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Megalamane S. Bootharaju, Chakra P Joshi, Mohammad J. Alhilaly, and Osman M. Bakr

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Switching a Nanocluster Core from Hollow to Non-hollow

Megalamane S. Bootharaju,[†] Chakra P. Joshi,[†] Mohammad J. Alhilaly,[†] and Osman M. Bakr^{*†}

[†]Division of Physical Sciences and Engineering, Solar and Photovoltaics Engineering Research Center, King Abdulah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

ABSTRACT: Modulating the structure-property relationship in atomically precise nanoclusters (NCs) is vital for developing novel NC materials and advancing their applications. While promising biphasic ligand-exchange (LE) strategies have been developed primarily to attain novel NCs, understanding the mechanistic aspects involved in tuning the core and the ligand-shell of NCs in such biphasic processes is challenging. Here, we design a single phase LE process that enabled us to elucidate the mechanism of how a hollow NC (e.g., $[\text{Ag}_{44}(\text{SR})_{30}]^{4+}$, -SR: thiolate) converts into a non-hollow NC (e.g., $[\text{Ag}_{25}(\text{SR})_{18}]$), and vice versa. Our study reveals that the complete LE of the hollow $[\text{Ag}_{44}(\text{SPhF})_{30}]^{4+}$ NCs (-SPhF: 4-fluorobenzenethiolate) with incoming 2,4-dimethylbenzenethiol (HSPhMe₂) induced distortions in the Ag_{44} structure forming the non-hollow $[\text{Ag}_{25}(\text{SPhMe}_2)_{18}]$ by a disproportionation mechanism. While the reverse reaction of $[\text{Ag}_{25}(\text{SPhMe}_2)_{18}]$ with HSPhF prompted an unusual dimerization of Ag_{25} , followed by a rearrangement step that reproduces the original $[\text{Ag}_{44}(\text{SPhF})_{30}]^{4+}$. Remarkably, both the forward and the backward reactions proceed through similar size intermediates that seem to be governed by the boundary conditions set by the thermodynamic and electronic stability of the hollow and non-hollow metal cores. Furthermore, the resizing of NCs highlights the surprisingly long-range effect of the ligands which are felt by atoms far deep in the metal core, thus opening a new path for controlling the structural evolution of nanoparticles.

INTRODUCTION

Control over size and structure of atomically precise nanoparticles¹⁻⁴ (NPs) has long been a subject of great interest. These compositionally precise NPs are usually designated by their distinct chemical formula similar to molecules, unlike average diameters that are used for describing the size of plasmonic NPs. As a result, these precise NPs are also called nanomolecules⁵ or nanoclusters^{6, 7} (NCs). Metal NCs are considered a missing link between NPs and atoms, filling the gap between these two distinct size regimes.⁸ NCs gained significant attention due to their unique optical⁹⁻¹³ and physicochemical¹¹⁻¹⁴ properties as well as intriguing electronic and redox behavior^{15, 16}. These characteristics made NCs a new class of functional materials for applications in catalysis,^{17, 18} sensing,¹⁹ biology,^{3, 6} energy,²⁰ and environment²¹.

The typical routes for metal NC synthesis are: i) direct reduction of metal precursors in the presence of desired ligands,²²⁻²⁸ ii) postsynthetic ligand-exchange (LE),²⁹⁻³⁵ and iii) metal-exchange^{15, 36-41}. Among these methods, LE has recently been widely adopted for preparing novel gold NCs⁴²⁻⁴⁴. The use of LE in other metal systems, such as silver is rare and its mechanism remains unexplored and poorly understood.^{29, 30} Particularly in silver, LE is exclusively based on a biphasic approach, where the starting and the final products move between two immiscible phases. Although biphasic (e.g., aqueous and organic) LE was shown to be a highly promising strategy to synthesize NCs due to the ease of extracting

the final NC product,^{29, 30} the abrupt NC transformations in these biphasic systems preclude the use of standard characterization tools such as mass spectrometry and optical spectroscopy to elucidate the LE mechanisms and the intricate cluster transformation steps involved. As a result, the LE mechanism in several NCs remains unknown. Revealing the complete details of the reaction pathways of LE in atomically precise NCs provides a view of the fundamental processes of LE chemistry of NPs that plasmonic NPs⁴⁵ and quantum dots⁴⁶ with their heterogeneous size distribution cannot afford.

In this work, we designed a single phase LE reaction to understand the step-by-step conversion of $\text{Ag}_{44}(\text{SR})_{30}$ NCs to $\text{Ag}_{25}(\text{SR})_{18}$ NCs, and vice versa, where studying the interconversion of these NCs was challenging in a biphasic LE. The single phase LE of $\text{Ag}_{44}(\text{SPhF})_{30}$ clusters (-SPhF: 4-fluorobenzenethiolate) with 2,4-dimethylbenzenethiol (HSPhMe₂) initially led to the partial LE and then complete LE. After complete LE, the Ag_{44} experienced structural distortions to form $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ and intermediate NCs of sizes larger than Ag_{44} . On the other hand, the formation of $\text{Ag}_{44}(\text{SPhF})_{30}$ from the $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ was observed to occur in a different pathway, wherein Ag_{25} dimerize and rearrange to reproduce the Ag_{44} along with the similar sized intermediates aforementioned. These intermediates and the nature of ligands appear to dictate the formation of hollow Ag_{44} and non-hollow Ag_{25} cores. Experimental results shed light into the LE mechanism and the effect of ligand structure

in governing the size and the structure of the final LE product.

EXPERIMENTAL SECTION

Chemicals

All chemicals of analytical grade were purchased from Sigma-Aldrich and used without further purification. Silver nitrate (AgNO_3), 4-mercaptobenzoic acid (HSPhCOOH), sodium borohydride (NaBH_4), tetraphenylphosphonium bromide (PPh_4Br), 2,4-dimethylbenzenethiol (HSPhMe_2), 2,4-difluorobenzenethiol (HSPhF_2), 2,4-dichlorobenzenethiol (HSPhCl_2), 4-methylbenzenethiol (HSPhMe), 4-fluorobenzenethiol (HSPhF), citric acid, sodium hydroxide pellets, triethylamine, methanol, acetonitrile (HPLC grade), dimethylformamide (DMF), and dichloromethane (DCM).

Synthesis of $\text{Ag}_{44}(\text{SPhCOOH})_{30}$ NCs

7.5 mg of HSPhCOOH was dissolved in 5 mL of deionized (DI) water using 400 μL of 1 M NaOH. To this solution, 7 mg of AgNO_3 in 1 mL of DI water was added and stirred for 20 minutes. After that, 2 mg of NaBH_4 in 1 mL of DI water was added. The light yellow Ag-thiolate solution turned dark red over 45 minutes indicating the formation of Ag NCs. The as-prepared clusters were precipitated and cleaned with excess methanol.

Transformation of $\text{Ag}_{44}(\text{SPhCOOH})_{30}$ NCs to $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ NCs

5 mL of methanolic PPh_4Br (1 mg/mL) solution was added to 5 mL of DCM that containing 5 μL of HSPhMe_2 . After that, 5 mL of aqueous $\text{Ag}_{44}(\text{SPhCOOH})_{30}$ NCs (5 mg/mL) was added and stirred for 2–3 minutes. The DCM layer that containing LE product was separated, dried, and then washed with methanol.

Conversion of $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ NCs to $\text{Ag}_{44}(\text{SPhCOOH})_{30}$ NCs

5 mL of $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ solution (2 mg/mL DCM) was added to 5 mL of alkaline aqueous HSPhCOOH (10 mg/mL) and stirred. The colorless aqueous layer turned pale pink indicating the LE of NCs.

LE of $\text{Ag}_{44}(\text{SPhF})_{30}$ NCs with various thiols

The $\text{Ag}_{44}(\text{SPhF})_{30}$ NCs were synthesized as per the literature¹¹ and also, see Supporting Information (SI) for details. About 5 mg of $\text{Ag}_{44}(\text{SPhF})_{30}$ NCs in 5 mL of DCM was stirred with 5 μL (2.3 times excess, in mmol, compared to the total ligand amount in the starting material) of a desired thiol HSPhMe_2 , HSPhF_2 , or HSPhCl_2 . The progress of LE reaction was examined using optical spectroscopy and mass spectrometry.

LE of $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ NCs with HSPhF

5 mg of $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ in 5 mL of DCM was reacted with 5 μL (2.8 times excess, in mmol, compared to the total

ligand amount in the starting material) of HSPhF and the formation of the LE products were tracked using UV-vis spectroscopy and mass spectrometry.

Characterization

UV-vis absorption spectra were collected using a JAZZ spectrophotometer (Ocean Optics). Electrospray ionization mass spectra (ESI MS) of NCs were acquired using a Bruker MicroTOF-II. Organic-soluble NCs were dissolved in a DCM+acetonitrile mixture and electrosprayed. The $\text{Ag}_{44}(\text{SPhCOOH})_{30}$ was dissolved in DMF after protonation with citric acid. The typical instrument parameters used were: mass range 100–10,000 Da; flow rate: 600 $\mu\text{L}/\text{h}$; capillary voltage 3.5–4.0 kV; source temperature 80–120 $^\circ\text{C}$; dry gas 0.2–0.4 L/min, and nebulizer gas 0.3–0.5 bar.

RESULTS AND DISCUSSION

We initially developed a biphasic, aqueous-organic, LE approach to convert $\text{Ag}_{44}(\text{SR})_{30}$ to $\text{Ag}_{25}(\text{SR})_{18}$, and vice versa. A purified aqueous solution of $\text{Ag}_{44}(\text{SPhCOOH})_{30}$ NCs that exhibit characteristic UV-vis and mass spectra (Figures 1 and S1 in SI) was used as a starting point for the LE reaction. After two minutes of LE of $\text{Ag}_{44}(\text{SPhCOOH})_{30}$ with HSPhMe_2 , the colorless DCM layer turned dark brown indicating a successful phase transfer, while the aqueous layer became colorless (Figure 1A inset). The absorption spectrum (Figure 1A) of cleaned dark brown solution displays unique features different from that of parent Ag_{44} indicating the transformation of the Ag_{44} cluster to a new size cluster. All of these UV-vis characteristics of new cluster are found to exactly match with those of recently reported $\text{Ag}_{25}(\text{SR})_{18}$ ²⁷ cluster inferring the LE product was likely $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ NC.

Figure 1. (A) UV-vis of $\text{Ag}_{44}(\text{SPhCOOH})_{30}$ and its HSPhMe_2 -exchanged product (red trace). Inset: photographs of $\text{Ag}_{44}(\text{SPhCOOH})_{30}$ LE from the top aqueous layer to the bot-

tom DCM layer. (B) ESI MS of $[\text{Ag}_{44}(\text{SPhCOOH})_{30}]^{4-}$ and its LE product $[\text{Ag}_{25}(\text{SPhMe}_2)_{18}]^{-}$ that are compared with their simulated mass spectra (see Figure S1 for full-range mass spectra).

This assignment was further confirmed by high-resolution ESI MS of the LE product, which shows a single peak at m/z 5167 (Figure S1B) corresponding to a molecular formula of $[\text{Ag}_{25}(\text{SPhMe}_2)_{18}]^{-}$ NCs. The simulated $[\text{Ag}_{25}(\text{SPhMe}_2)_{18}]^{-}$ mass spectrum and the experimental data are in excellent agreement (Figure 1B). The presence of a single peak of Ag_{25} and the absence of peaks of HSPHCOOH or its Ag-complexes are indicative of the formation of pure $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ from $\text{Ag}_{44}(\text{SPhCOOH})_{30}$. Similarly, Ag_{44} can be recovered by exchanging SPhMe₂ ligands of Ag_{25} with HSPHCOOH (Figure S2). Fascinatingly, $\text{Ag}_{44}^{10,11}$ and Ag_{25}^{27} NCs possess unique core structures in addition to differences in core charge and the arrangement of ligands. The $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ cluster consists of a hollow icosahedral Ag_{12} core encapsulated in a dodecahedral Ag_{20} that is stabilized by six three-dimensional (3D) $\text{Ag}_2(\text{SR})_5$ units.^{10,11} On the other hand, the $[\text{Ag}_{25}(\text{SR})_{18}]^{-}$ cluster has a non-hollow icosahedral Ag_{13} core protected with six 1D $\text{Ag}_2(\text{SR})_3$ units.²⁷

Although the biphasic LE shown here is a promising method for obtaining truly single sized $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ in good yield (80 wt%), the rapidity and dual phase nature of the approach hinder the investigation of the intricate reaction pathway that the clusters traversed to transform from a particle with a hollow core to a one with a non-hollow core, and vice versa. To elucidate the steps of this intriguing size and structural conversions through which these NCs occurred, we designed a single phase LE that enabled tracking the step-by-step changes in the reaction by ESI MS and optical absorption spectroscopy.

The Conversion of $\text{Ag}_{44}(\text{SPhF})_{30}$ NCs to $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ NCs in a Single Phase LE

Since $\text{Ag}_{44}(\text{SPhCOOH})_{30}$ was soluble only in aqueous and polar solvents, while the incoming ligand HSPHMe₂, and product $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ were soluble only in non-polar organic solvents, we searched for the set of ligands and resultant clusters that all could be solubilized in a single solvent. Therefore, we substituted SPhCOOH with SPhF, which is also a suitable ligand for Ag_{44} . However, HSPHMe₂, $\text{Ag}_{44}(\text{SPhF})_{30}$, HSPHMe₂, and $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ could all be solubilized in DCM. Notably, we optimized the concentration of the reactants in the single phase LE so that it occurs over the course of hours instead of seconds or minutes. Consequently, we were able to monitor the LE processes using mass spectrometry (Figure 2) and absorption spectroscopy (Figure 3).

In overall, single phase LE transformation of Ag_{44} to Ag_{25} can be categorized into four stages as described below.

Stage 1: Within 30 minutes of LE, $\text{Ag}_{44}(\text{SPhF})_{30}$ was found to exchange 18SPhF ligands with incoming 18SPhMe₂ ligands to produce a predominant product of $\text{Ag}_{44}(\text{SPhF})_{12}(\text{SPhMe}_2)_{18}$ and a less predominant product of

a nearly completely exchanged nanocluster of $\text{Ag}_{44}(\text{SPhF})_1(\text{SPhMe}_2)_{29}$. Note that we also observed several minor products with compositions $\text{Ag}_{44}(\text{SPhF})_{30-m}(\text{SPhMe}_2)_m$, where $m < 18$ and $m > 18$ (Figure S3A). The optical features of the transforming clusters display the same characteristics of an intact Ag_{44} structure but with a slight red-shift in 644 nm peak. After 1 h, nearly equal concentrations of $\text{Ag}_{44}(\text{SPhF})_{12}(\text{SPhMe}_2)_{18}$ and $\text{Ag}_{44}(\text{SPhF})_1(\text{SPhMe}_2)_{29}$ were observed as indicated by their mass peak intensities. The remnant absorption features of Ag_{44} are observed with the changes in peaks at 833, 537 and 644 nm, implying also the presence of an intact Ag_{44} core.

Figure 2. Time-dependent ESI MS study of $[\text{Ag}_{44}(\text{SPhF})_{30}]^{4-}$ LE with HSPHMe₂. The numbers with black, red, and blue color correspond to the number of Ag atoms, SPhF, and SPhMe₂ ligands, respectively. The numbers in green represent the charge of the clusters. Sharp peaks labeled with 'S' are unknown impurity artifacts in the mass-spectrometer without silver isotopic pattern, which are also present in the spectrum of a pure HPLC-grade DCM control. Mass spectral data reveal the conversion of Ag_{44} to Ag_{25} through intermediate NCs.

Stage 2: After 2 h, $\text{Ag}_{44}(\text{SPhF})_1(\text{SPhMe}_2)_{29}$ becomes the most predominant product. The presence of 29SPhMe₂ ligands on Ag_{44} at this stage would have created structural distortion that are also reflected in the absorption spectrum in which the 644 nm peak is broadened (denoted with asterisk in Figure 3) and shifted to 658 nm. The selective formation of two predominant LE products i.e., $\text{Ag}_{44}(\text{SPhF})_{12}(\text{SPhMe}_2)_{18}$ and $\text{Ag}_{44}(\text{SPhF})_1(\text{SPhMe}_2)_{29}$ (Figure S3), despite the myriad of other possible compositional possibilities is peculiar and requires some rationalization. Note that the Ag_{44} metal core is preserved until 29SPhF of the original $\text{Ag}_{44}(\text{SPhF})_{30}$ is replaced with SPhMe₂. Recall also that there are six 3D $\text{Ag}_2(\text{SPhF})_5$ motifs in $\text{Ag}_{44}(\text{SPhF})_{30}$ structure¹¹ (Figure S4A). The first predominant product would have thus formed by replacing three SPhF from each motif of $\text{Ag}_{44}(\text{SPhF})_{30}$ with three SPhMe₂

(Figure S4B) giving rise to $\text{Ag}_{44}(\text{SPhF})_{12}(\text{SPhMe}_2)_{18}$. At this stage, three of SPhMe_2 ligands are far apart to have little inter-ligand interactions and do not perturb the Ag_{44} structure. However, with passing of time, another predominant product $\text{Ag}_{44}(\text{SPhF})_1(\text{SPhMe}_2)_{29}$ forms likely by replacing all SPhF ligands of $\text{Ag}_{44}(\text{SPhF})_{12}(\text{SPhMe}_2)_{18}$. At this stage, five SPhMe_2 ligands are present (Figure S4C) in a motif. This situation leads not only to increased steric repulsions between bulky methyl groups, but also enhanced inter-ligand pi-pi interactions in 3D motifs of Ag_{44} that destabilizes the Ag_{44} structure.

Stage 3: After 2–3 h of LE, the distorted $\text{Ag}_{44}(\text{SPhF})_1(\text{SPhMe}_2)_{29}$ seems to dissociate disproportionately to form mixed ligand $\text{Ag}_{25}(\text{SPhF})_1(\text{SPhMe}_2)_{17}$ (Figure S5) while releasing fragments such as $\text{Ag}_n(\text{SPhMe}_2)_{n+1} + \text{Ag}_{19-n}$, $n \leq 11$ as observed in the mass spectrum (Figure S6). Some of these released fragments and the liberated SPhF 's (during exchange with SPhMe_2 in the previous stages) may further get absorbed by remaining $\text{Ag}_{44}(\text{SPhF})_1(\text{SPhMe}_2)_{29}$ to yield higher nuclearity intermediates such as $[\text{Ag}_{46}(\text{SPhF})_9(\text{SPhMe}_2)_{21}]^{2-}$, $[\text{Ag}_{48}(\text{SPhF})_7(\text{SPhMe}_2)_{23}]^{2-}$, and $[\text{Ag}_{50}(\text{SPhF})_4(\text{SPhMe}_2)_{26}]^{2-}$ (Figure 2 and S7).

Stage 4: After 3–4 h, previously formed intermediates Ag_{46} , Ag_{48} , and Ag_{50} were decomposed exclusively to an $\text{Ag}_{25}(\text{SPhF})_1(\text{SPhMe}_2)_{17}$ product as indicated by the gradual increase in its corresponding mass peak intensity (Figure 2). This size focusing process that is observed at 3–4 h is also reflected in the absorption spectra indicated by the characteristic features of Ag_{25} cluster. Finally, due to the presence of excess HSPHMe_2 in the reaction, the mixed ligand $\text{Ag}_{25}(\text{SPhF})_1(\text{SPhMe}_2)_{17}$ eventually gets transformed into a pure ligand system i.e., $[\text{Ag}_{25}(\text{SPhMe}_2)_{18}]^{1-}$ with ~80% purity. The change in overall charge from 4- (in Ag_{44}) to 1- (in Ag_{25}) occurred to impart the electronic stability to the final Ag_{25} product (Figure S5), which is governed by the shell-closing rule $[25-18-(-1)=8e^-]$.

photographs showing the $\text{Ag}_{44}(\text{SPhF})_{30}$ LE reaction with HSPHMe_2 as a function of time. A clear color change from red Ag_{44} to yellow indicates the formation of a new product Ag_{25} .

The formation of $\text{Ag}_{44}(\text{SPhF})_{30}$ NCs from $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ NCs in a Single Phase LE

$\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ in DCM was reacted with HSPHMe_2 and the time-dependent mass and absorption spectra (Figures 4 and S8) were acquired to elucidate the LE mechanism. The complete formation of Ag_{44} from Ag_{25} may also similarly be divided into four stages which we briefly summarize below.

Unlike $\text{Ag}_{44}(\text{SPhF})_{30}$, $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ undergoes rapid LE (typically within 60 minutes) with the incoming HSPHMe_2 . As a result, the first three stages seem to occur within 2–10 minutes. In the first stage, five SPhMe_2 of $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ were exchanged with five HSPHMe_2 to form a mixed ligand $[\text{Ag}_{25}(\text{SPhMe}_2)_{13}(\text{SPhF})_5]^{2-}$ (Figure 4A and S9A). Formation of this mixed ligand Ag_{25} would have removed special orientation²⁷ of SPhMe_2 ligands on Ag_{25} , which were originally of 1D $\text{Ag}_2(\text{SPhMe}_2)_3$ motifs. The incorporation of five SPhF ligands in 1D motifs would push them to rearrange into 3D motifs, as SPhF^n prefers 3D to 1D motifs. As a result, in the second stage, $[\text{Ag}_{25}(\text{SPhMe}_2)_{13}(\text{SPhF})_5]^{2-}$ species undergo dimerization, similar to Au_{25} polymerization,⁴⁷ to produce an intermediate product $[\text{Ag}_{50}(\text{SPhMe}_2)_{26}(\text{SPhF})_{10}]^{3-}$, which further forms $[\text{Ag}_{50}(\text{SPhMe}_2)_{26}(\text{SPhF})_9]^{3-}$ upon losing one SPhF ligand (Figure S9B). Here, the dimerization of $[\text{Ag}_{25}(\text{SPhMe}_2)_{13}(\text{SPhF})_5]^{2-}$ seems to follow an isoelectronic addition⁷ path giving rise to an electronically stable $[\text{Ag}_{50}(\text{SPhMe}_2)_{26}(\text{SPhF})_9]^{3-}$ intermediate with a close shell configuration $[50-35-(-3)=18e^-]$. In the third stage, this intermediate undergoes disproportionation to form two sets of new intermediates $[\text{Ag}_{47+n}(\text{SPhMe}_2)_{26}(\text{SPhF})_{6+n}]^{3-}$, $n=0-6$, and $[\text{Ag}_{41+n}(\text{SPhMe}_2)_{24}(\text{SPhF})_{3+n}]^{2-}$, $n=0-7$ along with the mixed ligand Ag_{44} i.e., $[\text{Ag}_{44}(\text{SPhMe}_2)_{24}(\text{SPhF})_6]^{2-}$. Finally, in the fourth stage (around 45 minutes), remaining 24 SPhMe_2 are replaced by SPhF ligands to produce a one ligand cluster i.e., $[\text{Ag}_{44}(\text{SPhF})_{30}]^{4-}$. This final product, with ~80% purity, is found to be electronically stable with a core charge of 4- contributing to a closed shell configuration $[44-30-(-4)=18e^-]$. These compositional changes in stages 1 to 4 were also manifested in the immediate disappearance of the characteristic Ag_{25} absorption features and appearance of Ag_{44} signature peaks (Figure 4B). Noteworthy, similar intermediate cluster sizes i.e., Ag_{46} , Ag_{48} , and Ag_{50} were identified during Ag_{44} to Ag_{25} interconversion (Figures 2 and 4). These intermediates appear to act as a switching state between the hollow and non-hollow core clusters, and were driven to either core state depending on the type of excess ligand in the reaction. Important observations during interconversion between Ag_{44} and Ag_{25} are depicted in Scheme 1.

Figure 3. Time-dependent absorption study of $\text{Ag}_{44}(\text{SPhF})_{30}$ LE with HSPHMe_2 . The asterisk on blue spectrum indicates the broadening and red-shifting of the 644 nm peak. Inset:

Figure 4. (A) Time-dependent ESI MS and (B) UV-vis study of $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ LE with HSPHF. Sharp peaks labeled with ‘S’ are unknown impurity artifacts in the mass-spectrometer without silver isotopic pattern, which are also present in the spectrum of a pure HPLC-grade DCM control. Red asterisk in B (on blue curve) shows the appearance of Ag_{44} features. Inset: photographs of $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ LE as a function of time. Color change from orange Ag_{25} to red indicates the formation of Ag_{44} cluster.

Scheme 1. Interconversion between $\text{Ag}_{44}(\text{SPhF})_{30}$ (inside red circle) and $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ (inside yellow circle) via LE. All color spheres: Ag atoms. Left half cycle: stage 1, partial LE; stage 2, nearly complete LE; stage 3, disproportionation; and stage 4, size focusing. Right half cycle: stage 1, partial LE; stage 2, dimerization; stage 3, disproportionation; and stage 4, size focusing.

From our experimental observations (see Scheme 1), the presence of electron releasing (e.g., methyl) or withdrawing (e.g., Cl, and F) groups in the ligand along with the steric hindrance that is provided by these groups while orienting themselves on a cluster are predicted to be crucial in determining the final cluster size during LE. To further examine this deduction, we designed additional experiments by choosing specific ligands such as HSPHF₂ and HSPHCl₂, in which the bulky methyl groups of HSPHMe₂ are replaced by less bulky F and Cl atoms. Surprisingly, we observed an intact Ag_{44} after complete LE of $\text{Ag}_{44}(\text{SPhF})_{30}$ with HSPHF₂ and HSPHCl₂ (Figure S10). On the other hand, the use of HSPHMe (4-methylbenzenethiol), with only one bulky methyl group, led to the decomposition of Ag_{44} after LE, clearly indicating the significant effect of ligand bulkiness along with the electronic effects of the substituent in defining the nature of core and the size of metal clusters.

CONCLUSION

We successfully designed a single phase LE reaction to completely elucidate the step-by-step transformation of $\text{Ag}_{44}(\text{SR})_{30}$ NCs to $\text{Ag}_{25}(\text{SR})_{18}$ NCs, and vice versa, where tracking the interconversion of these NCs was problematic in prior biphasic LE approaches. Our detailed investigations of the LE with unprecedented atomic detail reveal that the Ag_{44} to Ag_{25} transformation occurs via a disproportionation mechanism, whereas its reverse occurs through an uncommon dimerization prior to disproportionation.

tionation. Both the forward and the reverse LE processes are highly sensitive to the incoming ligand geometry and the nature of substituents in the ligand, whose effects are clearly manifested not only in the protecting-shell but also at the heart of the metal core. The presented single phase LE strategy and the fundamental understanding of NCs size- and structure-tuning provides a platform for exploring the interconversion of other nanoparticle systems and stimulates theoretical research in predicting the nanoparticle conversion reactions.

ASSOCIATED CONTENT

Supporting Information

ESI MS characterization of LE reactions of $\text{Ag}_{44}(\text{SPhF})_{30}$ and $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$; UV-vis spectra and ESI MS of various thiols reactions with $\text{Ag}_{44}(\text{SPhF})_{30}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: osman.bakr@kaust.edu.sa

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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Table of Contents