

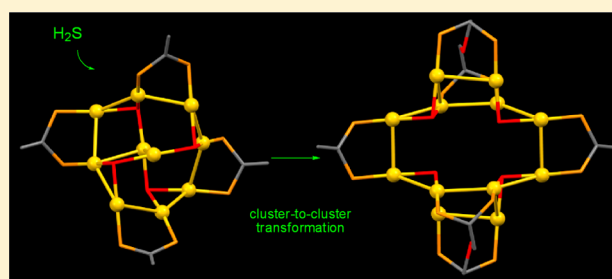
Addition Reaction-Induced Cluster-to-Cluster Transformation: Controlled Self-Assembly of Luminescent Polynuclear Gold(I) μ_3 -Sulfido Clusters

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Supporting Information

ABSTRACT: Unprecedented addition reaction-induced gold(I) cluster-to-cluster transformation has been observed in the present work. Reaction of the chlorogold(I) precursor, [vdpp(AuCl)₂] (vdpp = vinylidenebis(diphenylphosphine)) containing the diphosphine with unsaturated C=C bond, with H₂S resulted in a series of polynuclear gold(I) μ_3 -sulfido clusters bearing Au(I)⋯Au(I) interactions; the identities of which have been fully characterized by NMR, electrospray-ionization mass spectrometry, elemental analysis, and single crystal X-ray diffraction analysis. Diverse research methods, including UV–vis absorption, ¹H NMR, and ³¹P NMR spectroscopy, were employed to detect and monitor the transformation and assembly processes. Supported by single crystal structures, the existence of Au(I)⋯Au(I) bonding interactions sustains the diverse array of sophisticated polynuclear cluster structures and endues them with rich luminescence features.



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INTRODUCTION

In the past few decades, there has been an increasing research interest in the self-assembly of polynuclear gold(I) complexes via gold(I)–gold(I) interactions.^{1–8} With a closed-shell electronic configuration of d¹⁰, gold(I) adopts a linear two-coordinate coordination geometry and tends to form strong inter- or intramolecular homonuclear interactions.^{1n,q,r} This fascinating interaction, which has been termed auriphilic interaction by Schmidbaur,^{2c} is found in a number of polynuclear aggregates that possess a wide diversity of configurations and rich photophysical properties. Due to the high stability and the relative accessibility of synthetic routes, chalcogenide-based polynuclear gold(I) complexes, especially sulfido gold(I) complexes, are among one of the most popular systems in the gold family.^{1f,6a–d,7,8} Since 1999, our group has developed a series of polynuclear gold(I) clusters of bridging phosphane ligands, with pyramidal [Au₃(μ_3 -S)]⁺ units linked via metal–metal interaction directed self-assembly. Examples include the Au₆,^{6a} Au₁₀,^{6b} Au₁₂,^{6c} and Au₁₈ clusters.^{6d} In a number of these studies, there is the frequent coexistence of Au₆ and Au₁₀ clusters. Nevertheless, there was no evidence of the transformation between these gold(I) clusters. Although some examples of metal-based cluster transformation have been reported recently,⁹ to our knowledge, cluster-to-cluster transformations involving polynuclear gold(I) complexes are very rare.

In this work, the chlorogold(I) precursor containing the unsaturated vinylidenebis(diphenylphosphine) (vdpp) ligand,

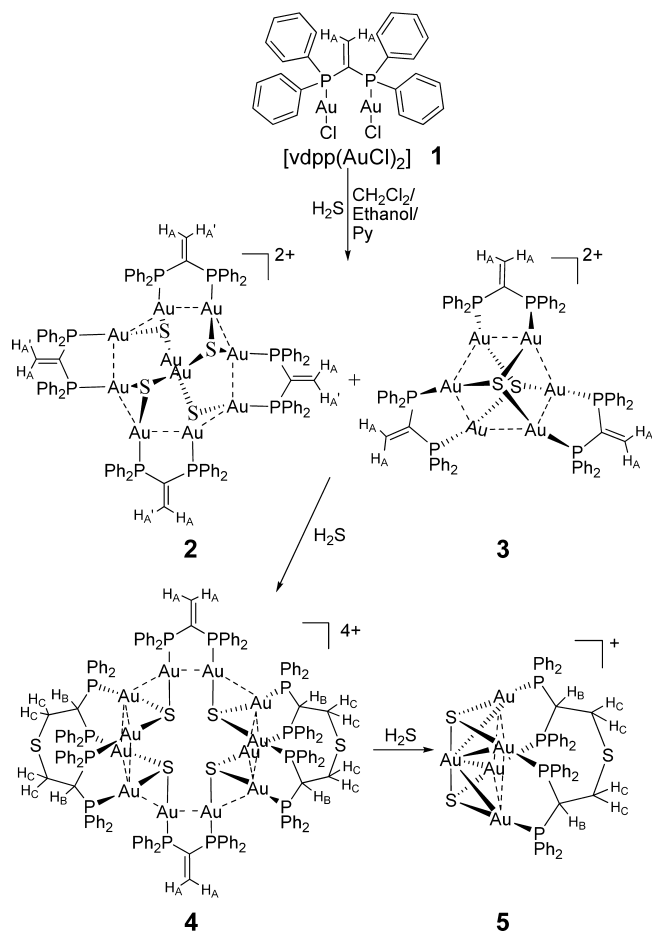
[vdpp(AuCl)₂]^{10,11} (**1**), has been employed to construct luminescent polynuclear gold(I) μ_3 -sulfido clusters. The introduction of active sites is anticipated to bring about unexpected functions and properties to these clusters. Interestingly, triggered by addition reaction between the vinyl group and H₂S, cluster-to-cluster transformation in this system has been observed, leading to the formation of four different types of clusters (Scheme 1). Similar activation of the C=C bond of the vdpp ligand by metal complexation has been reported by Schmidbaur and co-workers.¹⁰ These newly constructed luminescent polynuclear clusters based on gold(I)–gold(I) interactions have been well characterized. The self-assembly and transformation of these clusters could be monitored via ³¹P NMR, ¹H NMR, and UV–vis absorption spectroscopy. The present work demonstrates the possibility of constructing new gold(I) clusters on the basis of known cluster structures, which could largely expand the development of new libraries of novel gold(I) clusters and luminescent gold-based materials.

RESULTS AND DISCUSSION

Synthesis and Characterizations. Unlike previous studies in which reactions of H₂S with phosphine chlorogold(I) precursors usually would give rise to clear solutions, reaction of **1** with H₂S in this work initially led to a clear yellow solution

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Scheme 1. Proposed Self-Assembly of Gold(I) Clusters^a

^aThe counter anions (Cl^-) in the clusters have been omitted for clarity.

with yellow precipitate observed upon continuous bubbling of H_2S . The clear yellow solution afforded a yellow solid after evaporation. Vapor diffusion of diethyl ether into a dichloromethane-methanol solution of the yellow solid gave a mixture of yellow hexagonal block crystals and colorless needle-shaped crystals. ^{31}P NMR and 1H NMR analysis of the yellow crystals indicated two different phosphorus and proton environments, with the molecular ion cluster observed at m/z 1841 in positive-ion ESI-mass spectrum, attributed to $[Au_{10}(\mu-vdpp)_4(\mu_3-S)_4]^{2+}$ ($[2]^{2+}$), which has been confirmed by X-ray crystallography. Similar to our previously reported Au_{10} cluster,^{6b} complex 2 have a S_4 point group symmetry. The two P environments could not be interchanged by any symmetry operations of the S_4 point group, resulting in a pair of doublets in the ^{31}P NMR spectra. ^{31}P NMR analysis of the colorless needle-shaped crystals indicated the formation of a dodecagold(I) cluster, with a molecular ion peak at m/z 1234 ($[4]^{4+}$) in the positive-ion ESI-mass spectrum. Both the 1H NMR and the ESI-MS data did not agree with the formation of $[Au_{12}(\mu-vdpp)_6(\mu_3-S)_4]Cl_4$. The identity was eventually established by single crystal X-ray structure determination as $[Au_{12}(\mu-vdpp)_2(\mu-dppes)_2(\mu_3-S)_4]Cl_4$ ($[4]Cl_4$) (dppes = bis-(2,2-bis(diphenylphosphino)ethyl)sulfane), in which $vdpp$ was transformed to a new organic ligand via addition-reaction of the $C=C$ bond and H_2S . The presence of a local D_{2h} symmetry would account for the presence of two kinds of chemical

environments for the P atoms in solution. A hexagold(I) cluster, $[Au_6(\mu-vdpp)_3(\mu_3-S)_2]Cl_2$ ($[3]Cl_2$), was also isolated from the clear yellow solution. The yellow precipitate was demonstrated to be a pentagold(I) cluster, $[Au_5(\mu-dppes)(\mu_3-S)_2]Cl$ ($[5]Cl$). Both of these two clusters were well characterized by ^{31}P and 1H NMR spectroscopy, elemental analysis, and positive-ion ESI-MS.

Structure Determinations. The solid state structures of clusters 2 and 4 were further confirmed by single crystal X-ray diffraction analysis. $[2](PF_6)_2$ crystallizes in the triclinic space group $P\bar{1}$. Single crystal structure of $[2](PF_6)_2$ shows a decanuclear gold(I) μ_3 -sulfido cluster composed of four $vdpp-Au_2$ units linked together by four S atoms, whereby opposite pairs of S atoms are bonded to the two gold atoms (Au(9) and Au(10)) at the core in a linear fashion (Figure 1). Alternatively,

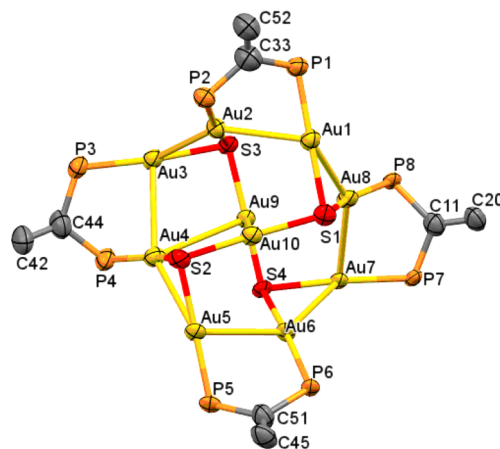


Figure 1. Perspective view of the complex cation of $[2](PF_6)_2$, showing the atomic numbering scheme. Phenyl rings and hydrogen atoms have been omitted for clarity.

cluster cation 2 can be viewed as a Au_8 macrocycle containing a Au_2 chain at the center. The majority of $Au\cdots Au$ distances of $[2](PF_6)_2$ are in the range of 2.98–3.17 Å, suggesting significant intramolecular $Au\cdots Au$ interactions.^{1d–f} The P–C–P angles of the $vdpp$ ligands are about 113°, and in each ligand two phosphorus and two carbon atoms of the vinyl group are all placed approximately on one plane. Such planar geometry has also been observed in P–N–P ligands of previously reported clusters.^{6a,b}

Complex $[4]Cl_4$ crystallizes also in the triclinic space group $P\bar{1}$ and consists of two (dppes) Au_4S_2 units linked together by two (vdpp) Au_2 connectors to give a dodecanuclear metal-lamacrocyclic cluster (Figure 2). Four gold atoms (Au(3), Au(4), Au(5), and Au(6)) form a distorted square in each (dppes) Au_4S_2 unit, which appears heart-shape from the side view. The $Au\cdots Au$ bond distances of $[4]Cl_4$ are in the range of 3.00–3.21 Å, and relatively long $Au\cdots Au$ separations of 3.40 and 3.61 Å are found for $Au(1')-Au(6)$ and $Au(2)-Au(4)$. As shown in Figure 2a, the top view of 4 is cross-shaped while the side view appears as two “hearts” connected by gold “chains” (Figure 2b). The bond lengths of the Au–P bonds in 2 and 4 are slightly shorter than 2.3 Å, while those of the Au–S bonds are slightly longer than 2.3 Å. In these two clusters, all the Au centers are two-coordinate with P–Au–S angles of 157.69(16) to 177.62(11)° that are distorted from the linear coordination geometry. The Au–S–Au angles range from 79.08(12) to 111.96(16)°, with most of them deviating from the 90°

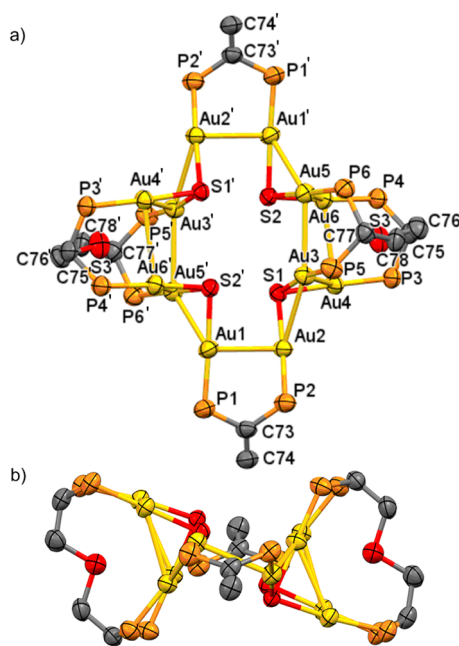


Figure 2. (a) Top and (b) side views of the crystal structure of the complex cation of $[4]Cl_4$. Phenyl rings and hydrogen atoms have been omitted for clarity.

expected for bonding involving the sulfur 3p orbitals^{1f} (Supporting Information, Tables S1 and S2).

Photophysical Studies. The UV–vis absorption spectra of gold(I) clusters 2–5 show an intense absorption at around 266 nm (Supporting Information, Table S3), which could also be observed in the UV–vis absorption spectrum of the chlorogold(I) precursor and is assigned to a metal-perturbed intraligand transition, while the low-energy absorption shoulders at ca. 305–355 nm are tentatively assigned as ligand-to-metal charge-transfer (LMCT) transitions modified by Au(I)⋯Au(I) interactions. These clusters are emissive in solution state while the emission becomes more intense in the solid state under excitation wavelengths greater than 350 nm. At low temperature (77 K), the solids of these polynuclear gold(I) clusters mainly emit in the green-yellow region at ca. 506–565 nm (Figure 3; Supporting Information, Table S3). The

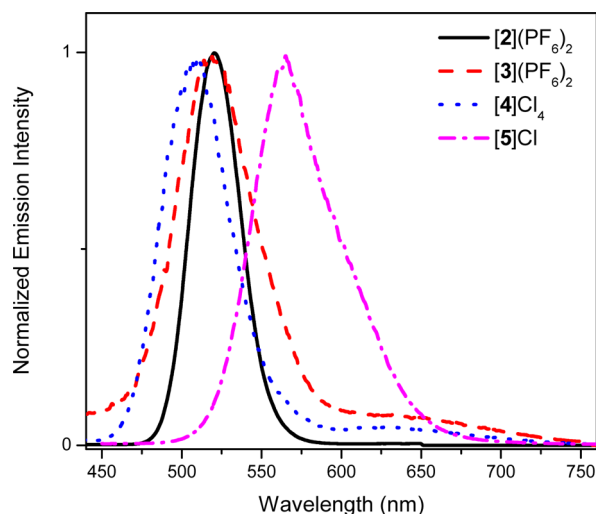


Figure 3. Low-temperature (77 K) solid-state emission spectra.

microsecond range of the radiative lifetime suggests the emission to be of a triplet parentage (Supporting Information, Table S3), which is tentatively assigned to a ligand-to-metal charge transfer (LMCT; $S \rightarrow Au$) origin modified by Au^I⋯Au^I interactions or, alternatively, as a ligand-to-metal–metal charge transfer (LMMCT) excited state.^{6a–d}

Monitoring of the Transformation and Assembly Process.

The existence of mixtures of clusters suggests the possibility of cluster-to-cluster transformation. Cluster reconfiguration might exist in the assembly process by the reaction with H₂S. Attempts were made to preliminarily monitor the assembly process by UV–vis absorption spectroscopy. Complex 1 and cluster $[5]Cl$ are only barely soluble in the reaction solution. In order to obtain a better understanding of the transformation and assembly, the progress of the reaction was monitored in DMSO solution. As the reaction proceeded in dichloromethane-ethanol-pyridine (3 mL, 1:1:1 v/v/v), aliquots of the reaction mixture (10 μL) were withdrawn, evaporated to dryness, and redissolved in DMSO for UV–vis absorption analysis. At about 5 min when the reaction mixture became a clear yellow solution, the absorption shoulder at around 300–350 nm rose dramatically from the baseline, corresponding to the formation of $[2]Cl_2$ and $[3]Cl_2$. When the reaction time reached about 15 min, two absorption maxima at ca. 310 and 360 nm, which could be unambiguously assigned to $[4]Cl_4$, were observed. As large amounts of yellow solid started to precipitate (at about 20 min), the absorption maximum at about 360 nm decreased dramatically, with the absorption shoulder at around 310 nm remaining (Supporting Information, Figure S4), suggesting the transformation of the decanuclear gold(I) clusters to $[5]Cl$.

To better uncover the mechanism of cluster-to-cluster transformation, NMR analysis including ¹H and ³¹P NMR spectroscopy was employed to monitor the assembly process. Equal aliquots of the reaction mixture were withdrawn from the reaction mixture at different times. After evaporation to dryness, the solid residues were dissolved in deuterated DMSO for NMR studies. The proton signals of the vinyl or/and the alkyl group (H_A, H_B, and H_C in Scheme 1) were monitored. As shown in Figure 4a, signals of H_A in 1 existed as a triplet at around δ 6.49 ppm. As the reaction proceeded, double–doublets at ca. δ 6.36 and 6.67 ppm attributed to protons of the vinyl group (H_A) of $[2]Cl_2$ and a triplet at δ 6.45 ppm assignable to H_A of $[3]Cl_2$ emerged. After about 5 min, the reaction mixture became clear and signals of 1 disappeared completely in the ¹H NMR spectra. Then signals of $[2]Cl_2$ and $[3]Cl_2$ started to vanish gradually, and three new triplets of $[4]Cl_4$ appeared at δ 2.30 (H_C), 6.10 (H_B), and 6.15 (H_A) ppm. The upfield shift and the observed integral ratio of 4:2:2 demonstrated the generation of the new dppes ligand, indicating that two of the vdpp ligands have reacted with H₂S to give rise to the coexistence of two types of ligands in $[4]Cl_4$. Finally, only signals assignable to H_B and H_C of $[5]Cl$ could be detected at δ 4.95 and 2.20 ppm after 30 min, which indicated the presence of only one type of phosphorus ligand, dppes, in the reaction mixture.

Further supporting evidence came from the ³¹P NMR spectral changes (Figure 4b). The initial ³¹P NMR signal of 1 appeared at about δ 32.2 ppm. After gently bubbling H₂S gas for around 3 min, the colorless suspension turned slightly yellow, and the ³¹P NMR spectra indicated the appearance of several new signals. The singlet at about δ 35.3 ppm could be assigned to $[3]Cl_2$, while the pair of doublets at ca. δ 34.0 and

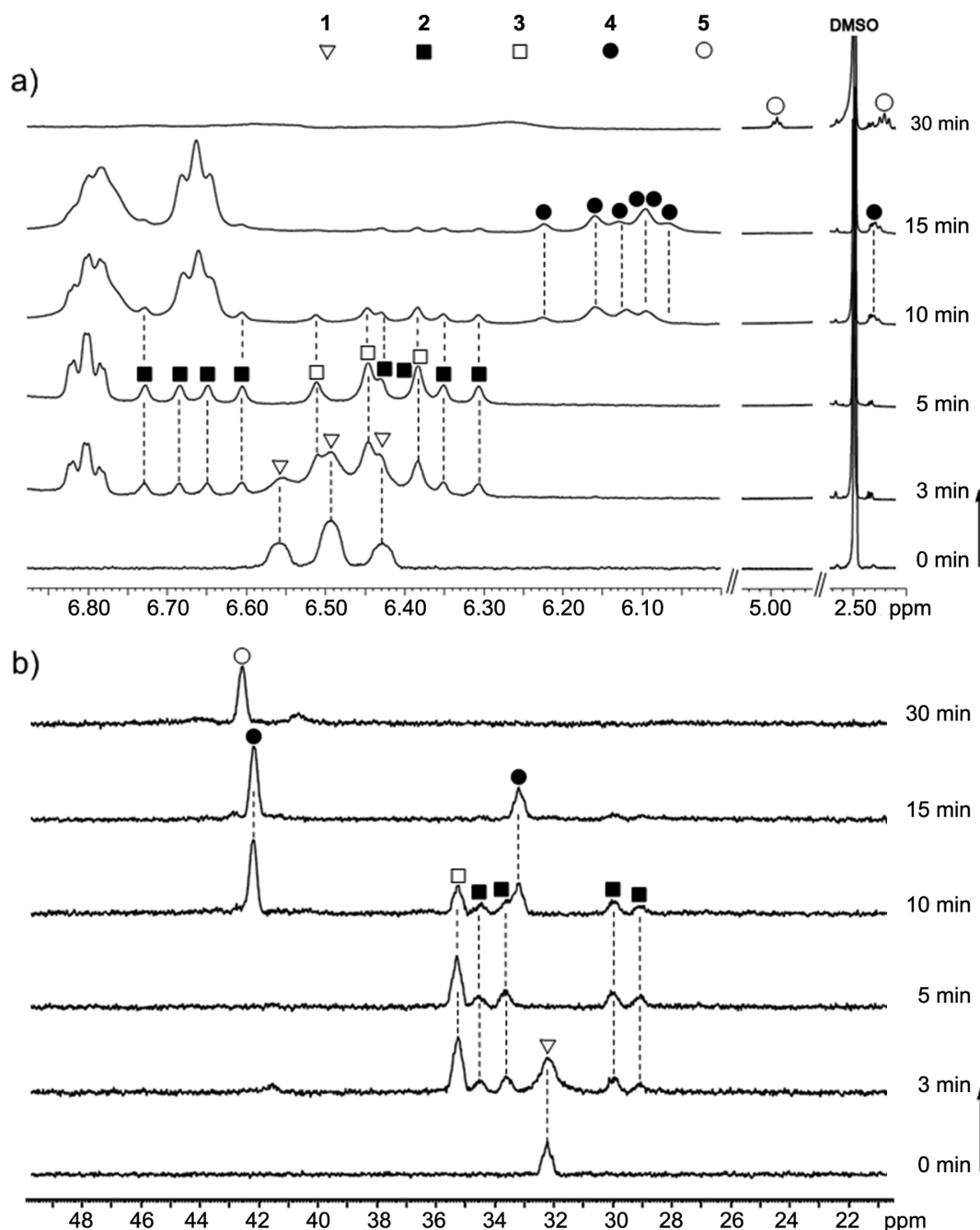


Figure 4. (a) ¹H NMR and (b) ³¹P NMR spectral changes in DMSO-*d*₆ during the assembly process.

29.5 ppm corresponded to signals of [2]Cl₂. As the reaction mixture became clear at about 5 min, the ³¹P NMR spectra showed the completion of reaction between 1 and H₂S. Then, at around 10 min, two singlets at ca. δ 42.2 and 33.2 ppm with integral ratio of 2:1 appeared, which corresponded to the formation of [4]Cl₄. The signals of [2]Cl₂ and [3]Cl₂ subsequently disappeared, leaving only [4]Cl₄ in the system. If H₂S was bubbled continuously, large amounts of yellow precipitate appeared and only one singlet at around δ 42.6 ppm in the ³¹P NMR spectra was observed, corresponding to signals of the final product, [5]Cl.

This addition reaction-induced cluster-to-cluster transformation is unprecedented and is the first of its kind. Similar reactions in the past with dppm and aminodiphosphine-bridged gold(I) systems did not yield similar phenomenon. The

monitoring experiments indicate that the most critical point of the transformation involves the addition reaction of the double bond of the vdpp ligand. In the current system, H₂S would first react with the gold(I) precursor to form a mixture of hexa- and decanuclear gold(I) clusters. After the sulfide has coordinated to the gold(I) atoms, H₂S would start to react with a portion of the vinyl groups, leading to the coexistence of two different phosphine ligands, vdpp and dppes. The increase in the rigidity and the steric hindrance of the organic phosphine ligands from vdpp to dppes would direct the cluster-to-cluster transformation from the decanuclear to the dodecanuclear gold(I) cluster, which is supported by the single crystal structures of cluster cation 2 and 4. According to the NMR analysis, the vinyl groups in cluster cation 4 would react with H₂S and vdpp would be completely transformed to dppes in

the mixture. Finally, the transformation process would end up with the formation of the pentagold(I) cluster.

CONCLUSIONS

Directed by gold(I)⋯gold(I) bonding interactions, different types of luminescent polynuclear gold(I) clusters have been assembled via addition reaction-induced cluster-to-cluster transformation. ³¹P NMR, ¹H NMR, and UV–vis absorption spectroscopy have been employed to monitor the self-assembly and transformation processes from **2** and **3**, to **4**, and finally to **5**. The sustained formation and existence of gold(I)⋯gold(I) interactions not only would support the high nuclearity structures of these clusters but also would impart them with their rich luminescence properties. This work has provided new strategies and insights into the self-assembly processes of polynuclear gold(I) clusters and the development of novel luminescent functional materials. Efforts are under way in our laboratory to extend such cluster-to-cluster transformation strategy to other cluster systems and to explore their potential applications in the development of luminescent functional materials.

EXPERIMENTAL SECTION

Materials and Reagents. Vinylidenebis(diphenylphosphine) (vdpp) and [vdpp(AuCl)₂] (**1**) were prepared according to literature procedures.^{10–12} All other solvents and reagents were used as received.

Instrumentation. ¹H NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz) Fourier transform NMR spectrometer with chemical shifts (δ, ppm) relative to tetramethylsilane (Me₄Si). ³¹P{¹H} NMR spectra were recorded on a Bruker AVANCE (162 MHz) Fourier transform NMR spectrometer with chemical shifts (δ, ppm) relative to 85% H₃PO₄. Electro spray ionization (ESI) mass spectra were recorded on a Finnigan LCQ mass spectrometer. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing.

Experimental details. As shown in Scheme 1, slow bubbling of H₂S gas into a suspension of **1** (30 mg) in dichloromethane-ethanol-pyridine (3 mL, 1:1:1 v/v/v) resulted in a series of polynuclear gold(I) μ₃-sulfido clusters, [Au₁₀(μ-vdpp)₄(μ₃-S)₄]Cl₂ ([**2**]Cl₂), [Au₆(μ-vdpp)₃(μ₃-S)₂]Cl₂ ([**3**]Cl₂), [Au₁₂(μ-vdpp)₂(μ-dppes)₂(μ₃-S)₄]Cl₄ ([**4**]Cl₄) (dppes = bis(2,2-bis(diphenylphosphino)ethyl)sulfane), and [Au₅(μ-dppes)(μ₃-S)₂]Cl ([**5**]Cl). Their PF₆ salts, such as [**2**](PF₆)₂ and [**3**](PF₆)₂, were obtained through metathesis reactions with NH₄PF₆ in methanol. The identities of cluster cations **2**, **3**, **4**, and **5** were confirmed by elemental analysis, electro spray ionization mass spectrometry (ESI-MS), and ¹H and ³¹P NMR spectroscopy. The yields of the complexes were variable, because all the clusters were obtained from the same reaction mixture and the yield of each would depend on the reaction time. For instance, when the H₂S bubbling was stopped at about 5 min, the majority of product is a mixture of cluster **2** (about 42%) and **3** (about 53%); the separation of which could be achieved by recrystallization. If the reaction was stopped at about 15 min, the yield of cluster **4** would be >90%, and finally, after 30 min, cluster **5** would be precipitated out as a yellow solid, with a yield of about 85%.

Characterizations. **Complex 2.** Point group symmetry in solution, S₄. [**2**]Cl₂: ¹H NMR (400 MHz, DMSO-*d*₆, 298 K): δ 6.36 (dd, ABXY-system (A, B = H; X, Y = P), 4H, ³J(PH) = 30.6 Hz, ³J(PH) = 17.8 Hz, =CH₂), 6.66 (dd, ABXY-system (A, B = H; X, Y = P), 4H, ³J(PH) = 30.6 Hz, ³J(PH) = 17.8 Hz, =CH₂), 6.80 (t, 8H, ³J(HH) = 6.2 Hz, –Ph), 7.12 (t, 8H, ³J(HH) = 6.2 Hz, –Ph), 7.25–7.37 (m, 20H, –Ph), 7.51–7.63 (m, 32H, –Ph), 7.91 (t, 4H, ³J(HH) = 6.8 Hz, –Ph), 8.17 (dd, 8H, ³J(PH) = 13.0 Hz, ³J(HH) = 7.6 Hz, –Ph); ³¹P{¹H} NMR (162 MHz, DMSO-*d*₆, 298 K): δ 29.54, 34.04 (dd, AB-system (A, B = P), ²J(PP) = 146 Hz, vdpp); positive ESI-MS: *m/z*: 1841 ([M]²⁺); elemental analysis calcd for [**2**]Cl₂·CH₂Cl₂·H₂O (found): C 32.69 (32.46), H 2.40 (2.27), N 0.00 (<0.3). [**2**](PF₆)₂:

¹H NMR (400 MHz, CDCl₃, 298 K): δ 6.23 (dd, ABXY-system (A, B = H; X, Y = P), 4H, ³J(PH) = 30.7 Hz, ³J(PH) = 17.6 Hz, =CH₂), 6.36 (dd, ABXY-system (A, B = H; X, Y = P), 4H, ³J(PH) = 30.7 Hz, ³J(PH) = 17.6 Hz, =CH₂), 6.80 (t, 8H, ³J(HH) = 7.7 Hz, –Ph), 7.08 (t, 8H, ³J(HH) = 7.7 Hz, –Ph), 7.19–7.25 (m, 8H, –Ph), 7.39–7.47 (m, 24H, –Ph), 7.53–7.62 (m, 20H, –Ph), 7.74 (t, 4H, ³J(HH) = 7.2 Hz, –Ph), 8.05 (dd, 8H, ³J(PH) = 13.1 Hz, ³J(HH) = 7.7 Hz, –Ph); ³¹P{¹H} NMR (162 MHz, CDCl₃, 298 K): δ 29.84, 34.21 (dd, AB-system (A, B = P), ²J(PP) = 146 Hz, vdpp), –144.22 (sept, PF₆); positive ESI-MS: *m/z*: 1841 ([M]²⁺); elemental analysis calcd for [**2**](PF₆)₂ (found): C 31.44 (31.30), H 2.23 (2.32), N 0.00 (<0.3).

Complex 3. Point group symmetry in solution, D₃. [**3**]Cl₂: ¹H NMR (400 MHz, DMSO-*d*₆, 298 K): δ 6.45 (t, AA'XX'-system (A, A' = H; X, X' = P), 6H, ³J(PH) = 25.7 Hz, =CH₂), 6.94–7.74 (br m, 60H, –Ph); ³¹P{¹H} NMR (162 MHz, DMSO-*d*₆, 298 K): δ 35.26 (s, vdpp); positive ESI-MS: *m/z*: 1217 ([M]²⁺). [**3**](PF₆)₂: ¹H NMR (400 MHz, CD₃CN, 298 K): δ 6.36 (t, AA'XX'-system (A, A' = H; X, X' = P), 6H, ³J(PH) = 25.7 Hz, =CH₂), 7.29–7.64 (br m, 60H, –Ph); ³¹P{¹H} NMR (162 MHz, CD₃CN, 298 K): δ 35.10 (s, vdpp), –144.53 (sept, PF₆); positive ESI-MS: *m/z*: 1217 ([M]²⁺); elemental analysis calcd for [**3**](PF₆)₂ (found): C 34.38 (34.07), H 2.44 (2.51), N 0.00 (<0.4).

Complex 4. Point group symmetry in solution, D_{2h}. [**4**]Cl₄: ¹H NMR (400 MHz, DMSO-*d*₆, 298 K): δ 2.32 (t, AA'BXX'-system (A, A' = H; X, X' = P), 8H, ³J(PH) = 16.6 Hz, –CH₂–), 6.00 (t, AA'BXX'-system (A, A' = H; X, X' = P), 4H, ²J(PH) = 13.2 Hz, –CH–), 6.15 (t, AA'XX'-system (A, A' = H; X, X' = P), 4H, ³J(PH) = 25.3 Hz, =CH₂), 6.69 (t, 16H, ³J(HH) = 7.0 Hz, –Ph), 6.79 (s, 16H, –Ph), 7.19–7.26 (m, 16H, –Ph), 7.33 (s, 24H, –Ph), 7.51–7.56 (m, 16H, –Ph), 8.08–8.15 (m, 32H, –Ph); ³¹P{¹H} NMR (162 MHz, DMSO-*d*₆, 298 K): δ 41.92 (s, 8H, dppes), 33.18 (s, 4P, vdpp); positive ESI-MS: *m/z*: 1234 ([M]⁴⁺); elemental analysis calcd for [**4**]Cl₄·2CH₂Cl₂ (found): C 36.15 (35.67), H 2.69 (2.80), N 0.00 (<0.3).

Complex 5. Point group symmetry in solution, C_{2v}. [**5**]Cl: ¹H NMR (400 MHz, DMSO-*d*₆, 298 K): δ 2.23 (t, AA'BXX'-system (A, A' = H; X, X' = P), 4H, ³J(PH) = 16.7 Hz, –CH₂–), 4.94 (t, AA'BXX'-system (A, A' = H; X, X' = P), 2H, ²J(PH) = 13.1 Hz, –CH), 7.13 (t, 8H, ³J(HH) = 7.4 Hz, –Ph), 7.20 (t, 4H, ³J(HH) = 7.4 Hz, –Ph), 7.32 (t, 8H, ³J(HH) = 7.4 Hz, –Ph), 7.53 (t, 4H, ³J(HH) = 7.4 Hz, –Ph), 7.77 (dd, 8H, ³J(PH) = 13.0 Hz, ³J(HH) = 7.0 Hz, –Ph), 8.18 (dd, 8H, ³J(PH) = 13.0 Hz, ³J(HH) = 7.0 Hz, –Ph); ³¹P{¹H} NMR (162 MHz, DMSO-*d*₆, 298 K): δ 42.52 (s, dppes); positive ESI-MS: *m/z*: 1875 ([M]⁺); elemental analysis calcd for [**5**]Cl·H₂O (found): C 32.37 (32.22), H 2.51 (2.43), N 0.00 (<0.3).

ASSOCIATED CONTENT

Supporting Information

X-ray structure determination, photophysical studies, and positive ESI mass spectra; Tables S1, S2 and S3, Figures S1–S8; crystallographic details (CIF) (CCDC 992317–992318). 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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