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Desorption Kinetics by Thermal Analysis Mass Spectrometry

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Teng-Yuan Dong,* Chih-Hung Tu, Heng-Hsi Wu, Chienlin Huang, Yuan-Sing Lin, and Ming-Cheng Lin

Department of Chemistry, Center for Nanoscience and Nanotechnology
National Sun Yat-Sen University, Kaohsiung, Taiwan

*Author to whom correspondence should be addressed.

Abstract

We describe a synthetic pathway to the formation of stable pyridine-functionalized octanethiolate mixed monolayer-protected Au clusters (MPCs). The spectroscopic characterization data of MPCs using NMR, UV-vis, TEM, XPS, and thermal-analysis-mass techniques are discussed. TEM analysis showed that spherical nanoclusters of 3-5 nm were produced. Furthermore, the particle sizes are uniform with a narrow size distribution. The pyridine-functionalized MPCs formed 2D superlattices with hexagonal packing covering on the carbon-coated copper grids during the toluene evaporation. For all samples, the S 2p3/2 and 2p1/2 components that appeared at ~162 and ~163 eV, respectively, in the XPS spectra compare very well with the typical value of chemisorbed S species. Thermal analysis mass spectrometer was used to analyze desorption behavior of octanethiolated MPCs or pyridine-functionalized mixed MPCs. The TA-mass spectra have revealed that MCPs exist monomer and dimer desorption behavior from monomeric thiolate adsorbed on the surface.

Keywords: Surface analysis; Adsorption, Chemisorption, Thermodynamics, Monolayer-protected gold nanoparticles.
1. INTRODUCTION

Very recently, extensive experimental work has been reported that it is relatively easy to prepare stable, densely packed, and well-ordered organosulfur self-assembled monolayers (SAMs) on gold surfaces.\textsuperscript{1-9} Chemisorption of alkanethiols on Au surface is believed to occur by oxidation addition to produce an alkanethiolate characterized by a wide variety of experimental methods. Tunneling microscopy and diffraction methods have found that SAMs display complex phase behavior that depends upon coverage, temperature, chain length, and method of preparation.\textsuperscript{1, 10-13} Long chain alkanethiols are easier to self-assemble on gold surface to form densely packed monolayers that the alkyl chains pack in an all-trans conformation and tilt ca. 27° to the normal.\textsuperscript{14} Electron microscopy and helium atom diffraction indicate a hexagonal lattice with a S-S distance of 5.0 Å which corresponds to the Au-Au (111) face lattice spacing and results in a surface density of 4.6 x 10\textsuperscript{14} molecule cm\textsuperscript{-2}.\textsuperscript{15}

Many mass spectrometric methods have been used to analyze the desorption behavior of thiolated SAMs. Temperature-programmed desorption (TPD) measurements for thiolated SAMs have detected a dimer species following desorption.\textsuperscript{16-18} Recently, SAMs of thiolated on Au were studied by N\textsubscript{2} laser desorption followed by vacuum ultraviolet photoionization mass spectrum in a time-of-flight mass spectrometer.\textsuperscript{19} Dimers (RSSR\textsuperscript{+}) dominated the photoionization mass spectrum from all chain lengths of alkanethiolated SAMs. It was suggested that dimerization occurs as a result of the recombination of surface thiolateds during desorption.

Alkanethiols with different chain lengths or terminal functional groups form mixed monolayers. Chidsey reported assembly of mixed monolayers of ferrocene-substituted and unsubstituted alkanethiols on Au(111) surface in a study of electron transfer rates.\textsuperscript{6, 20} Recently, functional groups on the outmost portion of the modified electrode surface, which can straightforwardly undergo many synthetic transformations, have been demonstrated. Furthermore, important recent reports describing the stabilization of monolayer-protected Au clusters (MPCs) with chemisorbed alkanethiols open the way to the studies of three-
dimensional monolayers by conventional methodologies such as NMR spectroscopy. There are particularly important for various applications, for examples, in molecular electronic devices and in the preparation of photo-electronic nano-devices. In particular, alkanethiolated Au clusters are stable in air, soluble in nonpolar organic solvents, and capable of facile modification with other thiols through exchange reactions. Many of functionalized MPCs described to date contain organic or bioorganic ligands such as dendrimers or DNA. Comparatively, the functionalization of MPCs by inorganic systems remains much less developed and usually involves alkanethiolated chains containing redox-active center. Murray and his coworkers have launched an investigation to study the core size and the chemical, electrochemical, structural and physical properties of ferrocenyl alkanethiolate Au clusters. Chen and his coworkers reported a study to construct 4-(1-oxo-7-mercaptohexyl)pyridine functionalized gold nanoparticles. The assembling of nanoparticles surface layers was effected by exploiting the complexation interactions between divalent metal ions and pyridine moiety. The number of the nanoparticle layers was controlled by the repetition of the dipping cycles. Recently, we described the synthesis of 4'-ferrocenyl-2,2':6',2''-terpyridine and 4'-biferrocenyl-2,2':6',2''-terpyridine ruthenium(II) terpyridyloctanethiolate complexes, and studied the molecular self-assembly of these inorganic complexes chemisorbed on Au nanoparticles. Very recent, Mayer reported functionalized gold and silver MPCs coated by polypyridyl ruthenium(II) complexes.

In this paper, we describe a synthetic pathway to the formation of stable pyridine-functionalized octanethiolate mixed monolayer-protected Au clusters. The spectroscopic characterizations for the Au MPCs are reported. Thermal analysis mass spectrometer (TA-MS) was used to analyze desorption behavior of octanethiolated MPCs or pyridine-functionalized mixed MPCs. Desorption of alkanethiols on metallic surfaces has been studied. Comparatively, desorption of alkanethiolate on nanoparticles has been scarcely studied and, to our knowledge, desorption of alkanethiolated Au MPCs has never been studied by TA-MS. The MPCs bearing Py ligand could provide systematic studies in application of their self-assembly using a variety of transition metals. Metal-ligand MPCs provide an expansion of
structural diversity of self-assembly processes, as well as imparting functional attributes such as redox and photochemical properties to the resulting constructs.

2. EXPERIMENTAL DETAILS

2.1. General Information

The preparations involving air sensitive materials were carried out by using standard Schlenk techniques under an inert atmosphere of N₂. Chromatography was performed on neutral Al₂O₃ (act. III). Dried THF was distilled from Na. All chemicals were reagent grade and used as received. Pyridine-functionalized octanethiolate monolayer protected clusters were prepared as illustrated in Scheme 1. Octanethiolated Au MPCs (AuC₈) were prepared as described by Murray²³,²⁴

2.2. Pyridyloctanethiol (2)

For 1, to the THF solution (100 ml) of 4-picoline (3.5 ml, 35.7 mmol) at -78 °C was added dropwisely a THF solution of lithium diisopropylamide (18 ml of 2.0 M, 35.7 mmol) to form an orange solution. The mixture was stirred for 1 h, and then the reaction mixture was added 1,7-dibromohpetane (6 ml, 35.7 mmol). The reaction mixture was continued stirring for 3 h, and then quenched with water. The crude product was extracted with hexane. The combined extracts were washed with saturated aqueous NaHCO₃ and it was then dried over MgSO₄. The solvent was removed under reduced pressure. The red residue was chromatographed, and elution with hexane/EA (1:1) gave the desired compound. The physical properties of 1 are following: ¹H NMR (500 MHz, CDCl₃): δ1.31 (m, 8H, -CH₂-), 1.61 (m, 2H, -CH₂-), 1.83 (m, 2H, -CH₂-), 2.58 (t, J = 10.8 Hz, 2H, -CH₂-), 3.38 (t, J = 12.0 Hz, 2H, -CH₂-), 7.07 (d, J = 6.9 Hz, 2H, py), 8.45 (d, J = 7.8 Hz, 2H, py); mass spectrum (EI): M⁺ at m/z 269, 271. Compound 1 (0.17 mmol) was reacted with excess NaSH in dried THF (60 ml) at reflux for 3 h, and then quenched with water. The crude product was extracted with ether. The combined extracts were washed with saturated aqueous NaHCO₃ and it was then dried over MgSO₄. The solvent was removed under reduced pressure. The crude product was chromatographed with hexane/EA (2:3) as elution solvent. The physical properties of 2 are following: ¹H NMR (CDCl₃, δ): ¹H NMR (500 MHz, CDCl₃): δ1.28 (m, 6H, -CH₂-), 1.34 (m, 2H, -CH₂-), 1.58 (m, 2H, -CH₂-), 1.63 (m, 2H, -CH₂-), 2.55 (2H, t, J =
8.0 Hz, -CH₂Py), 2.63 (t, J = 7.5 Hz, 2H, -CH₂S-), 7.06 (d, J = 6.0 Hz, 2H, py), 8.44 (d, J = 6.0 Hz, 2H, py); mass spectrum (EI): M⁺ at m/z 223.

2.3. AuC₈ MPCs

Octanethiol-modified Au MPCs were prepared by the method outlined in the literature published by Murray.23, 24 Briefly, a toluene solution (25 mL) containing octanethiol (0.301 g, 2.06 mmol) and TOAB (1.924 g, 3.53 mmol) was added to an aqueous solution (25 mL) of HAuCl₄ (0.333 g, 0.98 mmol). After phase transfer of the HAuCl₄ into the toluene had been accomplished, the mixture was reduced with NaBH₄ (0.448 g, 11.7 mmol). The organic layer was extracted with toluene. Following the steps of concentrating of the organic layer, pouring into ethanol, standing overnight at −4 ºC, centrifuging and rinsing with ethanol gave the desired Au MPCs. The Au MPCs had average core diameters of approximately 3.1 ± 0.5 nm. The ~3 nm sized particles were used to induce size and shape evolution with heating treatment in toluene or in TOAB (tetraoctylammonium bromide).

2.4. Heating Treatment of AuC₈ in Toluene (AuC₈-Ut)

Shape evolution with heating treatment in toluene was carried out by the method outlined in the literature published by Zhong.37 Briefly, particles of AuC₈ were redissolved in a small amount of toluene (2 mL) together with N(C₈H₁₇)₄Br (0.2 g). The resulting solution was heated in a silicon oil bath at 145 ºC. When the color of this solution changed from brown to dark red, the solution was heated further at 110 ºC for an additional 5 h. The change in color also included a size evolution. The solvent was removed in a rotary evaporator (under 50 ºC) followed by washing several times with ethanol and acetone. The Au MPCs created by using the heating treatment had average core diameters of approximately 4.1 ± 0.2 nm (measured by transmission electron microscopy).

2.5. Heating Treatment of AuC₈ in TOAB (AuC₈-Ua)

Shape evolution with heating treatment in molten TOAB was carried out by the method outlined in the literature published by Miyake.38 Briefly, a toluene solution containing a 2:1 mole ratio of octanethiol to HAuCl₄ was reduced using NaBH₄ at room temperature following the Murray’s procedure. The organic layer was extracted with toluene. Following the evaporation of the organic layer, particles of
**2.6. Synthesis of AuC₈-Py**

A mixture of AuC₈ (30 mg) and 2 (37 mg) in 1 mL toluene was stirred at room temperature for 48 hr. The solvent was removed under vacuum. The resulting product was suspended in a solution of acetone/ethanol and isolated with centrifuge. This procedure was repeated several times to obtain purified Py functionalized AuC₈-Py MPCs.

**2.7. Synthesis of AuC₈-Uₚ-Py and AuC₈-Uₚ-Py**

A mixture of uniformed Au MPCs (AuC₈-Uₚ or AuC₈-Uₚ, 30 mg) and 2 (37 mg) in 1 mL toluene was stirred at room temperature for 48 hr. The solvent was removed under vacuum. The resulting product was suspended in a solution of acetone/ethanol and isolated with centrifuge. This procedure was repeated several times to obtain purified Py functionalized MPCs (AuC₈-Uₚ-Py and AuC₈-Uₚ-Py).

**2.7. Physical Methods**

The ¹H and ¹³C NMR spectra were run on a Varian UNITY INOVA-500 spectroscopy. The UV spectra were obtained with a Hitachi U-4000 spectroscopy. Transmission electron microscopy (TEM) was performed in JEOL JEM-3010 Analytical Scanning Transmission Electron Microscope. The size and morphology of the nanoparticles were determined by transmission electron microscopy. The nanoparticles dissolved in toluene solution were then dropped into a 200 mesh carbon-coated copper grid sample holder, and then followed by natural evaporation at room temperature. The surface chemical composition of the copper nanoclusters was analyzed with a VG Scientific ESCALAB 250 operated at 400 W. A monochromatic Mg Kα X-ray source at 1253.6 eV was used, and the system was calibrated with respect to the C 1s peak. The desorption temperature of the adsorbed octanethiols
and the weight loss percentage of the nanoparticles were determined with a DTA-TG-MS spectroscopy by coupling Netzsch STA-409CD analyzer with Balzers QMA 400 spectroscopy under He (flow rate = 100 mL/min) at a heating rate rate of 10 deg/min. Mass spectra were obtained with electron ionization method (70 eV).

3. RESULTS AND DISCUSSION

3.1. Spectroscopic Analysis of Au MPCs

The schematic structures of the ligand and MPCs that are the focus of the present investigation are illustrated in Scheme 1. In the following sections, the characterization data of MPCs using NMR, UV-vis, and TEM techniques are discussed first, after which the XPS measurements and thermal analyses of MPCs.

3.1.1. NMR Spectroscopic Analysis.

The NMR technique was used to confirm an important question, which was whether or not the organic shell was functionalized by pyridyl octanethiol. Fig. 1 shows the pyridyl resonances in the $^1$H-NMR spectra for the free ligand, the $\text{AuC}_8$ and the pyridyl octanethiol functionalized mixed MPCs. As shown in Fig. 1, the confirmation of the functionalization of Au MPCs ($\text{AuC}_8$) by pyridyl octanethiol came from the low field peaks (7.2-8.6 ppm) which were established the resonances of the Py moiety. The chemical shift assignments for the pyridyl protons in the Au MPCs can be reasonably inferred by making a comparison with the pyridyl resonances in the free pyridyloctanethiol. It is interesting that the pyridyl protons of $\text{AuC}_8$-Ut-Py and $\text{AuC}_8$-Ua-Py MPCs give NMR signals at room temperature that are sharper than those of pyridyl $\text{AuC}_8$-Py MPCs. We would suggest that the smaller dipolar-dipolar interaction between the pyridyl moieties in the mixed monolayer decreases the efficiency of the nuclear relaxation mechanism, lengthening $T_1$ for the nucleus and causing the line to appear sharper.23 After the size and shape evolution, the core size was increased from $\sim$3 nm in $\text{AuC}_8$ to $\sim$5 nm in $\text{AuC}_8$-Ut-Py and $\text{AuC}_8$-Ua-Py MPCs. The desorption behavior of pyridine-functionalized mixed MPCs analyzed by thermal analysis mass spectrometer suggested that the mole fraction of pyridyloctanethiol chemisorbed in $\text{AuC}_8$-Ut-Py and $\text{AuC}_8$-
U₈-Py MPCs was decreased after the size and shape evolution. Consequently, the enlarged distance between the neighbouring pyridyl moieties results in a smaller dipolar-dipolar interaction.

### 3.1.2. TEM Imaging

The AuC₈ MPCs had 3.1 ± 0.5 nm average core diameters established by TEM. The ~3 nm particles were used to induce size and shape evolution with heating treatment in toluene or in TOAB (tetraoctylammonium bromide). The uniformed Au MPCs (AuC₈-U₁) created by using the heating treatment in toluene had 4.1 ± 0.2 nm core diameters established by TEM. The size-evolution Au MPCs (AuC₈-U₉) by heat treatment in TOAB had 5.2 ± 0.3 nm core diameters established by TEM.

The TEM images of the Py functionalized AuC₈-U₁-Py and AuC₈-U₉-Py MPCs showed an average core size of 4.4 ± 0.3 and 5.7 ± 0.3 nm, respectively. The representative TEM micrographs are shown in Fig. 2. The particle sizes are uniform with a narrow size distribution. As shown in Fig. 3, the Py functionalized AuC₈-U₉-Py MPCs formed 2D superlattices with hexagonal packing covering on the carbon-coated copper grids during the toluene evaporation.

### 3.1.3. UV-Vis Measurement

Optically, both intensity and energy of the surface plasmon (SP) resonance bands of nanoparticles have been known to be strongly dependent on size. Fig. 4 shows a set of UV-Vis spectra of AuC₈, AuC₈-U₁, AuC₈-U₉, AuC₈-U₁-Py and AuC₈-U₉-Py MPCs. The spectrum for each Au MPCs showed an identifiable SP band at ~520 nm. The shape and position of this band are in agreement with those previously reported. In the case of AuC₈, the SP band is not clear, indicating the broaden size distribution.

### 3.1.4. X-Ray Photoelectron Spectroscopy

The compositions of the samples were checked with XPS analysis. Fig. 5 depicts the XPS spectra of MPCs over the full range and the individual elemental peaks. For all samples, the S
2p\(_{3/2}\) and 2p\(_{1/2}\) components that appeared at \(\sim162\) and \(\sim163\) eV, respectively, in the XPS spectra (Table 1) compare very well with the typical value of chemisorbed S species.\(^{39}\) The slight downward shift relative to sulfur in the free alkanethiols indicates that the nanoclusters are alkanethiolate MPCs. Sulfonate signals were not detected, typically appeared at >167 eV. The Au 4f spectrum was resolved into a single spin-orbital pair (splitting 3.6 eV) with 4f\(_{7/2}\) and 4f\(_{5/2}\) appeared at \(\sim84\) and \(\sim87\) eV, respectively. As seen in the Table 1, the C:S atomic ratios in \(\text{AuC}_8\text{-U}_{\text{r}}\text{-Py}\) and \(\text{AuC}_8\text{-U}_{\text{a}}\text{-Py}\) were found higher than that in \(\text{AuC}_8\). This suggests that pyridyloctanethiols were adsorbed onto the Au nanoclusters.

3.2. Thermal Analysis-Mass Spectroscopy

Thermal analysis coupling with mass spectroscopy was used to analyze Au MPCs and provided information on the adsorption behavior. In the following sections, the in-situ TGA of Au MPCs is discussed first, after which the mass spectra and in-situ DSC analysis of Au MPCs.

3.2.1. In-Situ TGA

Fig. 6 shows the TGA results and the first derivative of weight loss for the \(\text{AuC}_8\), \(\text{AuC}_8\text{-U}_{\text{r}}\text{-Py}\) and \(\text{AuC}_8\text{-U}_{\text{a}}\text{-Py}\) MPCs. Weight loss percentage due to desorption of the organic fragments decreases for the \(\text{AuC}_8\text{-U}_{\text{r}}\text{-Py}\) (8.1 % loss) and \(\text{AuC}_8\text{-U}_{\text{a}}\text{-Py}\) (8.0 % loss) MPCs in comparison with \(\text{AuC}_8\) (24 % loss). This corresponds well with the increasing size established by TEM for \(\text{AuC}_8\text{-U}_{\text{r}}\text{-Py}\) and \(\text{AuC}_8\text{-U}_{\text{a}}\text{-Py}\) MPCs.

We also noticed from the derivative thermographs of \(\text{AuC}_8\text{-U}_{\text{r}}\text{-Py}\) and \(\text{AuC}_8\text{-U}_{\text{a}}\text{-Py}\) MPCs that the weight loss was not a simple one-step process. A peak was observed at the higher temperature side of the main peak. In the case of alkanethiolated Au MPCs, it was reported that the desorption behavior of the organics occurred in a stepwise manner due to the different binding sites on the nanoclusters.\(^{23,40}\) To consistent with our TA-mass results below, we would suggest that the pyridyloctanethiolate fragment was desorbed from the nanoclusters at higher temperature.
In the case of alkanethiolated Au MPCs studied by TGA, a slight increase in desorption temperature was observed with increasing thiol chain length.\textsuperscript{40} It has been suggested that the difference in desorption temperature is due to the van der Waals interaction between the chains, which is stronger for the longer alkanethiol chain.\textsuperscript{39b} For our mixed MPCs (\textit{AuC}_8-U_t-Py and \textit{AuC}_8-U_a-Py), it seems unlikely that the two thiols (pyridyloctanethiol and octanethiol) will show different Au-S bond strength of chemisorption. Furthermore, we have assumed the same van der Waals attraction between the mixed thiols. We would hence suggest that the difference in desorption onset is attributed to the different binding sites on the nanoclusters.

3.2.2. TA-Mass

Monomer ions (\textit{C}_8\textit{H}_{17}\textit{S}^+ and \textit{C}_8\textit{H}_{17}\textit{SSH}^+) and dimer ions ((\textit{C}_8\textit{H}_{17}\textit{S})_2^+ and (\textit{C}_9\textit{H}_{17})_2\textit{S}^+) dominated the mass spectra for octanethiolated gold nanoparticles. Figures 7-9 display the TA-mass spectra of \textit{AuC}_8, \textit{AuC}_8-U_t-Py and \textit{AuC}_8-U_a-Py MPCs, respectively. The most likely explanation for the dimer desorption product from \textit{AuC}_8 MPCs was the recombination of two thiolates during desorption. Desorption behavior studied with TPD (temperature-programmed desorption) experiments\textsuperscript{17, 18} and desorption mass spectrum methods\textsuperscript{19} with all chain lengths of alkanethiolated monolayers, such as octanethiolate monolayer, on Au(111) metal surface has been detected solely as dimers. It has been suggested that dimers are the most prevalent desorbed species due to favorable energetics: the energy needed to break two adsorbed-surface bonds (RS-Au = 40 kcal/mol) to the surface is mostly gained back by the formation of the disulfide bond (RS-SR = 74 kcal/mol).\textsuperscript{14a, 41} In our \textit{AuC}_8 MPCs case, both monomer ions and dimer ions were detected at same desorption maximum temperature of 480 K. Both monomer ions and dimer ions were also detected at same desorption maximum temperature of 463 K for \textit{AuC}_8-U_t-Py MPCs. We can not exclude that the monomer ion was probably the fragment from the dimmer ion. However, two desorption maximum temperatures for the monomer ion were seen at 457 and 480 K in the case of \textit{AuC}_8-U_a-Py MPCs, indicating some of octanethiolates on the nanoparticle surfaces would have geometries unfavorable to dimerization.
The thermal desorption of dimer from \textbf{AuC$_8$} MPCs argues for a common thermal mechanism of desorption. From desorption maximum temperature, the activation energy for desorption process could be calculated. It was reported that TPD of octadecanethiolated monolayer on Au(111) metal surface showed two dimer desorption peaks: one near 350 K corresponding to weakly chemisorbed thiolates and one near 500 K corresponding to strongly chemisorbed thiolates.\textsuperscript{17, 18} For simplicity, the activation energy calculation can be carried out by following Redhead’s analysis, assuming a first-order reaction.\textsuperscript{17}

\[ E_d = RT_p \ln (\frac{\nu_1 T_p}{\beta}) - 3.64 \]

Where $\nu_1$: pre-exponential factor, $E_d$: desorption activation energy, $R$: gas constant, $T_p$: desorption maximum temperature and $\beta$: linear heating rate. Redhead’s analysis has been applied to thermal desorption experiments by many researchers, especially for the first-order reaction. The simple characterization using Redhead’s analysis would yield some differences for a system with strong intermolecular interactions and dimerized desorption due to the assumption of a pre-exponential factor of 1 x 10$^{13}$ s$^{-1}$. TPD of octadecanethiolated monolayer on Au(111) metal surface revealed that monolayer desorbs to form a dimer with a desorption activation energy of 32 kcal/mol.\textsuperscript{17} From the TA-mass spectrum of \textbf{AuC$_8$} MPCs in Fig. 7, the desorption maximum temperature was seen at 480 K. Using the same equation, we obtained an activation energy of 32.5 kcal/mol for the desorption process in the \textbf{AuC$_8$} MPCs, assuming a pre-exponential factor of 1 x 10$^{13}$ s$^{-1}$. The activation energy in our system is similar with that of alkanethiolated monolayers on Au(111) metal surface. The desorption kinetics of uniform close-packed alkanethiolated SAMs on the Au(111) surface examined by TDS has revealed that there exists a dimerization process of SAM molecules, resulting in dimer desorption from monomer SAM adsorbed on solid Au surface.\textsuperscript{17, 18} To consistent with our in-situ DSC results below, on the other hand, we would believe that the alkyl sulfide monomer and dialkyl disulfide dimer were desorbed from the molten Au MPC surfaces, resulting in a desorption activation energy of 32.5 kcal/mol.

Mixed monolayers of MPCs (\textbf{AuC$_8$-U$_r$-Py} and \textbf{AuC$_8$-U$_a$-Py}) show great promise for engineering surface properties. Fig. 8 and Fig. 9 show the TA-mass spectra of \textbf{AuC$_8$-U$_r$-Py}
and AuC₈-Uₐ-Py. The mass peaks at \( m/z \) 290.2 and 145.1 corresponded to the monomer ion (C₈H₁₇S⁺) and dimer ion ((C₈H₁₇S)₂⁺). The desorption maximum temperature for the dimer ion was seen at 457 K (\( E_d = 31.0 \) kcal/mol). Furthermore, two desorption maximum temperatures for the monomer ion were seen at 457 and 480 K (\( E_d = 31.0 \) and 32.5 kcal/mol). The mass peaks at \( m/z \) 189.2 and 222.1 corresponded to the monomer pyridylalkanethiolate ions (C₁₃H₁₉N⁺ and C₁₃H₂₀NS⁺), while the dimer ion ((C₁₃H₂₀NS)₂⁺ \( m/z \) at 444.2) and mixed dimer (C₂₁H₃₇NS₂⁺ \( m/z \) at 367.2) were not detected. Desorption maximum temperature for the monomer pyridylalkanethiolate ion was seen at 519 K (\( E_d = 35.4 \) kcal/mol). Because of smaller interchain van der Waals interaction, we would expect that pyridylalkanethiolates are preferentially incorporated at the edge or corner of the nanoparticles. On the other words, edge or corner pyridylalkanethiolates would be desorbed at lower temperature than octanethiolates. Here, we could not find a reasonable explanation for this counterintuitive desorption behavior. Thermal desorption behavior for monolayers of mixed thiolates on Au(111) surface was studied previously by various MS methods. In a previous paper, Hanly et al. studied the desorption kinetics of C₁₁H₂₃SH/HOC₁₁H₂₂SH mixed monolayer on Au(111) surface prepared from a 1:5 molar ratio solution. The pure dimer ions ((C₁₁H₂₃S)₂⁺ and (HOC₁₁H₂₂S)₂⁺) and mixed dimer ion (C₁₁H₂₃S-SC₁₁H₂₂OH) were detected by 337 nm laser desorption mass spectrometry. Hanly suggested that near-random mixing on the surface between C₁₁H₂₃S thiolates and HOC₁₁H₂₂S thiolates. Simple surface-heating calculations indicated that 337 nm laser pulses could readily heat gold surface to ~1000 K. This temperature would have been more than sufficient to desorb simultaneously both C₁₁H₂₃S thiolates and HOC₁₁H₂₂S thiolates. The absence of the pure dimer ((C₁₃H₂₀NS)₂⁺ \( m/z \) at 444.2) and mixed dimer (C₂₁H₃₇NS₂⁺ \( m/z \) at 367.2) fragmentations in our system is due to the thermal nature of the desorption process. In our system, thermal desorption of alkanethiolates showed two desorption maximum temperatures: the dimer peak near 457 K corresponding to weakly chemisorbed octanethiolates and the peak near 519 K corresponding to strongly chemisorbed pyridyloctanethiolates. Low concentration of pyridyloctanethiolates on the nanoparticle surfaces would have geometries unfavorable to dimerization.

### 3.2.3. In-Situ DSC
In our *in-situ* DSC analysis (Fig. 10), an endothermic peak was detected respectively at 478, 433, and 439 K for $\text{AuC}_8$, $\text{AuC}_8$-$\text{U}_l$-$\text{Py}$ and $\text{AuC}_8$-$\text{U}_u$-$\text{Py}$. To understand the origin of this endothermic peak, we carried out the measurement of melting point. The results clearly suggested that our MPCs were melted at those temperatures. Dark brown-red nanoparticles were melted over a broaden temperature region, possibly caused by the melting of nanoparticles and alkanethiolate monolayers. Following desorption of alkanethiolates with continuous heating, melting nanoparticles were changed to golden solid Au. We expect that the mobility of the alkyl chains increases with temperature and hence behave more *liquid-like* at temperatures greater than melting point.

### 3.3. Desorption Kinetics of MPCs

The desorption kinetics of uniform close-packed alkanethiolated SAMs on the Au(111) surface examined by TPD has revealed that there exists a dimerization process of SAM molecules, resulting in dimer desorption from monomer SAM adsorbed on *solid* Au surface. Upon heating, the extended all-trans conformations of the alkanethiolate chains are retained. As shown in Fig. 11a, the two neighboring all-trans conformations of alkanethiolates would be in favorable geometry to dimerization. Therefore, desorption behavior studied with TPD experiments methods with all chain lengths of alkanethiolated monolayers on Au(111) metal surface has been detected solely as dimers. In our system, the trans conformations were disrupted upon heating. A phase transition of melting ($T_m$) involving conversion of trans conformations to a more disordered gauche conformations was detected in *in-situ* DSC. Some trans conformations were retained at temperatures greater than $T_m$, resulting in dimer desorption. Gauche conformations were unfavorable to dimerization, resulting in monomer desorption. In the case of mixed monolayer, low concentration of strongly chemisorbed pyridyloctanethiolates on the *molten* nanoparticle surfaces would have more conformational freedom, resulting in gauche conformations which were unfavorable to dimerization.

### 4. CONCLUSIONS
In summary, we have studied pyridine-functionalized thiolated gold nanoparticles prepared via an exchange method and investigated the monolayers of the thiolated chains chemisorbed on the nanocluster surfaces. TEM analysis showed that spherical nanoclusters of 3-5 nm were produced. Furthermore, the particle sizes are uniform with a narrow size distribution. The pyridine-functionalized \textbf{AuC₈-U₄-Py} MPCs formed 2D superlattices with hexagonal packing covering on the carbon-coated copper grids during the toluene evaporation. The regularity of the interdistance between the nanoparticles could be possibly attributed to the intermolecular Py-Py interaction, such as the $\pi-\pi$ interaction between pyridines on Au MPCs. Desorption kinetics of monolayer on the nanocluster surface was examined by thermal desorption spectroscopy. In addition, Redhead’s analysis for the desorption activation energy was calculated, assuming a pre-exponential factor of $1 \times 10^{13}$ s$^{-1}$. From the in-situ DSC analysis, we expect that the mobility of the alkyl chains increases with temperature and hence behave more liquid-like at temperatures greater than melting point.

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\textbf{References and Notes}


Scheme 1.

\[
\text{N-CH}_3 \cdot \text{Br-(CH}_2)_n\text{-Br} \xrightarrow{\text{LDA in THF}} \text{N-(CH}_2)_n\text{-Br} \xrightarrow{\text{NaSH}} \text{N-(CH}_2)_n\text{-SH}
\]

1) \(\text{N(C}_8\text{H}_17\text{)}_4\text{Br}\)
2) \(\text{C}_8\text{H}_17\text{SH}\)
3) \(\text{NaBH}_4\)

HAuCl\_4\_x\_H\_2\_O

1) \(\text{N(C}_8\text{H}_17\text{)}_3\text{Br}\)
2) \(\text{C}_8\text{H}_17\text{SH}\)
3) \(\text{NaBH}_4\)

\(\text{AuC}_8\text{-U}_{1} \xrightarrow{\text{Gold nanoparticles or Tol-SH}} \text{AuC}_8\text{-U}_{2}\)

\(\text{AuC}_8\text{-U}_{1}\text{-P} \text{y or AuC}_8\text{-U}_{2}\text{-P}y\)
FIGURE CAPTIONS

**Fig. 1.** $^1$H NMR spectra for the free ligand, $\text{AuC}_8$, $\text{AuC}_8$-$\text{Py}$, $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$, and $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$ in CDCl$_3$.

**Fig. 2.** TEM images of $\text{AuC}_8$-$\text{Ur}$ (a), $\text{AuC}_8$-$\text{Ur}$ (b), Py functionalized $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$ (c) and $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$ (d) MPCs, with histograms showing the respective size distribution.

**Fig. 3.** TEM images of the Py functionalized $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$ MPCs formed 2D superlattices with hexagonal packing.

**Fig. 4.** UV-Vis spectra of $\text{AuC}_8$, $\text{AuC}_8$-$\text{Ur}$, $\text{AuC}_8$-$\text{Ur}$, $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$, and $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$.

**Fig. 5.** Typical XPS spectra of $\text{AuC}_8$, $\text{AuC}_8$-$\text{Ur}$, $\text{AuC}_8$-$\text{Ur}$, $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$, and $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$. Inset: S and Au components.

**Fig. 6.** *In-situ* TGA (top) and the first derivative thermographs (bottom) of the thiolated MPCs.

**Fig. 7.** Thermal desorption mass spectrum of $\text{AuC}_8$.

**Fig. 8.** Thermal desorption mass spectrum of $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$.

**Fig. 9.** Thermal desorption mass spectrum of $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$.

**Fig. 10.** *In-situ* DSC on $\text{AuC}_8$, $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$, and $\text{AuC}_8$-$\text{Ur}$-$\text{Py}$.

**Fig. 11.** A schematic illustration of desorption behavior: (a) SAMs on Au(111); (b) mixed monolayer of Au nanoparticles; trans conformations of the alkanethiolates are disrupted.
Fig. 1. $^1$H NMR spectra for the free ligand, $\text{AuC}_8$, $\text{AuC}_8$-$\text{Py}$, $\text{AuC}_8$-$\text{U}_t$-$\text{Py}$, and $\text{AuC}_8$-$\text{U}_a$-$\text{Py}$ in CDCl$_3$ ($\delta$ at 7.24 ppm).
Fig. 2. TEM images of $\text{AuC}_8$-$\text{U}_1$ (a), $\text{AuC}_8$-$\text{U}_a$ (b), Py functionalized $\text{AuC}_8$-$\text{U}_1$-Py (c) and $\text{AuC}_8$-$\text{U}_a$-Py (d) MPCs, with histograms showing the respective size distribution.
Fig. 3. TEM images of the Py functionalized AuC$_8$-U$_c$-Py MPCs formed 2D superlattices with hexagonal packing.
Fig. 4. UV-Vis spectra of $\text{AuC}_8$, $\text{AuC}_8$-$\text{U}_t$, $\text{AuC}_8$-$\text{U}_a$, $\text{AuC}_8$-$\text{U}_t$-$\text{Py}$, and $\text{AuC}_8$-$\text{U}_a$-$\text{Py}$. 
Fig. 5. Typical XPS spectra of $\text{AuC}_8$, $\text{AuC}_8-\text{U}_t$, $\text{AuC}_8-\text{U}_a$, $\text{AuC}_8-\text{U}_t-\text{Py}$, and $\text{AuC}_8-\text{U}_a-\text{Py}$. 
Inset: S and Au components.
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Fig. 8. Thermal desorption mass spectrum of AuC₈-U₁-Py.
Fig. 9. Thermal desorption mass spectrum of AuC₆-U₆-Py.
Fig. 10. *In-situ* DSC on AuC$_8$, AuC$_8$-U$_r$-Py, and AuC$_8$-U$_a$-Py.
Fig. 11. A schematic illustration of desorption behavior: (a) SAMs on Au(111); (b) mixed monolayer of Au nanoparticles; trans conformations of the alkanethiolates are disrupted. $T_m$: melting point of MPCs. $T_p$: desorption maximum temperature observed by TA-mass.
Table 1

XPS Analysis of the Thiolated Au MPCs

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<th>Compd</th>
<th>C 1s BE, eV</th>
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<th>Au 4f(7/2) BE, eV</th>
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