In situ Raman monitoring triazole formation from self-assembled monolayers of 1,4-diethynylbenzene on Ag and Au surfaces via "click" cyclization

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Abstract

We prepared acetylenyl-terminated aromatic self-assembled monolayers (SAMs) of 1,4-diethynylbenzene on silver and gold. After the fabrication of pendent acetylenyl SAMs, the formation of triazoles was performed via Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition "click" chemistry. A density functional theory (DFT) calculation of Raman frequencies showed good agreement with our experimental data to provide evidence of the formation of the triazole molecule. Our results indicated that "click" chemistry could be successfully applied to simple aromatic SAMs proximate (<1 nm) to roughened gold surfaces. The reaction process could be monitored in real time by measuring intensity changes of the $\nu(C\equiv C)_{free}$ band in surface-enhanced Raman scattering (SERS) spectra.
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1. Introduction

Organic self-assembled monolayers (SAMs) prepared by spontaneous adsorption have drawn much attention, since they may provide a useful method of tailoring physiochemical properties on surfaces to various technical applications in biosensing, nanopatterning, and molecular electronic devices [1,2]. Despite many studies of SAMs derived from organosulfur reagents, relatively little work has been done to fabricate organic SAMs on metal surfaces without sulfur as the anchoring group.

Anchoring an aromatic ring via an alkynyl group may have the advantage of providing a π-conjugated linkage to the gold surface [3]. Rigid aromatic monolayers derived from α, ω-dithiols may provide the basis for studies leading to the design of molecular wires capable of bridging proximate gold surfaces [4]. Characterizing the interfacial structure of conjugated phenylethynyl SAMs should be important for understanding the

electronic and optical properties of materials and devices based on these molecules [5].

To introduce any required functionalities, it should be a significant step to conduct versatile organic reactions from the SAMs on metal surfaces [6]. The copper-catalyzed Huisgen dipolar cycloaddition of a terminal alkyne and an azide to form 1,2,3-triazole "click" chemistry has been extensively used in various organic reactions due to the high efficiency and technical simplicity of the reaction, which has great regioselectivity without requiring harsh reaction conditions [7]. In previous "click" chemistry reports [8,9], it has been shown that triazole formation can be achieved from SAMs on Au prepared from alkanethiols with relatively long carbon chains ($n \geqslant 8$), with some inconveniences in requiring additional time of synthesis for each chemical species.

The phenomenon of surface enhanced Raman scattering (SERS) has become one of the most sensitive techniques for monitoring the adsorbates of particularly short aromatic molecules on metal substrates at the submonolayer coverage limit [10–15]. One of the most widely used self-assembled monolayers (SAMs) may be organic adsorbates on Au or Ag surfaces [1]. We have continued to study SAMs on Au or Ag

surfaces [16–25], since they currently hold the best model system. Aromatic SAMs should have a number of advantages due to their rigidity and conjugated nature [26]. Despite quite a few studies [16–20] of aromatic SAMs disubstituted at their *para* positions, relatively little work has been done on SAMs prepared from those with the acetyleneic group on surfaces [21]. Surface enhanced Raman scattering (SERS) as an ultrasensitive spectroscopic tool for interface studies has been widely used to monitor chemical reactions occurring on Ag and Au metal surfaces [11]. We have used the SERS technique [16–25], since it can provide chemically specific information on the basis of the unique vibrational modes of target adsorbates. In this work we studied the surface "click" chemistry from 1,4-diethynyl-benzene SAMs on Au surfaces by means of SERS to aim at tailoring functionalized surfaces. To the best of our knowledge, this is the first Raman study to monitor triazole formation by "click" chemistry in real time from the simple aromatic SAMs on Au with the acetylene moiety as an anchoring group.

2. Experimental

2.1. Sample preparations

All chemicals used in this study were purchased from Aldrich without further purification. The methods of preparation of the aqueous Ag and Au colloidal nanoparticles have been reported previously [23–25]. For Ag, 90.0 mg of $AgNO_3$ in 500 ml of water was brought to boiling. A solution of 1% sodium citrate (10 ml) was then added to the $AgNO_3$ solution under vigorous stirring. A portion of $\sim 10^{-3}$ M $HAuCl_4$ aqueous solution (50 ml) was brought to boiling and a solution of 1% (w/w) sodium citrate (5 ml) was added to vigorously stirred $HAuCl_4$ solutions for Au nanoparticles. Boiling was continued for $\sim$20 min until the color of the mixed solution became wine red.

For the SERS-active Au surfaces [26], an Au plate (5 × 15 mm) is polished by sandpaper and then immersed into piranha solution. After the substrate was washed by absolute ethanol and the physically adsorbed species were removed by a highly purified nitrogen gas stream, the gold plate was roughened by oxidation–reduction cycles (ORC) using a CHI-700 potentiometer. A Pt wire and an Ag/AgCl were used as a counter and a reference electrode, respectively, in an electrolyte solution of KCl ($\sim$0.1 M). An SERS-active Ag substrate was obtained by immersion of the plate in a HNO_3 solution.

Before going into the surface "click" reaction, the triazole formation was tested in the bulk solution. 3-(4-Phenyl-1-*H*-1,2,3-triazol-1-yl)propan-1-ol was synthesized from ethynylbenzene with 3-bromopropanol. A NMR chemical shift for each proton clearly indicated triazole formation in $CDCl_3$ using a Bruker Avance 400 FT-NMR spectrometer. 1,4-Diethynyl-benzene was not used for a test due to a possible complex reaction from the two acetylenic moieties.

SAMs with pendent acetylenic groups were prepared by immersing SERS-active Ag and Au plates into an ethanolic solution of 1,4-DEB ($\sim 10^{-3}$ M) for over 12 h. The Au plate, self-assembled by 1,4-DEB, was taken out of the solution and then
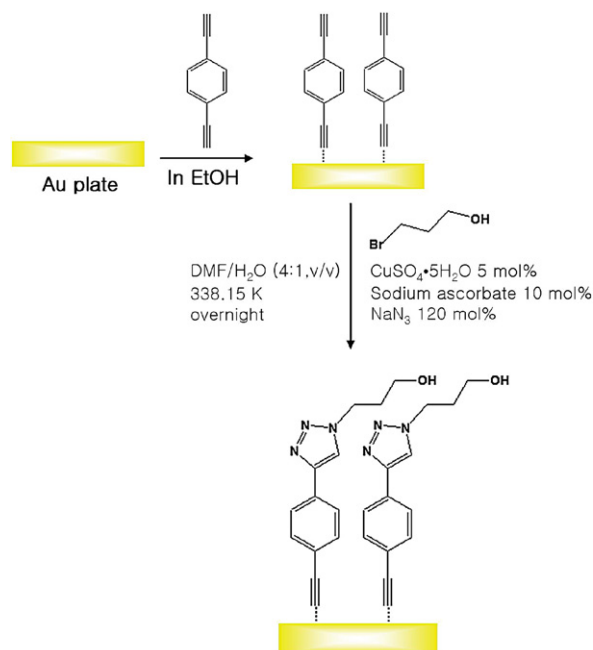

Fig. 1. Schematic presentation of the reaction process for 1,4-DEB adsorbed onto Au surfaces as the triazole compound by surface "click" chemistry. The scheme on Ag should be the same as that on Au.

washed in absolute ethanol and dried by a nitrogen gas stream. The SERS-active gold plate, self-assembled by 1,4-DEB, was reacted in 20 ml of DMF solution containing 5 ml of deionized water, 0.1 ml of 3-bromopropanol (1.47×10^{-3} mol), $CuSO_4 \cdot 5H_2O$ (7.35×10^{-5} mol), sodium ascorbate (1.47×10^{-4} mol), and sodium azide (1.76×10^{-3} mol) at 338 K. Fig. 1 is the schematic diagram for the reaction process. A roughened gold plate prepared by ORC was immersed into the ethanolic solution of 1,4-DEB. The pendent acetylene group of the adsorbed 1,4-DEB on Au was derivatized into the triazole compound by reacting with azide. The reaction process was monitored in real time by micro-Raman spectroscopy.

2.2. Instrumental measurements and DFT calculations

Raman spectra were obtained using a Renishaw Raman confocal system Model 1000 spectrometer equipped with an integral microscope (Leica DM LM). Raman scattering was detected with 180° geometry using a Peltier-cooled ($-70\,°C$) CCD camera (400 × 600 pixels). An appropriate holographic notch filter was set in the spectrometer. The 632.8 nm radiation from a 35-mW air-cooled He–Ne laser (Melles Griot Model 25 LHP 928) with the plasma line rejection filter was used as the excitation sources for the Raman experiments. Data acquisition time used in the Raman measurements was approximately 10 s. The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer. After a laser line rejection filter, the Raman-scattered light was collected to the detector through a holographic beam splitter. The sample was embedded to a glass capillary (Chase Scientific Glass, Inc.) with an outer diameter of 1.1–1.2 mm and ready for the Raman measurement. The laser beam was focused onto a spot approximately 2 μm
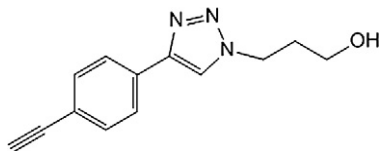
Fig. 2. Molecular structure used for DFT calculations to confirm "click" reaction on Au surfaces, 3-(4-(4-ethynylphenyl)-1H-1,2,3-triazol-1-yl)propan-1-ol.
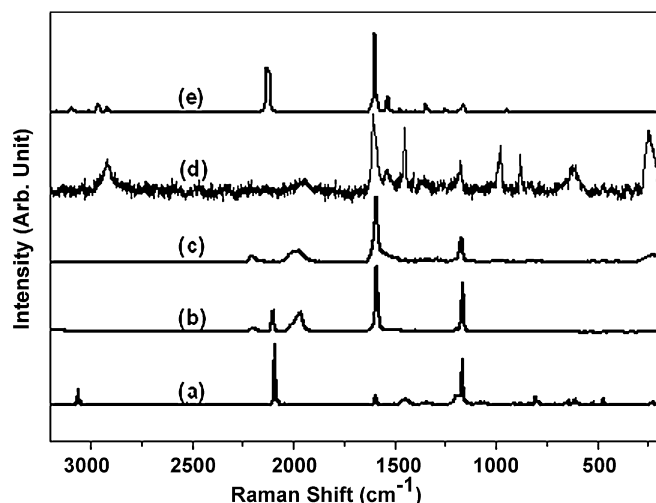

Fig. 3. (a) Ordinary Raman spectrum of 1,4-DEB in its solid state in 3200–200 cm⁻¹. SERS spectra of 1,4-DEB on (b) citrate-reduced Ag nanoparticles, (c) roughened Ag plate surfaces, and (d) modified 1,4-DEB on roughened Ag plates by the surface "click" reaction. (e) Simulated Raman spectrum of the molecule depicted in Fig. 2 from a DFT calculation.

in diameter with an objective microscope of order ×20. The Raman spectrometer was interfaced with an IBM PC and analyzed via a Renishaw WiRE software (v. 1.2) based on the GRAMS/32C suite program (Galactic). All ab initio molecular orbital calculations were carried out using the Gaussian '03 suite of programs [27]. Raman frequencies have been calculated at the level of B3LYP using 6-31 G++(d,p) basis sets for the triazole molecule 3-(4-(4-ethynylphenyl)-1H-1,2,3-triazol-1-yl)propan-1-ol via a "click" reaction as depicted in Fig. 2. The geometry optimization of the triazole–Au complex was carried out at the level of B3LYP using the LANL2DZ basis set.

3. Results and discussion

3.1. Raman spectra of 1,4-DEB on Ag and Au surfaces

Figs. 3a–3c show the ordinary Raman spectrum of 1,4-DEB in its solid state and the SERS spectra of 1,4-DEB on citrate-reduced Ag nanoparticles and roughened Ag plate surfaces, respectively. Figs. 4a–4c show the ordinary Raman (OR) spectrum of 1,4-DEB in its solid state and the SERS spectra on the Au nanoparticles and roughened Au plate surfaces, respectively. The concentration of the 1,4-DEB at $\sim 10^{-3}$ M should be much higher than that required for its monolayer coverage [22]. Consulting the earlier vibrational assignments [29,30], the Raman spectrum was analyzed. The in-plane benzene ring modes appeared at ca. 1178 (ν_{7a}) and 1595 (ν_{8a}) cm⁻¹. The weak band
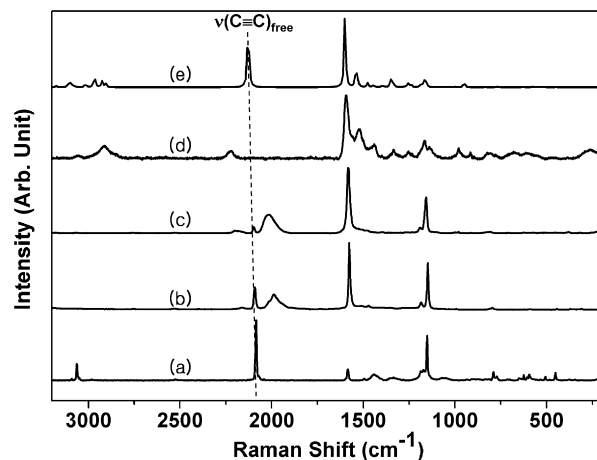

Fig. 4. (a) Ordinary Raman spectrum of 1,4-DEB in its solid state in 3200–200 cm⁻¹. SERS spectra of 1,4-DEB on (b) citrate-reduced Au nanoparticles, (c) roughened Au plate surfaces, and (d) modified 1,4-DEB on roughened Au plates by the surface "click" reaction. (e) Simulated Raman spectrum of the molecule depicted in Fig. 2 from a DFT calculation.

Table 1
Spectral data and vibrational assignment

1,4-DEB			Surface click triazole formation		Assignment[b,c]
OR	Ag plate SERS	Au plate SERS	Experiment	DFT[a]	
788	826	825	822		Benzene out-of-plane (17b)
			993	946	Triazole ring stretch (10)
1178	1170	1171	1153	1168	Benzene ring stretch (7a)
			1177		Triazole ring stretch (77)
			1266	1255	Triazole ring stretch (95)
			1348	1351	Triazole ring stretch (21)
			1533	1534	Triazole ring stretch (41)
1595	1591	1593	1606	1602	Benzene ring stretch (8a)
	1990				$\nu(C\equiv C)_{bound}$
2092	2100	2103		2127	$\nu(C\equiv C)_{free}$
	2208		2228	2150	$\nu(C\equiv C)_{bound}$
			2912	2924	$\nu(CH_2)$
3063		3065	3057	3098	CH stretch (2)

[a] The molecule is depicted in Fig. 2. Scale factor is 0.965.
[b] Based on Refs. [28,29] for 1,4-DEB and [30] for triazole.
[c] The numbers in the parentheses are the vibrational assignments in the references.

at ~ 800 (ν_{17b}) cm⁻¹ could be ascribed to the out-of-plane mode of the benzene ring. Their peak positions are listed in Table 1 along with the appropriate vibrational assignments.

Several C≡C stretching features were observed between 2200 and 1900 cm⁻¹ as shown in Figs. 3c and 4c, whereas only a single peak appeared at ~ 2092 cm⁻¹ for a free state in Figs. 3a and 4a. The sharp prominent band at 2092 cm⁻¹ may provide evidence that 1,4-DEB is adsorbed on gold through one of the two acetylene groups, with the other C≡C groups being pendent with respect to the gold surface. Also, it is noteworthy that the $\nu(C\equiv C)_{bound}$ band could be observed as high as ~ 2208 cm⁻¹ in the SERS spectrum of Fig. 3c. The Raman signal intensity of the $\nu(C\equiv C)_{free}$ band unbound to the surface appeared to be larger on colloidal nanoparticle surfaces than on

roughened surfaces [29]. It would presumably result from different adsorption behaviors of 1,4-DEB, ascribed to different crystal structure and surface morphology between nanoparticles and roughened plates. 1,4-DEB should adsorb onto Au surfaces after losing one of its two acetylenic protons. The pendent C≡C group on Au surfaces was modified by "click" chemistry.

3.2. Surface click chemistry from 1,4-DEB on Ag and Au surfaces

Figs. 3d and 4d show the SERS spectrum after derivatization of 1,4-DEB adsorbed onto Ag and Au plates, respectively, by "click" chemistry. The emerging band at $\sim$2900 cm^{-1} should be ascribed to the ν(CH$_2$) band. One of the most prominent differences between Figs. 3c and 3d (or Figs. 4c and 4d) is a spectral change of the C≡C stretching region. An absence of the relatively sharp peak in the region of $\sim$2100 cm^{-1} in Figs. 3d or 4d, representing the free C≡C group at the surface, dictates the derivatization of the pendent C≡C group by surface "click" chemistry. Also, the broad peak in the region of $\sim$2000 cm^{-1} of the ν(C≡C)$_{bound}$ band observed in Fig. 4d is up-shifted to $\sim$2200 cm^{-1}. Considering that its full width at half maximum (FWHM) bandwidth is as broad as $\sim$100 cm^{-1}, the up-shifted band at $\sim$2200 cm^{-1} should be due to a strong interaction with the surface. In comparison, the FWHM bandwidth of the ν(C≡C)$_{free}$ band was measured to be only $\sim$30 cm^{-1}. Since the frequency position of the azide band is found at $\sim$2110 cm^{-1}, it is not likely that the observed band can be ascribed to the neutral species of the azide. Considering the SERS spectra on Ag plates at $\sim$2208 cm^{-1}, it seems possible that the ν(C≡C)$_{bound}$ band could appear in such a high-frequency position after "click" cyclization. It has also to be mentioned that the vibrational band appeared at the high-frequency positions of $\sim$2170 and 2200 cm^{-1} for the Au sol and plate SERS, respectively, as shown in Figs. 4b and 4c, albeit more weakly than those at $\sim$1900 cm^{-1}.

To better check the formation of triazole, a DFT calculation was performed for 3-(4-(4-ethynylphenyl)-1H-1,2,3-triazol-1-yl)propan-1-ol, as depicted in Fig. 2. As illustrated in Figs. 3e and 4e, the simulated Raman spectrum matched quite well with the observed spectrum in Fig. 4d. The vibrational bands of the triazole could be assigned from Ref. [30] as listed in Table 1. It has to be mentioned that the ordinary Raman spectrum could be quite different from the SERS spectrum. We have also performed a DFT calculation for the triazole–Au complex to anticipate the Raman spectrum after adsorption onto Au. As compared in Figs. 5b and 5c, the Raman spectrum of the triazole–Au complex is predicted to be quite similar to that without the Au atom, except for the strongly estimated intensity of the ν(C≡C)$_{bound}$ band. Also, it is noteworthy that the position of the ν(C≡C)$_{bound}$ band at 2150 cm^{-1} is calculated to be 23 cm^{-1} above that in the ordinary spectrum at 2127 cm^{-1}, more closely in line with our experimental spectrum in Fig. 5a.

Numerous reports have indicated that the adsorption behavior depends on the metal substrates [31]. The detailed origins of the different orientations on Ag and Au have not been fully clarified yet. In this work, we found that the "click" reaction
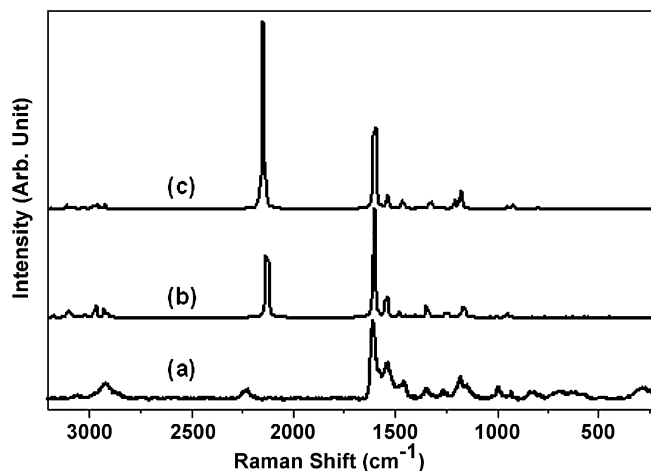

Fig. 5. (a) SERS spectrum of modified 1,4-DEB on roughened Au plates by the surface "click" reaction. Simulated Raman spectrum of (b) the molecule depicted in Fig. 2 and (c) the molecule-Au complex from a DFT calculation.

should occur on both Ag and Au and we could not tell the difference depending on the substrates. Considering that these cyclization reactions have been reported on silica [7] and carbon nanotubes [32], it is expected that the cyclization reaction should occur without the need for the metal surfaces.

In our recent SERS studies [21,29], the multiple ν(C≡C)$_{bound}$ were found to change significantly with the bulk concentration as well as the sol condition. The 2200 cm^{-1} band indicated a certain physicochemical change of the interfacial condition. To better monitor the triazole formation, we checked the SERS spectra after different reaction times by subsequently taking out the substrate from the reaction flask and examining vibrational features.

3.3. In situ monitoring of triazole formation in real time

Fig. 6 shows SERS spectra of 1,4-DEB after reaction with the azide for 1–60 h. A gradual spectral change indicated the formation of triazole via "click" chemistry. After 4 h of reaction time, the ν(C≡C)$_{free}$ at $\sim$2100 cm^{-1} appeared to be quite weakened. Also, the ν(C≡C)$_{bound}$ band was found to be quite blue-shifted from $\sim$1900 to $\sim$2200 cm^{-1}. Several vibrational features that could be ascribed to the triazole were observed to increase in reaction time. The vibrational bands at 993, 1177, 1266, 1348, and 1533 cm^{-1} could be due to the triazole band and their frequencies matched quite well with our simulated Raman frequencies from the DFT calculations, as shown in Figs. 5b and 5c.

Fig. 7 shows a plot of the decrease of the ν(C≡C)$_{free}$ band at $\sim$2100 cm^{-1} with respect to the ν(C≡C)$_{bound}$ band. Also, an increase of the triazole band could be monitored versus the reaction time. An exponential decay curve suggests a pseudo-first-order reaction. Our measure, k_{obs}, was estimated be 0.603 h^{-1}. This rate is considerable lower than the previous report [9]. A short carbon chain or the coverage of the acetylenic group may be related to the low rate of the surface "click" reaction. The percentage yield of 3-(4-phenyl-1-H-1,2,3-triazol-1-yl)propan-1-ol in the bulk solution was esti-
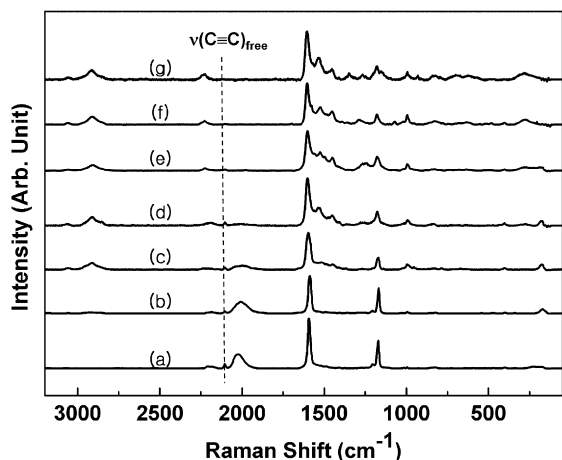
Fig. 6. SERS spectra of 1,4-DEB adsorbed on a roughened Au surface (a) before and after the surface "click" reaction with the azide for (b) 1, (c) 2, (d) 3, (e) 4, (f) 10, and (g) 60 h.
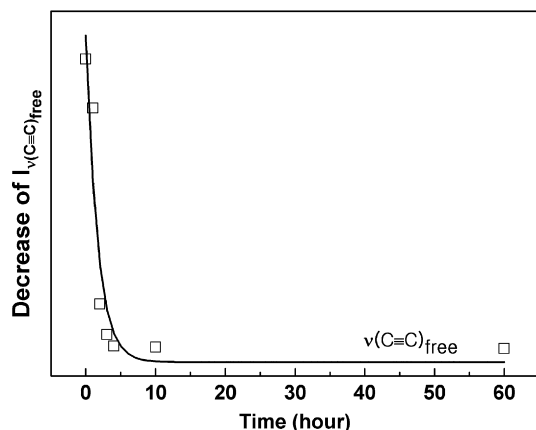

Fig. 7. Plot for the change of intensity in the region of the $\nu(C\equiv C)_{free}$ band at ~ 2100 cm^{-1} marked as squares ($\square$) with respect to those of the $\nu(C\equiv C)_{bound}$ band at ~ 2000 and ~ 2200 cm^{-1} on the basis of reaction time. The average time requiring for completion of the reaction is estimated to be ~ 2 h.

mated to be around 50% from the NMR measurements. It seems a matter of conjecture to estimate the percentage yield on the Au or Ag surfaces in an accurate way. From the changes in our Raman spectra, most assembled DEB SAMs on Au were expected to convert to triazole molecules, however. Our present work should provide a new method of monitoring Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition ("click" chemistry) on Au surfaces by means of Raman spectroscopy.

4. Summary and conclusions

We prepared acetylenyl-anchoring and -terminated aromatic self-assembled monolayers (SAMs) of 1,4-diethynylbenzene on gold. After the fabrication of pendent acetylenyl SAMs, the formation of triazoles was performed via Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition "click chemistry." A density functional theory (DFT) calculation of Raman frequencies was performed to better confirm the formation of the triazole molecule. Our results indicated that "click" chemistry could be successfully applied to simple aromatic SAMs proximate to Au

surfaces without any sulfur as an anchoring group. The reaction process was monitored in real time by means of surface-enhanced Raman scattering (SERS).

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