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Synthesis, Structures, and Luminescence Properties of Interconvertible $Au^{I}_{2}Zn^{II}$ and $Au^{I}_{3}Zn^{II}$ Complexes with Mixed Bis(diphenylphosphino)methane and D-Penicillaminate

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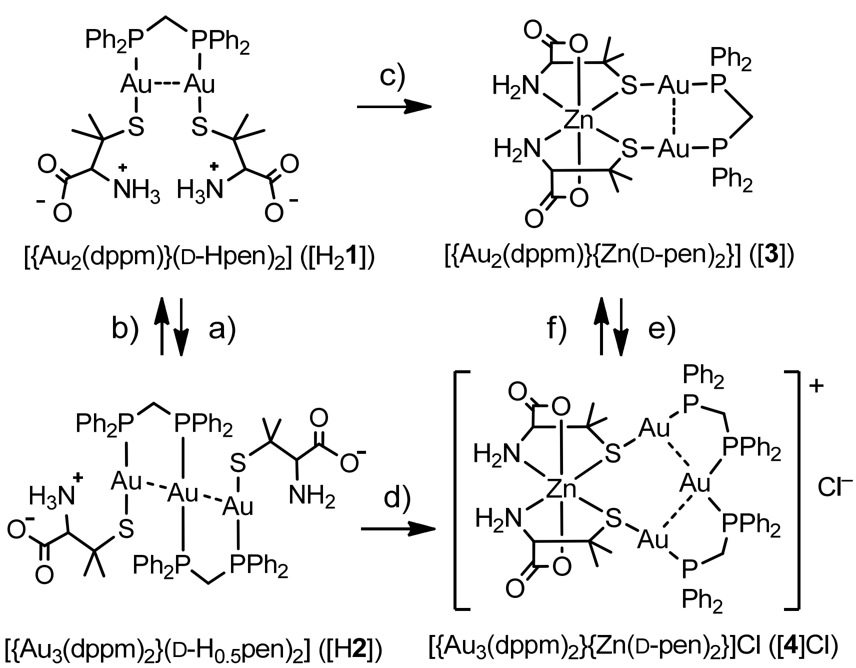
ABSTRACT: The reaction of the digold(I) complex, $[Au_2(dppm)(\text{D-pen})_2]^{2-}$ ($[\mathbf{1}]^{2-}$; dppm = bis(diphenylphosphino)methane and D-pen = D-penicillaminate), with Zn^{2+} in a 1:1 ratio gave the heterometallic $Au^I{}_2Zn^{II}$ trinuclear complex, $[Au_2Zn(dppm)(\text{D-pen})_2]$ ([**3**]), in which the Zn^{2+} ion is coordinated by $[\mathbf{1}]^{2-}$ in an $N_2O_2S_2$ octahedral geometry with the trans(O) configuration, forming an 8-membered $Au_2ZnS_2P_2C$ metalloring. A similar reaction using the newly prepared and crystallographically characterized trigold(I) complex, $[Au_3(dppm)_2(\text{D-pen})_2]^-$ ($[\mathbf{2}]^-$), produced a $Au^I{}_3Zn^{II}$ tetranuclear complex, $[Au_3Zn(dppm)_2(\text{D-pen})_2]^+$ ($[\mathbf{4}]^+$), in which the Zn^{2+} ion is coordinated by $[\mathbf{2}]^-$ in a similar octahedral geometry to form a $Au_3ZnS_2P_4C_2$ 12-membered metalloring. Complex [**3**] was converted to $[\mathbf{4}]^+$ by treatment with $[Au_2(dppm)_2]^{2+}$ in a 2:1 ratio, whereas $[\mathbf{4}]^+$ reverted to [**3**] upon treatment with a mixture of $[Au(\text{D-pen})_2]^{2-}$ and Zn^{2+} in a 1:1 ratio, indicative of the facile insertion/removal of the $[Au(dppm)]^+$ moiety with retention of the geometry of the *trans*(*O*)-$[Zn(\text{D-pen-}N,O,S)_2]^{2-}$ unit. An analogous interconversion that requires the insertion/removal of the $[Au(dppm)]^+$ moiety was also recognized between $[\mathbf{1}]^{2-}$ and $[\mathbf{2}]^-$. NMR spectroscopy revealed that $[\mathbf{4}]^+$ is in equilibrium with [**3**] and $[Au_2(dppm)_2]^{2+}$ in solution, the ratio of which is largely dependent on the solvent polarity. The luminescence properties of these complexes were also investigated, revealing the importance of the intramolecular aurophilic interaction, as well as the Zn^{II} coordination, for enhancement of the emission quantum efficiencies.

INTRODUCTION

In the past decade, molecular systems that contain two or more interconvertible structures have received increasing attention because of their potential applicability in molecular devices, actuators, and nanomachines.[1,2] Such molecular systems can be classified into two types on the basis of their operating principles: one type undergoes switching between two structural, conformational, or supramolecular isomers,[1] whereas the other type undergoes reversible structural expansion and contraction in the course of molecular assembling processes.[2] The former type of molecular systems has been considerably developed since the late 19th century, and many examples have been reported to date. These are relatively stable molecular systems supported by inert covalent bonds, and their molecular formulas remain unchanged before and after the conversion. In the latter type of systems, the molecular formulas and sizes can be altered, offering an advantage over the former in terms of control and switching of their functionalities. However, the structural expansion/contraction events require the facile, reversible reorganization of chemical bonds, and thus, this type of interconvertible molecular systems is relatively under-explored.[2,3] Almost all of the existing examples are limited to homometallic coordination systems with square-planar metal centers, of which $[Pd_3L_3]$ and $[Pd_4L_4]$ are representative examples that are composed of *cis*-protected $[Pd^{II}$(diamine or diphosphine)$]^{2+}$ units and polyimine bridging ligands (L).[2c,3]

In our ongoing studies on the rational construction of chiral heterometallic structures with thiol-containing amino acids,[4-9] we recently reported a digold(I) complex appended with dppm (bis(diphenylphosphino)methane) and D-pen (D-penicillaminate) ligands, $[Au_2(dppm)(D\text{-}pen)_2]^{2-}$ ($[\mathbf{1}]^{2-}$), that reacts with Ni^{2+} to form a $Au^{I}_2Ni^{II}$ trinuclear complex with an 8-membered metalloring, $[Au_2Ni(dppm)(D\text{-}pen)_2]$.[10] Notably, this $Au^{I}_2Ni^{II}$ trinuclear complex was interconvertible with a $Au^{I}_3Ni^{II}$ tetranuclear complex having a 12-membered metalloring, $[Au_3Ni(dppm)_2(D\text{-}pen)_2]^{+}$, accompanied by the insertion/removal of a $\{Au(dppm)\}^{+}$ moiety. Though gold(I) species with phosphine donors are often emissive, the $Au^{I}_2Ni^{II}$ and $Au^{I}_3Ni^{II}$ complexes were both non-emissive, presumably because of emission quenching through a lower-energy d-d transition state of the octahedral Ni^{II} center having a paramagnetic d^8 electronic configuration. Moreover, the paramagnetic nature of these complexes precluded evaluation of their structures in solution by means of NMR spectroscopic techniques. Thus, an analogous diamagnetic metalloring system, in which the octahedral Ni^{II} centers in $[Au_2Ni(dppm)(D\text{-}pen)_2]$ and $[Au_3Ni(dppm)_2(D\text{-}pen)_2]^{+}$ are replaced by Zn^{II} with a d^{10} configuration, was selected as the synthetic target. In this paper, we report the synthesis, characterization, and structural conversion of $[Au_2Zn(dppm)(D\text{-}pen)_2]$ ($[\mathbf{3}]$) and $[Au_3Zn(dppm)_2(D\text{-}pen)_2]^{+}$ ($[\mathbf{4}]^{+}$), along with those of their precursors, $[\mathbf{1}]^{2-}$ and $[Au_3(dppm)_2(D\text{-}pen)_2]^{-}$ ($[\mathbf{2}]^{-}$) (Scheme 1). The stability of $[\mathbf{3}]$ and $[\mathbf{4}]^{+}$ in solution, determined via ^{1}H and ^{31}P NMR spectroscopies, and their solid-state luminescence properties are also evaluated and compared with those of $[\mathbf{1}]^{2-}$ and $[\mathbf{2}]^{-}$ herein.



Scheme 1. Synthetic routes to [H_2**1**], [H**2**], [**3**], and [**4**]Cl. a) [$Au_2(dppm)_2]Cl_2$ (0.5 equiv) and NaOH (1 equiv). b) NH_4[Au(D-Hpen)$_2$] (1 equiv). c) $ZnCl_2$ (1 equiv) and NaOH (2 equiv). d) $ZnCl_2$ (1 equiv) and NaOH (1 equiv). e) [$Au_2(dppm)_2]Cl_2$ (0.5 equiv). f) NH_4[Au(D-Hpen)$_2$] (1 equiv), $ZnCl_2$ (1 equiv), and NaOH (4 equiv).

RESULTS AND DISCUSSION

Synthesis and characterization of [2]$^-$. The digold(I) complex, [Au_2(dppm)(D-Hpen)$_2$] ([H_2**1**]), which exhibits a methine and two methyl singlet signals due to D-pen at δ 3.57, 1.76, and 1.43 ppm in the ^1H NMR spectrum in methanol-d_4 (Figure 1a), was prepared from [Au_2Cl_2(dppm)] and D-H_2pen, according to the procedure described in a previous paper.[10] Complex [H**2**] was synthesized and isolated as pale yellow crystals by the reaction of the chlorido precursor, [$Au_3Cl_2(dppm)_2]^+$,[11] prepared *in situ* from [AuCl(tht)] (tht = tetrahydrothiophene) and dppm,[11,12] with D-H_2pen in a 1:2 ratio. A methine and two methyl singlet signals due to D-pen (δ 3.28, 1.32, and 1.17 ppm) are observed in the ^1H NMR spectrum of [H**2**] in methanol-d_4, in addition to broadened aromatic signals due to dppm (δ 7.9-7.1 ppm) (Figure 1b).[13] The integration ratio of these signals is 1:3:3:20, consistent with the presence of D-pen and dppm in a 1:1 ratio. The IR spectrum of [H**2**] shows a strong C=O stretching band at 1619 cm^{-1} corresponding to deprotonated carboxyl groups (Figure S2).[14] Based on these spectral features in conjunction with elemental analysis, [H**2**] is deduced to have a trigold(I) structure in [{$Au_3(dppm)_2$}(D-Hpen)(D-pen)], in which the amine group of one of the two D-pen ligands is protonated, rather than the carboxylate group.

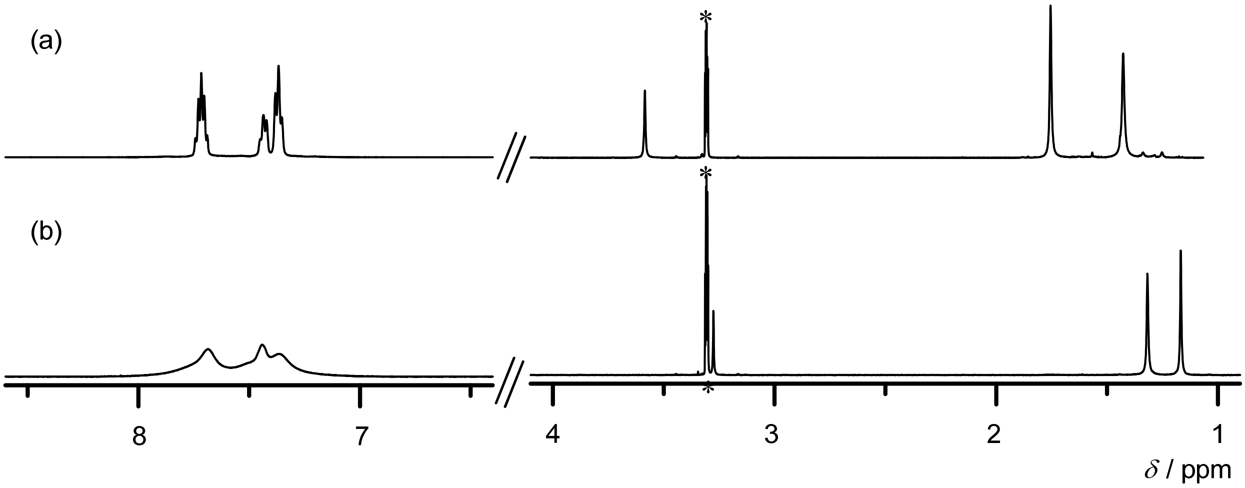


Figure 1. ^{1}H NMR spectra of (a) [H_2**1**] and (b) [H**2**] in methanol-d_4 at ambient temperature. (*) denotes the signals from solvents.

The structure of [H**2**] was established via single-crystal X-ray analysis, which revealed the presence of two crystallographically independent, yet nearly the same, trigold(I) complex molecules in the unit cell, in addition to several solvation water molecules (Figure 2). Each complex molecule contains three Au^I atoms that are linked by two dppm ligands to form a {$Au_3(dppm)_2$}$^{3+}$ core. The two terminal Au^I atoms in the {$Au_3(dppm)_2$}$^{3+}$ core are each bound by an S atom of D-pen, completing a non-linear trigold(I) structure (av. Au···Au···Au = 75.51(4)°), in which the terminal and the central Au^I ions forms Au···Au aurophilic interactions (av. Au···Au = 3.03(3) Å).[15] As a result, the two terminal Au^I atoms are situated in a linear P–Au–S geometry (av. Au–P = 2.273(12) Å, Au–S = 2.288(7) Å, P–Au–S = 176.8(6)°), whereas the central Au^I atom is located in a distorted P–Au–P linear geometry (av. Au–P = 2.318(7) Å, P–Au–P = 155.3(7)°). The overall arrangement in [H**2**] is very similar to that found in the

$\{Au_3(dppm)_2(D\text{-}pen)_2\}^-$ moiety in $[Au_3Ni(dppm)_2(D\text{-}pen)_2]^+$.[10] This implies that $[\mathbf{2}]^-$ serves as a hexadentate-N_2,O_2,S_2 metalloligand toward metal ion with retention of its trinuclear structure. Notably, the two complex molecules contact each other through D-pen amine groups (av. N···N = 2.82(10) Å), forming a dimeric unit. This is indicative of the presence of an $NH_3^+\cdots NH_2$ hydrogen bond,[16] although the proton between the two N atoms could not be detected via X-ray crystallography. Thus, it is concluded that [H**2**] has a neutral trigold(I) structure in $[Au_3(dppm)_2(D\text{-}Hpen)(D\text{-}pen)]$, consistent with the formula estimated from the spectroscopic and elemental analytical results.

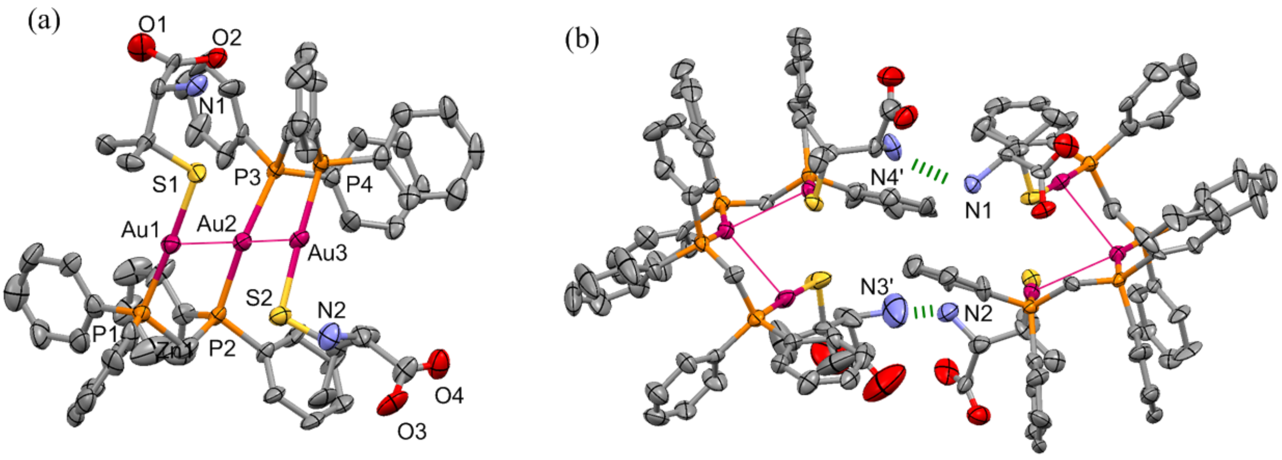


Figure 2. ORTEP drawings of (a) one of two crystallographically independent trigold(I) complex molecules of [H**2**] and (b) its dimeric structure. H atoms are omitted for clarity. Green dashed lines indicate the hydrogen bonding interactions. Symmetry code ('): x, 1+y, –1+z.

Synthesis and characterization of [3]. The coordination affinity of $[H_2\mathbf{1}]$ toward Zn^{2+} was evaluated by treating $[H_2\mathbf{1}]$ with 1 molar equiv of $ZnCl_2$ in ethanol, followed by the addition of NaOH. This reaction produced a colorless solution that yielded colorless crystals with a block-like morphology ([**3**]) in good yield (84%). Based on X-ray fluorescence analysis, it was found that [**3**] contains Au and Zn atoms in a 2:1 ratio; elemental analysis data were in agreement with the formula for a 1:1 adduct of $[\mathbf{1}]^{2-}$ and Zn^{2+}. The IR spectrum of [**3**] is essentially the same as that of $[Au_2Ni(dppm)(D\text{-}pen)_2]$ (Figure S2),[10] suggestive of the structural similarity between these complexes. Single-crystal X-ray structural analysis revealed that [**3**] is isomorphous with [Au_2Ni(dppm)(D-pen)$_2$],[10] and crystallized in a monoclinic system with a chiral space group, $P2_1$. There are two independent, yet nearly identical $Au^I_2Zn^{II}$ trinuclear complex molecules of [Au_2Zn(dppm)(D-pen)$_2$] in the asymmetric unit of [**3**], in which [**1**]$^{2-}$ chelates to the Zn^{II} atom in a hexadentate-N_2,O_2,S_2 mode, forming an 8-membered $Au_2ZnS_2P_2C$ metalloring (Figures 2 and S3). Of the three possible geometrical configurations (trans(N), trans(O), and trans(S)) for the [Zn(D-pen)$_2$]$^{2-}$ octahedral unit,[4b] [**3**] adopts the trans(O) configuration, as does the [Ni(D-pen)$_2$]$^{2-}$ octahedral unit in [Au_2Ni(dppm)(D-pen)$_2$].[10] However, the lengths of the bonds around the Zn^{II} atom in [**3**] (av. Zn–N = 2.13(2) Å, Zn–O = 2.14(2) Å, Zn–S = 2.514(13) Å) are slightly longer than those around the Ni^{II} atom in [Au_2Ni(dppm)(D-pen)$_2$] (av. Ni–N = 2.076(3) Å, Ni–O = 2.093(2) Å, Ni–S = 2.4267(8) Å). Furthermore, there is greater distortion of the bond angles surrounding the Zn^{II} atom in [**3**] (av. N–Zn–S = 172(3)°, O–Zn–O = 163.3(13)°) from an ideal octahedron compared with those about the Ni^{II} atom in [Au_2Ni(dppm)(D-pen)$_2$] (av. N–Ni–S = 175.54(8)°, O–Ni–O = 167.52(13)°); this is attributed to the weaker coordination of D-pen to the Zn^{II} center due to the lack of ligand field stabilization energy (LFSE) for an ion with d^{10} configuration. In [**3**], each of the two Au^I atoms is coordinated by P and S atoms in a slightly distorted linear geometry (av. Au–P = 2.269(5) Å, Au–S = 2.315(4) Å, P–Au–S = 174.5(15)°). The intramolecular Au···Au separation in [**3**] is 3.14(2) Å, which is indicative of the presence of an aurophilic interaction between the two Au^I atoms.[15] The two bridging S atoms in [**3**] have the *R* and the *S* chiral configurations such that the 8-membered metalloring adopts a twisted boat-like conformation, leading to the formation of an asymmetric $Au^I_2Zn^{II}$ structure. Notably, this is the first reported multinuclear complex containing both Au^I and Zn^{II} ions that are bridged by a chalcogen atom. In the crystal packing, complex molecules are connected to each other through CH···π interactions to construct a 2D layer structure in the *ac*-plane. The 2D layers are arranged in an antiparallel fashion such that the D-pen moieties are hydrogen-bonded with solvation water/ethanol molecules (Figure S4).

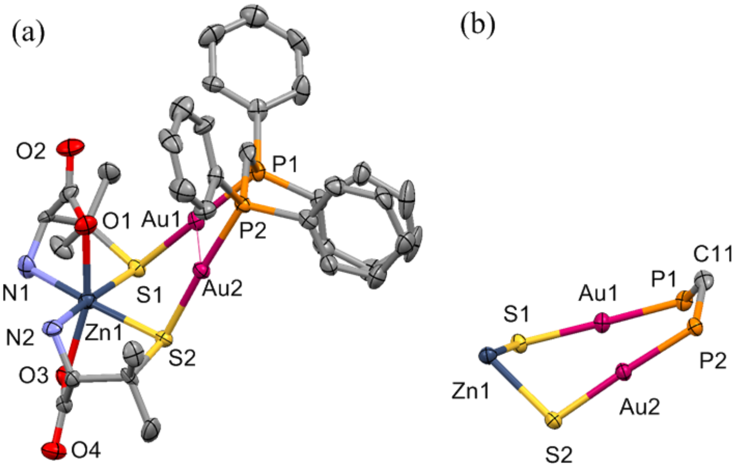


Figure 3. ORTEP drawings of (a) entire trinuclear complex molecule and (b) 8-membered metalloring structure in [**3**]. One of the two independent complex molecules is selected. H atoms are omitted for clarity.

Synthesis and characterization of [4]$^{+}$. Treatment of [H**2**] with 1 molar equiv of $\mathrm{ZnCl_2}$ in ethanol, followed by the addition of NaOH, produced colorless, needle-like crystals ([**4**]Cl) in good yield (85%). Based on X-ray fluorescence spectrometry, it was found that [**4**]Cl contains Au and Zn atoms in a 3:1 ratio, and its elemental analysis data were in agreement with the formula for a 1:1 adduct of [**2**]$^{-}$ and $\mathrm{Zn^{2+}}$. The IR spectrum of [**4**]Cl is essentially the same as that of $\mathrm{[Au_3Ni(dppm)_2(D\text{-}pen)_2]Cl}$ over the entire evaluated spectral region (Figure S2),[10] These results imply that [**2**]$^{-}$ coordinates to the $\mathrm{Zn^{2+}}$ ion with retention of its trigold(I) structure. Single-crystal X-ray analysis revealed that [**4**]Cl is isomorphous with $\mathrm{[Au_3Ni(dppm)_2(D\text{-}pen)_2]Cl}$,[10] and crystallized in the orthorhombic system in the chiral space group $P2_12_12$. The monocationic nature of the complex ion in this compound is indicated by the presence of complex ions and $\mathrm{Cl^{-}}$ ions in a 1:1 ratio. As shown in Figure 4, the complex cation [**4**]$^{+}$ has a $\mathrm{Au^{I}_{3}Zn^{II}}$ tetranuclear structure in $\mathrm{[Au_3Zn(dppm)_2(D\text{-}pen)_2]^{+}}$, in which [**2**]$^{-}$ chelates to the $\mathrm{Zn^{II}}$ ion in a hexadentate-$\mathrm{N_2,O_2,S_2}$ mode to form a skewed 12-membered $\mathrm{Au_3ZnS_2P_4C_2}$ metalloring. A C_2 axis passes through Zn1 and Au2 atoms, and thus only a half of the cation is asymmetric. The $\mathrm{Zn^{II}}$ atom in [**4**]$^{+}$ adopts a highly distorted octahedral geometry with the trans(O) configuration (Zn–N = 2.127(5) Å, Zn–

O = 2.112(4) Å, Zn–S = 2.5603(15) Å, N–Zn–S = 174.33(14)°, O–Zn–O = 165.8(2)°), similar to the Zn^{II} atom in [**3**]. The two symmetrically related Au^{I} atoms (Au1) are each coordinated by P and S atoms in an almost linear geometry (Au1–P = 2.2713(15) Å, Au1–S = 2.3183(14) Å, P–Au1–S = 174.99(5)°), whereas the central Au^{I} atom (Au2) is coordinated by two P atoms in a distorted linear geometry (Au2–P = 2.3357(13) Å, P–Au2–P = 162.53(7)°). The three Au^{I} atoms in [**4**]$^+$ are arranged in a non-linear fashion with a Au···Au···Au angle of 89.529(11)°. The distance between the terminal and the central Au^{I} atoms is 2.9929(3) Å, indicative of the presence of aurophilic interactions that are stronger than that in [**3**] with a Au···Au distance of 3.14(2) Å. These structural features of [**4**]$^+$ are comparable with those of [**2**]$^-$, and thus, it is deduced that [**2**]$^-$ functions as a hexadentate-$N_2O_2S_2$ metalloligand for Zn^{II} with retention of the trigold(I) structure. Both the bridging S atoms in [**4**]$^+$ adopt the *R* configuration, which is different from the *R* and *S* configurations adopted by the S atoms in [**3**]. No aggregation of the complex cations is observed in the crystal packing structure of [**4**]$^+$, unlike the case of [**3**] where aggregation of the complex molecules was observed. This is plausibly attributed to the cationic nature of [**4**]$^+$, which preferentially interacts with Cl^- anions through NH···Cl hydrogen bonds (Figure S5).

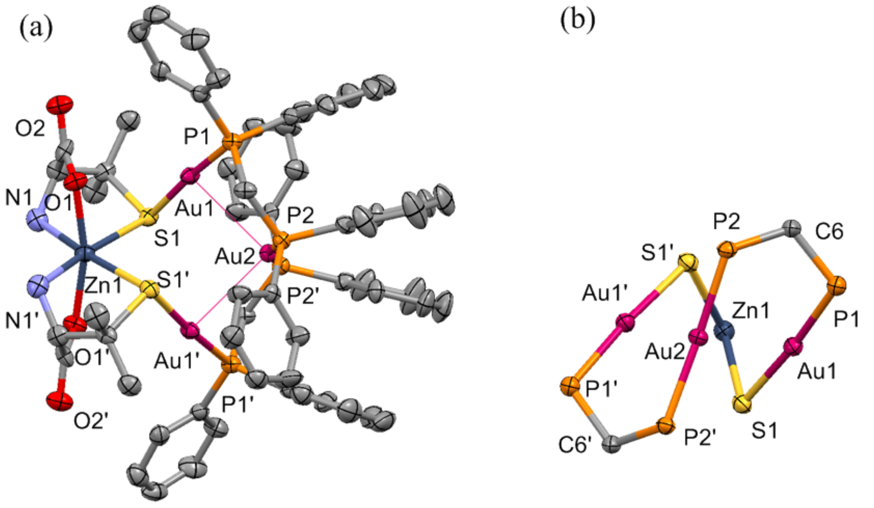


Figure 4. ORTEP drawings of (a) entire tetranuclear complex cation and (b) 12-membered metalloring structure in [**4**]Cl. H atoms are omitted for clarity.

Interconversion between [1]$^{2-}$ and [2]$^{-}$ and between [3] and [4]$^{+}$. Because it has been demonstrated that $[Au_2Ni(dppm)(\textsc{d}\text{-pen})_2]$ and $[Au_3Ni(dppm)_2(\textsc{d}\text{-pen})_2]Cl$ are interconvertible with each other, it was anticipated that a similar interconversion should occur in the metalloligand. Indeed, the 2:1 reaction of [H_2**1**] and $[Au_2(dppm)_2]Cl_2$ [17] in methanol-d_4 followed by addition of a base effected a change in the solution color from pale yellow to bright yellow. The ^1H NMR spectral features of the bright yellow reaction solution were essentially the same as that of [**2**]$^{-}$ (Figure S6a). On the other hand, the 1:1 reaction of [H**2**] and $NH_4[Au(\textsc{d}\text{-Hpen})_2]$ [18] in methanol-d_4 gave a pale yellow solution, the ^1H NMR spectral features of which were the same as those of [**1**]$^{2-}$ (Figure S6b). Thus, it is confirmed that [**1**]$^{2-}$ and [**2**]$^{-}$ are interconvertible with each other, accompanied by the insertion of a $\{Au(dppm)\}^+$ moiety in [**1**]$^{2-}$ and the removal of a $\{Au(dppm)\}^+$ moiety from [**2**]$^{-}$. The reactions are summarized in Equations 1 and 2.

$$[Au_2(dppm)(\textsc{d}\text{-pen})_2]^{2-} + 1/2[Au_2(dppm)_2]^{2+} \rightarrow [Au_3(dppm)_2(\textsc{d}\text{-pen})_2]^{-} \qquad (1)$$

$$[Au_3(dppm)_2(\textsc{d}\text{-pen})_2]^{-} + [Au(\textsc{d}\text{-pen})_2]^{3-} \rightarrow 2[Au_2(dppm)(\textsc{d}\text{-pen})_2]^{2-} \qquad (2)$$

Encouraged by the successful interconversion between [**1**]$^{2-}$ and [**2**]$^{-}$, we also investigated the possibility of interconversion between [**3**] and [**4**]$^{+}$. Based on the conversion reaction of [**1**]$^{2-}$ to [**2**]$^{-}$, [**3**] was allowed to react with 0.5 molar equiv of $[Au_2(dppm)_2]Cl_2$ in ethanol, which led to the isolation of colorless needle-like crystals of [**4**]Cl in good yield (79%). Conversely, colorless crystals of [**3**] were isolated in good yield when a pale yellow solution of [**4**]Cl in ethanol was treated with 1 molar equiv of $NH_4[Au(\textsc{d}\text{-Hpen})_2]$ and $ZnCl_2$, followed by addition of NaOH. Thus, [**3**] having an 8-membered metalloring is converted to [**4**]$^{+}$ having a 12-membered metalloring by the insertion of a $\{Au(dppm)\}^+$ moiety, whereas [**4**]$^{+}$ reverts to [**3**] by the removal of the $\{Au(dppm)\}^+$ moiety.[19] The overall reactions are summarized in Equations 3 and 4.

$$[Au_2Zn(dppm)(\textsc{d}\text{-pen})_2] + 1/2[Au_2(dppm)_2]^{2+} \rightarrow [Au_3Zn(dppm)_2(\textsc{d}\text{-pen})_2]^{+} \qquad (3)$$

$$[Au_3Zn(dppm)_2(\text{D-pen})_2]^{+} + [Au(\text{D-pen})_2]^{3-} + Zn^{2+} \rightarrow 2[Au_2Zn(dppm)(\text{D-pen})_2] \quad (4)$$

Stability of [3] and $[4]^{+}$ in solution. Complexes [**3**] and [**4**]Cl contain only closed-shell atoms and thus are diamagnetic in nature. This enabled investigation of their structures in solution via NMR spectroscopy. The ^{1}H NMR spectrum of [**3**] in methanol-d_4 shows three singlet signals at δ 3.40, 1.55, and 1.47, assignable to methine and two diastereotopic methyl groups of D-pen, in addition to aromatic multiplet signals due to the phenyl groups of dppm in the range δ 7.72–7.32 (Figure 5a). The NMR profile in conjunction with the 1:2 integration ratio of proton signals for dppm and D-pen ligands are compatible with the presence of a single species of [**3**] in solution. However, the appearance of only a single set of proton signals in the ^{1}HNMR spectrum is inconsistent with the asymmetric structure determined via X-ray crystallography. In addition, only a singlet signal is observed at δ 35.2 in the ^{31}P NMR spectrum of [**3**] (Figure S8). Based on these NMR spectral features, it is postulated that the facile inversion of the bridging S atoms in [**3**], which is fast on the NMR time scale, takes place in solution, rather than the presence of a single symmetrical isomer with *R*,*R* or *S*,*S* configurational S atoms.

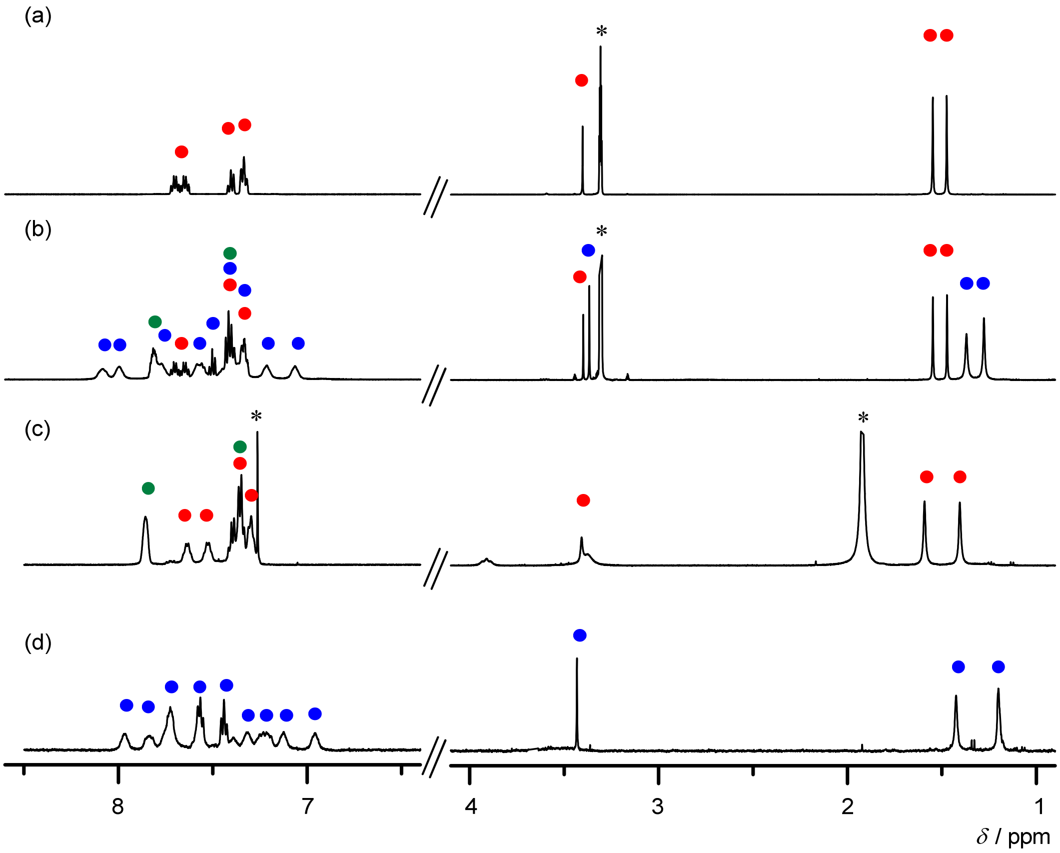
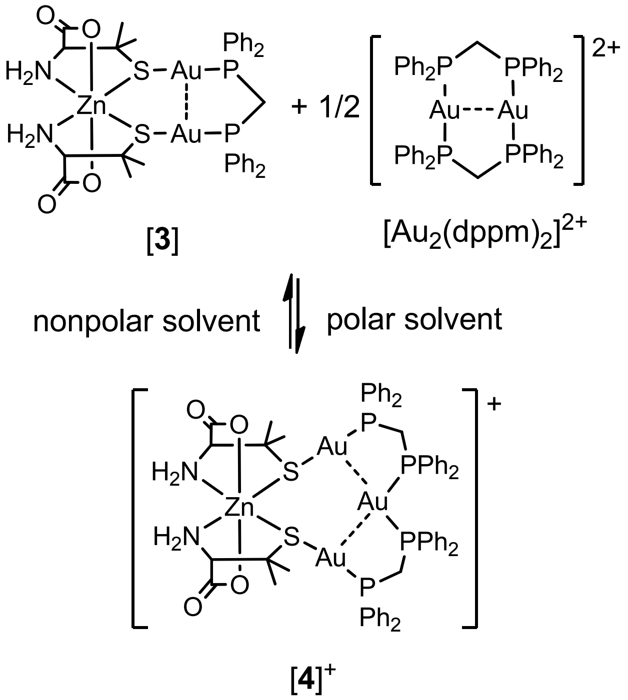


Figure 5. ^{1}H NMR spectra of (a) [**3**] and (b) [**4**]Cl in methanol-*d*$_4$, (c) [**4**]Cl in chloroform-*d*, and (d) [**4**]Cl in D$_2$O. Red, blue, and green circles indicate the signals from [**3**], [**4**]$^+$, and [Au$_2$(dppm)$_2$]Cl, respectively. (*) denotes the signals from solvents.

In comparison, the ^{1}H NMR spectrum of [**4**]Cl in methanol-*d*$_4$ is somewhat complicated, characterized by several proton signals due to [**3**] and [Au$_2$(dppm)$_2$]$^{2+}$, along with a single set of signals assignable to [**4**]$^+$ (Figure 5b). Based on the relative intensities of the D-pen methyl signals in the range of δ 1.2-1.6, it is estimated that [**4**]$^+$ and [**3**] co-exist in a 2:1 ratio. This implies that one third of [**4**]$^+$ is decomposed into [**3**] and [Au$_2$(dppm)$_2$]$^{2+}$ in this solvent. The ^{31}P NMR spectrum of [**4**]Cl in methanol-*d*$_4$ is characterized by two phosphorous signals due to [**3**] (δ 35.2) and [Au$_2$(dppm)$_2$]$^{2+}$ (δ 36.5), in addition to two signals due to [**4**]$^+$ (δ 37.5 and 35.8), which supports the decomposition of [**4**]$^+$ into [**3**] and [Au$_2$(dppm)$_2$]$^{2+}$ (Figure S8). Given that no significant NMR spectral changes were noticed in analyses over the course of a few days, it is considered that [**4**]$^+$ is in equilibrium with [**3**] and [Au$_2$(dppm)$_2$]$^{2+}$ in methanol-d_4 (Scheme 2).



Scheme 2. Equilibrium between [**3**] and [**4**]$^+$ in solution.

When [**4**]Cl was dissolved in D_2O, only a single set of signals for [**4**]$^+$ was detected in the ^{1}H and ^{31}P NMR spectra (Figures 5d and S8d). In contrast, no detectable signals of [**4**]$^+$ were observed in the ^{1}H and ^{31}P NMR spectra upon dissolution of [**4**]Cl in chloroform-*d*, and only signals due to [**3**] and [Au$_2$(dppm)$_2$]$^{2+}$ were observed in a 2:1 integration ratio (Figures 5c, S8c, and S9). Thus, the equilibrium between [**4**]$^+$, [**3**], and [Au$_2$(dppm)$_2$]$^{2+}$ is strongly dependent on the solvent employed. It is assumed that in a less polar solvent such as chloroform, the ionic species [**4**]$^+$ and Cl$^-$ are not stabilized via solvation and are converted into neutral species of [**3**] and [Au$_2$(dppm)$_2$Cl$_2$].[20] On the other hand, a polar solvent such as water can effectively stabilize ionic species, preventing the dissociation of [**4**]$^+$ into [**3**] and [Au$_2$(dppm)$_2$]$^{2+}$.

Luminescence properties. The excitation and emission spectra of solid samples of [H_2**1**], [H**2**], [**3**], and [**4**]Cl were acquired at ambient temperature as summarized in Table 1. [H_2**1**] and [H**2**] were almost non-emissive ($\Phi = 0.004$ for [H_2**1**] and $\Phi < 0.001$ for [H**2**]), whereas [**3**] and [**4**]Cl displayed yellow and green emission, respectively. The emission bands for [**3**] and [**4**]Cl were respectively centered at 546 nm and 522 nm with corresponding quantum yields of $\Phi = 0.033$ and $\Phi = 0.13$ (Figure 6). Because [H_2**1**] and [H**2**] are emissive at 77 K (Figure S10), it is assumed that immobilization of the two D-pen moieties respectively present in [**1**]$^{2-}$ and [**2**]$^{-}$ by chelation with the Zn^{II} ion prevents quenching of the emission, leading to the drastic increase in their quantum yields. The larger quantum yield for [**4**]Cl is compatible with its rigid Au$^{I}_{3}$Zn^{II} tetranuclear structure having two Au···Au contacts, which are shorter than the Au···Au contact found in the Au$^{I}_{2}$Zn^{II} trinuclear structure in [**3**]. The origin of the emission for these complexes is assigned to phosphorescence arising primarily from a ^{3}LMMCT (S → Au···Au) transition, similar to the assignment for related luminescent gold(I) species having both phosphine and thiolate ligands.[15b,21] Consistent with this assignment, the emission lifetimes of [**3**] (4.3, 0.54, and 0.049 μs) and [**4**]Cl (12, 2.9, and 0.61 μs) are on the order of microseconds (Table 1).[22]

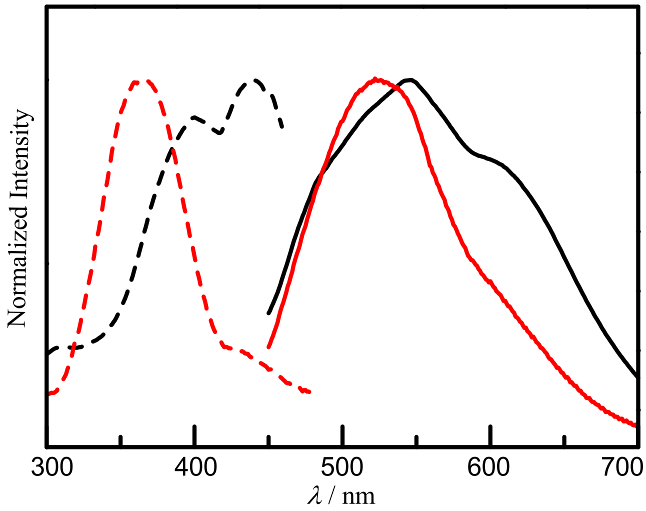


Figure 6. Emission (solid line) and excitation (dashed line) spectra of [**3**] (black) and [**4**]Cl (red) in the solid state.

CONCLUDING REMARKS

In this study, we showed that the digold(I) complex ([H$_2$**1**]) readily reacts with Zn^{2+} to produce the Au$^{I}_{2}$Zn^{II} trinuclear complex ([**3**]) with an 8-membered metalloring, which indicates the functionality of [H$_2$**1**] as a hexadentate-N$_2$,O$_2$,S$_2$ metalloligand to a Zn^{2+} ion on deprotonation. This was also the case for the trigold(I) complex ([H**2**]) that was newly prepared and structurally characterized, producing the Au$^{I}_{3}$Zn^{II} tetranuclear complex ([**4**]$^{+}$) with a 12-membered metalloring by the reaction with Zn^{2+}. It was evidenced that [**3**] and [**4**]$^{+}$, as well as [**1**]$^{2-}$ and [**2**]$^{-}$, are interconvertible to each other with the insertion/removal of a [Au(dppm)]$^{+}$ unit, as in the case of the analogous Au$^{I}_{2}$Ni^{II} and Au$^{I}_{3}$Ni^{II} complexes.[10] In addition, [**4**]$^{+}$ was found to be converted into [**3**] and [Au$_2$(dppm)$_2$]$^{2+}$ in solution, the degree of which is largely dependent on the solvent polarity. These results clearly indicate that not only Au-S bonds but also Au-P bonds are to be cleaved in solution in this system. Remarkably, [**3**] and [**4**]Cl were highly emissive in the solid state at ambient temperature, although [H$_2$**1**] and [H**2**] are almost non-emissive under the same conditions. In addition, the emission intensity, as well as the emission energy, is increased on going from [**3**] to [**4**], in parallel with the increase of Au···Au aurophilic interactions. Thus, the present study demonstrated the importance of the formation of Zn-S bonds and Au···Au contacts, for the emission enhancement of gold(I) complexes with mixed thiolate and phosphine donors. Finally, it should be noted that the interconvertible structures in [**3**] and [**4**]Cl, which show different emission colors and intensities, have a potential for switchable luminescent sensors and probes.[23] With this in mind, the exploration of other interconvertible coordination systems with mixed thiol-containing amino acid and diphosphine ligands, as well as the preparation of other heterometallic complexes derived from [H$_2$**1**] or [H**2**], are underway in our laboratory.

Experimental Section

Preparation of [Au$_3$(dppm)$_2$(D-Hpen)(D-pen)] ([H2]). To a colorless solution containing 1.00 g (1.30 mmol) of dppm in 25 mL of dichloromethane was added 0.63 g (1.95 mmol) of [AuCl(tht)] (tht = tetrahydrothiophene).[12] The mixture was stirred at room temperature in the dark, and 0.20 g (1.31

mmol) of D-H_2pen suspended in 8 mL of ethanol was added to the mixture. After additional 1 hour of stirring, 20 mL (2.0 mmol) of a 0.1 M NaOH ethanolic solution was added to the resulting pale yellow solution to give a yellow suspension. The yellow suspension was evaporated to dryness, and the resulting yellow residue was dissolved in 16 mL of methanol. After addition of 26 mL of water, the yellow solution was stood at room temperature for 5 weeks, which gave pale yellow crystals. Yield: 1.14 g (95%). Anal. Calcd for $[Au_3(dppm)_2(D\text{-}Hpen)(D\text{-}pen)]\cdot 10H_2O = C_{60}H_{83}N_2O_{14}P_4S_2Au_3$: C, 39.27; H, 4.56; N, 1.53%. Found: C, 39.05; H, 4.45; N, 1.56%. IR spectrum (cm^{-1}, KBr disk): 1619 (ν_{COO^-}), 1436 (ν_{Ph}), 1101 and 782-690 ($\nu_{P\text{-}Ph}$). ^1H NMR spectrum (ppm from TMS, methanol-d_4): δ 7.9-7.1 (broad, 40H), 3.28 (s, 2H), 1.32 (s, 6H), 1.17 (s, 6H). ^{31}P NMR spectrum (ppm from H_3PO_4, methanol-d_4): δ 34.5 (s).

Conversion from [$H_2$1] to [H2]. To a pale yellow solution containing 13 mg (11 μmol) of [H_2**1**]·$5H_2O$ in 0.6 mL of methanol-d_4 was added 7 mg (5 μmol) of $[Au_2(dppm)_2]Cl_2$,[17] which gave a bright yellow solution. The ^1H NMR spectrum of this solution was consistent with that of $[Au_3(dppm)_2(D\text{-}Hpen)(D\text{-}pen)]$ ([H**2**]) in methanol-d_4.

Complex [H**2**] was isolated from [H_2**1**] as follows. To a colorless solution containing 0.10 g (0.087 mmol) of [H_2**1**]·$5H_2O$ in 4 mL of methanol was added 0.06 g (0.05 mmol) of $[Au_2(dppm)_2]Cl_2$, followed by the addition of 0.9 mL (0.09 mmol) of a 0.1 M NaOH aqueous solution, which gave a bright yellow solution, by way of a pale yellow solution. After addition of 5 mL of water, the yellow solution was stood at room temperature for 3 days, which gave pale yellow crystals of [H**2**]·$10H_2O$. Yield: 0.10 g (63%).

Conversion from [H2] to [$H_2$1]. To a bright yellow solution containing 17 mg (9.0 μmol) of [H**2**]·$10H_2O$ in 0.6 mL of methanol-d_4 was added 5.5 mg (9.5 μmol) of $NH_4[Au(D\text{-}Hpen)_2]\cdot 3.5H_2O$,[18] which gave a pale yellow solution. The ^1H NMR spectrum of this solution was consistent with that of $[Au_2(dppm)(D\text{-}Hpen)_2]$ ([H_2**1**]) in methanol-d_4.

Preparation of [Au_2Zn(dppm)(D-pen)$_2$] ([3]). To a colorless solution containing 0.30 g (0.24 mmol) of [H_2**1**]·5H_2O in 10 mL of ethanol was added 2.6 mL (0.26 mmol) of a 0.1 M $ZnCl_2$ ethanolic solution and 5.2 mL (0.52 mmol) of a 0.1 M NaOH aqueous solution, which gave a colorless solution. After addition of 10 mL of water, the resulting solution was stood at room temperature for 5 weeks, which gave colorless block crystals. Yield: 0.27 g (84%). Anal. Calcd for [Au_2Zn(dppm)(D-pen)$_2$]·7H_2O = $C_{35}H_{54}N_2O_{11}P_2S_2ZnAu_2$: C, 33.25; H, 4.31; N, 2.22%. Found: C, 33.35; H, 4.24; N, 2.28%. IR spectrum (cm^{-1}, KBr disk): 1592 (ν_{COO^-}), 1436 (ν_{Ph}), 1101 and 776-691 ($\nu_{P\text{-}Ph}$). ^{1}H NMR spectrum (ppm from TMS, methanol-d_4): δ 7.72-7.63 (m, 8H), 7.40 (t, 4H), 7.35-7.32 (m, 8H), 4.21 (t, 0.1H), 3.40 (s, 2H), 1.55 (s, 6H), 1.47 (s, 6H). ^{31}P NMR spectrum (ppm from H_3PO_4, methanol-d_4): δ 35.2 (s).

Preparation of [Au_3Zn(dppm)$_2$(D-pen)$_2$]Cl ([4]Cl). To a yellow solution containing 0.30 g (0.16 mmol) of [H**2**]·10H_2O in 3 mL of ethanol were added 4 mL of water, 1.7 mL (0.17 mmol) of a 0.1 M $ZnCl_2$ ethanolic solution, and 1.6 mL (0.16 mmol) of a 0.1 M NaOH aqueous solution, which gave a pale yellow solution. The addition of 25 mL of water and 1.6 mL (82. mmol) of a 5 M NaCl aqueous solution to this solution gave a white suspension, which turned to an almost clear solution by adding 3 mL of ethanol. After 4 days, a small amount of a white powder was precipitated. The white powder was removed by filtration through Celite, and the filtrate was stood at room temperature in the dark. After 1 month, the resulting colorless needle-like crystals were collected by filtration. Yield: 0.28 g (85%). Anal. Calcd for [Au_3Zn(dppm)$_2$(D-pen)$_2$]Cl·14.5H_2O = $C_{60}H_{91}N_2O_{18.5}P_4S_2ClZnAu_3$: C, 35.74; H, 4.55; N, 1.39%. Found: C, 35.76; H, 4.66; N, 1.40%. IR spectrum (cm^{-1}, KBr disk): 1612 (ν_{COO^-}), 1436 (ν_{Ph}), 1102 and 784-691 ($\nu_{P\text{-}Ph}$). ^{1}H NMR spectrum (ppm from TMS, methanol-d_4): δ 8.09 (s, 4H), 7.99 (s, 4H), 7.83-7.31 (m, 42H), 7.21 (s, 4H), 7.06 (s, 4H), 3.40 (s, 0.8H), 3.37 (s, 2H), 1.55 (s, 2.5H), 1.47 (s, 2.5H), 1.37 (s, 6H), 1.27 (s, 6H). ^{31}P NMR spectrum (ppm from H_3PO_4, methanol-d_4): δ 37.5 (s, 1P), 36.5 (s, 0.4P), 35.8 (s, 1P), 35.2 (s, 0.4P).

Conversion from [3] to [4]Cl. To a colorless solution containing 0.10 g (0.08 mmol) of [**3**]·7H_2O in 3 mL of ethanol was added 0.05 g (0.04 mmol) of [Au_2(dppm)$_2$]Cl_2, which gave a pale yellow solution. The addition of 15 mL of water and 0.80 mL (4.0 mmol) of a 5 M NaCl aqueous solution gave a white suspension, which turned to an almost clear solution by adding 1 mL of ethanol. After filtration, the resulting solution was stood at room temperature in the dark. After 6 weeks, the resulting colorless needle-like crystals of [**4**]Cl were collected by filtration. Yield: 0.13 g (79%).

Conversion from [4]Cl to [3]. To a solution containing 0.050 g (0.025 mmol) of [**4**]Cl·14.5H_2O in 3 mL of ethanol were added 0.015 g (0.025 mmol) of $NH_4[Au(\text{D-Hpen})_2]\cdot 3.5H_2O$ and 1 mL of a 0.1 M ethanolic NaOH solution. After the mixture was stirred at room temperature for a few minutes, 0.25 mL (0.025 mmol) of a 0.1 M ethanolic $ZnCl_2$ solution was added to it. The colorless reaction solution was evaporated to dryness, and the white residue, which showed a ^{1}H NMR spectrum (methanol-*d*$_4$) essentially the same as that of [**3**], were recrystallized from 3 mL of ethanol/water (1:1) to give colorless crystals of [**3**]. Yield: 0.034 mg (54%).

Measurements. The ^{1}H and ^{31}P NMR spectra were measured on a JEOL ECA-500 NMR spectrometer at room temperature using tetramethylsilane (TMS, δ 0.0 ppm) as the internal standard for ^{1}H NMR and triphenyl phosphate (δ –17.6 ppm) as the external standard for ^{31}P NMR. The solid-state luminescence spectra were measured on a JASCO FP-6600 spectrometer at room temperature. The emission quantum yields (Φ) were measured with a lab-made absolute emission quantum yield measuring system using an integrating sphere (6 inch, Labsphere Inc.) of which the internal surface was coated with highly reflective Spectralon. A sample powder in a flat quartz cell (10mm diameter, 1mm height) placed at the bottom of the integrating sphere was excited with a monochromated light (355 – 365 nm) introduced from the top of the integrating sphere through a liquid light guide (deep UV model, Newport Co.). The emission from a detection exit of the integrating sphere was focused into a grating spectromator (Triax 1900, Jobin Yvon) equipped with a CCD image sensor (S7031, Hamamatsu). The absolute quantum yield of emission was calculated according to the method described in the literature.[24] The emission lifetimes were determined using the measuring system previously reported.[25] The sample was photoexcited using the third harmonic of a Q-switched Nd^{3+}:YAG laser (Continuum Surelite I-10, λ=355 nm). The observed decay profile of the emission intensity was fit to two or three exponential functions with convolution of the instrumental response function of the measuring system. The IR spectra were measured on a JASCO FT/IR-4100 spectrometer using KBr disks at room temperature. The elemental analyses (C, H, N) were performed at Osaka University. The X-ray fluorescence spectrometries were performed on a HORIBA MESA-500 spectrometer.

X-ray Structural Determinations. Single-crystal X-ray diffraction measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71075$ Å) at 200 K. The intensity data were collected by the ω scan technique with $2\theta_{\mathrm{max}} = 54.9°$ and were empirically corrected for absorption. The structure was solved by direct methods using SIR97 [25] or SHELXS-97 [26] and refined by fullmatrix least-squares techniques using SHELXL-97.[26]

For [H**2**]·10H$_2$O, two crystallographically independent complex-molecules existed in the asymmetric unit. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, except those of solvated water molecules and those on amine/ammonium nitrogen atoms. Phenyl groups were refined by using AFIX 66 constraints. Several non-hydrogen atoms were refined by using DELU restraints.

For [**3**]·7H$_2$O·0.5EtOH, two crystallographically independent complex-molecules existed. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, except those of solvated water molecules.

For [**4**]Cl·17H$_2$O, a half of the trinuclear complex-cation was crystallographically independent. The chloride anion and some of water molecules were disordered. All non-hydrogen atoms, except disordered O atoms, were refined anisotropically. Hydrogen atoms were included in calculated positions, except those of solvated water molecules.

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Supporting Information Available. X-ray crystallographic files in CIF format for the structures in this work, temperature dependent ^{1}H NMR spectra of [H**1**] (Figure S1), IR spectra of [H_2**1**], [H**2**], [**3**], and [**4**]Cl (Figure S2), two independent molecules of [**3**] (Figure S3), packing structures of [**3**] $\cdot 7H_2O \cdot 0.5EtOH$ and [**4**]Cl$\cdot 17H_2O$ (Figures S4 and S5), ^{1}H NMR spectra of interconversion reaction solution between [H_2**1**] and [H**2**] and between [**3**] and [**4**] (Figures S6 and S7), ^{31}P NMR spectra of [**3**] and [**4**]Cl (Figure S8), ^{1}H NMR spectrum of [**3**] in $CDCl_3$ (Figure S9), and emission and excitation spectra of [H_2**1**] and [H**2**] at 77 K (Figure S10). These materials are available free of charge via the Internet at http://pubs.acs.org.

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TABLES

Table 1. Luminescent properties of [H_2**1**], [H**2**], [**3**], and [**4**]Cl in the solid state.

complex	$\lambda_{max,em}$/nm^a (solid, r.t.)	Lifetime/μs^b (solid, r.t.)	Quantum yield, Φ^c
[H_2**1**]	546	0.024 (86%), 0.47 (11%), 3.4(3%)	0.004
[H**2**]	554	0.023 (91%), 0.32 (7%), 3.6(2%)	<0.001
[**3**]	546	0.049 (76%), 0.54 (27%), 4.3 (7%)	0.033
[**4**]Cl	522	0.61 (51%), 2.9 (36%), 12 (13%)	0.13

a The excitation wavelength was set to 400 nm. *b* Determined with excitation at 355 nm. A value in parenthesis denotes the fraction of each component in triple exponential decay. *c* Error ± 10%.

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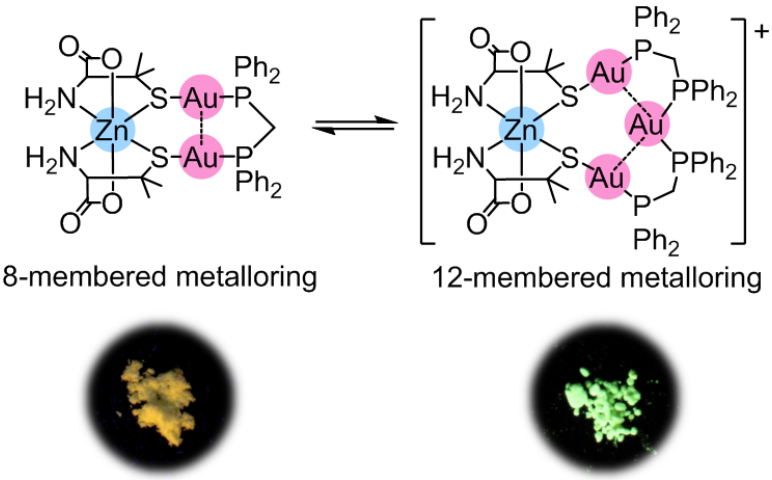

A trinuclear $Au^{I}_{2}Zn^{II}$ cyclic complex with an 8-membered metalloring structure, [$\{Au_2(dppm)\}\{Zn(D\text{-}pen)_2\}$] was reversibly expanded to the tetranuclear $Au^{I}_{3}Zn^{II}$ cyclic complex with a 12-membered metalloring structure, [$\{Au_3(dppm)_2\}\{Zn(D\text{-}pen)_2\}]^{+}$, by adding an $\{Au(dppm)\}^{+}$ unit. The Au^{I}-Zn^{II} complexes show photoluminescence with different color and brightness, by changing intramolecular aurophilic interactions.