

Substituent-Mediated Transformation of Polynuclear Gold(I)-Sulfido Complexes—From Pentanuclear to Octadecanuclear Cluster-to-Cluster Transformation

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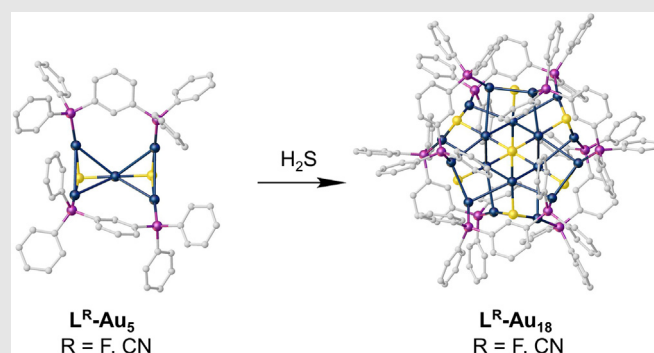
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Polynuclear gold complexes show diverse structures and bonding. An exploration into their transformation represents a challenging area of research. Herein, an unprecedented substituent-mediated transformation from pentagold(I) to octadecagold(I) complexes has been observed. These gold(I)-sulfido complexes with distinct structures have been fully characterized, and the transformation process has been monitored by NMR spectroscopy in solution state. The electron-withdrawing effects of the substituent groups on the diphosphine ligands have given rise to subtle changes in the electron density on the gold(I) center, which has resulted in the structural reorganization of the clusters to maximize Au...Au interactions. This compensates for the loss of electron density at the metal center, leading to different symmetries and nuclearities of gold(I)-sulfido complexes with distinctly different photophysical properties. Our findings offer a simple and

effective cluster-to-cluster transformation strategy for the development of novel luminescent gold(I)-sulfido clusters with controlled structures by varying the electronic nature of the substituent on the phosphine ligand.



Keywords: supramolecular self-assembly, polynuclear gold(I)-sulfido complexes, substituent-mediated, cluster-to-cluster transformation, electron density

Introduction

Aurophilicity-directed self-assembly has emerged as an effective approach for the construction of diverse architectures.^{1–15} In recent decades, growing research interest has focused on the self-assembly of polynuclear gold(I)

aggregates via Au...Au interactions that show strengths similar to that of hydrogen bonding.^{16–47} To date, polynuclear gold(I)-sulfido complexes have become a particularly interesting subclass in the gold family due to the comparatively facile synthesis and highly stable structure.^{48–56} Recently, our group has made efforts not only to

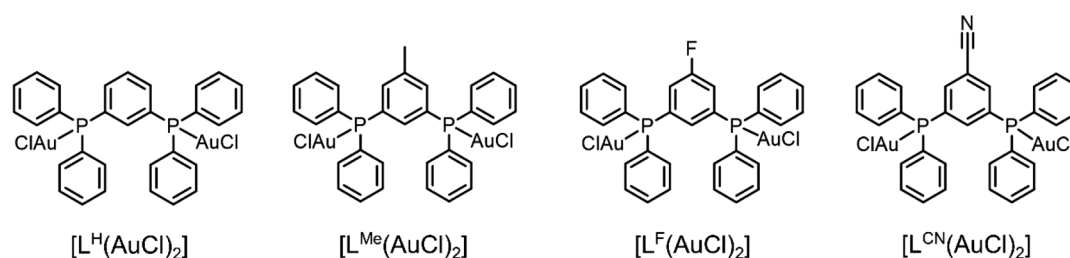


Chart 1 | Chemical structures of $[L^H(AuCl)_2]$, $[L^{Me}(AuCl)_2]$, $[L^F(AuCl)_2]$, and $[L^{CN}(AuCl)_2]$.

build new structures of polynuclear μ_3 -sulfido gold(I) complexes with rich luminescence properties, but also to study their interesting polynuclear gold(I)-based cluster-to-cluster transformations.^{51–54,56} Introducing reactive sites, such as alkynyl groups,⁵⁰ vinyl groups,⁵⁴ or cis-trans isomerizable groups,⁵⁶ to bring about cluster-to-cluster transformation and changes in luminescence properties has led to fascinating structures and properties. However, reactive sites capable of such conversions, while interesting, are rather limited. Thus, a search for a simple but controllable method for the structural regulation of gold(I) clusters is still a major challenge. If the transformation could be extended from the use of specific reactive functional groups to more general ligand design principles, myriad possibilities in the area of transformation would result.

Moreover, ligands with rigid backbones have played important roles in the field of luminescent materials, owing to their abilities of providing extended π -conjugation and molecular rigidity.^{57–60} Phosphine ligands with rigid aromatic backbones are widely used in organometallic catalysis and blue phosphorescent organic light-emitting diode materials.^{61,62} In polynuclear gold(I)-sulfido complexes, the most commonly used ligands are phosphine ligands with flexible linkers, such as dppm,⁵² dpepp,⁵¹ and so on,⁵⁰ while ligands based on rigid aromatic skeletons are rarely used. Since the configurations of polynuclear gold(I)-sulfido complexes are sensitive to the P–P bite distances of phosphine ligands, the employment of rigid diphosphine ligands with well-defined P–P bite distances is a feasible and precise way to optimize P–P bite distances for the controlled synthesis of various polynuclear complex structures. Since linear diphosphine ligands $PPh_2(p-C_6H_4)_n PPh_2$, ($n = 1–4$) have been shown to prefer the formation of supramolecular aggregates ($n = 1$) and cage-like ($n = 2–4$) structures rather than discrete polynuclear gold(I)-sulfido complexes,^{39,40} an exploration in the use of V-shaped ligands based on 1,3-bis(diphenylphosphino)benzene with a shorter P–P bite distance for the assembly of discrete polynuclear gold(I) complexes is worth pursuing. Furthermore, to the best of our knowledge, the role of the substituents of the rigid aromatic skeleton of diphosphine ligands in facilitating the transformation of

the structure of the polynuclear gold(I)-sulfido complexes has rarely been reported.

Herein, we report an interesting finding, in which a minor difference in the substituent group of the rigid diphosphine ligands has resulted in the formation of different structures of the polynuclear gold(I)-sulfido complexes. By employing chlorogold(I) precursors, $[L^H(AuCl)_2]$, $[L^{Me}(AuCl)_2]$, $[L^F(AuCl)_2]$, and $[L^{CN}(AuCl)_2]$ (Chart 1), a novel series of luminescent polynuclear gold(I)-sulfido complexes, $[Au_5(L^H)_2S_2]Cl$ ($[L^H-Au_5]Cl$), $[Au_5(L^{Me})_2S_2]Cl$ ($[L^{Me}-Au_5]Cl$), $[Au_5(L^F)_2S_2]Cl$ ($[L^F-Au_5]Cl$), $[Au_{18}(L^F)_6S_8]Cl_2$ ($[L^F-Au_{18}]Cl_2$), $[Au_5(L^{CN})_2S_2]Cl$ ($[L^{CN}-Au_5]Cl$), and $[Au_{18}(L^{CN})_6S_8]Cl_2$ ($[L^{CN}-Au_{18}]Cl_2$), have been constructed. These gold(I) complexes have been well characterized. Furthermore, it was found that the electron-withdrawing substituent on the benzene core of 1,3-bis(diphenylphosphino)benzene is of vital importance for the regulation of the cluster transformation process. Intriguingly, the pentagold(I) complexes with electron-withdrawing substituents such as $-F$ and $-CN$ were found to transform to octadecagold(I) complexes in solution in the presence of H_2S . The transformation process has been monitored by NMR spectroscopy. This work not only reveals the transformation process but also provides a simple and convenient strategy to develop controlled transformation for the development of luminescent gold-based materials.

Experimental Methods

Synthesis of polynuclear gold(I)-phosphine complexes

$[L^H-Au_5]Cl$

Freshly produced H_2S gas was bubbled into a solution of $[L^H(AuCl)_2]$ (91.1 mg, 0.10 mmol) in 11 mL dichloromethane-pyridine (10:1, v/v) at room temperature, resulting in a clear colorless solution. Subsequent evaporation and purification by layering of diethyl ether onto a dichloromethane solution of the complex gave $[L^H-Au_5]Cl$ as white crystals. Yield: 53 mg (67% based on the Au content). 1H NMR (400 MHz, CD_2Cl_2), δ (ppm): 9.38 (t, $J = 15.8$ Hz, 1H, phenyl), 7.60–7.32 (m, 17H, phenyl), 7.30–7.19 (m, 2H, phenyl), 7.06–6.86 (m, 4H, phenyl).

$^{31}\text{P}\{\text{H}\}$ NMR (162 MHz, CD_2Cl_2), δ (ppm): 31.5. Positive high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) (m/z): calcd for $[(\text{C}_{30}\text{H}_{24}\text{P}_2)_2\text{Au}_5\text{S}_2]^+$, 1941.0471; found, 1941.0506. White crystals of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$ suitable for X-ray structural determination were obtained by slow vapor diffusion of diethyl ether into a CH_2Cl_2 and MeOH mixture (1:1, v/v) solution of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$.

$[\text{L}^{\text{Me}}\text{-Au}_5]\text{Cl}$

This was prepared according to a procedure similar to that described for $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$, except $[\text{L}^{\text{Me}}(\text{AuCl}_2)]$ (93 mg, 0.10 mmol) was used instead. Yield: 58 mg (72% based on the Au content). ^1H NMR (400 MHz, CD_2Cl_2), δ (ppm): 9.23 (t, $J = 15.9$ Hz, 1H, phenyl), 7.64–7.18 (m, 18H, phenyl), 7.10–6.84 (m, 4H, phenyl), 2.38 (s, 3H, $-\text{CH}_3$). $^{31}\text{P}\{\text{H}\}$ NMR (162 MHz, CD_2Cl_2), δ (ppm): 31.3. Positive HR-ESI-MS (m/z): calcd for $[(\text{C}_{31}\text{H}_{26}\text{P}_2)_2\text{Au}_5\text{S}_2]^+$, 1969.0784; found, 1969.0712.

$[\text{L}^{\text{F}}\text{-Au}_5]\text{Cl}$

This was prepared according to a procedure similar to that described for $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$, except $[\text{L}^{\text{F}}(\text{AuCl}_2)]$ (93 mg, 0.10 mmol) was used instead. Yield: 85 mg (84% based on the Au content). ^1H NMR (400 MHz, CDCl_3), δ (ppm): 9.10 (t, $J = 15.2$ Hz, 1H, phenyl), 7.55–7.29 (m, 16H, phenyl), 7.12–6.97 (m, 6H, phenyl). $^{31}\text{P}\{\text{H}\}$ NMR (162 MHz, CDCl_3), δ (ppm): 30.4. $^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3), δ (ppm): -106.4. Positive HR-ESI-MS (m/z): calcd for $[(\text{C}_{30}\text{H}_{23}\text{FP}_2)_2\text{Au}_5\text{S}_2]^+$, 1977.0282; found, 1977.0137. White crystals of $[\text{L}^{\text{F}}\text{-Au}_5]\text{Cl}$ suitable for X-ray structural determination were obtained by slow vapor diffusion of diethyl ether into a CH_2Cl_2 and MeOH mixture (1:1, v/v) solution of $[\text{L}^{\text{F}}\text{-Au}_5]\text{Cl}$.

$[\text{L}^{\text{CN}}\text{-Au}_5]\text{Cl}$

Freshly produced H_2S gas was bubbled into a solution of $[\text{L}^{\text{CN}}(\text{AuCl})_2]$ (46.8 mg, 0.05 mmol) in dichloromethane-pyridine (22 mL, 10:1, v/v) at room temperature, resulting in a clear solution in 5 min. Subsequent evaporation and purification by layering diethyl ether onto a dichloromethane solution of the complex gave $[\text{L}^{\text{CN}}\text{-Au}_5]\text{Cl}$ as a white solid. Yield: 23.1 mg (57% based on the Au content). ^1H NMR (400 MHz, CD_2Cl_2), δ (ppm): 9.41 (t, $J = 14.9$ Hz, 1 H, phenyl), 7.80–7.30 (m, 18H, phenyl), 7.30–7.00 (m, 4H, phenyl). $^{31}\text{P}\{\text{H}\}$ NMR (162 MHz, CD_2Cl_2), δ (ppm): 31.5. Positive HR-ESI-MS (m/z): calcd for $[(\text{C}_{31}\text{H}_{23}\text{NP}_2)_2\text{Au}_5\text{S}_2]^+$, 1991.0376; found, 1991.0417.

$[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$

Freshly produced H_2S gas was bubbled into a solution of $[\text{L}^{\text{F}}(\text{AuCl})_2]$ (186 mg, 0.20 mmol) in dichloromethane-pyridine (11 mL, 10:1, v/v) at room temperature, resulting in a clear colorless solution in 10 min. Further bubbling of

H_2S gas for 5 h, followed by evaporation of the solvent and recrystallization from dichloromethane solution gave $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$ as yellow tetrahedron-shaped crystals. Yield: 78 mg (53% based on the Au content). ^1H NMR (400 MHz, CD_2Cl_2), δ (ppm): 9.83 (t, $J = 14.2$ Hz, 1H, phenyl), 7.81–6.22 (m, 22H, phenyl). $^{31}\text{P}\{\text{H}\}$ NMR (162 MHz, CD_2Cl_2), δ (ppm): 29.4. $^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CD_2Cl_2), δ (ppm): -110.24. Positive HR-ESI-MS (m/z): calcd for $[(\text{C}_{30}\text{H}_{23}\text{FP}_2)_6\text{Au}_{18}\text{S}_8]^{2+}$, 3293.9670; found, 3293.9475. Yellow crystals of $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$ suitable for X-ray structural determination were obtained by slow vapor diffusion of diethyl ether into a dichloromethane solution of $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$.

$[\text{L}^{\text{CN}}\text{-Au}_{18}]\text{Cl}_2$

Freshly produced H_2S gas was bubbled into a solution of $[\text{L}^{\text{CN}}(\text{AuCl})_2]$ (46.8 mg, 0.05 mmol) in dichloromethane-pyridine (22 mL, 10:1, v/v) at room temperature, resulting in a clear red solution in 10 min. Further bubbling of H_2S gas for 1 h, followed by evaporation of the solvent and recrystallization from slow vapor diffusion of diethyl ether into a dichloromethane solution gave $[\text{L}^{\text{CN}}\text{-Au}_{18}]\text{Cl}_2$ as red crystals, suitable for X-ray structural determination. Yield: 15.1 mg (41% based on the Au content). ^1H NMR (400 MHz, CD_2Cl_2), δ (ppm): 10.00 (t, $J = 13.5$ Hz, 1H, phenyl), 7.61–7.23 (m, 14H, phenyl), 7.18 (d, $J = 8.5$ Hz, 2H, phenyl), 7.02–6.89 (m, 2H, phenyl). 6.58–6.40 (m, 4H, phenyl). $^{31}\text{P}\{\text{H}\}$ NMR (162 MHz, CD_2Cl_2), δ (ppm): 30.3. Positive HR-ESI-MS (m/z): calcd for $[(\text{C}_{31}\text{H}_{23}\text{NP}_2)_6\text{Au}_{18}\text{S}_8]^{2+}$, 3314.9810; found, 3314.9650.

Results and Discussion

Synthesis and characterization

A series of pentanuclear and octadecanuclear gold(I)-sulfido complexes, denoted as $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$, $[\text{L}^{\text{Me}}\text{-Au}_5]\text{Cl}$, $[\text{L}^{\text{F}}\text{-Au}_5]\text{Cl}$, $[\text{L}^{\text{CN}}\text{-Au}_5]\text{Cl}$, $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$, and $[\text{L}^{\text{CN}}\text{-Au}_{18}]\text{Cl}_2$, were synthesized by bubbling H_2S into a dichloromethane-pyridine mixture of respective chlorogold(I) precursors. All polynuclear gold(I) complexes were characterized by NMR, HR-ESI-MS, and electronic absorption and emission spectroscopies (Supporting Information Figures S1–S21). The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$ in CD_2Cl_2 shows only one singlet at $\delta = 31.5$ ppm (Supporting Information Figure S3), indicating that the two phosphorus atoms of L^{H} are in the same environment. The other pentanuclear gold(I)-sulfido complexes show similar $^{31}\text{P}\{\text{H}\}$ NMR spectra (Supporting Information Figures S5, S7, and S13), suggesting that the structures of these Au_5 complexes are similar to phosphorus atoms in the same environment. Upon diffusion of diethyl ether vapor into a concentrated solution of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$ in CH_2Cl_2 and MeOH (1:1, v/v) mixture, single crystals of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$ were obtained. Single-crystal X-ray diffraction analysis further confirms

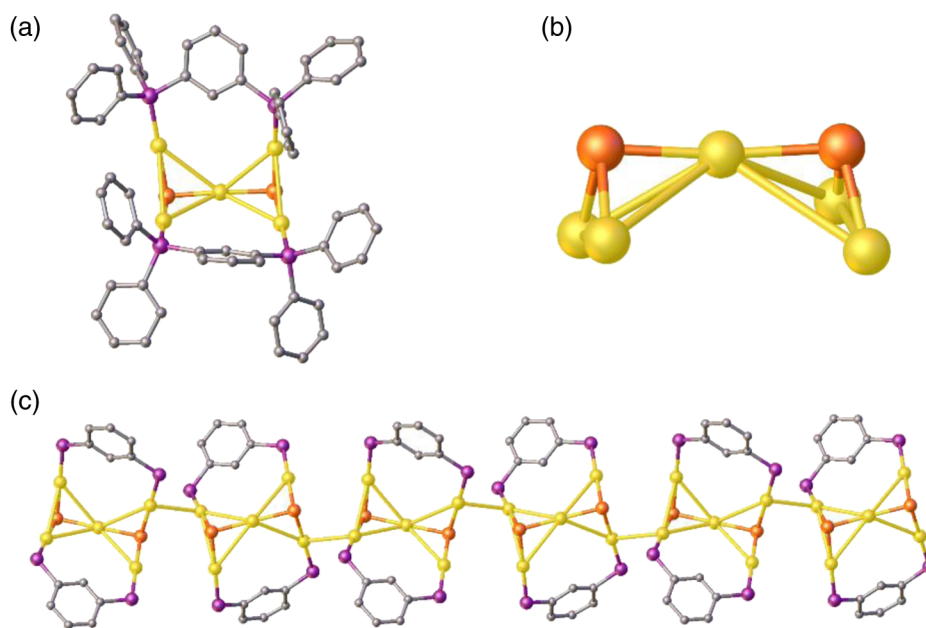


Figure 1 | (a) Crystal structure of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$. (b) Core of the crystal structure of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$. (c) Packing of linear 1-D molecular arrays in the crystal structure of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$ (gray, C; purple, P; yellow, Au; orange, S).

the formation of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$, which crystallizes in the monoclinic $P2_1$ space group (Supporting Information Table S1). The five gold(I) atoms are surrounded by two nearly trans-disposed diphosphine ligands (Figures 1a, 1b and Supporting Information Figures S22) and bridged by two μ_3 -S atoms with Au-S-Au angles in the range of $86.87\text{--}96.53^\circ$ (Supporting Information Table S3). The Au...Au distances range from 3.08 to 3.37 Å, which are in the normal range for aurophilic interactions (Supporting Information Table S2). More interestingly, the discrete complex $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$ can further assemble to form one-dimensional linear supramolecular aggregates via intermolecular gold...gold interactions in the crystal-line state (Figure 1c). Cl[−] counterions were found to be located around the phosphine ligand with hydrogen-bonding distances ranging from 2.66–3.24 Å (Supporting Information Figure S23). This represents the first example of the crystal structure of pentanuclear gold (I)-sulfido complex based on diphosphine ligands. There is no symmetry in the solid state observed in the single-crystal structure determination. However, only one P environment is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Supporting Information Figure S3), suggesting a local C_{2v} symmetry of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$ in the solution state. Similarly, single crystals of $[\text{L}^{\text{F}}\text{-Au}_5]\text{Cl}$ have also been obtained under the same conditions. The related information of the crystal structure data is summarized in Supporting Information Tables S4–S6 and Figure S24.

Interestingly, with exposure to H₂S atmosphere overnight, the solution colors of $[\text{L}^{\text{F}}\text{-Au}_5]\text{Cl}$ and $[\text{L}^{\text{CN}}\text{-Au}_5]\text{Cl}$ slowly change from colorless to yellow and red, respectively. However, similar phenomena are not observed for

the solutions of $[\text{L}^{\text{H}}\text{-Au}_5]\text{Cl}$ and $[\text{L}^{\text{Me}}\text{-Au}_5]\text{Cl}$ under similar conditions. The yellow complex product, $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$, has been isolated as tetrahedron-shaped crystals by the diffusion of diethyl ether into the dichloromethane solution, which was found to be suitable for single-crystal X-ray diffraction analysis. The single-crystal X-ray structure shows that $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$ is $[\text{Au}_{18}(\text{L}^{\text{F}})_6(\mu_3\text{-S})_8]^{2+}$ ($[\text{L}^{\text{F}}\text{-Au}_{18}]^{2+}$) (Figure 2a). The crystal structure of $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$ is refined in the cubic $I43d$ space group (Supporting Information Tables S7–S9). Intriguingly, the F...F distance between every two adjacent Au₁₈ complexes in the crystal structure is shown to be 2.94 Å (Figure 2c), suggesting the presence of F...F interactions, which helps to stabilize crystal packing.⁶³ The complex cation $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$ is comprised of six diphosphine ligands, eighteen gold(I) atoms, and eight μ_3 -bridging S atoms (Figure 2a) to give an octadecanuclear gold(I)-sulfido cluster structure, which is similar to the related Au₁₈ clusters, $[\text{Au}_{18}\text{Se}_8(\text{dppe})_6]^{2+}$,²¹ $[\text{Au}_{18}\text{S}_8(\text{dppe})_6]^{2+}$,⁶⁴ and $[\text{Au}_{18}\text{S}_8(\mu\text{-trans-dppee})_3]^{2+}$.⁵⁶ The gold skeleton of $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$ consists of a peripheral Au₁₂ macrocycle linked by Au...Au and Au–S interactions (Figure 2b) and the kernel of the gold skeleton can be viewed as a twisted cube consisting of a Au₆S₂ core (Figure 2a). The Au...Au contacts range from 2.95 to 3.27 Å, which are in the range of aurophilic interactions (Supporting Information Table S8). Also, in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$, only one singlet at $\delta = 29.4$ ppm was found, suggesting that two phosphorus atoms on the same ligand are equivalent (Supporting Information Figure S10). The identity of $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$ was further confirmed by HR-ESI-MS analyses. A prominent cluster peak at

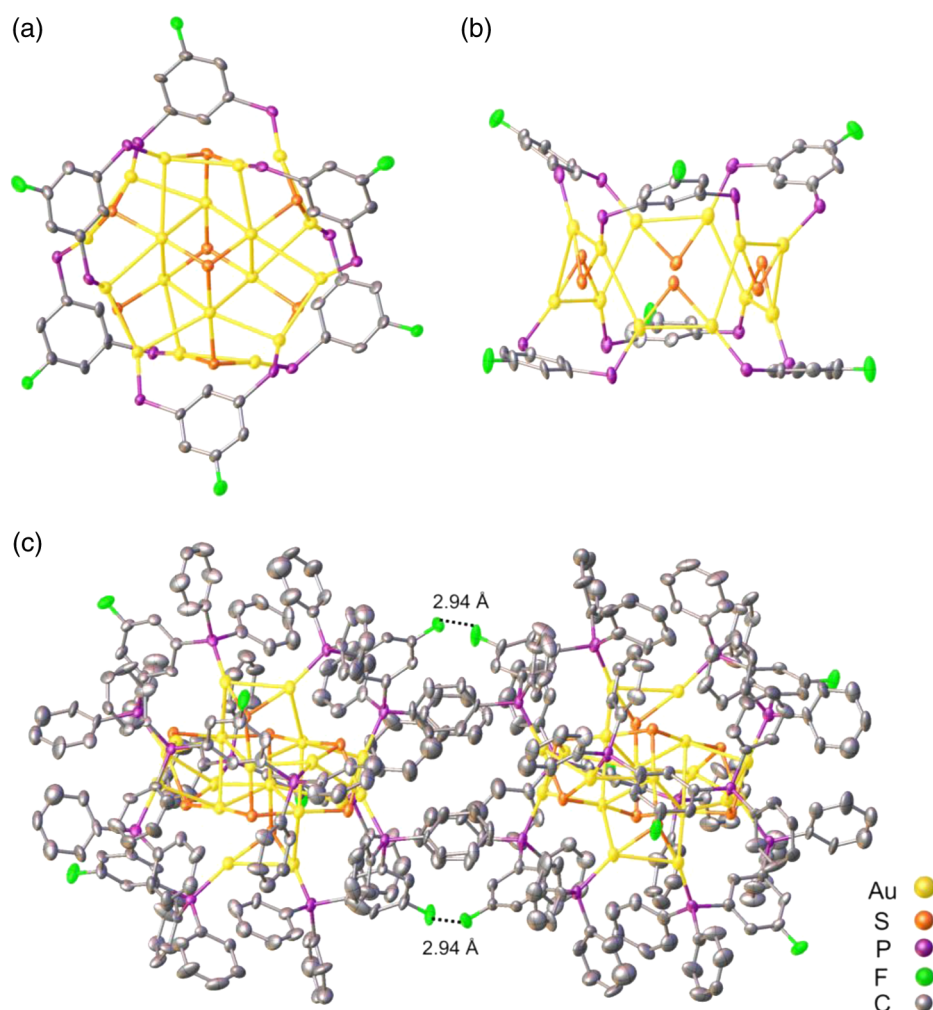


Figure 2 | (a) Perspective view of $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$. (b) Side view of peripheral Au_{12} macrocycle skeleton in $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$. (c) Packing of adjacent molecules in the crystal structure of $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$. Thermal ellipsoids are shown at a 50% probability level. The counteranions, solvent molecules, and hydrogen atoms are omitted for clarity (gray, C; green, F; purple, P; yellow, Au; orange, S).

$m/z = 3293.95$ can be attributed to the doubly charged molecular ion cluster, $[\text{Au}_{18}(\text{L}^{\text{F}})_6\text{S}_8]^{2+}$, with the loss of Cl^- counterions. This assignment is supported by the good agreement of the simulated isotopic pattern of the ion cluster with the high-resolution experimental MS isotopic pattern (Supporting Information Figure S19). The ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR spectral data also support the assignment (Supporting Information Figures S9 and S11). Similarly, NMR, HR-ESI-MS spectroscopy, and single-crystal X-ray diffraction studies have also been used to establish the structure of $[\text{L}^{\text{CN}}\text{-Au}_{18}]\text{Cl}_2$ (Supporting Information Tables S10–S12, Figures S14, S15, S21, and S25), indicating that the structure of $[\text{L}^{\text{CN}}\text{-Au}_{18}]\text{Cl}_2$ is similar to that of $[\text{L}^{\text{F}}\text{-Au}_{18}]\text{Cl}_2$.

Photophysical studies

A cluster-to-cluster conversion from Au_5 to Au_{18} has brought about a dramatic red shift in the UV-vis

absorption spectra (Supporting Information Figure S1). The UV-vis absorption spectra of these pentanuclear and octadecanuclear gold(I)-sulfido clusters show low-energy absorption shoulders at 320 and 400 nm, respectively (Supporting Information Figure S1), which are absent in the chlorogold(I) precursors and are tentatively assigned as ligand-to-metal-metal charge transfer (LMMCT; $\text{S} \rightarrow \text{Au}_n$) or ligand-to-metal charge transfer (LMCT; $\text{S} \rightarrow \text{Au}$) transitions modified by $\text{Au}(\text{I})\cdots\text{Au}(\text{I})$ interactions. The red shift may be due to the increase in nuclearity from pentanuclear to octadecanuclear and the shorter $\text{Au}\cdots\text{Au}$ distances observed in octadecanuclear clusters that narrow the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gap. The luminescent properties of the complexes were found to be different, and the pentanuclear clusters are nonemissive in solution. It is possible that the open structure and fluxionality of pentanuclear clusters allow their emission to be readily quenched by

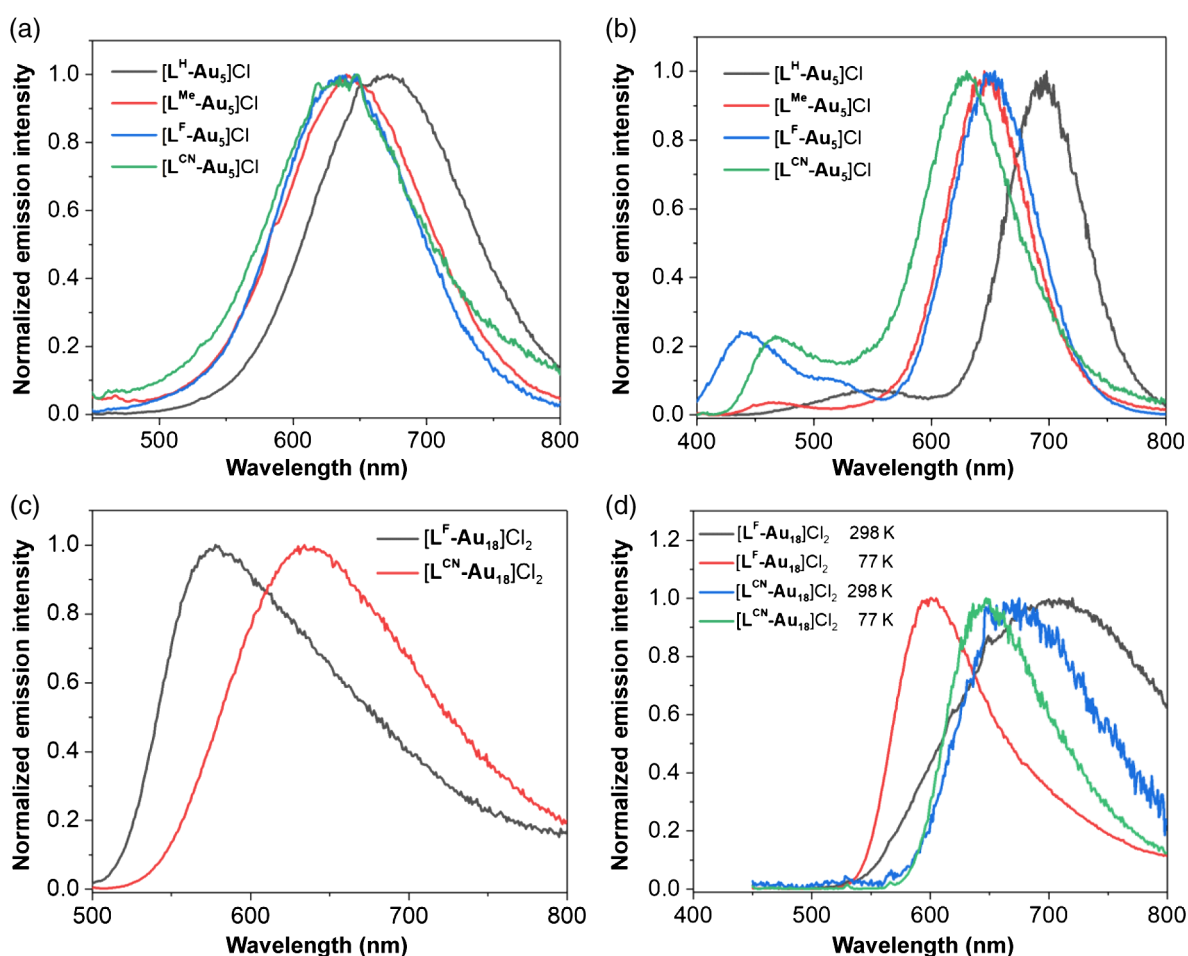


Figure 3 | Solid-state emission spectra of $[L^H-Au_5]Cl$, $[L^{Me}-Au_5]Cl$, $[L^F-Au_5]Cl$, and $[L^{CN}-Au_5]Cl$ (a) at room temperature and (b) low temperature (77 K). (c) Solution-state emission spectra of $[L^F-Au_{18}]Cl_2$ and $[L^{CN}-Au_{18}]Cl_2$ in dichloromethane. (d) Solid-state emission spectra of $[L^F-Au_{18}]Cl_2$ and $[L^{CN}-Au_{18}]Cl_2$ at room temperature and low temperature (77 K).

solvent and molecular motion. However, they emit red light in the solid state at ambient temperature with photoluminescence quantum yield (PLQY) up to around 10.8% (Figure 3a and Table 1), possibly attributable to the rigid environment exerted by the rigid ligands in the solid lattice. These pentanuclear clusters show a dual blue-green and orange-red luminescence in the solid state at 77 K (Figure 3b). In contrast, the octadecanuclear clusters not only are emissive in dichloromethane with PLQY of up to around 3.7% in solution (Figure 3c and Table 1), but also give an orange-red emission in the solid state at room temperature upon excitation with PLQY up to around 6.0% (Figure 3d and Table 1). The low-energy emission bands for these complexes near 570–710 nm can be assigned as arising from 3LMMCT excited-state origin or 3LMCT excited-state origin modified by metal...metal interactions, while the high-energy blue-green emission bands can be assigned as arising from the metal-perturbed ligand-centered phosphorescence, similar to that reported in previous studies.⁶⁵

Study of the transformation process

To better understand the mechanism of cluster-to-cluster transformation, the assembly process has been monitored by 1H , $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectroscopies in $CDCl_3$ -pyridine (10:1 v/v) (Figure 4). The signal of the proton (H_A) in the ligand backbone between the two phosphorus atoms has been monitored (Figure 4a). As shown in Figure 3b, the initial proton signal in the precursor $[L^F(AuCl)_2]$ occurs at around $\delta = 7.05$ ppm. Continuous bubbling of H_2S for around 5 min has led to the appearance of a new and broad signal around $\delta = 9.12$ ppm. Meanwhile, the disappearance of the ^{19}F and ^{31}P signals of the $[L^F(AuCl)_2]$ precursor and the appearance of the new signals of $[L^F-Au_5]Cl$ at around $\delta = -106.50$ and 30.50 ppm can unambiguously confirm the complete consumption of the precursor, giving only $[L^F-Au_5]Cl$ in solution (Figures 4d and 4c). As the reaction proceeded for approximately 30 min, another proton signal at $\delta = 9.83$ ppm attributed to the proton of

Table 1 | Photophysical Properties of Complexes

Complex	Media (T [K])	UV-vis λ_{\max} (nm) ($\epsilon \times 10^{-5}$ [dm ³ mol ⁻¹ cm ⁻¹])	Emission λ_{em} (nm)	Emission Quantum Yield (%) ^a
[L ^H -Au ₅]Cl	CH ₂ Cl ₂ (298)	287 sh (0.09)	— ^b	— ^b
	Solid (298)		668	~10.8
	Solid (77)		550, 695	
[L ^{Me} -Au ₅]Cl	CH ₂ Cl ₂ (298)	293 sh (0.17)	— ^b	— ^b
	Solid (298)		644	~7.4
	Solid (77)		465, 646	
[L ^F -Au ₅]Cl	CH ₂ Cl ₂ (298)	293 sh (0.13)	— ^b	— ^b
	Solid (298)		651	~7.7
	Solid (77)		440, 650	
[L ^{CN} -Au ₅]Cl	CH ₂ Cl ₂ (298)	289 sh (0.08)	— ^b	— ^b
	Solid (298)		633	~1.9
	Solid (77)		469, 629	
[L ^F -Au ₁₈]Cl ₂	CH ₂ Cl ₂ (298)	390 sh (0.16)	580	~2.0
	Solid (298)		705	~5.7
	Solid (77)		600	
[L ^{CN} -Au ₁₈]Cl ₂	CH ₂ Cl ₂ (298)	384 sh (0.22)	637	~3.7
	Solid (298)		670	~6.0
	Solid (77)		645	

^a Solution emission quantum yields were measured with reference to [Ru(bpy)₃]Cl₂ in H₂O.

^b No emission was detected for complexes in dichloromethane solution.

[L^F-Au₁₈]Cl₂ emerged. The formation of [L^F-Au₁₈]Cl₂ can also be observed in the ¹⁹F{¹H} and ³¹P{¹H} NMR spectra, such as a new signal at $\delta = 29.1$ ppm in the ³¹P{¹H} NMR spectra and a new signal at $\delta = -109.1$ ppm in the ¹⁹F{¹H} NMR spectra assigned to [L^F-Au₁₈]Cl₂ (Figures 4c and 4d). As the reaction proceeds, the colorless solution turns yellow (Figure 4e) and signals characteristics of [L^F-Au₅]Cl disappear; meanwhile that of [L^F-Au₁₈]Cl₂ are growing in intensity (Figures 4b–4d). Finally, after 2 h, only the signals of [L^F-Au₁₈]Cl₂ can be observed in solution, indicating the completion of the transformation process.^a Similarly, the cluster-to-cluster transformation process has also been confirmed by HR-ESI-MS (Supporting Information Figure S26). The control experiments involving the mixing of [L^F-Au₅]Cl with excess acetic acid or pyridine, respectively, do not lead to similar observations (Supporting Information Figures S27–S30). It is likely that the acid and base do not play a key role in cluster-to-cluster transformation. In addition, the S to Au atomic ratio in [L^F-Au₅]Cl was 1:2.5, which is smaller than 1:2.25 in [L^F-Au₁₈]Cl₂. It is suggested that the H₂S could provide the necessary S source of the reaction. Further control experiments involving the mixing of [L^F(AuCl)₂] with different ratios of Li₂S confirm the hypothesis (Supporting Information Figure S31). [L^F-Au₅]Cl was found to transform to [L^F-Au₁₈]Cl₂ with increasing ratios of Li₂S.

The Au₃S unit is the smallest building block in the gold(I) μ_3 -sulfido clusters. Given that the distance

between the two gold atoms in [L^F-Au₅]Cl is 5.03 Å, which is about twice the length of the Au–S bond (Figure 5a), it is rather conducive for [L^F-Au₅]Cl to be formed initially within the first 5 min. With time, [L^F-Au₅]Cl is transformed into [L^F-Au₁₈]Cl₂, which has a larger number of Au...Au contacts, as well as Au–S bonds, and relatively shorter Au...Au distances, providing [L^F-Au₁₈]Cl₂ its thermodynamic stability. The rearrangement of the diphosphine ligands has led to the reconfiguration of the cluster structures. It was found that the diphosphine ligands and two gold atoms lie nearly on the same plane in the single-crystal structure of [L^F-Au₅]Cl, indicating that the lone pairs on the two P atoms also lie on the same plane as the ligand (Figure 5b), with the distance of the two P atoms 5.53 Å apart, bringing the two gold atoms to a separation of 5.03 Å (Figure 5a); while in [L^F-Au₁₈]Cl₂, the separations of the two P atoms and the two gold atoms were 5.49 and 5.96 Å, respectively (Figure 5a). Compared with [L^F-Au₅]Cl, the distance between the two gold atoms in [L^F-Au₁₈]Cl₂ is 0.93 Å longer and the two gold atoms are deviated from the plane of the ligand (Figure 5). It is a result of the rotation of the C–P bond, which renders the lone pairs on the two P atoms pointing toward a direction out of the plane. Such rearrangement of the diphosphine ligands affects the initial weaker aurophilic interactions to maximize the gold(I)...gold(I) interactions with increasing reaction time, resulting in the transformation of the cluster from [L^F-Au₅]Cl to more stable [L^F-Au₁₈]Cl₂ units.

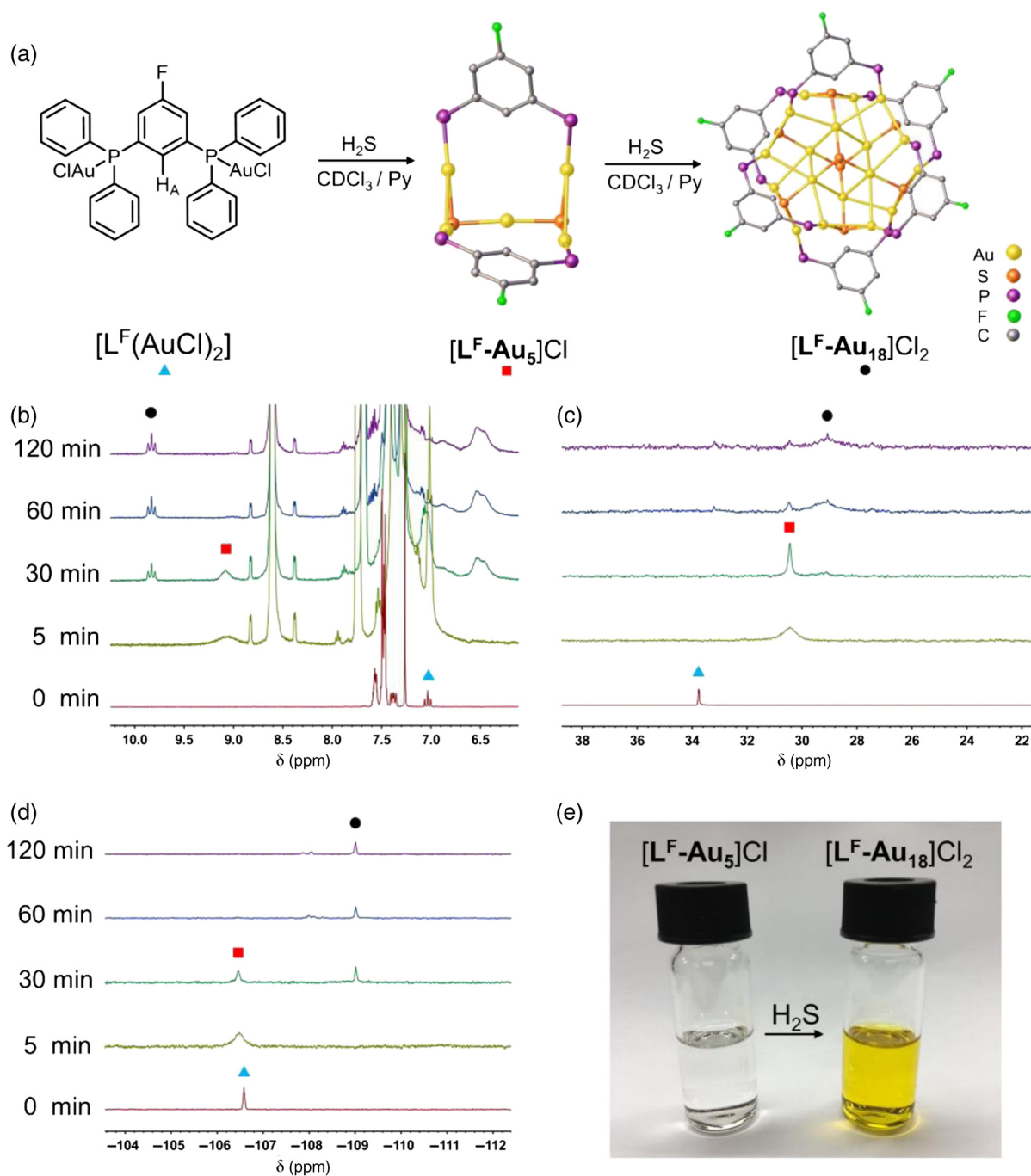


Figure 4 | (a) Self-assembly and transformation process of polynuclear gold(I) complexes (other ligands, counter-ions, and hydrogen atoms are omitted for clarity). (b) 1H NMR, (c) $^{31}P\{^1H\}$ NMR, and (d) $^{19}F\{^1H\}$ NMR spectral changes and (e) solution color changes in $CDCl_3$ during the assembly process (gray, C; green, F; purple, P; yellow, Au; orange, S).

However, similar transformation processes cannot be found in the other two Au_5 complexes ($[L^H-Au_5]Cl$ and $[L^{Me}-Au_5]Cl$) under the same conditions. It is suggested that the electron-withdrawing substituents (such as $-F$ and $-CN$) on the rigid skeleton of the diphosphine ligand may be a key factor in the cluster transformation. With reference to our previous works on gold(I)-phosphine complexes,^{66,67} it is likely that the more electron-

withdrawing substituent groups on the diphosphine ligands would lead to reduced electron densities at the gold(I) centers that induce a structural reorganization of the clusters ($[L^F-Au_{18}]Cl_2$ and $[L^{CN}-Au_{18}]Cl_2$) to compensate for the loss of electron density at the gold(I) centers through an increase in the number of $Au\cdots Au$ contacts as well as an enhancement of the $Au\cdots Au$ interactions. The reduction in electron density at the gold(I) centers by the

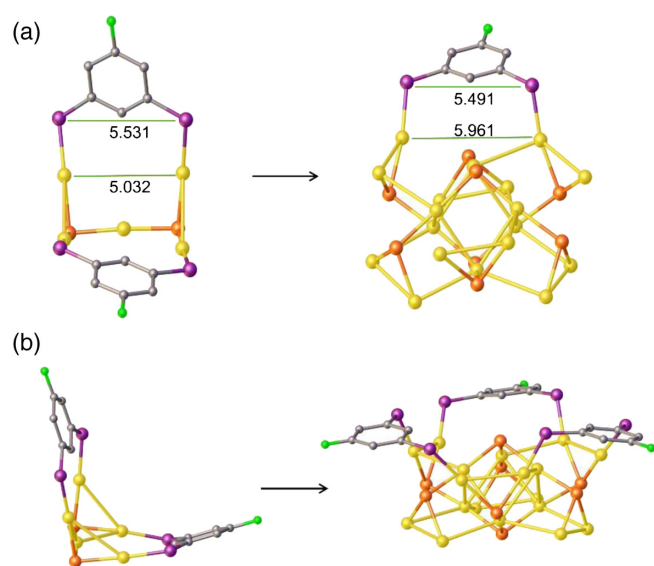


Figure 5 | (a) Bridging models and (b) side view of bridging models in the solid state; selected distances are shown. Other ligands, counteranions, and hydrogen atoms are omitted for clarity (gray, C; green, F; purple, P; yellow, Au; orange, S).

electron-withdrawing substituent groups on the diphosphine ligands has also been supported by density functional theory (DFT) calculations (Supporting Information Figures S32–S41).

Conclusions

An unprecedented cluster-to-cluster transformation from Au₅ to Au₁₈ is reported in this work. The self-assembly and transformation processes have been monitored by ¹H, ³¹P {¹H}, and ¹⁹F {¹H} NMR spectroscopies and revealed by single-crystal structural analysis combined with UV–vis absorption and emission spectroscopies. The subtle changes in the electron density on the gold(I) center have resulted in different reorganization abilities of the clusters. Such a significant conversion of the nuclearity of gold(I) clusters has resulted in different photophysical behaviors. This work has provided a new way of exploring cluster-to-cluster transformation, which can control structural reorganization by changing the electronic nature of the substituents of the ligand. Further work in our laboratory on modulating the structures of gold(I) clusters with various bridging ligands is in progress.

Footnote

^a Upon monitoring the transformation process, there are some signals in the ¹⁹F {¹H} and ³¹P {¹H} NMR spectra that cannot be identified. Attempts to identify the byproducts using HR-ESI-MS were not successful, probably due to the difficulty in the ionization of these unidentifiable species.

Supporting Information

Supporting Information is available and includes general, synthesis and characterization, X-ray crystallography, photophysical studies, computational details, and supplementary figures.

Conflict of Interest

There are no conflicts of interest to report.

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