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Photoinduced Isomerization-Driven Structural Transformation Between Decanuclear and Octadecanuclear Gold(I) Sulfido Clusters

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S *Supporting Information*

ABSTRACT: Upon photoirradiation, isomerization of the ligands, 1,2-bis(diphenylphosphino)ethene (dppee) from the cis to the trans form in polynuclear gold(I) sulfido clusters, led to the structural transformation of the decagold(I) cluster to the octadecagold(I) cluster. Both polynuclear μ_3-sulfido gold(I) clusters have been fully characterized by NMR, mass spectrometry, elemental analysis, and single crystal X-ray diffraction analysis. The transformation process could be readily detected and monitored by UV−vis absorption, emission, and ^{31}P NMR spectroscopy in solution. Supported and driven by Au(I)···Au(I) bonding interactions, the nuclearity and symmetry of these clusters were largely different from each other, resulting in completely distinct photophysical features.
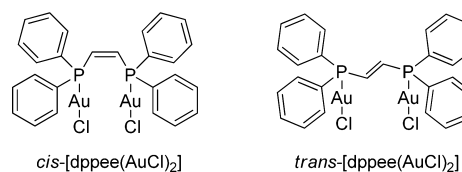
Aurophilic interaction,[1] with the interaction energy comparable to that of hydrogen bond,[2] has been widely utilized to construct diverse architectures.[2,3] Perturbed by gold(I) and gold(I)···gold(I) interactions, the energy gap between the HOMO and the LUMO of these assemblies could be largely narrowed, resulting in promising luminescent properties.[2,3] In the past decades, there has been an increasing research interest in the construction of polynuclear gold(I) aggregates via gold(I)···gold(I) interactions.[2−8] Polynuclear sulfido gold(I) complexes, as one of the most stable systems, are ubiquitous in the gold family.[2a,3,6,7,8a−f] Much attention has been focused on the development of polynuclear gold(I) complexes with rich luminescence properties in recent years,[6−8] especially the polynuclear μ_3-sulfido gold(I) clusters bridged by bi- or tridentate phosphine ligands,[8a−f] via metal···metal interaction directed self-assembly.

On the other hand, cis−trans isomerization can frequently be observed in C=C,[9a,b] C=N,[9c,d] and N=N[9e,f] bond containing derivatives, which have been widely used to design and synthesize functional molecular switches.[9] Generally, the trans forms of these double bond based compounds are thermodynamically more stable than the cis forms.[9,10] Bruce and coworkers have reported that the trans isomer of the uncoordinated 1,2-bis(diphenylphosphino)ethene (dppee) ligand is 23 kJ mol^{-1} more stable than *cis*-dppee.[10a] Nevertheless, the free *cis*-dppee could not undergo isomerization upon photoirradiation.[10a,c] By coordination to gold(I), several dinuclear gold(I) *cis*-dppee complexes have been demonstrated to possess photochemical isomerization reactivity.[10] However, to the best of our knowl-

edge, similar photoisomerization properties have never been applied to the polynuclear gold(I) cluster system.

Here we report the unprecedented photoinduced isomerization-driven structural reconfiguration of polynuclear gold(I) complexes. The chlorogold(I) precursors, *cis*-[dppee(AuCl)$_2$] and *trans*-[dppee(AuCl)$_2$] (Chart 1),[10,11] have been employed to

Chart 1. Chemical Structures of the *cis*- and *trans*-dppee Based Chlorogold(I) Precursors, *cis*-[dppee(AuCl)$_2$], and *trans*-[dppee(AuCl)$_2$]

cis-[dppee(AuCl)$_2$]   *trans*-[dppee(AuCl)$_2$]

assemble luminescent polynuclear gold(I) μ_3-sulfido clusters, **1** (Au$_{10}$) and **2** (Au$_{18}$), respectively. Interestingly, the decagold(I) cluster could be quantitatively transformed to octadecagold(I) clusters in solution, mediated by the transformation of the organic ligands from *cis*- to *trans*-dppee, which could be monitored by ^{31}P{^{1}H} NMR, UV−vis absorption, and emission spectroscopy. This work shows promises to the uncovering of the nature and the mechanism for the formation of polynuclear gold(I) clusters.

Reaction of *cis*-[dppee(AuCl)$_2$] with H$_2$S led to a clear yellow solution, which after evaporation afforded a yellow solid. Yellow block crystals of **1** could be obtained by recrystallization of the yellow solid from a dichloromethane−methanol−diethyl ether system. The ^{31}P{^{1}H} NMR spectrum of the yellow crystals in CD$_3$OD shows a pair of doublets of a two-spin AX pattern at $\delta =$ 13.7 and 17.0 ppm ($J_{P-P} =$ 56.8 Hz), indicating two different phosphorus environments. The molecular ion cluster observed at m/z 1841.5 in the MALDI-TOF and ESI mass spectra is attributed to [Au$_{10}$(μ-*cis*-dppee)$_4$(μ_3-S)$_4$]$^{2+}$ ([**1**]$^{2+}$) (Figure S1 and S2). The formation of cluster **1** has been further confirmed by single-crystal X-ray diffraction analysis. The chloride salt [**1**]Cl$_2$ crystallizes in orthorhombic space group $Pna2_1$. The ten gold(I) atoms are bridged by four μ_3-S atoms and surrounded by four diphosphine ligands (Figure S3). The cis forms of the dppee ligands are unambiguously observed in the cluster structure, with two P atoms and two bridging C atoms all on the same plane. The Au···Au bond distances are in the range of 2.88−3.16 Å,

suggesting the presence of aurophilic interactions (Table S1). Single crystal structure determination indicates no symmetry in the solid state. However, similar to our previously reported Au_{10} clusters,[8b,e,f] only two nonexchangeable P environments are observed in the $^{31}P\{^{1}H\}$ NMR spectrum, indicating the local S_4 symmetry of cluster **1** in solution (Figure S4). The fluxionality of the cluster in solution might be responsible for the symmetry increase.

Interestingly, on exposure to ambient light irradiation for several days, the solution color of [**1**]Cl$_2$ changes slowly from bright yellow to orange-red (Figure S5). A red crystalline solid ([**2**]Cl$_2$) has been isolated from the orange-red solution. By exchanging the counter-anions of the red complex from Cl$^-$ to PF$_6^-$ by metathesis reaction, red needle-shaped crystals of [**2**](PF$_6$)$_2$ suitable for single crystal X-ray diffraction analysis have been obtained and determined. The identity of the cluster cation was established by single crystal X-ray structure determination as [Au$_{18}$(μ-*trans*-dppee)$_6$(μ_3-S)$_8$]$^{2+}$ ([**2**]$^{2+}$), in which *cis*-dppee was transformed to *trans*-dppee via photochemical isomerization. [**2**](PF$_6$)$_2$ crystallizes in the monoclinic $C2/c$ space group, and the cluster cation **2** consists of 18 gold(I) atoms, eight μ_3-bridging S atoms, and six *trans*-dppee diphosphine ligands (Figure S6). Similar to its related [Au$_{18}$Se$_8$(dppe)$_6$]$^{2+}$ and [Au$_{18}$S$_8$(dppe)$_6$]$^{2+}$,[5b,7g] the gold skeleton of **2** consists of two Au$_9$ macrocycles interlocked with each other through aurophilic and Au−S interactions (Figure S7). The cluster cation could also be viewed as one Au$_6$S$_2$ center surrounded by two Au$_6$S$_3$(*trans*-dppee)$_3$ crowns (Figure S8). The Au⋯Au contacts are in the range of 2.95−3.17 Å (Table S2). Relatively long Au⋯Au distances (about 3.6 Å) could be found between the three gold(I) atoms (Au(7), Au(8), and Au(9)) coordinated to the same μ_3-S (S(3)) center in each Au$_6$S$_2$ unit (Figure S8).

On the other hand, starting from the chlorogold(I) precursor, *trans*-[dppee(AuCl)$_2$], cluster **2** could also be assembled by reaction of the *trans*-[dppee(AuCl)$_2$] with H$_2$S in solution (Scheme 1). $^{31}P\{^{1}H\}$ NMR analysis of [**2**]Cl$_2$ shows only one

Scheme 1. Self-Assembly Processes of Gold(I) Clusters and Photoinduced Isomerization-Driven Transformations[a]

[a]Cluster cations **1** and **2** are represented by their crystal structures (gray wire, C; orange ball, P; yellow ball, Au; red ball, S; protons and counter-anions are omitted).

downfield-shifted singlet at δ = 39.8 ppm. On the basis of the NMR spectrum and single crystal structure study, a local D_{3d} point group symmetry in solution could be assigned to cluster **2**. In the MALDI-TOF mass spectrum of cluster **2**, the observed fragments [Au$_{17}$(μ-*trans*-dppee)$_3$(μ_3-S)$_8$]$^+$, [Au$_{17}$(μ-*trans*-dppee)$_2$(μ_3-S)$_8$]$^+$, and [Au$_{13}$(μ-*trans*-dppee)$_3$(μ_3-S)$_6$]$^+$ with loss

of several organic ligands and gold atoms (Figure S9) establishes the formation of an octadecanuclear gold(I) cluster. The high resolution molecular peak observed at m/z 3089.4 in the ESI mass spectrum is in good agreement with the simulated isotopic distribution of [Au$_{18}$(μ-*trans*-dppee)$_6$(μ_3-S)$_8$]$^{2+}$ (Figure S10). These two clusters have been further characterized by ^{1}H NMR spectroscopy and elemental analysis (see Supporting Information, experimental section).

On going from the cis to the trans products in *cis*-[dppee(AuCl)$_2$] and *trans*-[dppee(AuCl)$_2$], a blue shift in the UV−vis absorption spectra was observed. This has been attributed to aurophilic interactions that stabilize the first excited singlet state of *cis*-[dppee(AuCl)$_2$].[10b] Similar blue shifts could also be found in other *cis*-to-*trans*-dppee-containing dinuclear gold(I) complexes.[10] On the contrary, in the polynuclear gold(I) cluster system, a cis-to-trans conversion from **1** to **2** results in a dramatic red shift in electronic absorption spectra. The UV−vis absorption spectra of **1** and **2** show several low-energy absorption shoulders at ca. 320, 365, and 425 nm and at ca. 380 and 465 nm (Figure 1), respectively, which are tentatively assigned to ligand-
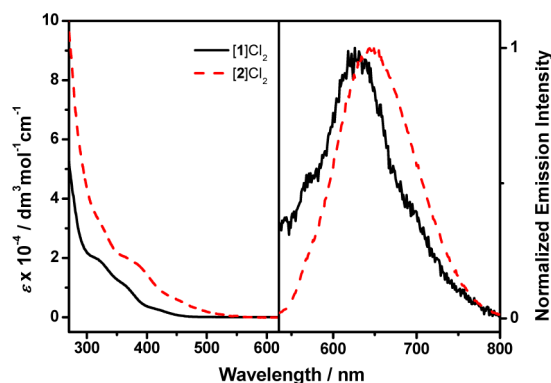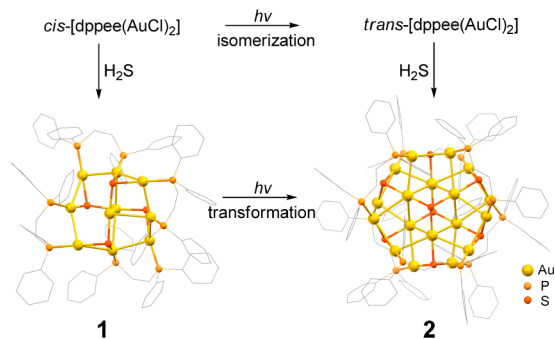

Figure 1. UV−vis absorption (left) and emission (right) spectra of [**1**]Cl$_2$ and [**2**]Cl$_2$ in degassed methanol at ambient temperature.

to-metal charge transfer (LMCT; S → Au) transitions modified by Au(I)⋯Au(I) interactions.[8a−f] The red shift might be attributed to the increase in nuclearity from the Au$_{10}$ to the Au$_{18}$ cluster that narrows the HOMO−LUMO energy gap. Their luminescence properties are also found to behave differently. Upon excitation at 450 nm, emission of cluster **1** both in solution and in the solid state are weak with band maxima at around 630 nm, while cluster **2** emits much more intensely in the red region both in solution and in the solid state at ca. 645 nm (Figures 1 and S11).

Under irradiation of a high intensity Xe lamp, structural transformation of the cluster could be largely accelerated and completed within several minutes. When the isomerization and transformation were monitored by UV−vis absorption spectroscopy in dilute methanol solution (5×10^{-5} M), the absorption shoulder at around 450−550 nm was found to rise dramatically (Figure 2), indicating the transformation of the clusters in solution from **1** to **2**. From the plot in Figure 2, the enhancement of absorbance was found to slow down after 1 min, and finally the transformation was completed within 2 min in dilute solution. Meanwhile, with photoexcitation, the emission intensity would increase significantly with emission maxima at around 645 nm, corresponding to the formation of cluster **2** and suggesting the transformation of the decanuclear to the octadecanuclear gold(I) clusters (Figure S12).
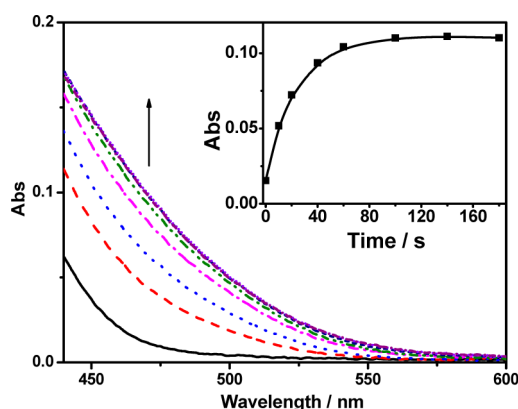
Figure 2. UV−vis spectral traces of [**1**]Cl$_2$ at different times in dilute methanol solution (5 × 10^{-5} M) under photoirradiation. The inset shows the plot of absorbance at 465 nm at different irradiation time.

Further supporting evidence came from the ^{31}P{^{1}H} NMR spectral changes (Figure 3). The initial ^{31}P{^{1}H} NMR signals of
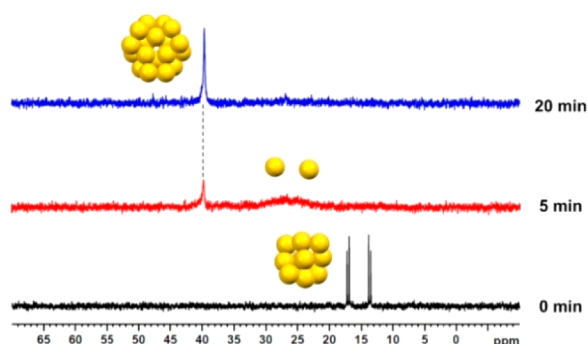

Figure 3. ^{31}P{^{1}H} NMR spectral changes in CD$_3$OD during the photoirradiation, with the initial concentration of [**1**]Cl$_2$ at 10^{-3} M (black, Au$_{10}$; red, intermediate; blue, Au$_{18}$).

1 appear at δ 13.7 and 17.0 ppm as a pair of doublets. After photoirradiation with the Xe lamp for around 5 min, the yellow solution turns to orange-yellow slightly, and the ^{31}P{^{1}H} NMR spectrum indicates the appearance of a new singlet at δ 39.6 ppm and a very broad signal at around δ 27 ppm, with the disappearance of the signals of cluster **1**. The singlet at ca. δ 39.6 ppm could be unambiguously assigned to [**2**]Cl$_2$. The broad signal indicates the existence of an intermediate[12] before the eventual assembly to octadecagold(I) cluster **2**. Finally, after 20 min, only the signal of cluster **2** could be observed in solution, indicating the completion of the photochemical isomerization and cluster transformation processes.

The isomerization of the organic diphosphine ligands from *cis*- to *trans*-dppee has resulted in the reconfiguration of the cluster structures. In the single crystal structure of cluster **1**, the distance of the two P atoms in the *cis*-dppee ligand is 3.60 Å, with the short Au···Au distance of 2.99 Å between two coordinated gold atoms (Figure 4a). This indicates that the lone pairs on the two P atoms in one *cis*-dppee ligand point to the same direction (Figure 4b), while in each *trans*-dppee ligand of cluster **2**, the separations of the two P atoms and the two neighboring gold atoms are 4.45 and 5.61 Å, respectively. Compared to cluster **1**, the separations of the two P atoms of cluster **2** in one ligand become 0.85 Å larger, and the lone pairs on the two P atoms in *trans*-dppee are disposed toward opposite directions, which renders the retention of short Au···Au contacts impossible. Therefore, triggered by photo-
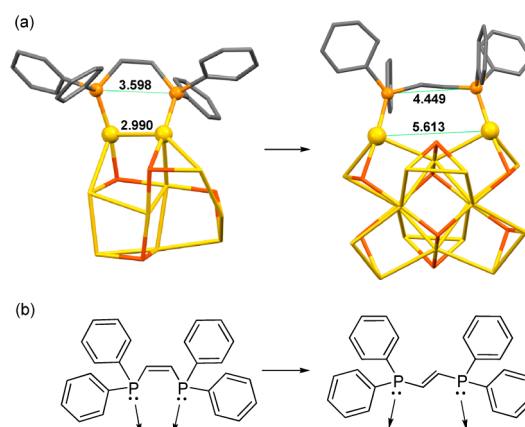

Figure 4. (a) Bridging models and (b) illustrations of the coordination orientations of *cis*-dppee and *trans*-dppee in the solid state; selected distances and bond lengths are shown. Other ligands, counter-anions, and hydrogen atoms are omitted for clarity (gray, C; orange, P; yellow, Au; red, S).

irradiation, the photochemical isomerization of the diphosphine ligand would disrupt the initial aurophilic interactions. These, together with development of new gold(I)···gold(I) attractions, have led to the configuration transformation of the cluster from Au$_{10}$ to Au$_{18}$ units.

In summary, an unprecedented cluster transformation involving a change in the cluster nuclearity has been mediated by light. Upon photoirradiation, the decagold(I) cluster would transform to an octadecagold(I) cluster in solution. UV−vis absorption, emission, and ^{31}P{^{1}H} NMR spectroscopy, combined with single crystal structural analysis, have been employed to monitor the self-assembly processes and reveal the transformation mechanism. Driven by cis-to-trans isomerization of the organic diphosphine ligand dppee, the nuclearity and the symmetry of the polynuclear sulfido gold(I) clusters have switched significantly, resulting in different photophysical behaviors. These properties endow polynuclear gold(I) sulfido clusters **1** and **2** as attractive applications in novel photochromic materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental details, X-ray structure determination, photophysical studies, and Figures S1−S12; crystallographic details (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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