Synthesis of an N-Heterocyclic Carbene-based Au(I) Coordinate Surfactant: Application for Alkyne Hydration Based on Au Nanoparticle Formation

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Abstract: In this study, an N-heterocyclic carbene (NHC)-based metal coordinate surfactant (MCS), NHC-Au-MCS, in which the NHC framework afforded the bonding of the Au(I) at the linkage of the hydrophilic and hydrophobic moieties, was synthesized. The structure of NHC-Au-MCS was confirmed by ¹H and ¹³C NMR spectroscopic measurements together with elemental analysis. Matrix-assisted laser desorption/ionization (MALDI), laser desorption/ionization (LDI), and electrospray ionization mass spectrometry (ESI-MS) indicated the distinct reactivity of NHC-Au-MCS, such as the exchange of Br to Cl and the formation of a cationic Au complex, where the two NHC ligands were coordinated to an Au(I) center upon laser activation. The surface tension and dynamic light scattering (DLS) measurements revealed that the coordination of Au(I) to NHC reduced the critical micelle concentration (CMC) of NHC-Au-MCS (1.3 × 10⁻⁴ M), which resulted in the formation of micelles at concentrations higher than the CMC in water. We also confirmed that the surface-active Au(I) complex of NHC-Au-MCS catalyzed the hydration of 1-dodecyn to 2-dodecanone in water in the absence of an organic solvent. On the basis of the detailed mechanistic investigations regarding the reactivity of NHC-Au-MCS, we revealed that NHC-Au-MCS partially translated into Au nanoparticles (AuNPs), which facilitated alkyne hydration. These mechanistic studies were supported by UV-vis measurements, transmission electron microscopy (TEM), and LDI-MS.

Key words: surfactant, N-heterocyclic carbene, gold, nanoparticle, catalysis

1 Introduction

Metal coordinate surfactants (MCSs) are a new class of materials, in which the ligand moieties present in the surfactant framework are bound to various metal ions¹⁻⁴. Owing to their surface activity and the variety of functions resulting from the nature of the metal centers utilized, MCSs possess a potential for use as catalysts⁵, electronic materials⁶, mesoporous material templates⁷, and precursors for nanoparticles (NPs)⁸. MCSs typically consist of a cationic metal center, which is bound to anionic surfactants via weak ionic or coordination bonds. Therefore, the metal center tends to dissociate in water, which presents a challenge in understanding the relationship between the nature of the metal center and its impact on MCS functions. We previously reported an N-heterocyclic carbene (NHC)-based Pd(II)-coordinated MCS, NHC-Pd-MCS, where the Pd(II) was bound to the NHC framework, which was composed of an octaethylene glycol monomethyl ester and an n-dodecyl chain⁹,¹⁰. Owing to a strong Pd–carbene bond and the presence of NEt₃ as a co-ligand, NHC-Pd-MCS exhibited remarkable stability even in water, thereby allowing us to study the relationship between the Pd(II) and the self-assembling properties of NHC-Pd-MCS. We observed that the coordination of the MCS precursor to Pd(II) significantly influenced the surface activities, micelle size, and self-assembling behavior of NHC-Pd-MCS in water. Importantly, this MCS can be employed as a recyclable catalyst for the aqueous Mizoroki–Heck reaction.

Herein, we report the synthesis of an NHC-based Au(I) coordinate surfactant (NHC-Au-MCS, Fig. 1) and the investigation of its various properties. We observed that the critical micelle concentration (CMC) of NHC-Au-MCS was an order of magnitude lower than that of NHC-Pd-MCS despite both MCSs containing the same NHC ligands. The
application of NHC-Au-MCS for the catalytic hydration of alkynes was also studied. Furthermore, our studies revealed that Au nanoparticles (AuNPs) formed from NHC-Au-MCS could facilitate the hydration of 1-dodecyn. The formation of AuNPs was also observed by UV–vis and transmission electron microscopy (TEM) measurements. Additionally, the reaction profile was monitored, and these revealed that NHC-Au-MCS was first adsorbed at the air/water interface before it partially translated into AuNPs.

2 Experimental

2.1 Materials

The imidazolium bromide MCS precursor was synthesized according to a method in the literature. Me$_2$AuCl (>95%), AgSbF$_6$ (>97.0%), 1-dodecyn (95.0%), and trans-2-[3-(4-tert-butylyphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) were purchased from Tokyo Chemical Industry, Co., Ltd. β-cyclodextrin (97.0%), K$_2$CO$_3$ (99.5%), acetone (99.0%), dichloromethane (CH$_2$Cl$_2$) (99.5%), methanol (99.5%), chloroform (CHCl$_3$) (99.0%), and tetrahydrofuran (THF) were purchased from FujiFilm Wako Pure Chemical Industries, Ltd. and were utilized as received. Sodium trifluoroacetate (NaTFA) was purchased from Sigma-Aldrich (St Louis, MO, USA).

2.2 Synthesis and characterization

$^1$H NMR spectra were recorded on a Bruker NMR spectrometer (Avance 400, Bruker Biospin Co., Inc., USA) operated at 400 MHz. $^{13}$C NMR spectra were recorded on the same instrument at 100 MHz. All the NMR spectra were recorded in CDCl$_3$. Both the $^1$H NMR and $^{13}$C NMR spectra were calibrated using tetramethylsilane as an internal reference. Elemental analyses were carried out using a Flash 2000 instrument (Thermo Fisher Scientific Inc., USA).

Laser desorption/ionization mass spectrometry (LDI-MS) and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) were conducted using a JMS-S3000 SpiralTOF mass spectrometer (JEOL, Tokyo, Japan) equipped with a neodymium-doped yttrium lithium fluoride laser. For the LDI-MS analysis, the sample was prepared by depositing 0.5 μL of the THF solution (concentration: 1 μg mL$^{-1}$) of NHC-Au-MCS on a 384-circle disposable target (Hudson Surface Technology, Old Trappan, NJ), which was air-dried prior to the laser irradiation. For the solvent-based MALDI-MS analysis, 1 μL of the sample solution was mixed with 1 μL of the THF solution of DCTB (concentration: 15 mg mL$^{-1}$) and 1 μL of the THF solution of NaTFA (concentration: 1 mg mL$^{-1}$), followed by the deposition on the disposable target and air-drying. For the solvent-free MALDI-MS analysis, ~0.5 μL of NHC-Au-MCS was mixed with solid DCTB and solid NaTFA in a mortar to obtain a homogeneous paste, which was deposited as a thin film on the target with a spatula. The parameters of the ion source were adjusted to maintain a peak width of ΔM = ~0.02 Da, over the mass range of interest (resolving power was ~4.5 × 10$^4$ at m/z 900). The accurate mass-to-charge ratios were measured with an internal calibration procedure using the sodium adducts of a poly(methyl methacrylate) 1.31 × 10$^3$ g mol$^{-1}$ standard, which was added to half of the solvent-based and solvent-free deposits. The msTornado control/analysis (JEOL) was employed to record data and for preliminary data treatment, while mMass 5.5.0.0$^2$ was utilized for further data treatment and artwork.$^{12}$

Electrospray ionization (ESI) MS analysis was performed on an amaZon SL-STT2 ion trap instrument (Bruker, Bremen, Germany) equipped with an ES ion source. NHC-Au-MCS (concentration: ~1 mg mL$^{-1}$) was dissolved in CHCl$_3$ and was further diluted in methanol. The sample solution was introduced into the ionization source in the infusion mode at a flow rate of 5 mL min$^{-1}$ using a syringe pump. Instrument control, data acquisition, and processing were performed by Bruker Compass 1.3 SR2 software (trap control 7.0), and mMass 5.5.0.0 was employed for the data treatment and artwork.

The imidazolium bromide (1.00 g, 1.46 mmol) MCS precursor, K$_2$CO$_3$ (0.21 g, 1.46 mmol), chloro(dimethylsulfide) gold (0.43 g, 1.46 mmol), and acetone (30 mL) were placed in a 200 mL flask equipped with a magnetic stir bar. The mixture was stirred for 4 h at 60°C. The solvent evaporated under reduced pressure, and the crude product was purified by silica gel chromatography ($R_f$ = 0.21, CHCl$_3$/MeOH = 9:5/0.5). NHC-Au-MCS was obtained as a pale-yellow oil (1.13 g, 1.29 mmol, 88%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 (s, 1H, NCH = CH$_2$), 6.90 (s, 1H, NCH = CH$_2$), 4.36 (t, J = 6.0 Hz, 2H, NCH$_2$), 4.14 (t, J = 6.0 Hz, 2H, NCH$_2$), 3.82 (t, J = 6.0 Hz, 2H, CH$_2$), 3.74–3.48 (m, 28H, CH$_3$), 3.38 (s, 3H, CH$_3$), 1.83 (t, J = 8.0 Hz, 2H, CH$_2$), 1.35–1.18 (m, 18H, CH$_3$), and 0.88 (s, J = 6.0 Hz, 3H, CH$_3$).$^{13}$C NMR δ 173.6, 122.2, 119.9, 71.9, 70.6, 70.5, 70.4 (2C), 70.3, 59.0, 53.5, 51.5, 51.4, 51.2, 51.1, 31.9, 31.1, 29.6, 29.5, 29.4, 29.3, 29.1, 26.5, 22.7, and 14.2; Anal. Calcd. for C$_{59}$H$_{40}$AuBrN$_4$O$_3$: C, 43.69; H, 7.70; and N, 3.18. Found: C, 43.95; H, 7.25; and N, 3.19. High-resolution MALDI-MS analysis of NHC-Au-MCS, measured m/z (lightest isotope): 901.3243; proposed elemental...
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composition: $\text{C}_{32}\text{H}_{62}\text{AuBrN}_2\text{O}_8\text{Na}^+$; calculated $m/z = 901.3247$; error: -0.4 ppm; assignment:[NHC-Au-MCS + Na]$^+$.  

2.3 Surface activities

The surface tension analyses of the surfactant solutions were conducted by the Wilhelmy plate method at 25°C using a DY-500 surface tension meter (Kyowa Kaimen Kagaku Co.), whose accuracy was intermittently monitored with ultrapure water. The Pt plate was cleaned by flaming, and the glassware was rinsed sequentially with tap and ultrapure waters.

2.4 Catalytic hydration of alkenes

2.4.1 Procedure A

NHC-Au-MCS (0.018 mmol) and AgSbF$_6$ or NaB($\text{C}_6\text{F}_5$)$_4$ (0.018 mmol) were added to a screw-cap vial equipped with a stir bar. Thereafter, 1-dodecyné (0.30 mmol) and the solvent (1.5 mL) were added, and the mixture was vortexed for several seconds. The mixture was vigorously stirred (1,000 rpm) for 24 h at 80°C and cooled to ambient temperature. Further, the crude product was extracted with CH$_2$Cl$_2$. After washing with brine, the organic phase was dried over MgSO$_4$. The organic solvent was evaporated to obtain the crude product. The conversion reaction was monitored by $^1$H NMR spectroscopy.

2.4.2 Procedure B

NHC-Au-MCS (0.018 mmol), AgSbF$_6$ (0.018 mmol), and CH$_2$Cl$_2$ (5 mL) were added to a screw-cap vial equipped with a stir bar. The mixture was stirred for 1 h at ambient temperature to produce [NHC-Au-MCS]$^+ \cdot [\text{SbF}_6]^-$. The catalyst was filtered through a pad of silica gel, and the solvent was evaporated. The obtained catalyst and 1-dodecyné (0.30 mmol) were added to a 15 mL test tube equipped with a stir bar. Water (1.5 mL) was then added, and the mixture was vortexed for several seconds. The mixture was vigorously stirred (1,000 rpm) for 24 h at 80°C, after which it was cooled to ambient temperature. The crude product was extracted with CH$_2$Cl$_2$. After washing with brine, the organic phase was dried over MgSO$_4$. The organic solvent was evaporated to obtain the crude product. The conversion reaction was monitored by $^1$H NMR spectroscopy.

2.5 Formation of AuNPs

An NHC-Au-MCS (1.0 mM) aqueous solution was prepared in a vial tube and was maintained at ambient temperature. The formation of AuNPs was monitored by observing the changes in the adsorption bands centered at 535 nm and originating from the surface plasmon resonance (SPR) of AuNPs on a UV–vis spectrometer (V-560, JASCO).

2.6 LDI-MS analysis and TEM observation of AuNPs

NHC-Au-MCS was dissolved in water (1 mM), and the solution was maintained at ambient temperature for 1 h. The obtained pink solution (1 μL) was deposited on a 384-circle disposable target and air-dried. The thin-film deposit was then analyzed by LDI-MS in both the positive and negative ion modes (denoted LDI (+) and LDI (−), respectively) on a JMS-S3000 SpiralTOF mass spectrometer by laser irradiation at “low” and “high” fluences (50 and 70% from the arbitrary scale of mS Tornado). The pink solution (2 μL) was also dropped on a glow-discharged copper grid (200 mesh) coated with C (Excel support film, Nisshin EM Co.). The solution was blotted using a filter paper, and the grid was thoroughly dried. Images were acquired on an H-7650 transmission electron microscope (Hitachi High-Technologies) at 120 kV. The particle size and distribution were determined by counting 276 particles using the WinRoof image processing software (Mitani Co., Ltd, Fukui, Japan). The size distributions of AuNPs were also measured with a dynamic light scattering (DLS) instrument (DLS-7000, Otsuka Electronics Co., Japan) employing a 488 nm Ar laser (75 mW) as the light source (25°C). The time-dependent correlation function of the scattered light intensity was measured at a scattering angle of 90°. The particle size distributions were determined using the software provided with the instrument. In this study, the autocorrelation function was analyzed by the histogram method.

3 Results and Discussion

3.1 Synthesis and structural properties

The novel Au-coordinated MCS was prepared, and its structural properties were investigated by a variety of techniques. Figure 1 shows the molecular structure of the surface-active NHC-Au complex (NHC-Au-MCS). NHC-Au-MCS was synthesized by the reaction of the MCS precursor with a 1.0 equivalent of Me$_2$SbCl in the presence of K$_2$CO$_3$ in acetone at 60°C for 4 h with 88% yield. The elemental analysis of NHC-Au-MCS (C: 43.95, H: 7.25, and N: 3.19) was largely consistent with the calculated values (C: 43.69, H: 7.10, and N: 3.18). The same consistency was observed in the accurate mass measured by high-resolution MALDI-MS (measured $m/z$ (lightest isotope): 901.3243; and the elemental composition: $\text{C}_{32}\text{H}_{62}\text{AuBrN}_2\text{O}_8\text{Na}^+$; calculated $m/z = 901.3247$; error: -0.4 ppm), thus confirming the assigned composition of NHC-Au-MCS. The $^1$H NMR spectrum of NHC-Au-MCS in CDCl$_3$ exhibited protons corresponding to the $\text{N}$-heterocycle at $\delta = 7.20$ and 6.90 ppm, whose positions were shifted upfield by 0.51 and 0.49 ppm, respectively, compared to those of the NHC precursor. Additionally, the disappearance of the C2 acidic proton ($\delta = 10.17$ ppm from the MCS precursor) indicated the Au–C...
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bond formation. Indeed, the $^{13}$C NMR spectrum of NHC-Au-MCS exhibited C2 at 173.6 ppm and the free carbene signal that is typically present around 200 ppm was not observed on the spectrum, further confirming the formation of the Au–C bond.

To estimate the reactivity of NHC-Au-MCS, several MS techniques were employed. The MALDI mass spectrum of the initial NHC-Au-MCS is depicted in Fig. 2(A). Employing a regular solvent-based sample preparation method and utilizing a high molar ratio of the matrix/analyte ($\approx 3 \times 10^3$), an intact Au(NHC)Br species together with a minor Au(NHC)Cl species were detected as their corresponding sodium adducts at m/z 901/903 (isotopes $^{79}$Br and $^{81}$Br) and m/z 857/859 (isotopes $^{35}$Cl and $^{37}$Cl), respectively. A favorable in situ transmetalation with traces of NaCl solvent, vials was proposed to account for the detection of the sodiated Au(NHC)Br. The mass spectral assignments were further validated by the accurate mass measurements (measured m/z: 857.3770; elemental composition: C$_{32}$H$_{62}$O$_8$N$_2$AuCl; calculated m/z: 857.3752; error: $\approx 2.1$ ppm) and multistage ESI-MS analysis (data not shown).

Interestingly, another large molecular weight compound, which was larger than Au(NHC)Cl was also observed at m/z 1402 as a minor component and was assigned as Au(NHC)$_2$ according to the accurate mass measurements, which suggested the coordination of the two MCS precursors to the Au(I) center (measured m/z [lightest isotope] 1401.8645; elemental composition: C$_{64}$H$_{124}$AuN$_4$O$_{16}$; calculated m/z: 1401.8672; error: $\approx 1.9$ ppm). The MALDI-MS analysis of the same sample employing a solvent-free sample preparation method, which greatly reduced the molar ratio of the matrix/analyte (estimated at $3 \times 10^3$ and noticeably enhanced the detection of Au(NHC)$_2$ (Fig. 2(B)), suggesting its formation in situ upon laser irradiation. This hypothesis was further supported by a comparison of the MALDI mass spectra with those of LDI (Fig. 2(C)) and ESI-MS fingerprints (Fig. 2(D)). The LDI mass spectrum displayed Au(NHC)$_2$ exclusively, while the ESI mass spectrum displayed only the sodiated Au(NHC)Br adduct. These simple experiments validated the role of laser irradiation and the non-implication of the matrix in the formation of the ionic dimer, which in turn, revealed the potential reactivity of the Au–Br bond upon laser activation. Additionally, the changes in the ESI-MS fingerprint regions over time confirmed the increasing abundance of Au(NHC)Cl compared to that of Au(NHC)Br (inset of Fig. 2(D)) until Au(NHC)Cl became the major component. These changes demonstrated the possibility of a rapid Br $\rightarrow$ Cl transmetalation without requiring an external activation. Overall, the structural properties suggest the distinctive reactivity of NHC-Au-MCS.

3.2 Surface activities

The surface tension-lowering activity of NHC-Au-MCS...
was determined by the Wilhelmy plate method. Solutions of various concentrations were prepared and maintained overnight. The color of the solutions changed gradually from colorless to pink, indicating the partial formation of AuNPs (vide infra). The surface tension of water decreased with increasing concentration of NHC-Au-MCS from 72.0 to 44.9 mN/m, as shown in Fig. 3(A), and the CMC, obtained from the intersection of the two fitted lines, was $1.3 \times 10^{-5}$ M. The CMC of the MCS precursor was two orders of magnitude higher than that of NHC-Au-MCS\(^{19}\). Interestingly, the CMC of NHC-Pd-MCS ($1.4 \times 10^{-4}$ M) was one order of magnitude higher than that of NHC-Au-MCS\(^{13}\), despite both complexes possessing the same NHC ligands. These results point to the importance of the metal center in determining their surface properties. The low CMC of NHC-Au-MCS may result from the attractive intermolecular interaction of Au centers, such as Au–Au interactions\(^{20}\). It was reported that the Au atom, in Au(Ⅰ) oxidation state, is a hydrogen bond acceptor\(^{17}\). These properties characterize Au as the most electronegative among all metals\(^{8}\). Moreover, Au possesses very small atomic and ionic radii and, therefore, the lowest possible coordination number (CN = 2), which is lower than that of Pd(CN = 4) with a square planer geometry. The open space around Au atoms should facilitate the approach of other elements. Consequently, NHC-Au-MCS exhibits distinctive properties compared to NHC-Pd-MCS. The alignment of the Au atom in NHC-Au-MCS at the air/water interface may hamper the disruption of the hydrogen bonds of water. Therefore, the surface tension at the CMC ($\gamma_{\text{CMC}}$) of NHC-Au-MCS was higher than that of NHC-Pd-MCS. The relative scattering intensity suddenly increased above the CMC (Fig. 3(B)), indicating that the formation of micelles by NHC-Au-MCS commenced above its CMC. Indeed, the DLS measurement of the NHC-Au-MCS solution after filtration (PVDF filter with 0.45 μm pore size) confirmed the presence of the NHC-Au-MCS micelles with an average diameter of $5.7 \pm 1.1$ nm.

### 3.3 Catalytic activities

Having studied the physical characteristics of the prepared surface-active NHC-Au-MCS, we turned attention to its potential applications in catalysis. To examine its applicability for aqueous catalysis, we attempted the hydration reaction of alkynes since it is a classical methodology that afforded rapid access to a variety of ketone products\(^{19}\). The utilization of NHC-Au catalysts for alkyne hydration and the associated mechanisms have been reported. In 2009, Nolan et al. reported the use of NHC-Au(Ⅰ) catalysts in the development of a highly efficient catalytic system in the presence of AgSbF$_6$ for the hydration of various alkynes in the absence of a strong acid\(^{20}\). The reaction mechanism studies revealed that the initiation step of the reaction was the formation of a cationic [NHC-Au]$^+$ . Recent reports on the AuNP-catalyzed alkyne hydration indicated the different mechanisms for the NHC-Au(Ⅰ) heterogeneous and homogeneous catalyzed reactions\(^{21}\).

To study the alkyne hydration reaction using NHC-Au-MCS, we selected 1-dodecynedic, which possesses the same alkyl chain length as that of NHC-Au-MCS, as the model substrate. A vigorously stirred mixture of 1-dodecynedic and NHC-Au-MCS (20 mol %) in water facilitated the formation of an oil-in-water type emulsion. AgSbF$_6$ (20 mol %) was added to the emulsion, and the mixture was heated at 80°C. After 10 min, the color of the solution changed to deep purple, and thereafter, to a black suspension after 1 h, implying the formation of AuNPs in the reaction mixture. After 24 h, the reaction achieved an 84% conversion to 2-dodecanone (Table 1, Entry 1). A 40 mol % loading of NHC-Au-MCS and AgSbF$_6$ was required for the quantitative

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Fig. 3 (A) Surface tension vs. concentration plot of NHC-Au-MCS at 25°C. (B) Light-scattering intensity vs. concentration plot of NHC-Au-MCS at 25°C. The light scattering intensity of NHC-Au-MCS was detected using an Ar laser (488 nm).
conversion of 1-dodecyne under the condition presented in Entry 2. A low catalytic loading below the CMC (0.005 mol%) did not form 2-dodecanone. We explored other additives for this reaction and observed that KB(C₆F₅)₄ was an effective additive that favors activation at a low catalytic loading (10 mol%) without conversion losses (Entries 3 and 4). B(C₆F₅)₄, as a weakly coordinating anion, could stabilize the [NHC-Au]+ moiety during a catalytic cycle and thus facilitate the reactions. Next, we examined the typical two-phase reaction systems for alkyne hydration. Mixtures of water and ethanol or propanol produced homogeneous solutions and achieved high conversions (>99% for ethanol and propanol, Entries 6 and 7) while mixtures of water and methanol, butanol, octanol, or dodecanol were heterogeneous and achieved low conversions (83% for methanol, 63% for butanol, 9% for octanol, and 6% for dodecanol, corresponding to Entries 5, 8, 9, and 10, respectively). Similar tendencies were observed when polyalcohols were utilized as co-solvents. Both 1,2- and 1,4-butanediols exhibited good solubility in both 1-dodecyne and water, resulting in the quantitative formation of the product (Entries 12 and 13). However, both substrates were poorly soluble in 1,2-propanediol and achieved low conversions (Entry 11). These results indicate that the reaction of 1-dodecyne with water was facilitated by the surface-active NHC-Au-MCS.

To confirm the reaction mechanism, the cationic complex ([NHC-Au-MCS]⁺[SbF₆]⁻), which is typically expected to be the active species of a homogeneous reaction, was prepared separately by the reaction of NHC-Au-MCS with AgSbF₆. Thereafter, we attempted the hydration of 1-dodecyne to 2-dodecanone using the preformed[NHC-Au-MCS]⁺[SbF₆]⁻ in water via the procedure described in Table 1. Contrary to the results obtained in Table 1, this reaction achieved only 25% conversion although it formed a stable emulsion (Fig. 4). These results suggest that the catalytic hydration of 1-dodecyne in water was facilitated mainly by the formation of AuNPs under heterogeneous conditions. Further, the amount of catalytically active AuNPs was likely insufficient, and a relatively large catalytic loading might be required for effecting this conversion.

### 3.4 Formation of AuNPs

To investigate the reaction mechanism of NHC-Au-MCS-mediated alkyne hydration, we studied the formation of AuNPs in water and observed that AuNPs were formed upon dissolving NHC-Au-MCS (0.1 mM) in water, followed by maintaining it at ambient temperature. An aliquot of the resulting pink solution was analyzed by TEM (Fig. 5(A)). The images show the formation of AuNPs, whose shapes appeared to be generally spherical. Additionally, some hexagonal and triangle-shaped AuNPs were also present (Figs. 5(B) and (C)). Interestingly, the triangle-shaped AuNPs with layer structures were also observed (Fig. 5(D)). We expected that NHC-Au-MCS may be covered by AuNPs, consequently.

The calculated mean size of the AuNPs was 50.1 ± 15.9 nm (Fig. 5(B)), which is in agreement with the acquired DLS measurements (47.3 ± 10.5 nm). Figure 6(A) shows the reaction profile that was monitored using the UV–vis absorption spectra. The peak centered at 535 nm originated from the SPR of AuNPs. It is well known that the wavelength and magnitude of SPR depend on the con-
centration and structure of AuNPs. The size of each of the AuNPs was ~50 nm (estimated from the wavelengths), which also agrees with TEM and DLS measurements. A similar reaction of NHC-Au-MCS below CMC (9.0 \times 10^{-6} \text{ M}) did not obtain the absorbance at 535 nm. Next, we studied the time profile of the reaction, which indicated that the AuNP formation completed after 100 min (Fig. 6). Control experiments were conducted to understand the role of the NHC-Au-MCS surface activity toward AuNP formation. The mixing of β-cyclodextrin (β-CD) with NHC-Au-MCS in water resulted in a reduction in the absorption corresponding to AuNP at 535 nm. The apparent rate of AuNP formation in the presence of β-CD (1.4 \times 10^{-3} \text{ min}^{-1}) was obtained from the slope at the initial region of the reaction profile, was approximately two times lower than that in its absence (2.5 \times 10^{-3} \text{ min}^{-1}). It is well known that β-CD forms a host-guest complex with surfactants, thereby inhibiting the adsorption by surfactants at the air/water interface. Moreover, the reaction of NHC-Au-MCS in ethanol, whose interfacial tension (21.8 mN/m at 25°C) is lower than that of water, did not produce AuNPs. These control experiments suggested that AuNPs were formed from NHC-Au-MCS, which was adsorbed at the air/water interface. The addition of β-CD in water and the use of ethanol as a solvent inhibited the adsorption behavior of NHC-Au-MCS.

AuNPs obtained from NHC-Au-MCS were stable in water even after heating at 80°C for 24 h. Furthermore, the absorbance at 535 nm did not decrease; it rather increased from 0.15 to 0.21 after the thermal treatment. AuNPs also exhibited resistance to 2 M NaCl, in the presence of which their absorbance at 535 nm did not change even after 24 h. Sakai et al. reported the formation of AuNP in an aqueous mixture of HAuCl₄·3H₂O and amphiphilic block copoly-
AuNPs by the NHCs in NHC-Au-MCS. Moreover, the Au stabilizers of the AuNPs. Moreover, the Au-isotopic Au clusters Au \(_n\) and displayed mo-

mers, such as poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), in the absence of any other reducing agent\(^{20}\). The block copolymers play a beneficial role as the stabilizers of the AuNPs. Moreover, the Au–C\(_{\text{NHC}}\) bond is ~20 kcal \(\text{mol}^{-1}\) stronger than the typical Au–S bond of thiols\(^{27}\). These results explain the excellent stabilization of AuNPs by the NHCs in NHC-Au-MCS.

The MALDI-MS spectrum of NHC-Au-MCS also supported the formation of AuNPs (Fig. 7). Upon solubilizing NHC-Au-MCS in water and maintaining the sample for 2 min, the solution changed into a deep-pink. Further, the MALDI(+/−) mass spectra of the two air-dried droplets that were de-

posited on the target, using the stable NHC-Au-MCS solutions in THF and water, were the same (data not shown), and their MALDI-MS fingerprints depicted in Figs. 7A and B varied greatly. As partly reported in Fig. 2, the MALDI mass spectra of unreacted NHC-Au-MCS displayed the formation of the laser-induced Au(NHC)\(_2\)\(^{+}\) at \(m/z\ 1.4 \times 10^3\) in LDI(+) and AuBr\(_2\)\(^−\) in LDI(−). A second peak, observed at \(m/z\ 679\), remains unassigned. The laser fluence used to desorb/ionize these species was set at 70% in the arbitrary scale of msTornado, which is a typical setting in an LDI as it does not benefit from matrix assistance. The first set of LDI(+/−) mass spectra obtained using a solution of NHC-Au-MCS in water, which was maintained for 20 min, were recorded using a laser fluence at 50% and displayed mono-isotopic Au clusters Au\(_{\text{n}}\) = 1−3\(^{+}\) and Au\(_{\text{n}}\) = 1−2\(^{−}\), which are typical fingerprints of AuNPs\(^{28–30}\). These peaks were further employed as internal calibrants in addition to the larger Au\(_{\text{n}}\)Br\(_{\text{n}}\) clusters in LDI(−) and a remaining Au(NHC)\(_2\)\(^+\) in LDI(+). The observed detection by LDI at a low laser fluence, which is typically employed for the MALDI-MS analysis, further suggested that AuNPs are indeed deposited on the target and that the transfer of species to the gas phase was facilitated by a surface-assisted LDI (SALDI) process\(^{31}\). Upon increasing the laser fluence to 70% to facilitate a better comparison with the LDI pattern of unreacted NHC-Au-MCS, much larger Au\(_{\text{n}}\)\(^+/−\) clusters were clearly observed in LDI(+/−). The detection of the intact sodiated Au(NHC)Br in LDI(+) was an important result, which confirmed a) the occurrence of the SALDI process involving AuNPs and b) the completion of the transformation of Au(NHC)Br to AuNPs. When the same laser fluence was utilized, and the detection range for the mass was set to a higher mass range, only large Au\(_{\text{n}}\)\(^+/−\) clusters were observed, ranging to \(n = 30\) in LDI(+) and \(n = 19\) in LDI(−), which favored the detection of odd clusters. This observation is similar to the report by Kolář\(á\) et al. on the LDI-MS of synthetic AuNPs\(^{32}\). These preliminary results afforded the assessment of the presence and chemical nature of AuNPs formed upon the solubilization of NHC-Au-MCS in water.

Overall, the results suggested that the formation of AuNPs from NHC-Au-MCS, as the Au source, comprises two steps: first, the surface-active Au\(_{\text{n}}\) complex of NHC-Au-MCS was absorbed at the air/water interface to form an integrated Au cluster via the van der Waals interaction between the n-dodecyl chains. This may also involve the participation of the Au(1)–Au(1) interactions\(^{16}\). The formation of Au(NHC)\(_2\)\(^+\) during the reaction was considered as an indirect proof of AuNP formation and the presence of NHCs at the surface of AuNPs\(^{15,16}\). Secondly, NHC-Au-MCS at the air/water interface translated into AuNPs since the octaethylene glycol monomethyl ester moiety may have acted as a reducing agent. During the transformation from NHC-Au-MCS to AuNPs, NHC-Au-MCS can produce reac-

\[ \text{Au(NHC-MCS)} \rightarrow \text{AuNP} + \text{NHC} \]

\(\text{Au}(\text{NHC-MCS}) \rightarrow \text{AuNP} + \text{NHC} \]

\[ \text{Au}(\text{NHC-MCS}) \rightarrow \text{AuNP} + \text{NHC} \]

Fig. 6 (A) UV-vis spectra of NHC-Au-MCS (0.1 mM) in water at 25°C. (B) Reaction profile monitored by absorption at 535 nm (circle: the reaction of NHC-Au-MCS (0.1 mM) in water at 25°C; square: the reaction of NHC-Au-MCS (0.1 mM) in the presence of β-cyclodextrin (10 mM) in water at 25°C; triangle: the reaction of NHC-Au-MCS (0.1 mM) in ethanol at 25°C).
N-Heterocyclic Carbene-based Au Coordinated Surfactant

In this study, we reported the synthesis of an NHC-based MCS comprising an Au(I) center (NHC-Au-MCS), in which the metal center was bound to the linkage of the hydrophilic and hydrophobic portions of the surfactant via a robust Au–carbene bond. The MALDI-, LDI-, and ESI-MS measurements indicated a distinctive reactivity for NHC-Au-MCS, which underwent transmetalation from Au(NHC)Br to Au(NHC)Cl, and formed Au(NHC)₂⁺ under laser activation conditions. Surface tension measurements revealed that the CMC of NHC-Au-MCS (1.3 × 10⁻⁵ M) was two orders of magnitude lower than that of its MCS precursor. Moreover, the CMC of NHC-Au-MCS was one order of magnitude lower than that of NHC-Pd-MCS despite both complexes possessing the same NHC ligand. Notably, the surface-active Au(I) complex of NHC-Au-MCS catalyzed the hydration of 1-dodecyne in water. The reaction proceeded with the formation of a heterogeneous Au(I) complex, along with the formation of AuNPs, which were characterized using UV–vis, TEM, and MS measurements, in water. The obtained AuNPs were stable in water even after

4 Conclusions

Fig. 7  LDI(+) and LDI(−) mass spectra of the dried droplets from (A) the unreacted NHC-Au-MCS in THF and (B) the aqueous NHC-Au-MCS.
heating at 80°C for 24 h and were remarkably stable even in the presence of 2 M NaCl, suggesting that the surface of AuNPs was protected by the NHC ligands via a strong Au-C(NHC) bond. Thus, the mixture of NHC-Au-MCS and its AuNPs facilitated the hydration of alkynes under aqueous conditions.

AuNPs have attracted particular interest for their size-and shape-dependent properties. So far, many types of capping agents have been employed in the synthesis of AuNPs. Among them, NHCs have attracted significant interest as neutral and electron-rich ligands, which form a strong M–C bond with metallic surfaces. Particularly, the use of a well-defined NHC-Au(1) complex as a precursor is regarded as a novel approach for controlling the size and stability of AuNPs. However, the reaction typically required strong reducing reagents, such as 9-BBN. Further, the use of an NHC-based MCS as a precursor of AuNPs has not been reported. Thus, the AuNP-catalyzed hydrations of alkynes, mediated by NHC-Au-MCS in water, can be an invaluable tool in organic synthesis for the rapid generation of structural complexity and are prime examples of green sustainable chemistry.

Conflicts of Interest:
There are no conflicts of interest to declare.

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