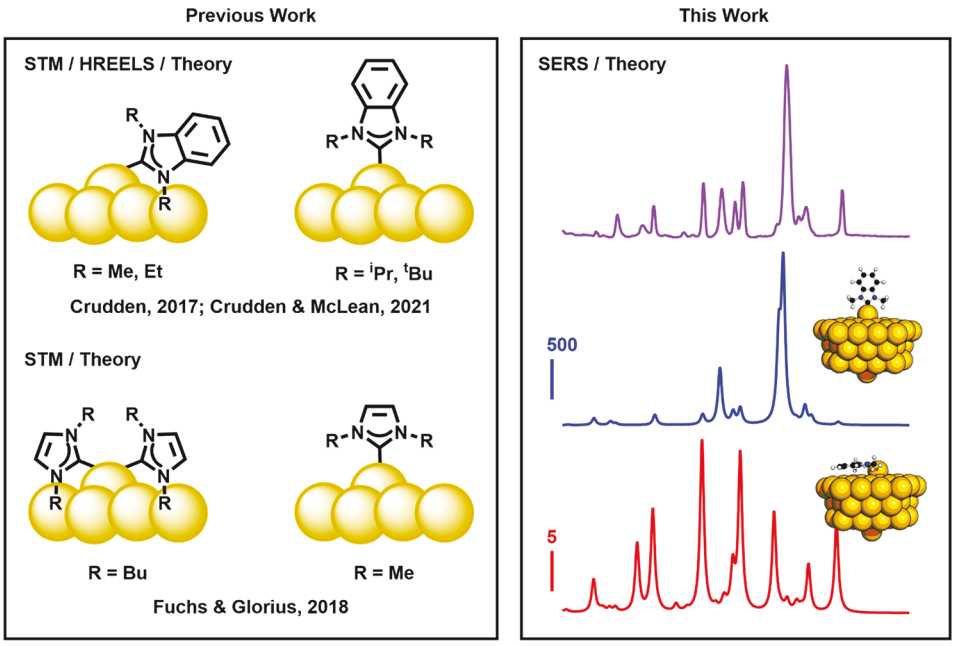

Figure 1. Wingtip-dependent orientation of NHCs on gold surfaces. Left: previous work utilizing STM, HREELS, and theory. Crudden and McLean[18,19] found that benzimidazolium NHCs with smaller alkyl chain wingtip groups adopt flat orientations, while NHCs with bulky wingtip groups adopt vertical orientations. Fuchs and Glorius[20] found that imidazolium NHCs with longer alkyl chain wingtip groups form dimeric species on the surface, while shorter alkyl chain wingtip groups adopt vertical orientations. Right: this work investigates NHC orientation on AuNP using SERS and theory. The blue and red scale bars have units of 10^{-32} cm^2 sr^{-1}. Abbreviations: Me = methyl, Et = ethyl, ^{i}Pr = isopropyl, ^{t}Bu = *tert*-butyl, and Bu = butyl.

and benzimidazolium NHCs on gold film-over-nanospheres (AuFONs).[32]

In this Letter, we present a spectroscopic study of the wingtip-dependent NHC orientation on spherical gold nanoparticles (AuNPs). Benzimidazolium Au(I) complexes with methyl, *tert*-butyl, hexyl, and ethyl wingtip groups (Figure 2) were synthesized according to previously published procedures (see the Supporting Information)[33,34] and then appended to 50 nm citrate-capped AuNPs using the simple top-down approach of Camden and Jenkins.[2] The NHC ligands in this study employed shorter (methyl and ethyl) and longer (hexyl) alkyl chains as well as sterically bulky wingtip groups (*tert*-butyl). The resulting NHC-AuNPs were characterized with SERS, and the most favorable binding configurations for each NHC were modeled using DFT calculations of a single ligand on a Au_{58} cluster. Simulations revealed that the flat configuration is the most stable for the NHCs investigated here. The SERS results reveal that the flat configuration is indeed the most dominant form for all NHCs; however, a small population of vertically oriented carbenes also coexist on the nanoparticle surfaces.

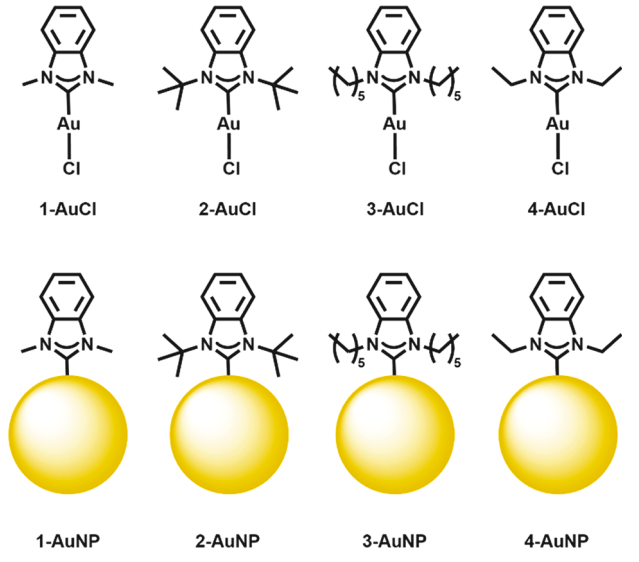

Figure 2. Structures of NHC−Au complexes and NHC modified AuNPs examined in this work.

Figure 3 displays the optimized geometries and binding energies of NHC ligands **1**−**4** adsorbed to a Au_{58} cluster with either a flat or vertical configuration. The Au_{58} cluster was chosen for this study to generate a small cluster model for a AuNP with an adatom. In all calculations, a gold adatom was included in the surface model, which is consistent with a previous report by Glorius and Fuchs.[20] The presence of an adatom provides enough room for the NHCs with sterically bulky wingtips to adopt flat orientations on the surface, as compared to binding directly to the surface. Comparison of the experimentally measured SERS spectra with the simulated SERS spectra for each configuration (Figure 4) allows us to explore the most prevalent configuration adopted by the NHCs on the AuNP surface. The Raman cross sections for the flat spectra (Figure 4, red traces) are about 2 orders of magnitude lower than their corresponding simulated vertical spectra (Figure 4, blue traces). The effects of ligand loading on NHC orientation were also explored, as previous work indicates that surface packing density can influence the NHC geometry. Over the concentration range studied here (0.2−83 μM), the SERS spectra are unchanged (Figures S2 and S3).

Figure 4a shows the comparison between the experimental and theoretical (flat and vertical) spectra for **1-AuNPs**. Neither simulated configuration alone captures the qualitative features

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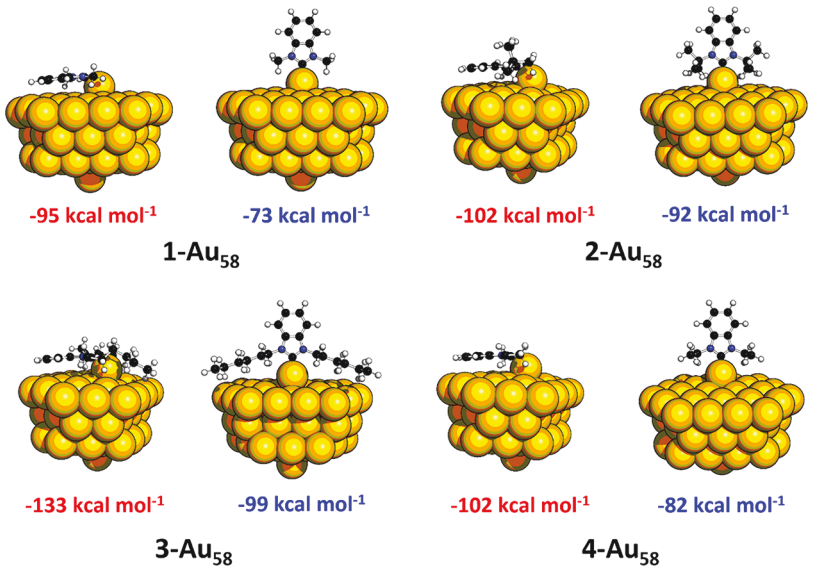

Figure 3. Optimized geometries and calculated binding energies for the flat (red) and vertical (blue) orientations of NHC ligands **1**−**4** on a Au_{58} cluster.

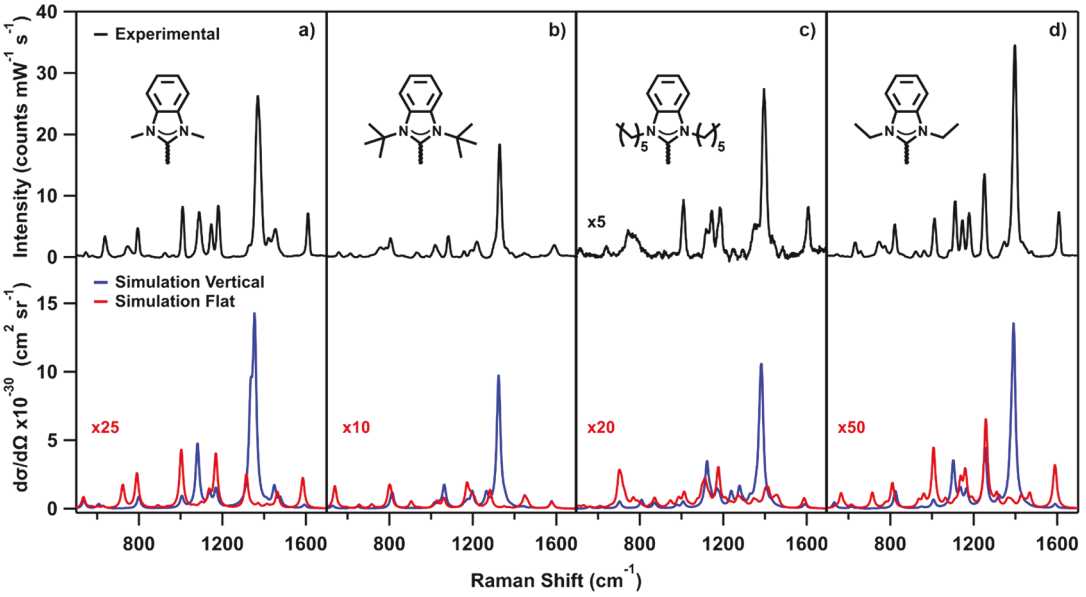

Figure 4. Comparison of the experimental (top) and theoretical (bottom) SERS spectra of flat (red) and vertical (blue) oriented NHCs for (a) **1-AuNPs**, (b) **2-AuNPs**, (c) **3-AuNPs**, and (d) **4-AuNPs**.

of the experimental spectrum, but rather a combination of the two provides a more accurate representation, alluding to the presence of both configurations on the AuNP surface. For example, the large band observed at ∼1370 cm^{-1} arises primarily from the vertically oriented carbenes (∼1354 cm^{-1} in the simulated spectrum). Next, a peak in the simulated flat spectrum at 1585 cm^{-1} is only minimally present in the simulated vertical but is prevalent in the experimental spectrum at 1610 cm^{-1}. Because calculations of the SERS cross sections reveal the flat orientation to be almost 2 orders of magnitude weaker than the vertical orientation, there must be considerably more of the flat orientation on the AuNP surface for its features to be so prevalent in the experimental spectrum.[29] Therefore, while SERS can simultaneously detect both the flat and vertical orientation of **1-AuNPs**, there is likely a much larger population of the flat orientation. Using the theoretically determined Raman cross sections, the best agreement with the experimental spectrum of **1-AuNPs** is achieved when approximately 4% (1 in 25) of ligand **1** are oriented vertically on the AuNP surface (Figure S4). This result is consistent with the lower calculated binding energy of the flat configuration and current literature that NHCs with methyl wingtips form flat lying species on gold surfaces.[18] When the NHCs have small wingtips and low coverage, they can dimerize on gold surfaces;[18,20,22,35] therefore, we also explored this possibility. Theoretical calculations employing a flat dimer of ligand **1** on a Au_{58} cluster yield a spectrum that is very similar to the flat monomer, **1-Au_{58}** (Figure S6). Therefore, no conclusions can be made regarding the presence of monomeric or dimeric NHCs on the AuNP surface.

The experimental and theoretical spectra of **2-AuNPs** are compared in Figure 4b. Despite previous literature concluding

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that NHCs with *tert*-butyl wingtips will adopt vertical orientations,[19] there are features in the experimental spectrum suggesting the presence of both flat and vertical configurations. For example, the most intense peak in the experimental spectrum (1328 cm^{-1}) arises from a vertical configuration of **2**. The experimental spectrum additionally displays bands that are uniquely associated with the flat configuration (experiment/theory: 929/904 cm^{-1} and 1448/1449 cm^{-1}). The best agreement between the theoretical and experimental spectra of **2-AuNPs** is achieved when approximately 10% (1 in 10) of ligand **2** are vertically oriented on the AuNP surface (Figure S4).

Figures 4c and 4d compare the experimental and calculated SERS spectra for **3-AuNPs** and **4-AuNPs**, respectively. Similar to the patterns observed for **1-AuNPs** and **2-AuNPs**, the most intense peak in the experimental spectrum arises from the vertical NHCs, while other bands can only be attributed to flat NHCs. The best agreement between the theoretical and experimental spectra of **3-AuNPs** and **4-AuNPs** is achieved when approximately 5% (1 in 20) of ligand **3** and 2% (1 in 50) of ligand **4** are vertically oriented (Figure S5). The experimental spectrum of **3-AuNPs** is considerably weaker in intensity than the others, which could allude to a lower packing density on the AuNP surface.

The preference for flat orientations is consistent with our calculations of the binding energies, which find the flat configuration to be much more stable (by 10−30 kcal mol^{-1}) than a vertical configuration. On purely thermodynamic grounds, this difference is large enough to exclude the possibility of vertically oriented carbenes; however, experiments indicate a small population of vertically oriented NHCs (Table S1). This is not unexpected as the calculations do not account for solvent effects or the presence of kinetically trapped states. Additionally, the simulations only consider one isolated NHC ligand on a Au_{58} cluster; therefore, no crowding effects or NHC−NHC interactions are included. Taken together, our work indicates that the local NHC geometry depends on the complex interplay between carbene structure, binding motif, and deposition method.

In summary, we have systematically investigated the effects of wingtip size on the orientation of NHCs on AuNPs. Consistent with previous literature, smaller wingtip groups lead to stable flat configurations; surprisingly, bulkier wingtips also have stable flat configurations likely due to the presence of an adatom. Comparison of experimental SERS results with the theoretically calculated spectra for flat and vertical configurations shows that we are simultaneously detecting both NHC configurations. Our combined results also showcase the strengths and weaknesses of SERS for molecular orientation studies.[36−39] Despite the flat configurations having lower calculated binding energies, SERS can detect even small populations of the less stable vertical configuration. Alternatively, a weakness of SERS for investigating molecular orientation lies in the reduced sensitivity to molecules with modes parallel with the surface.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.3c00588.

Additional experimental and calculation details; TEM and UV−vis characterization of the AuNPs; additional SERS spectra from concentration dependence studies (PDF)

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Notes

The authors declare no competing financial interest.

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