Luminescence color switching of supramolecular assemblies of discrete molecular decanuclear gold(I) sulfido complexes

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A series of discrete decanuclear gold(I) μ₃-sulfido complexes with alkyl chains of various lengths on the aminodiphosphine ligands, [Au₁₀(Ph₂PNC₆H₄₂n₊₁)₃Ph₂PPh₂]₄(μ₃-S₄)(ClO₄)₂, has been synthesized and characterized. These complexes have been shown to form supramolecular nanoaggregate assemblies upon solvent modulation. The photoluminescence (PL) colors of the nanoaggregates can be switched from green to yellow to red by varying the solvent systems from which they are formed. The PL color variation was investigated and correlated with the nanostructured morphological transformation from the spherical shape to the cube as observed by transmission electron microscopy and scanning electron microscopy. Such variations in PL colors have not been observed in their analogous complexes with short alkyl chains, suggesting that the long alkyl chains would play a key role in governing the supramolecular nanoaggregate assembly and the emission properties of the decanuclear gold(I) sulfido complexes. The long hydrophobic alkyl chains are believed to induce the formation of supramolecular nanoaggregate assemblies with different morphologies and packing densities under different solvent systems, leading to a change in the extent of Au(I)–Au(I) interactions, rigidity, and emission properties.

Significance

Polynuclear gold(I) complexes have attracted enormous attention over the past decades owing to their intriguing luminescence behavior and their interesting structural and bonding properties, especially with regard to their propensity to form noncovalent short gold–gold contacts. Most works in polynuclear gold(I) clusters involve structural studies in the solid state, with less attention focused on supramolecular assembly in solution. Herein, discrete decanuclear gold(I) μ₃-sulfido complexes with long alkyl chains are found to form supramolecular assemblies with different luminescence and morphologies that are tunable by solvent modulation. This has demonstrated the importance of the control and manipulation of intercluster assembly in influencing the photophysical properties and morphologies of the clusters. Such findings have not been previously reported in discrete molecular gold(I) systems.


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Data deposition: The atomic coordinates and structure factors have been deposited in the Cambridge Structural Database, Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk/data_request/cif (CSD reference no. 964914).

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groups, can serve as building blocks for the construction of novel hierarchical nanostructured materials with environment-responsive properties, and it represents a rare example in which nanoaggregates have been assembled with the use of discrete molecular metal clusters as building blocks.

Results and Discussion

The syntheses and isolation of the discrete propeller-like decanuclear gold(I) μ₁-sulfido complexes, 1–4 (Fig. 1), were achieved by the reaction of the corresponding \[\text{Au}_2(\text{Ph}_2\text{PN(C}_3\text{H}_7)\text{PPh}_2)\text{Cl}_2\] with H₂S in a dichloromethane–methanol mixture at 50 °C to give the products in moderate yields.

The identity of complexes 1–4 has been confirmed by positive electrospray ionization (ESI) mass spectrometry, in which the ion cluster due to [M]\(^{2+}\) was observed. The \(^{31}\text{P}(\text{H})\) NMR spectra of the complexes in CDCl₃ at 298 K show a pair of doublets, indicating the presence of two different phosphorus environments. The structure of the decanuclear complex, 3, was revealed by X-ray crystal analysis. Fig. S1 depicts the perspective drawing of the complex cation of 3 with atomic numbering. The crystallographic determination data and the average bond lengths and distances are listed in Tables S1–S3. Similar to \([\text{Au}_{10}(\text{Ph}_2\text{PN(C}_3\text{H}_7)\text{PPh}_2)\text{Cl}_2]_4(\mu_3-\text{S})_4(\text{ClO}_4)_2\) (45), the complex cation possesses a propeller-like structure with four \([\text{Au}_2(\text{Ph}_2\text{PN(C}_3\text{H}_7)\text{PPh}_2)]^{2+}\) units, connected together by four μ₁ sulfides.

The two interstitial gold(I) atoms are arranged in the center with the S₄ symmetry axis passing through them. Intramolecular Au(I)–Au(I) contacts of 2.956 Å (11) to 3.329 Å were observed. The \(^{31}\text{P}(\text{H})\) NMR spectra of the complexes in CDCl₃ at 298 K show a pair of doublets, indicating the presence of two different phosphorus environments. The structure of the decanuclear complex, 3, was revealed by X-ray crystal analysis. Fig. S1 depicts the perspective drawing of the complex cation of 3 with atomic numbering. The crystallographic determination data and the average bond lengths and distances are listed in Tables S1–S3. Similar to \([\text{Au}_{10}(\text{Ph}_2\text{PN(C}_3\text{H}_7)\text{PPh}_2)\text{Cl}_2]_4(\mu_3-\text{S})_4(\text{ClO}_4)_2\) (45), the complex cation possesses a propeller-like structure with four \([\text{Au}_2(\text{Ph}_2\text{PN(C}_3\text{H}_7)\text{PPh}_2)]^{2+}\) units, connected together by four μ₁ sulfides.

Interestingly, the emission colors of complexes 1–4 are found to depend significantly on the solvent systems from which they are prepared. The solvent-induced emission changes of complex 3 are illustrated by the emission spectra (Fig. 2) with changing methanol–water content and the photographs (Fig. 2). Inset) taken under UV irradiation. It can be seen that the colors of the emission change from green to red with increasing methanol content. These clear solutions have been obtained by rapidly injecting the stock acetone solutions (1 × 10⁻³ M, 50 μL) of complex 3 into pure water or water–methanol mixture. It is likely that these clear solutions contain well dispersed nano-sized aggregates of the discrete gold(I) sulfido clusters (see below). Complex 3 in acetone (1 × 10⁻³ M) emits mainly at 514 nm; however, upon addition of water, a drastic enhancement of the green emission at 514 nm becomes apparent, and upon increasing the methanol content (15%, 25%, 38%, and 50%) in water, the emission at 514 nm shows a drop in intensity, with a concomitant increase in the intensity of a low-energy emission band at 650 nm. Similar emission spectral changes have also

![Fig. 1. Structures of complexes 1–4.](image1)

![Fig. 2. Emission spectra of 3 (1 mM) in 50 μL acetone upon addition of 2 mL of water (black) (photograph A), 13% methanol–water (red) (B), 25% methanol–water (green) (C), 38% methanol–water (blue) (D), and 50% methanol–water (cyan) (E). (Inset) Photographs showing the luminescence color changes under UV irradiation.](image2)

![Fig. 3. Emission spectra of the related \([\text{Au}_{10}(\text{Ph}_2\text{PN(C}_3\text{H}_7)\text{PPh}_2)\text{Cl}_2]_4(\mu_3-\text{S})_4(\text{ClO}_4)_2\) (1 mM) as control in 50 μL acetone upon addition of 2 mL of water (black) (photograph A), 13% methanol–water (red) (B), 25% methanol–water (green) (C), 38% methanol–water (blue) (D), and 50% methanol–water (magenta) (E). (Inset) Photographs showing the luminescence color changes under UV irradiation.](image3)
been observed for complexes 2 and 4 (Figs. S4 and S5), but not in complex 1 (Fig. S6) and the related \([\text{Au}_{10}(\text{Ph}_2\text{PN(C}_3\text{H}_7)\text{PPb}_2)_4(\text{H}_2\text{S})_4]^{2+}\text{ClO}_4_2\), which show consistently green emission in different solvent systems (Fig. 3), indicating that the long aliphatic alkyl chains are essential in governing the behavior. The differences in emission color are also not mainly due to solvatochromism, as the shifts of emission energies of the two bands from less polar solvent systems to more polar ones are minute, but rely on the changes in the relative intensities of the two emission bands in the green and orange-red region. The plot of the ratio of the low-energy band to the high-energy band \((I_{655}/I_{515})\) against different solvent composition is shown in Fig. 4. From the plot, the ratio does not show any obvious change with solvent composition in the gold(I) clusters with short C₈ alkyl chains, while significant changes are observed in the gold(I) clusters with long alkyl chains. Interestingly, less methanol is needed for the low-energy emission band to become saturated when the alkyl chain becomes longer. This plot clearly shows that the low-energy emission is alkyl chain length dependent. It is likely that the addition of the acetone solution of the complexes into nonsolvents would generate nanoaggregates of the discrete molecular complexes with long alkyl chains.

The formation of nanoaggregates in 2–4 has been confirmed by visible light scattering (Fig. 5) and dynamic light scattering (DLS) experiments (Fig. 6). In DLS experiments, different sizes of nanoaggregates have been recorded; with increasing methanol contents in water, the size of the nanoaggregates becomes larger, and this may arise from the slower precipitation and growth rate of the discrete molecular aggregates in the less polar solution mixture of MeOH–H₂O that would lead to larger-sized nanoaggregates than that in the very polar pure water.

To establish the identity of the aggregate species in the presence of methanol and methanol–water mixture, respectively, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to probe the morphological changes in various methanol–water compositions. Surprisingly, interesting morphological changes have been observed in the presence of various methanol–water compositions. The TEM images of 4 injected into 100% aqueous solutions showed spheres with diameters of about 70 nm (Fig. 7A). Upon the addition of methanol, the emission color turns red with the evolution of the shape of the nanoaggregates from sphere to cube of about 200 nm (Fig. 7B and C). The size increase also matches the results obtained from the DLS studies.

It is remarkable that the size of the nanoaggregates generated from the acetone–methanol–water mixture is found to be generally larger than those obtained from the acetone–water mixture, as revealed by DLS, TEM, and SEM experiments, and the aggregate patterns are also found to be different, indicating that they are packed in different ways.

The proposed packing patterns of the nanoaggregates of 2–4 under different conditions are illustrated in Fig. 8. In acetone–water mixture, the long hydrophobic alkyl chains of 2–4 might be contracted with hydrophobic–hydrophobic interactions and 2–4 are likely to be densely aggregated, such that the gold(I) core is distorted and the Au(I)–Au(I) distances are perturbed, in particular the interstitial ones, and/or the distortion of the excited states is restricted to a certain degree, resulting in the emission being dominated by the high-energy phosphorescence. However, it is likely that 2–4 are packed in a different way in the less polar acetone–methanol–water mixture. The condition might allow the long hydrophobic alkyl chains to be more extended and well dispersed, rendering 2–4 to be less strained and loosely packed such that intercluster interactions would also become possible. The close Au(I)–Au(I) contacts including the interstitial ones are probably retained, and/or the
distortion of the excited states is much less restricted, facilitating the low-energy emission.

The hypothesis is supported by the NMR spectroscopic studies, with the \(^{1}H\) NMR spectra of 4 under different solvent compositions shown in Fig. 9. In [D\(_{6}\)]-acetone, complex 4 shows a well-resolved \(^{1}H\) NMR spectrum, while the chemical shifts of the aromatic signals of the bis(diphosphino)amine ligand would show an upfield shift with broad and poorly resolved NMR signals in [D\(_{6}\)]-acetone-D\(_{2}\)O (1:1, vol/vol) mixture, indicating that the complex molecules would undergo self-assembly to form aggregate species in the acetone–water mixture. In contrast, the NMR signals become better resolved in [D\(_{6}\)]-acetone-D\(_{2}\)O-[D\(_{3}\)]-methanol (1:1:1, vol/vol) mixture, which may be ascribed to the different packing mode. In [D\(_{6}\)]-acetone-D\(_{2}\)O (1:1, vol/vol) mixture, the nanoaggregates would pack more densely, while the nanoaggregates in [D\(_{6}\)]-acetone-D\(_{2}\)O-[D\(_{3}\)]-methanol (1:1:1, vol/vol) mixture are packed more loosely. The denser nanoaggregates with hydrophobic–hydrophobic interactions will give rise to less well-resolved NMR signals. Furthermore, the variable-temperature \(^{1}H\) NMR spectra of 4 in [D\(_{6}\)]-acetone-D\(_{2}\)O (1:1, vol/vol) and [D\(_{6}\)]-acetone-D\(_{2}\)O-[D\(_{3}\)]-methanol (1:1:1, vol/vol) mixture have also been examined (Figs. S7 and S8). Upon increasing the temperature, the NMR signals become better resolved in [D\(_{6}\)]-acetone-D\(_{2}\)O (1:1, vol/vol) mixture. In contrast, less significant changes have been observed in [D\(_{6}\)]-acetone-D\(_{2}\)O-[D\(_{3}\)]-methanol (1:1:1, vol/vol) mixture. This indicates that the proposed hierarchical structures are perturbed thermally and the perturbation due to hydrophobic–hydrophobic interactions is more significant in the densely aggregated acetone–water mixture than the loosely aggregated acetone–water–methanol mixture. The hypothesis is also supported by the differences observed in the emission lifetimes of 4 obtained from 50% methanol–water (\(\tau_{\text{em}} = 490 \text{ nm}, \tau_{\text{o}} = 0.9 \mu\text{s}\) and from 100% water (\(\lambda_{\text{em}} = 700 \text{ nm}, \tau_{\text{o}} = 2.0 \mu\text{s}\)), resulting from a change in the microenvironment of the emissive gold(I) nanoaggregates.

In summary, a series of discrete molecular Au\(_{10}\) clusters with alkyl chains of different lengths on the amidophosphine ligands has been synthesized and demonstrated to show intercluster supramolecular nanoaggregate assembly to afford nanoaggregates of different emission colors and morphologies that are dependent on the alkyl chain lengths and the solvent environment. Correlation of the emission color to the morphological transformation has been made. The unique photophysical properties of this class of compounds should form the basis for the future design and development of luminescent nanomaterials and supramolecular assemblies.

Materials and Methods. Potassium tetrachloroaurate(III) (Strem), iron(II) sulfdide (FeS, Acros), and lithium perchlorate trihydrate (LiClO\(_{4}\), Strem) were purchased and used as received. Hydrogen sulfide (H\(_{2}\)S) was freshly generated by reaction of solid FeS with dilute HCl using the Kipp apparatus. Pyridine (Acros) was distilled over KOH and stored in the presence of KOH.

Physical Measurements and Instrumentation. Elemental analyses of the complexes were preformed on a Flash EA 1112 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences in Beijing. The electronic absorption spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission spectra were recorded on a Spex Fluorolog-3 Model FL3-211 fluorescence spectrophotometer with Corning filters. The degassed solutions for photophysical studies were deaerated on a high-vacuum line in a two-compartment cell consisting of a 10-cm\(^{2}\) round-bottomed flask equipped with a side-arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Solutions were rigorously degassed with less than four successive freeze–pump–thaw cycles. Luminescence lifetime measurements were performed using a conventional laser system. The excitation source was the 355-nm output (third harmonic) of a Spectra-Physics Quanta-Ray Q-switched GCR-150-10 pulsed Nd:YAG laser. Luminescence decay signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix Model TDS-620A (500 MHz, 2 GS/s) digital oscilloscope, and analyzed using a program for exponential fits on a PC computer. Dynamic light-scattering experiments were performed with a Malvern Zetasizer 3000HS. TEM experiments were performed on a Philips Tecnai G2 20 S-TWIN transmission electron microscope with an accelerating voltage of 200 kV. SEM experiments were performed on a Leo 1530 field emission gun (FEG) scanning electron microscope operating at 4.0–6.0 kV.
Synthetic Details. The synthesis and isolation of the discrete propeller-like decanuclear gold(I)μ₃-sulfido complexes, 1–4, were achieved by the reaction of the ligands [(Au₂{P(N(CH₃)₂)₃})₅(C₅H₅N)], [(Au₂{P(N(CH₃)₂)₃})₅(C₅H₅N)], [(Au₂{P(N(CH₃)₂)₃})₅(C₅H₅N)] with H₂S in a dichloromethane–ethanol–pyridine mixture at ca. 50 °C to give the product in moderate yield. Pyridine was used as a mild base to deprotonate H₂S, forming the pyridinium chloride, which is rather unreactive toward the soft gold(I) metal center. The preparation of related [Au₅{P(P(CH₃)₃)₃}]₄(μ₃-S)₄(μ₃-S)₄ has been reported previously (45). The details of the synthesis and characterization are given in SI Text.

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