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NHC-Stabilized Au_{10} Nanoclusters and Their Conversion to Au_{25} Nanoclusters

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NHC-Au-X complexes (X = Cl, Br, I). The significant effect of the halide ligands on the formation, stability, and further conversions of these clusters is presented. While solutions of the chloride derivatives of Au_{10} show no change even upon heating, the bromide derivative readily undergoes conversion to form a biicosahedral Au_{25} cluster at room temperature. For the iodide derivative, the formation of a significant amount of Au_{25} was observed even upon the reduction of NHC-Au-I. The isolated bromide derivative of the Au_{25} cluster displays a relatively high (*ca.* 15%) photoluminescence quantum yield, attributed to the high rigidity of the cluster, which is enforced by multiple CH- π interactions within the molecular structure. Density functional theory computations are used to characterize the electronic structure and optical absorption of the Au_{10} cluster. ¹³C-Labeling is employed to assist with characterization of the products and to observe their conversions by NMR spectroscopy.



KEYWORDS: gold, N-heterocyclic carbenes, metal nanoclusters, nanocluster interconversion, density functional theory calculations, NMR analysis, ¹³C-labeling, photoluminescence

INTRODUCTION

N-Heterocyclic carbenes (NHCs) are widely employed ligands in transition-metal and main-group chemistry^{1–3} and have recently attracted interest in materials chemistry,⁴ providing robust monolayers on planar gold surfaces^{5–8} and nanoparticles.^{9–15} Known NHC-stabilized gold nanoclusters are predominantly smaller Au₁₁ or Au₁₃ species,^{16–20} however, Au₂₃ and Au₄₄ cores have also been reported for mixed-ligand systems.^{21,22} Despite the high prevalence of Au₂₅ cores in thiolate-stabilized clusters, there is only one example of this cluster size for NHC-stabilized systems.²³

Our group recently reported that the reduction of NHC– Au–X complexes resulted in a series of icosahedral Au_{13} clusters (Figure 1) when benzylic groups on the NHC nitrogens of substituted benzimidazole were employed.¹⁷ Although a range of benzylic substituents was tolerated, increasing the steric size of the substituents led to a decrease in the yield of the target Au_{13} clusters, and the formation of polydisperse cluster mixtures. It was surprising then that the use of an NHC ligand with even more sterically hindered 2,4,6trimethylbenzyl (from here on, MesCH₂) wingtip groups gave well-defined cluster species, specifically an Au_{10} cluster with a toroidal core. Subsequent conversion of Au_{10} to a biicosahedral Au_{25} cluster strongly depends on the nature of the halide employed.

Herein, we document the synthesis of these Au_{10} and Au_{25} clusters and provide evidence that small, isolable clusters are precursors to the formation of larger clusters. The extreme effect that seemingly innocent counterions have on the conversion of Au_{10} to Au_{25} is also described, along with the effect of the solvent. The use of ¹³C labeling on the carbene carbon provides unprecedented insight into the transformation.

RESULTS AND DISCUSSION

Synthesis and Characterization of Au₁₀ Nanoclusters

Molecular gold complexes MesCH2 BimyAuX **2a**-c (X = Cl, Br, I) were synthesized from the corresponding benzimidazolium

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Figure 1. Synthesis of NHC-stabilized Au nanoclusters by direct reduction of NHC-Au-X complexes.

salts 1a-b via established procedures^{24,25} (see the SI for details). The reduction of these complexes was carried out with NaBH₄ at room temperature (Figure 2A). In all cases, UV-vis absorbance spectroscopy revealed the presence of cluster species with absorbance profiles notably different from previously reported Au₁₃ clusters.¹⁷ For instance, in the case of 2b (X = Br), the reaction mixture after 12-20 h at room temperature shows distinct absorbance bands at \sim 320, 368, and 470 nm (Figure S2). Analysis of the crude reaction mixture by electrospray ionization mass spectrometry (ESI-MS; Figure S3) identified the major cluster species to be $[Au_{10}({}^{\rm MesCH2}Bimy)_6Br_3]^+$ ([3b]+). The reaction times for the formation of Au₁₀ clusters as well as the composition of the crude reaction mixtures depended on the halide employed but all MesCH2BimyAuX precursors produced $[Au_{10}(^{MesCH2}Bimy)_{6}X_{3}]X$ clusters (3a, X = Cl; 3b, X = Br; 3c, X = I). *In situ* monitoring of the reduction of 2b by UV-vis absorbance spectroscopy at short reaction times (<6 h) showed intermediate gold species with absorbance bands at ~325, 424, and 532 nm (Figures S11 and 12). Due to their transient nature, these species could not be unequivocally identified by ESI-MS and NMR spectroscopy (Figures S13 and 14). At longer reaction times, these intermediate species converted to [3b]Br.

Clusters [3a]Cl and [3b]Br were purified by column chromatography, recrystallization, and anion exchange with NH₄PF₆ (see the SI for details). ESI-MS of $[3b][PF_6]$ shows a dominant molecular ion peak at 4504.9 *m/z* corresponding to $[Au_{10}(^{MesCH2}Bimy)_6Br_3]^+$ (Figure 2B). Good agreement was observed between the experimental and theoretical isotope distribution patterns. A minor peak at 4460.0 *m/z* was also observed in the cluster region; this peak was attributed to exchange species $[Au_{10}(^{MesCH2}Bimy)_6Br_2Cl]^+$, most likely formed by halide exchange during ionization. UV–vis absorbance profiles of purified clusters $[3a][PF_6]$ (Figure S67) and $[3b][PF_6]$ (Figure 2C) are largely the same, although the exact band positions and intensities were found to be dependent on the halide. Halogen effects on optical properties are consistent with previous observations with phosphinestabilized Au nanoclusters;²⁶ however, a dramatic difference in the reactivity of gold clusters depending on the halide present has not been previously reported, to the best of our knowledge. In our experiments, iodide cluster [3c]I proved to be difficult to isolate in high purity due to its facile conversion to other clusters (*vide infra*), and [3c]I was therefore only partially characterized (Figures S6–8 and S15).

X-ray quality single crystals of the triflate salt [**3b**][OTf] were characterized by single-crystal X-ray crystallography. The solid-state structure (Figure 3) reveals a toroidal Au₁₀ core similar to $[Au_{10}(PCy_2Ph)_6Cl_3][NO_3]$ reported by Mingos et al.²⁷ but [**3b**]⁺ has a different arrangement of halide ligands. Cluster [**3b**]⁺ has pseudo C_{2V} symmetry, with two Au₃(NHC)₃ rings capping either side of a planar Au₄Br₃ core. The Au–Au distances range from 2.6271(9) Å to 2.936(1) Å, with the average radial Au–Au bonds being shorter than the average peripheral Au–Au separations (2.700 and 2.832 Å, respectively; see Table S7 for summarized data). Au–C bond lengths are between 2.026(9) Å and 2.041(9) Å (average 2.034 Å; Table S7), which is slightly shorter compared with Au–C_{NHC} bond lengths in previously reported NHC-stabilized gold nanoclusters.^{17–20,23}

The cluster core of $[3b]^+$ is relatively more open than in previously reported NHC-stabilized gold nanoclusters: unlike Au₁₃ and Au₁₁, $[3b]^+$ does not have any inner gold sites. Moreover, the gold atom at the central site of $[3b]^+$ is not bonded to NHC or halide ligands, which makes $[3b]^+$ potentially more reactive.

Synthesis and Characterization of Au₂₅ Nanoclusters

Although [**3b**]Br is sufficiently stable to survive column chromatography, its solutions in ethanol change color over time, which prompted us to investigate whether a new cluster was being formed. As expected, the UV–vis absorbance spectra reflect this change, most notably through the appearance of a new band at 658 nm (Figure S16). ESI-MS analysis identified $[Au_{25}(^{MesCH2}Bimy)_{10}Br_7]^{2+}$ ([**4b**]²⁺) as the new cluster species. This formulation is similar to an Au_{25} cluster stabilized by ^{iPr}Bimy NHCs reported by Zheng et al.,²³ in which five



Figure 2. (A) Preparation of Au_{10} clusters 3a-c; (B) ESI-MS of $[3b][PF_6]$; and (C) UV-vis absorbance spectrum of $[3b][PF_6]$ in dichloromethane.

bridging bromide ligands link two Au_{13} icosahedra with a shared central atom. In Zheng's report, the Au_{25} cluster was the result of prolonged treatment of a molecular gold precursor without the observation of intermediate cluster species.

Purification of cluster $[4b]^{2+}$ could be achieved by anion exchange with NH₄PF₆ followed by column chromatography (see the SI for details). In the ESI-MS of $[4b][PF_6]_2$ (Figure 4B), the dominant molecular ion peak at 4654.5 *m/z* shows good agreement with the theoretical isotope distribution pattern of $[Au_{25}(^{MesCH2}Bimy)_{10}Br_7]^{2+}$. Trace amounts of $[Au_{25}(^{MesCH2}Bimy)_{10}Br_6Cl]^{2+}$ (see the small peak at 4632.1 on Figure 4B) were also observed, consistent with Br/Cl exchange.²⁸ The main UV-vis absorbance bands of [4b]- $[PF_6]_2$ were found at 325, 338, 377, 413, 467 (with a shoulder at ~510), and 658 nm (Figure 4C).

Though the conversion of one metal nanoclusters to another is common, reports on such transformations involving biicosahedral M_{25} nanoclusters are scarce. A few publications describe the preparation of phosphine/thiolate or phosphine/ halide stabilized biicosahedral M_{25} nanoclusters by conversion from other species, such as a mixture of gold nanoparticles,^{29–32} spherical M_{25} clusters,³³ and smaller Au_{11}



Figure 3. (A) Molecular structure of [3b][OTf] with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and anions have been omitted, and NHCs are shown as a wireframe for increased clarity. (B, C) Alternative view of the $[3b]^+$ core with bromide ligands only. Color key: Yellow = Au, Orange = Br, Gray = C, Blue = N.

nanoclusters.³⁴ In all of these cases, there was a specific trigger for the transformations of the metal core, for example, the addition of different ligands.^{31,32} Seemingly triggerless conversion of otherwise stable Au_{10} into biicosahedral Au_{25} is unprecedented. This prompted us to look into details of the Au_{10} to Au_{25} conversion.

Kinetics of Au₁₀ to Au₂₅ Conversion in Solution

To probe the conversion of Au_{10} to Au_{25} clusters, we leveraged the differences in the UV-vis absorbance spectra of the two species to monitor reaction progress over time. Specifically, we tracked the increase in the absorbance of the Au_{25} characteristic band at 658 nm (Figure 5). It was found that the conversion of [**3b**]Br is solvent dependent, occurring readily in protic or mildly acidic solvents such as alcohols (methanol, ethanol) or chloroform, but not in other solvents examined such as dichloromethane or tetrahydrofuran (THF) (Figure **S16**). The conversion rate for [**3b**]Br depends on its concentration, temperature, and the nature of the solvent. At room temperature in alcohol solvents, over a week is required to reach an appreciable concentration of Au_{25} , while the same conversion takes only 2 days at 55 °C in methanol. The conversion is the fastest in chloroform at 55 °C, taking only hours (Figure 5).³⁵ Unfortunately, in chloroform, this conversion is accompanied by the formation of unidentifiable byproducts, which complicated attempts at quantitative kinetic experiments.

To confirm the results obtained by UV–vis absorbance spectroscopy and gain insight into the mechanism of Au_{25} formation, conversion of [**3b**]Br was also monitored by ESI-MS and NMR spectroscopy (Figures S19–S21). Similar trends were also observed using these techniques. In particular, the conversion was faster in chloroform compared to methanol, as monitored by NMR spectroscopy (Figures S20–S21). Note that no intermediate cluster species were observed by ESI-MS while monitoring the conversion of Au_{10} to Au_{25} (Figure S19), and therefore, greater detail concerning the mechanism for this conversion could not be obtained using this method.

The nature of the outer sphere anion also has a significant effect on the rate of conversion. Cluster $[3b][PF_6]$ shows only partial conversion after 20 h at 60 °C in methanol,³⁶ while



Figure 4. (A) Preparation of Au_{25} cluster [4b]Br₂; (B) ESI-MS of [4b][PF₆]₂; and (C) UV-vis absorbance spectrum of [4b][PF₆]₂ in dichloromethane.



Figure 5. Conversion of [3b]Br in chloroform (blue) and methanol (green) at 55 °C, monitored *in situ* by the change in absorbance at 658 nm over time.

under the same conditions [3b]Br converts significantly to Au₂₅, as observed by UV-vis absorbance and NMR spectroscopy, and ESI-MS (Figures S17–21). Inner sphere halides also have a significant effect. For example, the Au_{10} cluster with chloride ligands [3a]Cl showed no evidence of conversion to Au₂₅ even after several weeks in ethanol at room temperature or with heating at 60 °C in methanol. By contrast, the bromide derivative [3b]Br is readily converted to Au₂₅ clusters $[4b]^{2+}$ in specific solvents, and iodide cluster [3c]I gave significant amounts of Au_{25} clusters $[4c]^{2+}$ even during the reduction of 2c (Figure S15). Attempts to isolate pure samples of [3c]I via the established methods for [3b]Br also led to the isolation of a significant amount of $[4c]^{2+}$ without the need for further conversion, although instability of $[4c]^{2+}$ prevented full purification and characterization (Figures S6-8). These results demonstrate the pivotal role not only of the outer sphere counterions but also of the ligated halide ligands in cluster conversion from Au₁₀ to Au₂₅ and the overall stability of the clusters. Our observations agree with the previous reports that

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halides can affect the growth and conversions of metal nanoclusters. $^{\rm 37-39}$

Structural Characterization of Au_{25} Clusters in the Solid State

In an early attempt to isolate pure Au_{25} cluster $[4b]^{2+}$ for structural characterization, [3b]Br was dissolved in ethanol and kept at room temperature for 7 days. Purification by dialysis and anion exchange with $K[B(C_6F_5)_4]$ led to the isolation of crystals of a closely related cluster $[Au_{25}(^{MesCH2}Bimy)_{10}Br_8]$ - $[B(C_6F_5)_4]$ ($[5b]^+$, Figure 6). This cluster closely resembles



Figure 6. (A) Molecular structure of $[5b][B(C_6F_5)_4]$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and anions have been omitted, and NHCs are shown as a wireframe for increased clarity. (B) Alternative view of the $[5b]^+$ core with bromide ligands only. Color key: Yellow = Au, Orange = Br, Gray = C, Blue = N.

 $4b^{2+}$ with the exception of having an additional inner sphere bromide ligand and therefore only a +1 charge. The parent mass peak for $[5b]^+$ could not be observed by ESI-MS, with the sample showing only a peak for $[4b]^{2+}$, likely due to the facile loss of one bromide ligand on the core during ionization.

X-Ray crystallographic analysis indicated that $[5b]^+$ features a twisted biicosahedral structure where the two central Au₅ pentagons making up the core of the structure are in a partially staggered orientation. The structure also features four bridging and two terminal bromide ligands connecting the two central Au₅ pentagons, instead of the expected symmetric five bridging bromide ligands (Figures 6B and S63). The Au–Br bond distances at the waist sites are in the range of 2.5316(8) Å— 2.5794(7) Å for the doubly bridging bromides and 2.455(1) Å—2.4609(9) Å for the terminal ones. The latter distances are slightly shorter compared with the terminal Au–Br bond distances at the vertex sites (2.4706(9) Å—2.4718(9) Å; see Table S8 for summarized data). The co-existence of different (*i.e.*, bridging and terminal) metal-halide connection modes at the waist sites of biicosahedral nanoclusters is extremely rare; it was reported only once for related phosphine/ halide-ligated AgAu bimetallic M₂₅ clusters by Huang et al.⁴⁰

Subsequently, we established an optimized procedure for the isolation and purification of the Au₂₅ cluster, specifically, the conversion of [**3b**]Br in methanol at 60 °C, followed by anion exchange of the crude mixture with excess NH₄PF₆ and purification by column chromatography (see details in the SI). We note that the anion exchange was used here to facilitate purification, though later we discovered that anions may also play role in transformations between [**5b**]⁺ and [**4b**]²⁺ (*vide infra*). We were successful in growing crystals of [**4b**][B-(C₆F₅)₄]₂ from Au₂₅ clusters isolated *via* this route, after anion exchange with the borate anion. The solid-state structure (Figure 7) shows the expected Au₂₅ core structure with five symmetric bridging bromide ligands and not six as for [**5b**]⁺.

The two central Au₅ pentagons are slightly twisted from an eclipsed orientation, although less than that in $[5b]^+$, most likely due to the steric constraints of the bulky mesityl substituents. Structures with five bridging halides and different degrees of rotation of the vertex-sharing icosahedra had been reported for related phosphine/halide-ligated heterometallic M_{25} nanoclusters⁴¹⁻⁴⁴ and, more recently, for an NHC/halideligated Au₂₅ nanocluster.²³ In particular, [Au₂₅(^{iPr}Bimy)₁₀Br₇]²⁺ (bearing significantly less bulky *i*Pr wingtip groups as compared with MesCH₂ in $[4b]^{2+}$) was reported to have an eclipsed configuration of two icosahedra;²³ this nanocluster conforms to idealized D_{5h} symmetry with somewhat shorter icosahedron-icosahedron separations than in $[4b]^{2+}$ (see Table S8). Of note, the asymmetric unit contains two molecules of $[4b]^{2+}$ and three $[B(C_6F_5)_4]^-$ counterions. The fourth counterion was not resolved; this $[B(C_6F_5)_4]^-$ counterion is likely significantly disordered due to the large solvent accessible void in the unit cell (see Figure S65).

The fact that the Au₁₀ cluster with chloride ligands [**3a**]Cl showed no conversion to Au₂₅ (while [**3b**]Br and [**3c**]I convert readily) may be explained both by the steric environment imposed by the bulky mesityl-substituted NHC ligand, as well as steric and electronic factors introduced by the smaller chloride ligands. Though multiple examples of phosphine, thiolate, or NHC-protected gold clusters with halides as co-ligands have been reported, chlorides are commonly found terminally bound to gold, and clusters with Au–Cl bridging bonds are extremely rare.^{45,46}

Structural Characterization of Au₁₀ and Au₂₅ Clusters in Solution by NMR Spectroscopy

To further probe the reactivity and structures of $[3b]^+$ and $[4b]^{2+}/[5b]^+$ in solution,¹³C(2)-labeled benzimidazolium salt **1b*** was synthesized and used to prepare the corresponding ¹³C-labeled gold complex **2b*** and cluster [3b*]X (see the SI for details). The ¹³C{¹H} NMR spectrum of labeled [3b*]X (X = Br or PF₆) has two carbene peaks at 200.7 and 214.9 ppm in a 2:1 ratio, respectively, as expected from the two different ligand environments predicted from the solid-state structure of the Au₁₀ clusters (Figure 8A; see Figure S45 for full-spectrum



Figure 7. (A) Molecular structure of $[4b][B(C_6F_5)_4]_2$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and anions have been omitted, and NHCs are shown as a wireframe for increased clarity. The asymmetric unit has two cluster molecules; only one is shown for clarity. (B) Alternative view of the $[4b]^{2+}$ core with bromide ligands only. Color key: Yellow = Au, Orange = Br, Gray = C, Blue = N.



Figure 8. ${}^{13}C{}^{1}H$ NMR spectra (600 MHz, CD_2Cl_2) of (A) ${}^{13}C{}^{1}$ labeled [3b*][PF₆]; (B) column-purified [4b*][PF₆]₂, and (C) crude reaction mixture from conversion of [3b*]Br in MeOH at 60 °C for 4 days.

and Figure S56 for assignment). The ¹H NMR spectrum of $[3b^*]X$ (Figure S44) is also in agreement with this structure and is consistent with the nonlabeled cluster (Figure S40), showing only minor broadening of the benzylic proton peaks, in contrast to the diastereotopic benzylic proton peaks observed in the spectra of related Au₁₃ clusters.¹⁷

Conversion of $[3b^*]$ Br in methanol or CHCl₃ at 60 °C, followed by exchange with NH₄PF₆ and purification by column chromatography led to the isolation of a major cluster species with only one carbene peak in the ¹³C{¹H} NMR spectrum at 206.7 ppm (Figures 8B and S47). The ¹H NMR spectrum (Figure S46) is consistent with the NMR spectrum of the isolated crystals of $[4b][B(C_6F_5)_4]_2$ as well as nonlabeled Au₂₅ clusters isolated by NH₄PF₆ exchange and column chromatography, and shows a single, albeit asymmetric, ligand environment, due to the fixed arrangement of the ligands across the cluster (see Figures S57 and S58 for assignment). For example, six distinct methyl resonances can be found for the mesityl groups (Figure S46). Due to the expected symmetry of the ten ligands in cluster $[4b]^{2+}$, as well as the consistency of the NMR and other spectroscopic data with the crystals isolated for $[4b][B(C_6F_5)_4]_2$ we assign this species as $[4b^*][PF_6]_2$ (see the SI for full characterization data).

To obtain more insight into the conversion of Au_{10} to Au_{25} , and the possible distinction between clusters $[\mathbf{4b}]^{2+}$ and $[\mathbf{5b}]^+$ in solution, we monitored the conversion of $[\mathbf{3b^*}]X$ under various conditions by NMR spectroscopy. In crude samples, we can indeed confirm the presence of two major sets of cluster ligand peaks by ¹H NMR spectroscopy, in addition to the expected gold complex byproducts ($^{\text{MesCH2}}Bimy$)AuX and $[(^{\text{MesCH2}}Bimy)_2Au]X$. In particular, a second set of six methyl resonances distinct from those confirmed to be $[\mathbf{4b}]^{2+}$ is evident in the reaction mixtures before anion exchange and purification (Figure S22), along with a second carbene signal in the ¹³C{¹H} NMR spectra of ¹³C-labeled samples at 206.9 ppm (Figures 8C and S23). It also appears that this species is either converted to $[\mathbf{4b}]^{2+}$ or decomposed during anion exchange and/or column purification.

Interestingly, the ¹H NMR spectrum of a pure sample of $[4b][PF_6]_2$ in the presence of excess tetrabutylammonium bromide showed mostly this second set of signals in dichloromethane-d2 (see Figures S22 and 23), suggesting that it exists in this form in the presence of excess bromide ions. Although the asymmetry of the solid-state structure of [5b]⁺ would suggest the presence of multiple carbene signals for this cluster, similar phosphine ligated AgAu bimetallic M₂₅ clusters with six bridging halides have been found to exhibit only a single ligand environment in solution by NMR spectroscopy.47 It is difficult to confirm the assignment of this species as [5b]⁺, as the parent mass peak cannot be observed by ESI-MS likely due to facile loss of one bromide ligand on the core during ionization, and unfortunately the crystal yield of $[5b][B(C_6F_5)_4]$ was not high enough for detailed NMR studies. However, these NMR studies confirm that multiple cluster species, likely the two Au₂₅ clusters characterized in the solid-state, are generated from the conversion of Au_{10} , with $[4b]X_2$ appearing to be the dominant structure isolated after purification in most cases.

Theoretical Calculations

The electronic structure of $[3b]^+$ was investigated by density functional theory (DFT) using experimental coordinates as a starting point (see the SI for technical details of the DFT



Figure 9. (A) HOMO (left) and LUMO (right) orbitals of $[3b]^+$ and (B) calculated (red) and measured (green) UV-vis spectrum of $[3b]^+$.

calculations and analysis). We used the real-space GPAW code⁴⁸ and optimized the structure with the Perdew–Burke– Ernzerhof (PBE)⁴⁹ exchange–correlation (xc) functional to describe the electron–electron interactions. The PBEoptimized structure of $[\mathbf{3b}]^+$ in the gas phase is shown in Figure S74 and compared to the crystal structure in Table S9. We see that the gas-phase model overestimates the Au–Au bonds by 2–5%, Au–Br bonds by 2%, and Au–C bonds by 2% while keeping the overall symmetry unchanged.

This behavior is similar to what we have found previously for NHC-stabilized Au clusters,^{16,17,23} and we consider it an acceptable compromise between numerical efficiency and accuracy. We note that the use of the gas-phase model for $[3b]^+$ itself may account partially for the small structural discrepancies between the experiment and theory, regardless of the used xc functional, due to omission of effects from counterions and crystal packing.

To study the symmetry of the frontier orbitals and the magnitude of the HOMO-LUMO energy gap, we also employed the GLLB-SC xc functional, which was originally developed to improve the band gap of semiconductor materials.⁵⁰ Figure S75 compares the electronic density of states calculated both from the PBE functional and the GLLB-SC functional for the PBE-optimized cluster structure. Both functionals yield similar symmetries for the frontier orbitals, with the HOMO and HOMO-1 orbitals being of T1_u (spherical P-symmetry), as expected for a cluster with 6 "superatom" electrons,⁵¹ while the LUMO orbital has an eg (D) symmetry (Figures 9A and S76). GLLB-SC yields a significantly larger energy gap as compared to PBE (2.26 and 1.98 eV, respectively). The larger gap is consistent with the measured optical band gap as discussed later. For this reason, we performed further analyzes of the electronic structure and optical properties using the GLLB-SC functional.

Bader charge analysis (Table S10) reveals that the central Au atom in the cluster is slightly negatively charged, while the Au atoms in contact with the ligands are close to neutral. Bromines are clearly electron-withdrawing ligands (-0.49 e per Br), as expected, and the NHC ligands act as weak electron donors (0.45 e per ligand) to balance the total charge to +1.

The calculated UV-vis absorbance spectrum of the gasphase model of $[3b]^+$ is compared to the experimental data recorded in dichloromethane (Figure 9B). The first experimental absorption peak observed at around 505 nm as well as the experimental optical band gap at around 550 nm (2.25 eV) are reproduced well by the theory. The computations predict two distinct optical absorptions at the band edge (see the blue sticks in Figure 9B) that are likely to split to a larger degree in terms of energy at finite temperature due to atom dynamics. This explains the broader asymmetric first feature (two merging peaks) observed in the experiment. The third and fourth peaks (at 366 and 317 nm, respectively) in the experimental spectrum are reproduced well by the theory. We analyzed the four peaks in the computed spectrum by decomposing them to single electron-single hole excitations with dipole contributions. The so-called dipole transition contribution maps (DTCM) showing these decompositions (Figures S77-S81) indicate that the lowest-energy peak has a clear gold-gold character, having electrons removed from HOMO and HOMO-1 orbitals and placing them to the LUMO orbital. The second absorption peak has a mixed character by including gold-gold transitions from HOMO/ HOMO-1 to LUMO+2 as well as ligand-to-gold transitions. The weight of ligand-to-gold transitions increase as the peak energy increases for the third and fourth absorbance peaks.

The electronic structure of phosphine/thiolate or NHC-protected biicosahedral Au_{25} clusters was previously rationalized^{23,52} as a "dimer" of two closed-shell superatoms. Clusters $[4b]^{2+}$ and $[5b]^+$ described herein, likely possess similar electronic configurations, and therefore detailed calculations were not carried out on these systems.

Photoluminescence Studies

Given the high PLQY (ca. 16%) observed for our previously reported NHC-stabilized Au13 clusters,17 an investigation into the emission properties of both Au₁₀ and Au₂₅ clusters was undertaken. Excitation and emission spectra of $[3b]^+$ and [4b]²⁺ were acquired, as well as fluorescence excitationemission matrix (EEM) data (see the SI for details). Photoluminescence from $[4b]^{2+}$ was found to be significantly brighter as compared with $[3b]^+$ (Figure 10, inset). Emission maxima were observed at ~795 and 785 nm for $[3b]^+$ and $[4b]^{2+}$, respectively (Figure 10). The excitation spectrum of $[4b]^{2+}$ matches very well with its absorbance spectrum (Figure S69); the position and profile of the emission band are independent of the excitation wavelength. Both these observations confirm the absence of emissive impurities in the cluster sample. Of note, the presence of O2 does not decrease or quench the emission, suggesting that no triplet state is involved in the emission.

The observed optical band gap is 550 nm for $[3b]^+$ (2.25 eV), demonstrating the high stability of this cluster. This matches well with the computed value as discussed above. The PLQY was determined by the comparative method using zinc phthalocyanine as a standard (Figures S72 and S73). Cluster $[3b]^+$ was shown to have a PLQY of *ca*. 0.9%, which is of the order expected for Au nanoclusters. The Au₂₅ cluster $[4b]^{2+}$



Figure 10. Emission spectra (excited at 336 nm) of deoxygenated solutions of $[3b][PF_6]$ (black) and $[4b][PF_6]_2$ (red) in dichloromethane. The concentration of solutions was adjusted so the absorbance at 336 nm matches. Inset: photographs of the corresponding samples under visible (top) and UV (bottom) light.

showed a dramatically increased PLQY of 15%, which is significantly higher than that observed for most Au clusters. As was suggested previously,^{17,18} the rigidity imparted upon the cluster through inter-ligand $CH-\pi$ and $\pi-\pi$ interactions most likely enhances the emission by restricting the nonradiative decay pathways of the excited state, and in the case of $[4b]^{2+}$, the two fused Au₁₃ icosahedra of the core are also further rigidified by bridging bromide ligands. However, relating the cluster structure to photophysical properties is challenging because PLQY measurements are carried out in solution, while detailed structural characterization is performed in the solid-state. Efforts to study photoluminescence properties in the solid-state are ongoing in our laboratories.

CONCLUSIONS

In conclusion, we have described a series of new NHC-stabilized $[Au_{10}(^{MesCH2}Bimy)_6X_3]^+$ clusters $[3a-c]^+$ (X = Cl, Br, I) with a novel core architecture. The use of the bulky bis(2,4,6-trimethylbenzyl)benzimidazolium-2-ylidene ligand is important to drive cluster formation away from the more common Au_{13} clusters. Cluster $[3b]^+$ undergoes a solvent- and counterion-dependent conversion into larger Au_{25} clusters, with both $[Au_{25}(^{MesCH2}Bimy)_{10}Br_8]^+$ and $[Au_{25}(^{MesCH2}Bimy)_{10}Br_7]^{2+}$ observed experimentally in the solid state by X-ray crystallography and in solutions by NMR using the clusters bearing 13 C-labeled NHC ligands. The nature of the halide is critically important, with chloride-containing Au_{10} clusters showing no propensity to convert to Au_{25}.

Theoretical analysis showed that the conversion is connected to the increase of "metallicity" of the cluster from a 6-electron system to an unusual 16-electron system reported previously²³ and the conversion was monitored using ESI-MS and *in situ* NMR spectroscopy, in addition to UV–vis absorbance spectroscopy. While Au_{10} was only weakly emissive, the Au_{25} cluster displayed significantly increased photoluminescence, with the maximum emission wavelength of 785 nm, and PLQY of *ca.* 15%. Work to further tailor the emission of these clusters, understand the mechanism of cluster interconversion, and investigate further properties is underway at this time.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.2c00004.

Synthetic procedures, characterization data, and experimental results of monitoring the reaction progress using UV–vis absorbance, ESI-MS, and NMR spectroscopies; X-ray crystallographic data for [3b][OTf] (CCDC 2127768), $[4b][B(C_6F_5)_4]_2$ (CCDC 2127770), and $[5b][B(C_6F_5)_4]$ (CCDC 2127779) are available free of charge at www.ccdc.cam.ac.uk/structures/ (PDF)

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The authors declare no competing financial interest.

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