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Direct self-focusing synthesis of monodisperse [Au₈(PPh₃)₇]²⁺ nanoclusters

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Abstract: Direct and scalable synthesis of monodisperse gold nanoclusters is highly desired but remains a great challenge due to the complexity of chemical reactions. Toward this goal, a suitable precursor is important as it can simplify the synthesis processes and offer controllability in tuning the product. In this work, we find that Au(PPh₃)₂Cl could be used as an effective precursor for the direct synthesis of atomically monodisperse $[Au_8(PPh_3)_7]^{2+}$ nanoclusters, without the need of tedious post-synthetic purification steps. The Au(PPh₃)₂Cl precursor could be directly reduced by NaBH₄ (0.25 molar equivalent) in dichloromethane solution, producing Au₈ clusters with a 35% reaction yield. Time-dependent mass spectrometry and in-situ UV-vis absorption spectra reveal that the synthesis process is initiated by the rapid formation of Au₆–Au₈ mixture, followed by a slow spontaneous self-focusing process that converges the mixture into atomically monodisperse Au₈. The success of this direct synthesis is hypothesized to arise from the relatively stronger Au(I)…Au(I) aurophilic attraction between Au(I)-PPh₃ complexes that facilitates the aggregation of Au(I)-PPh₃ on Au(0) cores.

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Introduction

Atomically-precise gold nanoclusters have acted as a category of nanomaterials and attracted wide scientific attention, due not only to their unique structures and properties intermediate between those of the atomic and bulk states, but also to their potential in developing novel optical nanomaterials¹⁻⁶ and catalysts.⁷⁻¹³ The scalable synthesis of Au nanoclusters with size-dependent chemical and physical properties could promote their fundamental science and applications, and has been an active subject of research in the last decade. To obtain atomically monodisperse Au nanoclusters in a controllable way, tremendous efforts have been made and great progresses have been achieved.^{4, 14-19} However, to date it is still highly desired but remains great challenge to develop more facile and effective routes for synthesis of Au nanoclusters.

So far, numerous synthetic routes of Au nanoclusters have been exploited. They could be grouped into two categories: direct synthetic route and post-synthetic route.¹⁵ The direct synthesis refers to reduction of the precursor complexes (most commonly, AuPPh₃Cl and HAuCl₄) by a certain reducing agent to yield atomically monodisperse nanoclusters. Staring from the pioneering work of the Brust-Schiffrin method,²⁰ the direct synthetic route has been used for preparation of various phosphine- and thiol-stabilized Au nanoclusters via the borohydride or borane reduction of gold complexes in homogeneous solutions. It is successful in the synthesis of stable Au₉/Au₁₁, Au₁₃, and Au₂₅ nanoclusters during the reduction processes of mono-, di-phosphine, or thiolate Au(I) complexes.²¹⁻²⁵ However, the direct reduction route is unsuccessful in preparing many other core-sized Au nanoclusters due to the complexity of the chemical reaction systems that produce a mixture of nanoclusters with various sizes; especially, direct synthesis of ultrasmall gold clusters consisting of several Au atoms (Au₄, Au₆, Au₇, and Au₈) is still difficult. To solve this problem, many post-synthetic methods have been exploited which can be regarded as a core-size conversion or transformation process, where preformed larger core-sized nanoclusters are converted into smaller, single-sized molecular

nanoclusters. Typical examples of post-synthetic methods are the synthesis of Au₂₅ nanorods using thiolate-induced size-conversion of polydisperse Au-triphenylphosphine (PPh₃) nanoparticles (1–3.5 nm),^{26, 27} and HCl-etching induced synthesis of di-phosphine protected Au₁₃ clusters from polydisperse clusters.²⁸⁻³⁰ Although ultrasmall gold nanoclusters (Au₄, Au₆, Au₇, and Au₈) can be synthesized through post-synthetic routes,^{18, 22, 31-34} they suffer from several drawbacks, such as complicated synthesis process, low reaction yield, and limited choice of inductive agents. Ultrasmall gold clusters with Au atoms ranging from 6 to 13 are commonly coordinated by phosphine ligands, and form an important family of molecular nanoclusters. Therefore, seeking more pathways for facile and effective synthesis of Au-phosphine nanoclusters has been a long-standing objective of cluster science and deserves further study.

It has been known that precursor is of great importance in nanocluster synthesis, at least in two aspects that a good precursor can simplify the synthesis processes, and can offer more controllability in targeting the desired nanoclusters and tuning their property.¹⁴ Hence, choosing a suited precursor may be a critical factor in a rational design of the synthetic chemistry of nanoclusters. In this work, we show that reducing the Au(PPh₃)₂Cl precursor by NaBH₄ (0.25 molar equivalent) could yield atomically monodisperse $[Au_8(PPh_3)_7]^{2+}$ nanoclusters, which were obtained previously with complicated post-synthetic route via multi-step conversion from $[Au_9(PPh_3)_8]^{3+}$ to $[Au_8(PPh_3)_8]^{2+}$, and then $[Au_8(PPh_3)_8]^{2+}$ to $[Au_8(PPh_3)_7]^{2+}$.³⁵ The reaction yield of this synthesis is 35% on the basis of Au atom and could be easily scaled up for large-quantity synthesis. Time-dependent mass spectrometry and UV-vis absorption spectra were used to trace this synthesis and revealed the two-step processes, including the first kinetic reduction and the second self-focusing steps. Similar reaction starting from the commonly used AuPPh₃Cl precursor yields mainly $[Au_{11}(PPh_3)_8Cl_2]^{3+}$ but no sign of $[Au_8(PPh_3)_7]^{2+}$, highlighting the critical role of the Au(PPh_3)_2Cl precursor in this synthesis.

Experimental

Chemicals: Chloroauric acid (HAuCl₄, Alfa Aesar), triphenylphosphine (99%, Alfa Aesar), sodium borohydride (98%, Aldrich). All solvents were obtained from Aldrich and employed as received. The Au(PPh₃)₂Cl and Au(PPh₃)₂Cl precursors were prepared according to the protocols in the literature.³⁶

The synthesis of $[Au_8(PPh_3)_7]^{2+}$ clusters: NaBH₄ (0.0562 mmol) was added to the Au(PPh_3)₂Cl precursor (20 mmol/L, 10 mL of CH₂Cl₂) solution, under rapid stirring at 25 °C for 168 h. The final solution was precipitated after addition of 200 mL of n-hexane for 24 h. The supernatant was discarded and the precipitates obtained through centrifugation were redissolved in 2 mL of ethanol. After the solution was centrifuged at 15000 rpm for 5 min to remove insoluble Au(I) complexes, the supernatant containing $[Au_8(PPh_3)_7]^{2+}$ clusters was evaporated to dryness by vacuum rotary. The obtained solid was re-dissolved in ethanol and collected by centrifugation/evaporation again. This step was repeated for 2 times, giving the yield of ~ 35% $[Au_8(PPh_3)_7]^{2+}$ cluster on the basis of Au atom.

The effect of the reaction temperature on the synthesis was also tested. It was found that within a narrow temperature range from 25 to 40 °C, the formation process of the end product could not be accelerated remarkably with increase of temperature. However, further elevating the reaction temperature to beyond 40 °C led to the growth into much larger clusters or even nanoparticles, instead of monodisperse $[Au_8(PPh_3)_7]^{2+}$ clusters.

The reaction starting from the AuPPh₃Cl instead of Au(PPh₃)₂Cl as precursor: It was conducted under the otherwise same reaction conditions as those using the Au(PPh₃)₂Cl precursor. And all its characterizations were the same with those in the case of Au(PPh₃)₂Cl.

To two as-prepared Au₈ cluster solutions (1.2 μ mol/L, 10 mL of CH₂Cl₂), Au(PPh₃)₂Cl and AuPPh₃Cl precursor with the same mole of 0.05 mmol was added, and

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then the reaction solution was stirred rapidly at 20 °C for 168 h. Finally, the obtained solutions were characterized by mass spectrometry and UV-vis absorption spectra.

Characterizations: Electrospray ionization mass spectrometry (ESI-MS) analysis was carried out by ESI-TOF with a Bruker Microtof mass-spectrometer operating in positive ionization mode. The ionization process needed Temperature (100 °C) control and nitrogen drying gas (1 μ L/min) in ESI source. All spectra were obtained in reflection mode of the TOF mass spectrometer equipped with multi-step detection for maximum sensitivity; isotopic resolution was obvious throughout the entire detection mass range of m/z 800 to 2000. Calibration was conducted by reserving (609 m/z) in FIA 10 pg (100:1 S/N 200 μ L/min). The detection of clusters was carried out with 10 μ L of sample at flow rate of 0.1 ml/min in 0.1% formic acid in acetonitrile/H2O (1:1). The Au L₃-edge X-ray absorption near-edge structure (XAFS) spectra were obtained in transmission mode at the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF), China, with electron storage ring operated at 2.5 GeV and a maximum current of 250 mA. The UV-vis absorption data were collected by a Purkinje General TU-9001 spectrometer in the wavelength range of 250–800 nm, following the correction of the background absorption by utilizing pure ethanol. X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a VG Thermo ESCALAB 250 spectrometer operated at 120 W with the binding energy calibrated against the carbon 1s line.

Results and Discussions

The reaction procedure for the direct one-pot synthesis of $[Au_8(PPh_3)_7]^{2+}$ nanoclusters is shown schematically in Fig. 1. It involves the reduction of Au(PPh_3)_2Cl to produce polydisperse Au₆-Au₈ intermediates, and their subsequent self-focusing toward monodisperse Au₈ clusters. Upon the addition of NaBH₄ to the Au(PPh_3)_2Cl precursor solution, the reduction occurs rapidly in 1 h, producing a red-brown solution. Then the solution color undergoes non-obvious change till the completion of the reaction (168 h). After repeated centrifugation/evaporation for the reaction product, the synthetic reaction yields ~35% $[Au_8(PPh_3)_7]^{2+}$ clusters on the basis of Au atom. To the best of our knowledge, this is the first time for direct synthesis of monodisperse $[Au_8(PPh_3)_7]^{2+}$ nanoclusters through using the Au(PPh_3)_2Cl precursor. Previously, $[Au_8(PPh_3)_7]^{2+}$ nanoclusters could only be obtained via multi-step post-synthetic conversion from $[Au_9(PPh_3)_8]^{3+}$ to $[Au_8(PPh_3)_8]^{2+}$, and then $[Au_8(PPh_3)_8]^{2+}$ to $[Au_8(PPh_3)_7]^{2+35}$



Figure 1. Direct synthesis of Au_8 nanoclusters via the self-focusing process during NaBH₄ reduction of $Au(PPh_3)_2Cl$.

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Next, time-dependent ESI-MS and *in-situ* UV-vis absorption spectra were used to identify the intermediate species and monitor their evolution during the direct synthesis of $[Au_8(PPh_3)_7]^{2^+}$. Aliquots of the solution were taken at regular time intervals and subject to characterizations. Seen from the ESI mass spectra shown in Fig. 2(a), over the range of *m/z* 900-2000 Da, the precursor prior to the reaction (0 h) exhibits a strong peak at *m/z* 919 Da corresponding to $[Au_2(PPh_3)_2]^+$. After reduction for 1 h, besides weak signals over the range of *m/z* 900-1200 assigned to Au(I) complexes (mainly Au₂ and Au₃ complexes), distinct peak at *m/z* 1706 Da appears, which could be assigned to the molecular formula of $[Au_8(PPh_3)_7]^{2^+}$ (calculated *m/z* = 1706.19 Da). Other weaker peaks at *m/z* 1377 and 1608 Da are also observable, and they are related to $[Au_6(PPh_3)_6]^{2^+}$ (calculated *m/z* = 1378.10 Da) and $[Au_7(PPh_3)_7]^{2^+}$ (calculated *m/z* = 1608.42 Da), respectively. The determinations of these molecular formulas are confirmed by the good match between the experimental data and the calculated isotope patterns Fig. 2(b). This

indicates that the reduction products of $Au(PPh_3)_2Cl$ at 1 h are mainly composed of polydisperse Au_6-Au_8 cluster mixture. With increasing reaction time, the Au_8 signal is gradually enhanced, and the Au_6 and Au_7 signals are gradually damped. Finally, at 168 h, one intense peak corresponding to Au_8 is observed in the mass spectrum, while the peaks of Au_6 and Au_7 clusters are nearly invisible, implying the atomical monodispersity of the Au_8 product.



Figure 2. (a) Time-dependent ESI-MS of Au₈ synthetic process via the direct reduction of Au(PPh₃)₂Cl precursor. (b) Comparison between the experimental ESI mass spectra and the calculated isotope patterns of $[Au_8(PPh_3)_7]^{2+}$, $[Au_7(PPh_3)_7]^{2+}$ and $[Au_6(PPh_3)_6]^{2+}$. (c) Time-dependent UV-vis absorption spectra of the reduction process as in (a).

The findings of the ESI mass spectrometry could be confirmed by the time-dependent UV-vis absorption spectra (Fig. 2(c)). A featureless monotonous decrease is observed in the absorption spectrum of the Au(PPh₃)₂Cl precursor (0 h). Then absorption peaks at 412 and 460 nm, characteristic of $[Au_8(PPh_3)_7]^{2+}$ clusters, start to appear after 1 h of reduction reaction. Compared with the standard spectrum of pure $[Au_8(PPh_3)_7]^{2+}$ cluster that exhibit three distinct absorption peaks at 370, 412 and 460 nm,¹⁸ at this time the 370 nm absorbance is absent and the 460 nm absorbance is too weak in intensity, suggesting the polydispersity of the clusters. With prolonged reaction

time, the absorption peaks become more and more distinct; at 48 h the absorbance at 370 nm appears. Finally, the absorption spectrum shows a well-defined feature of $[Au_8(PPh_3)_7]^{2+}$ clusters, indicative of the obtainment of monodisperse $[Au_8(PPh_3)_7]^{2+}$ clusters evolved from mixed clusters. Since in this later stage of the synthesis, no additional reagent was added to converge the sizes of the intermediate clusters, the spontaneous size-convergence in the Au(PPh_3)_2Cl circumstance could be called a "self-focusing" process.



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Figure 3. (a) Time-dependent ESI-MS of the direct reduction process of AuPPh₃Cl precursor by NaBH₄. (b) Comparison between the experimental ESI mass spectra and the calculated isotope patterns of $[Au_2(PPh_3)_2Cl]^+$, $Au_2(PPh_3)_3Cl]^+$, $[Au_3(PPh_3)_2Cl_2+H^+]^+$, $[Au_9(PPh_3)_8]^{3+}$, $[Au_9(PPh_3)_8]^{2+}$ and $[Au_{11}(PPh_3)_8Cl_2+2H^+]^{3+}$. (c) Time-dependent UV-vis absorption spectra of the reduction process as in (a).

The combined analyses of ESI-MS and UV-vis absorption spectra manifest that the $Au(PPh_3)_2Cl$ precursor is beneficial to the one-pot synthesis of monodisperse $[Au_8(PPh_3)_7]^{2+}$ clusters. One may wonder what happens if the commonly used Au(I) precursor of AuPPh_3Cl precursor is employed instead. To clarify this issue, we performed parallel experiments by using the AuPPh_3Cl precursor to replace Au(PPh_3)_2Cl under the otherwise same reaction conditions. The reaction process was also monitored by ESI-MS

and UV-vis absorption spectra as shown in Fig. 3. Compared with the Au(PPh₃)₂Cl case, the mass spectrum of AuPPh₃Cl reduction product at 1 h indicates a wider size distribution. Apart from the $[Au_6(PPh_3)_6]^{2+}$ (m/z = 1377 Da) and $[Au_7(PPh_3)_7]^{2+}$ (m/z = 1608 Da) peaks, other intense peaks at $m/z \sim 1290$, 1446, and 1936 Da are apparent which could be assigned to the molecular formulas of $[Au_9(PPh_3)_8]^{3+}$ (calculated m/z = 1290.08Da), $[Au_{11}(PPh_3)_8Cl_2+2H^+]^{3+}$ (calculated m/z = 1446.11 Da), and $[Au_9(PPh_3)_8]^{2+}$ (calculated m/z = 1936.52 Da), respectively, as evidenced by the excellent match between experimental and calculated isotope patterns (Fig. 3(b)). The major mass peaks are the ones of $[Au_9(PPh_3)_8]^{2+}$, $[Au_9(PPh_3)_8]^{3+}$ and $[Au_6(PPh_3)_6]^{2+}$. As the reaction continues to 10 and 22 h, the Au₁₁ mass peak is gradually enhanced. After 168 h of reaction time, the dominant cluster is [Au₁₁(PPh₃)₈Cl₂+2H⁺]³⁺, accompanied by the [Au₆(PPh₃)₆]²⁺ and $[Au_9(PPh_3)_8]^{3+}$ species. It should be noted that almost no $[Au_8(PPh_3)_7]^{2+}$ peak could be observed throughout the synthesis course. This is in good agreement with the literature report that NaBH₄ reduction of AuPPh₃Cl is the traditional way to synthesize Au₁₁ and Au₉ clusters.^{18, 25} The eventual formation of $[Au_{11}(PPh_3)_8Cl_2]^{3+}$ and $[Au_9(PPh_3)_8]^{3+}$ is also indicated by the time-dependent UV-vis absorption spectra (Fig. 3(c)), which well resembles those of the standard spectrum of Au₁₁ clusters in both the spectral shape and peak positions (312, 380, 416, and 500 nm).^{18, 25, 31} Again, no sign of [Au₈(PPh₃)₇]²⁺ could be observed. All these observations indicate that $[Au_8(PPh_3)_7]^{2+}$ could be hardly obtained through the direct reduction of the AuPPh₃Cl precursor.

Summarizing the above results, the stable cluster of $[Au_8(PPh_3)_7]^{2+}$ is formed through the direct reduction of Au(PPh_3)_2Cl by NaBH₄ (0.25 molar equiv), while the same reaction starting from the AuPPh_3Cl precursor produces $[Au_{11}(PPh_3)_8Cl_2]^+$ clusters. Because the only changed parameter in these two synthesis reactions is the precursor, the results suggest that the Au(PPh_3)_2Cl precursor is vital to the direct synthesis of $[Au_8(PPh_3)_7]^{2+}$. In order to shed some light on the correlation between the precursors and cluster products, the electronic features of Au atoms were investigated by Au L_3 -edge

X-ray absorption near-edge structure (XANES) spectra and X-ray photoelectron spectroscopy (XPS). The normalized XANES spectra of the Au(PPh₃)₂Cl and AuPPh₃Cl precursors show that the former exhibits a much more intense white-line peak at ~11925 eV than that of the latter (Fig. 4 (a)). This indicates the more electronic transitions from the $2p_{3/2}$ to the $5d_{5/2, 3/2}$ states, resulting in higher Au valence state in Au(PPh₃)₂Cl. Similar phenomenon could also be observed from the XPS spectra in Fig. 4 (b). The Au $4f_{7/2}$ peak of Au(PPh₃)₂Cl is located at 85.6 eV, showing a 0.3 eV shift toward the higher binding energy side as compared with the peak (85.3 eV) of AuPPh₃Cl. Intriguingly, analogous difference persists in the Au valence states of their reduction products. The $[Au_8(PPh_3)_7]^{2+}$ cluster exhibits stronger white-line intensity and higher absorption edge position than $[Au_{11}(PPh_3)_8Cl_2]^+$ (Fig. 4 (c)), and the Au $4f_{7/2}$ XPS peak of $[Au_8(PPh_3)_7]^{2+}$ is also ~0.6 eV higher (85.3 vs 84.7 eV) than that of $[Au_{11}(PPh_3)_8Cl_2]^+$ (Fig. 4 (d)). We also performed the Au L₃-edge XANES calculations for $[Au_8(PPh_3)_7]^{2+}$ and $[Au_{11}(PPh_3)_8Cl_2]^+$ clusters using the FEFF8.0 code³⁷ based on their known structures. The results are shown in Figure 4(c), which indicates that with decreasing cluster size from $[Au_{11}(PPh_3)_8Cl_2]^+$ to $[Au_8(PPh_3)_7]^{2+}$, the white-line is intensified due to stronger Au \rightarrow P charge transfer, in agreement with the experimental observations. Hence, the Au valence state in $[Au_8(PPh_3)_7]^{2+}$ is remarkably higher than that in $[Au_{11}(PPh_3)_8Cl_2]^+$, just like their corresponding precursors.



Figure 4. (a)/(c) XANES, and (b)/(d) XPS spectra of the precursors/clusters. The dashed lines in (c) show the calculated XANES spectra for $[Au_8(PPh_3)_7]^{2+}$ and $[Au_{11}(PPh_3)_8Cl_2]^+$ clusters.

As for why Au(PPh₃)₂Cl and AuPPh₃Cl give quite different cluster products under the same reduction conditions, we hypothesize that this is related to the different valence states of Au atoms in the precursors. Figure 5 illustrates schematically the formation process of $[Au_8(PPh_3)_7]^{2+}$. After addition of the reducing agent NaBH₄, zerovalent Au cores are produced and initiate the growth of clusters. However, owing to the insufficient reducing agent (merely 0.25 molar equiv), a significant part of precursors remains unreduced and releases into the solution Au(I)-PPh₃ complexes that acts as reactive species during the subsequent cluster growth. According to the "grow and passivate" model,¹⁴ these active Au(I)-PPh₃ complexes progressively aggregate on the freshly generated Au(0) cores and passivate the structure until a stable $[Au_8(PPh_3)_7]^{2+}$ cluster configuration is achieved. The impetus for the aggregation growth of the clusters is provided by the direct Au(I)–Au(0) bonding in the clusters that results in the short Au–Au distance (2.63–2.72 Å, average 2.68 Å) in $[Au_8(PPh_3)_7]^{2+}$, as well as the

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Au(I)...Au(I) aurophilic attraction between the Au(I) complexes.³⁸ The aurophilic interactions, whose strength is in the order of tens of $kJ \cdot mol^{-1}$ and comparable with hydrogen bonds, arise from the hybridization between the empty 6s/6p shells and filled $5d^{10}$ shells due to the relativistic effect.³⁹ As a result of the weaker Au(I)...Au(I) aurophilic attraction than the direct Au(I)-Au(0) binding, the Au(I)-Au(I) distances (2.71-2.94 Å) with an average value of 2.85 Å, ³⁵ is longer than the Au(I)-Au(0) distances. Therefore, the formation of the target Au nanoclusters relies on the accessibility of the Au(I)-PPh₃ complexes to the Au(0) cores and the Au(I) \cdots Au(I) aurophilic attraction strength as well, which are affected by the valence of the precursor complexes. The higher Au valence state in Au(PPh₃)₂Cl strengthens the Au(I) \cdots Au(I) aurophilic attraction and facilitates the aggregation of the Au(I)-PPh₃ complexes around the Au(0) cores, leading to the formation of thermodynamically stable cluster [Au₈(PPh₃)₇]²⁺ with a higher Au valence. As a comparison, the AuPPh₃Cl precursor has a relatively lower Au valence, and hence the aurophilic attraction between the detached Au(I) complexes is relatively weaker. Consequently, $[Au_{11}(PPh_3)_8Cl_2]^+$ clusters are finally formed due to the relatively weaker aurophilic attraction, as suggested by the considerably longer Au(I)-Au(I) distances (in the range of 2.86-3.13 Å, 2.95 Å in average)⁴⁰ than those in $[Au_8(PPh_3)_7]^{2+}$.

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Figure 5. Schematic illustration of the aggregation growth mode of $[Au_8(PPh_3)_7]^{2+}$ reduced from Au(PPh_3)₂Cl. The Au(I)…Au(I) aurophilic attraction between Au(I)-PPh_3 complexes provides impetus for the stabilization of the clusters.

Conclusions

In conclusion, we report a direct one-pot synthetic protocol for monodisperse $[Au_8(PPh_3)_7]^{2^+}$ cluster through reducing the Au(PPh_3)_2Cl precursor by NaBH₄. Our synthesis is facile and simple, and could be used for large-scale synthesis of monodisperse Au₈ clusters. Time-dependent ESI-MS and UV-vis absorption spectra reveal the two-step processes of this synthesis. The first step is the rapid formation of the Au₈-dominated cluster mixture, and the second step involves a slow self-focusing process in which the cluster mixture grows into monodisperse Au₈ cluster in excess Au(PPh_3)_2Cl. The comparative study by using the AuPPh_3Cl precursor shows that Au₁₁, rather than Au₈, is eventually formed, reflecting the critical role of Au(PPh_3)_2Cl in the one-pot direct synthesis of the Au₈ clusters. The success of this direct Au₈ synthesis possibly arises from the relatively stronger Au(I)…Au(I) aurophilic attraction between Au(I) complexes detached from Au(PPh_3)_2Cl molecules than from AuPPh_3Cl.

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Table of Contents Entry



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