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Author(s)	Yoshinari, Nobuto; Konno, Takumi
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Metallosupramolecular Structures Derived from a Series of Diphosphine-bridged Digold(I) Metalloligands with Terminal D-Penicillamine

Nobuto Yoshinari ^[a] and Takumi Konno ^{*[a]}

Abstract: In this report, we describe our recent work on the development of a new family of chiral heteroleptic digold(I) metalloligands with mixed diphosphine and D-penicillamine (D-pen), $[\text{Au}_2(\text{dppx})(\text{D-pen-S})_2]^{2-}$ (dppx = $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$, $n = 1-5$) and their application for the construction of chiral multinuclear and metallosupramolecular structures. The reactions of the metalloligands with 3d metal ions produce a variety of chiral heterobimetallic structures retaining the digold(I) metalloligand structure, ranging from discrete trinuclear to infinite helix structures that depend on the type of dppx. In addition, monophosphine and triphosphine analogues of the metalloligands were designed, and their coordination behavior is discussed to show the essential properties and potential extensibility of this class of metalloligands.

Takumi Konno received his B.Sc., M.Sc., and Dr. Sc. degrees from the University of Tsukuba (Japan). He continued his work there before moving to the University of Cincinnati in 1986. He became a research associate at the University of Tsukuba in 1987 and was promoted to lecturer in 1994. In 1997, he moved to Gunma University as an associate professor and was promoted to a full professor in 1998. He was appointed as a professor at Osaka University in 2000. He was selected as a project leader of CREST in 2013. His research interests are currently focused on the preparation and stereochemistry of a new class of multinuclear metal complexes and metallosupramolecules created through the use of sulfur-containing metalloligands.



Nobuto Yoshinari received his B.Sc. degree in 2005, M.Sc. degree in 2007, and Dr. Sc. degree in 2010 from Osaka University (Japan). During 2007-2010, he was a research fellow of the Young Scientists of Japan Society for the Promotion of Science (DC1). He started his academic career at the Department of Chemistry of Osaka University as an assistant professor in 2010. His research interests are focused on the rational creation of supramolecular assemblages of multinuclear metal clusters and the development of their unique stereochemical, photophysical, and dielectric functionalities.



[a] Dr. N. Yoshinari, Prof. T. Konno*
Department of Chemistry, Graduate School of Science,
Osaka University
Toyonaka, Osaka 560-0043, Japan
E-mail: konno@chem.sci.osaka-u.ac.jp

1. Introduction

In recent decades, heterometallic coordination compounds, which include more than one type of metal ion, and their supramolecular assemblages have been continuously explored in the fields of coordination chemistry and supramolecular chemistry. This exploration has mainly been motivated by their unique physical and chemical properties, which arise from the heterometallic cores, in addition to their structural beauty.^[1] In general, this class of heterometallic compounds has been prepared by a one-step self-assembly of well-designed organic ligands and a mixture of metal ions.^[2] However, this approach may result in the formation of undesired homometallic species, and the structures of the products are left to chance. To overcome these problems, a metalloligand approach, in which a pre-prepared homometallic complex with coordination donor sites (so-called metalloligand) is reacted stepwise with secondary metal ions, has recently become popular.^[3]

It has been recognized that a thiolate group (RS^-) coordinated to a metal center (M) possesses a relatively high nucleophilicity to form $\text{M}'\text{-S}$ bonds by reacting with thiophilic transition metal ions (M') (Figure 1).^[4,5] We focused on the reactivity of the coordinated thiolato group and began to employ thiolato metal complexes as metalloligands for the stepwise construction of S-bridged heterometallic multinuclear complexes in 1984.^[5-13] Currently, the metalloligand approach is being established for the rational construction of S-bridged heterometallic multinuclear complexes.^[4,14] A continuing challenge we face is the control of heterometallic structures by choosing reacting metal ions and reaction conditions appropriately without the use of finely designed organic ligands. Thus, we investigated the coordination ability of thiolate metal complexes derived from selected simple aliphatic aminothiols—2-aminoethanethiol (Haet),^[5,6] L-cysteine ($\text{L-H}_2\text{cys}$),^[7,8] and D-penicillamine ($\text{D-H}_2\text{pen}$)^[9-12] (Figure 2)—for constructing heterometallic multinuclear and metallosupramolecular products.

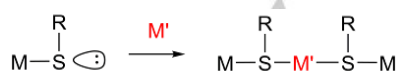


Figure 1. The reactivity of a thiolato metal complex (MSR) with M' ion.

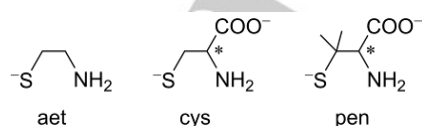


Figure 2. Three simple aliphatic aminothiols used in our research.

During these investigations, we found that a mononuclear gold(I) complex with D-pen, $[\text{Au}(\text{D-pen-S})_2]^{3-}$,^[15] in which a linear gold(I) ion is coordinated by two D-pen through S atoms, acts as a multidentate metalloligand using coordinated thiolato and non-coordinated amine and carboxylate groups to form a variety of heterometallic structures responding to the reacting metal ions

and reaction conditions.^[10,11] This result suggested that the monodentate-S coordination of the D-pen moiety is a key factor for the coordination versatility of the metalloligand. To expand the range of this chemistry, we recently designed a series of diphosphine-bridged digold(I) metalloligands, $[\text{Au}_2(\text{dppx})(\text{D-pen-S})_2]^{2-}$ ($[\mathbf{1}]^{2-}$ – $[\mathbf{5}]^{2-}$),^[16-19] by introducing a digold(I) unit with diphosphine as a linker in place of the Au^{I} atom in $[\text{Au}(\text{D-pen-S})_2]^{3-}$ ($\text{dppx} = \text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$; $n = 1-5$) (Figure 3).

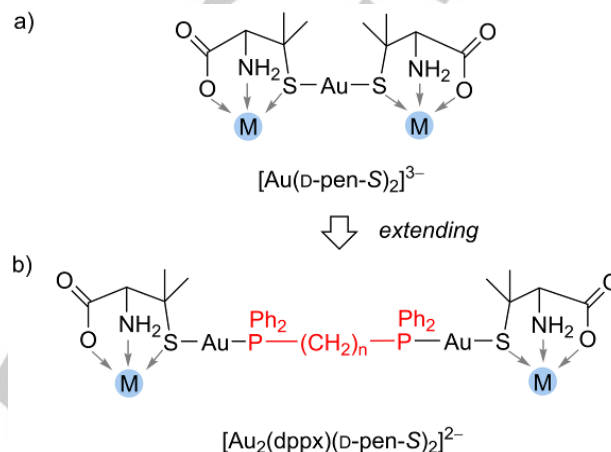


Figure 3. Coordination systems based on (a) $[\text{Au}(\text{D-pen-S})_2]^{3-}$ and (b) $[\text{Au}_2(\text{dppx})(\text{D-pen-S})_2]^{2-}$.

In this paper, we outline the background of gold(I) complexes with phosphine and thiolate ligands. Then, we review our recent work on the creation of chiral heterometallic multinuclear complexes based on $[\text{Au}_2(\text{dppx})(\text{D-pen-S})_2]^{2-}$ and their self-assembling behavior through non-covalent interactions.^[16-20] The coordination mode of $[\text{Au}_2(\text{dppx})(\text{D-pen-S})_2]^{2-}$ to second metal ions is categorized into three types: chelating, closed-bridging, and extended-bridging; these types will be discussed in terms of the alkyl chain length of the dppx linker (Figure 4). The coordination behavior of monophosphine and triphosphine analogues, $[\text{Au}(\text{PPh}_3)(\text{D-pen-S})]^-$ ($[\mathbf{6}]^-$)^[21] and $[\text{Au}_3(\text{tdme})(\text{D-pen-S})_3]^{3-}$ ($[\mathbf{7}]^{3-}$; $\text{tdme} = 1,1,1\text{-tris(diphenylphosphinomethyl)ethane}$),^[22] will also be reviewed.

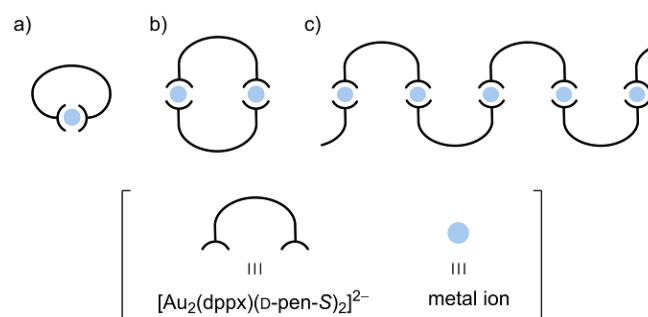


Figure 4. Three possible coordination modes of $[\text{Au}_2(\text{dppx})(\text{D-pen-S})_2]^{2-}$: (a) chelating, (b) closed-bridging, and (c) extended-bridging.

2. Diphosphine-bridged Digold(I) Metalloligands

2.1 Brief History of Gold(I) Complexes Possessing Both Phosphine and Thiolate Ligands.

Since the observation of anti-rheumatoid activity in Auranofine ([[(1-thio-β-D-glucopyranose-2,3,4,6-tetraacetato-S)-(triethylphosphine)gold(I)] ([8]; Figure 5) in 1972^[23] and its X-ray structural determination by Hill and co-workers in 1985,^[24] several hundred gold(I) complexes coordinated by both thiolates and phosphines have been prepared and structurally characterized to date.^[25,27–30] The early development of this class of materials was motivated by potential anti-rheumatoid and anti-tumor applications.^[26–28] In addition, the excellent photoluminescence properties of this class of materials were observed in the 1990s,^[29] thereby attracting additional researchers to exploring this class of compounds.^[30]

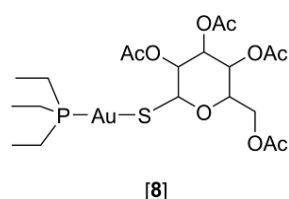


Figure 5. A drawing of Auranofine ([8]).

Most compounds in this class contain non-bridging thiolato groups. Therefore, they are expected to act as S-donating metalloligands, similar to other thiolato metal complexes. Indeed, several previous papers have reported the coordination behavior of this class of gold(I) complexes as an S-donating metalloligand.^[31–39] The reactivity of this class of gold(I) metal complexes for metal ions or metal units was initially established by Laguna and co-workers.^[31–34] They found that a dithiolate-bridged digold(I) metal complex, $[\text{Au}_2(\mu\text{-S-S})(\text{PPh}_3)_2]$ ([9]), readily reacts with the $[\text{Au}(\text{PPh}_3)]^+$ fragment to produce an S-bridged Au_3 complex $[\text{Au}_3(\mu\text{-S-S})(\text{PPh}_3)_3]\text{ClO}_4$ ([10] ClO_4) (S-S = 3,4-S₂C₆H₃CH₃) (Figure 6a).^[31] In [10]⁺, the digold(I) complex chelates to the additional Au^{I} center through two thiolato S atoms, with the formation of two $\text{Au}\cdots\text{Au}$ interactions of 2.96 Å. The chelating coordination mode of this class of metalloligands was also observed in the reaction with $[\text{M}(\text{cod})_2]^+$ (M = Ir^I, Rh^I; cod = 1,5-cyclooctadiene).^[32] Additionally, they reported that a diphosphine-bridged digold(I) complex with two terminal thiolate ligands, $[\text{Au}_2(\text{SC}_6\text{F}_5)_2(\mu\text{-dppf})]$ ([11]) (dppf = 1,1'-bis-(diphenylphosphino)ferrocene), readily reacts with a square-planar organogold(III) unit $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)]$ in dichloromethane to form S-bridged tetranuclear gold(I)-gold(III) complexes, $[\text{Au}_4(\text{SC}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_6(\mu\text{-dppf})]$ ([12]) (Figure 6b).^[33] Two neutral $\{\text{Au}(\text{C}_6\text{F}_5)_3\}$ units bind on each S atom of [12], which confirmed that complex [11] acts as an S-donating metalloligand with a bis(monodentate-S) coordination mode. The reactivity of [11] with d^{10} metal centers, such as Cu^I, Ag^I, Au^I, and Hg^{II}, has also been investigated.^[33] The luminescence quenching of an S–Au^I–

P-type metalloligand $[\text{Au}_2(\mu\text{-dppm})(2\text{-aminobenzenethiolate})_2]$ (dppm = Bis(diphenylphosphino)methane) by attaching an Au^{III} unit $[\text{Au}(\text{C}_6\text{F}_5)_3]$ on the S atoms was also reported.^[34] Additionally, a rare gold-chromium compound with Au–S–Cr bridging, $[\text{AuCr}(\text{CO})_5(\text{SPh})(\text{PPh}_3)]$, was also obtained from the reaction of $[\text{Au}(\text{PPh}_3)(\text{SPh})]$ with $[\text{Cr}(\text{CO})_5(\text{thf})]$ (thf = tetrahydrofuran).^[35]

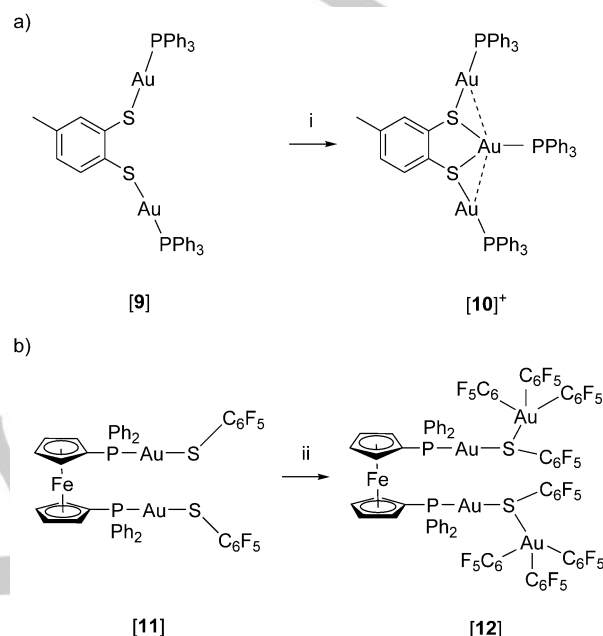


Figure 6. Coordination behavior of (a) $[\text{Au}_2(\mu\text{-S-S})(\text{PPh}_3)_2]$ ([9]) and (b) $[\text{Au}_2(\text{SC}_6\text{F}_5)_2(\mu\text{-dppf})]$ ([11]). (i): $[\text{Au}(\text{PPh}_3)(\text{ClO}_4)]$ in CH_2Cl_2 . (ii): $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)]$ in CH_2Cl_2 .

The introduction of donor groups other than coordinated thiolato group was also found to provide the resulting heterometallic structures with structural diversity and unique properties.^[36–39] Eisenberg and co-workers designed a linear-type mononuclear gold(I) complex with two uncoordinated pyridyl groups, $[\text{Au}(\text{Spy})(\text{PPh}_2\text{py})]$ ([13]) (Figure 7a).^[36] Through the metalation of S and N atoms by $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$, the monomeric [13] dimerized to a heterobimetallic complex $[\text{Au}_2\text{Cu}_2(\mu\text{-Spy})(\mu\text{-PPh}_2\text{py})](\text{PF}_6)_2$ ([14] $(\text{PF}_6)_2$) with increased luminescence relative to parental [13] in solution at 77 K because of the formation of strong $\text{Au}\cdots\text{Cu}$ interactions (2.63–2.64 Å). Gimeno and co-workers reported significantly enhanced photoluminescence in $\text{Au}^{\text{I}}\text{-Cu}^{\text{I}}$ and $\text{Au}^{\text{I}}\text{-Ag}^{\text{I}}$ heterometallic coordination systems derived from mononuclear gold(I) complexes with thiolate- and pyridylphosphine-type ligands.^[37] The introduction of carboxylate groups in the thiolate ligand has also been successful. The reaction of $[\text{Au}(\text{PPh}_3)(\text{Hcpa})]$ ([15]) (H_2cpa = 2-cyclopentylidene-2-sulfanylacetic acid) with $[\text{Ag}(\text{PPh}_3)(\text{NO}_3)]$ in the presence of base produced a dinuclear $\text{Au}^{\text{I}}\text{Ag}^{\text{I}}$ complex, $[\text{AgAu}(\text{PPh}_3)_2(\text{cpa})]$ ([16]), in which not only S but also carboxylate O atoms of the gold(I) complex coordinate to the silver center (Ag–S = 2.431(3) Å, Ag–O = 2.374(8) Å) (Figure 7b).^[38] Interestingly, when the pendant cyclopentyl group in cpa was replaced by aryl groups

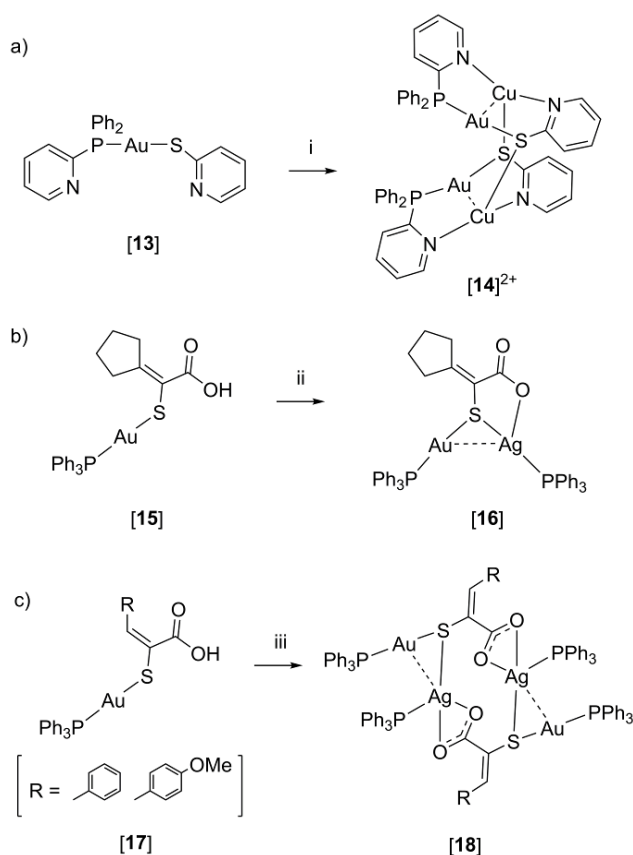


Figure 7. Coordination behavior of (a) $[\text{Au}_2(\text{SPy})(\text{PPh}_2\text{py})]$ (**[13]**), (b) $[\text{Au}(\text{Hcpa})(\text{PPh}_3)_2]$ (**[15]**), and $[\text{Au}(\text{Hxspa})(\text{PPh}_3)_2]$ (**[17]**). (i): $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ in CH_2Cl_2 , (ii): $[\text{Ag}(\text{PPh}_3)(\text{NO}_3)]$ in methanol, and (iii) $[\text{Ag}(\text{PPh}_3)(\text{NO}_3)]$ in methanol.

in $[\text{Au}(\text{PPh}_3)(\text{Hxspa})]$ (**[17]**), the coordination mode changed from S,O-chelating to S,O-bridging, producing a cyclic tetranuclear Ag_2Au_2 complex, $[\text{Ag}_2\text{Au}_2(\text{PPh}_3)_4(\text{xspa})_2]$ (**[18]**) ($\text{H}_2\text{xspa} = 3\text{-(aryl)-2-sulfanylpropenoic acids}$) (Figure 7c). Compound **[18]** shows high cytotoxicity against a cisplatin-resistant cancer cell line, *A2780cis*.^[39]

As briefly described above, this class of heteroleptic gold(I) complexes can generally act as S-donating metalloligands in the rational synthesis S-bridged hetero- and homo-metallic multinuclear structures. However, the following issues remain to be addressed in this class of compounds: (i) The examined second metal ions are typically limited to noble metals, such as Au^{I} , Au^{III} , Ag^{I} , Cu^{I} , and Ir^{I} . Therefore, the reactivity of this class of gold(I) complexes toward 3d metal ions has been poorly investigated. (ii) Only achiral thiolate and phosphine ligands were employed for the construction of heterometallic products previously, although several optically active gold(I) complexes have been reported.^[24,40] (iii) Finally, the supramolecular structures of the heterometallic products have not been thoroughly discussed, although this class of compounds is highly expected to show a variety of intermolecular supramolecular interactions, such as aurophilic interactions,^[41] $\pi \cdots \pi/\text{CH} \cdots \pi$

interactions between phosphine ligands, and hydrogen bonds based on the heterometallic and heteroleptic structures.

2.2 Design of Diphosphine-bridged Digold(I) Metalloligands.

As mentioned in the introduction, we recently reported that the mononuclear gold(I) complex with D-pen, $[\text{Au}(\text{D-pen-S})_2]^{3-}$, can act as a chiral multidentate metalloligand for transition metal ions using coordinated thiolato and non-coordinated amine and carboxylate groups. Interestingly, $[\text{Au}(\text{D-pen-S})_2]^{3-}$ changes its coordination mode when responding to the reacting metal ions and reaction conditions.^[10,11] To date, a total of four types of coordination modes have been identified for $[\text{Au}(\text{D-pen-S})_2]^{3-}$: (i) bis(monodentate-S) mode in $[\text{Ag}_2\{\text{Au}(\text{D-pen})_2\}_2]^{4-}$,^[11a] (ii) bis(bidentate-N,S) mode in $[\text{Co}_2\{\text{Au}(\text{D-pen})_2\}_3]^{3-}$,^[11e] $[\text{M}_2\{\text{Au}(\text{D-pen})_2\}_2]^{2-}$ ($\text{M} = \text{Ni}^{\text{II}}$, Pd^{II} , Pt^{II}),^[11b,11c,11d] and $[\text{Ni}_2\{\text{Au}(\text{D-pen})_2\}_3]^{5-}$,^[11b] (iii) bis(bidentate-O,S) mode in $[\text{Ni}_2\{\text{Au}(\text{D-pen})_2\}_2]^{4+}$,^[11b] and (iv) bis(tridentate-N,O,S) mode in $[\text{Ni}_2\{\text{Au}(\text{D-pen})_2\}_2]^{2-}$ ^[11b] and $[\text{Co}_3\{\text{Au}(\text{D-pen})_2\}_3]$.^[11e] However, all four coordination modes are bridging-type and produce discrete cyclic structures. This is probably because of the rigid linear geometry of the gold(I) ion, which fixes the orientation of the D-pen moieties on opposite sides. To overcome these limitations, we newly designed a series of linear digold(I) metalloligands, $[\text{Au}_2(\text{dppm})(\text{D-Hpen-S})_2]$ (**[H₂1]**), $[\text{Au}_2(\text{dppe})(\text{D-Hpen-S})_2]$ (**[H₂2]**), $[\text{Au}_2(\text{dppp})(\text{D-Hpen-S})_2]$ (**[H₂3]**), $[\text{Au}_2(\text{dppb})(\text{D-Hpen-S})_2]$ (**[H₂4]**), and $[\text{Au}_2(\text{dpppe})(\text{D-Hpen-S})_2]$ (**[H₂5]**) ($\text{dppx} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$; $n = 1$ (dppm), 2 (dppe), 3 (dppp), 4 (dppb), 5 (dpppe)) (Figure 8). In these metalloligands, two-terminal $\{\text{Au}(\text{D-pen-S})\}^-$ coordination arms are linked by bis(diphenylphosphino)alkane (dppx) through Au–P bonds. This new family of metalloligands possesses (i) directional flexibility because of the presence of an alkyl backbone that spans two gold(I) ions, (ii) both hydrophilic and hydrophobic characteristics because of the presence of amino and carboxylate groups and phenyl groups, (iii) coordination ability toward transition metal ions through two terminal D-pen moieties, and (iv) optical activity on the S-configurational D-pen moieties.

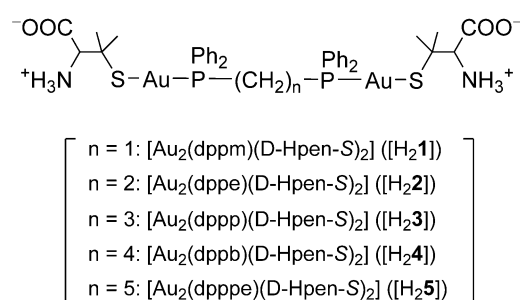


Figure 8. A series of diphosphine-bridged digold(I) metalloligands, $[\text{Au}_2(\text{dppx})(\text{D-Hpen-S})_2]$.

2.3 Synthesis, Molecular Structure, and Reactivity of Dppx-bridged Gold(I) Complexes with D-Pen.

The optically active diphosphine-bridged digold(I) metalloligands $[H_21]$ – $[H_25]$ are prepared from chloridogold(I) diphosphine precursors— $[Au_2(dppm)Cl_2]$,^[42] $[Au_2(dppe)Cl_2]$,^[43] $[Au_2(dppp)Cl_2]$,^[44] $[Au_2(dppb)Cl_2]$,^[45] and $[Au_2(dpppe)Cl_2]$ ^[45]—by treating two equivalents of D-Hpen in the presence of a base. They are isolated as a neutral form of $[Au_2(dppx)(D-Hpen-S)_2]$, in which two terminal D-pen ligands are partially protonated to create D-Hpen. The C=O stretching bands of $[H_21]$ – $[H_25]$ in the infrared spectra appear at approximately 1625 – 1628 cm^{-1} , which is typical for zwitterionic amino acids ($NH_3^+-R-COO^-$) (1620 – 1630 cm^{-1}) but not un-ionized ones ($NH_2-R-COOH$) (1700 – 1730 cm^{-1}).^[46] Thus, D-Hpen[−] in $[H_21]$ – $[H_25]$ is assumed to exist in a zwitterionic form with protonated amine and deprotonated carboxyl groups, such as free D-Hpen[−]^[47] and $NH_4[Au(D-Hpen-S)_2]$.^[15]

Three of the five metalloligands ($[H_22]$, $[H_23]$, $[H_24]$) were characterized by single-crystal X-ray crystallography (Figure 9). Each Au^I atom has an almost linear geometry (av. S–Au–P = 172.9° ($[H_22]$), 175.1° ($[H_23]$), 174.1° ($[H_24]$)), coordinated by a P atom from dppx and an S atom from D-Hpen[−]. Because there is no intramolecular contact between two Au^I atoms in these complexes, the digold(I) molecules are connected to one another through intermolecular auropophilic interactions (av. Au⋯Au = 3.13 Å ($[H_22]$), 3.08 Å ($[H_23]$), 3.20 Å ($[H_24]$)), resulting in 1D polymeric structures. Because of the auropophilic interactions, the complexes exhibit photoluminescence at room

temperature in the solid state. Focusing on the conformation of the alkyl chain backbone of $[H_22]$ – $[H_24]$, they clearly adopt a thermodynamically stable all-trans conformation with gauche C–P lines. This leads to the difference in the orientations of the two-terminal $\{Au(D-Hpen-S)\}$ coordination arms among $[H_22]$ – $[H_24]$, depending on the odd or even number of their methylene groups. That is, $[H_22]$ and $[H_24]$, which contain two and four methylene groups, respectively, adopt anti-orientation with respect to the two-terminal D-pen moieties, whereas $[H_23]$, which contains three methylene groups, exhibits syn-orientation. Molecular modeling studies revealed that this correlation between the parity (odd vs. even) of the alkyl chains and the orientation (syn vs. anti) of the two D-Hpen moieties is applicable to the shortest $[H_21]$ and the longest $[H_25]$. The ‘odd-even rule’ in the molecular conformation of the metalloligands is strongly related to the difference in their coordination modes and the resulting molecular/metalloligand structures, as will be described in the following chapters.

In 1994, Lin and co-workers reported that a trigold(I) complex cation bridged by a two-dppm linker, $[Au_3(dppm)_2Cl_2]Cl$, equilibrates with a mixture of $[Au_2(dppm)Cl_2]$ and $[Au_2(dppm)_2Cl_2]$ in solution.^[48] This is suggestive of the structural expansion of $\{Au_2(dppm)\}^{2+}$ species to $\{Au_3(dppm)\}^{3+}$ species by reacting with $[Au_2(dppm)_2Cl_2]$. Indeed, we have demonstrated that the 2:1 reaction of dppm-bridged digold(I) metalloligand $[H_21]$ with $[Au_2(dppm)_2Cl_2]$ in methanol yielded a trigold(I) complex, $[Au_3(dppm)_2(D-Hpen-S)(D-Hpen-S)]$ ($[H19]$), the molecular structure of which was confirmed by X-ray analysis (Figure 10a).^[17] In $[H19]$, a 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 nonlinear trigold(I) structure (av. Au⋯Au⋯Au = $75.51(4)^\circ$), in which the terminal and central Au^I ions form auropophilic interactions (av. Au⋯Au = $3.03(3)\text{ Å}$). In contrast, the trigold(I) complex $[H19]$ reverts back to $[H_21]$ through the 1:1 reaction of $[H19]$ and $NH_4[Au(D-Hpen-S)_2]$ in methanol in the presence of a base. Thus, it is confirmed that $[H_21]$ and $[H19]$ are interconvertible with each other, accompanied by the insertion of a $\{Au(dppm)\}^+$ moiety in $[H_21]$ and the removal of a $\{Au(dppm)\}^+$ moiety from $[H19]$. These reactions are summarized in Figure 10b.

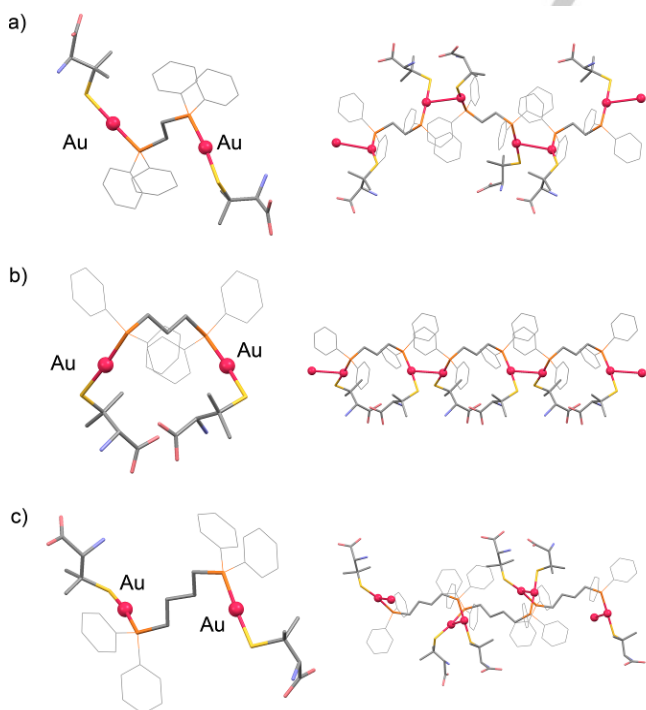


Figure 9. (left) Molecular structures and (right) 1D chain structures in (a) $[H_22]$, (b) $[H_23]$, and (c) $[H_24]$.

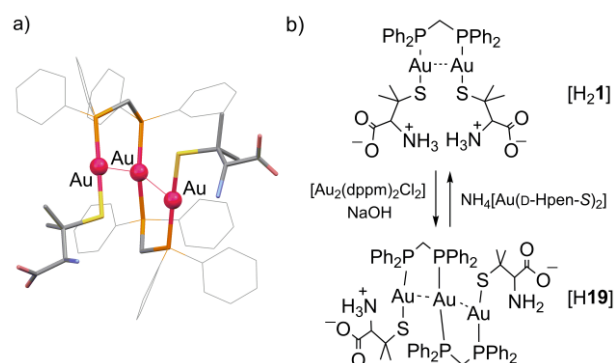


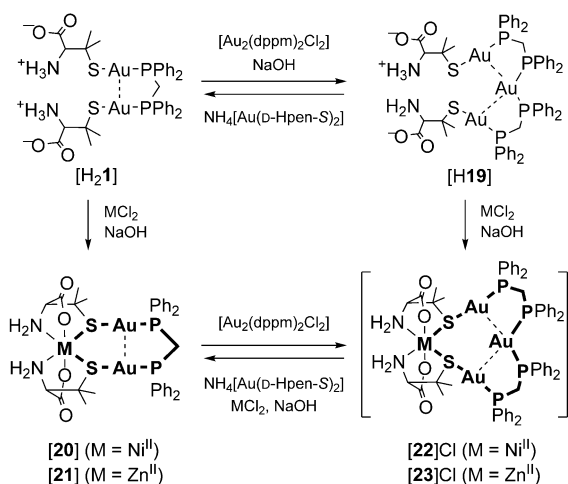
Figure 10. a) Molecular structure of $[H19]$ and b) interconversion between $[H_21]$ and $[H19]$.

Our attempts at the structural expansion of [H₂2]-[H₂5] by treating the corresponding [Au₂(dppx)₂Cl₂] have not been successful to date. The specific strong intramolecular aurophilic interactions in the dppm system may play an important role in the expansion reaction from [H₂1] to [H19].

3. Coordination Behavior of Diphosphine-bridged Digold(I) Metalloligands with Penicillamate.

3.1. Polynuclear structures constructed from [Au₂(dppm)(D-pen-S)₂]²⁻.

The coordination behavior of the shortest dppm-bridged digold(I) metalloligand [H₂1] was investigated first. We found that [H₂1] coordinates to divalent transition metal ions (M = Ni^{II}, Zn^{II}) in a chelating manner, forming an S-bridged Au₂M trinuclear structure with an 8-membered MAu₂S₂P₂C metalloring, [M{Au₂(dppm)(D-pen-S)₂}] ([20] for M = Ni^{II}, [21] for M = Zn^{II}) (Scheme 1).^[16,17] This is in sharp contrast to the coordination mode of [Au(D-pen-S)₂]³⁻, which uniformly adopts a bridging-type mode.^[10,11]



Scheme 1. Syntheses and conversions of [20], [21], [22]Cl, and [23]Cl.

Single-crystal X-ray crystallography revealed that the crystals of [20] and [21] are isomorphous and that the molecular structures of the trinuclear structures are essentially isostructural with each other (Figure 11a,b). The difference lies in the longer coordination bonds around the Zn^{II} center in [21] compared with those around the Ni^{II} center in [20], which can be reasonably explained by the weaker coordination resulting from the lack of ligand field stabilization energy (LFSE) of the Zn^{II} ion. The trinuclear complexes [20] and [21] contain an octahedral [M(D-pen-S)₂]²⁻ unit that is bound to a [Au₂(dppm)]²⁺ moiety through S atoms. The M atom selectively adopts a distorted N₂O₂S₂ octahedral geometry with a trans(O) geometric configuration.^[10] The two bridging S atoms are asymmetric and have the *R* chiral configuration. For both crystals, an intramolecular aurophilic

interaction was observed between two Au^I atoms (Au...Au = 3.1346(2) Å for [20], 3.14(2) Å for [21]). A similar aurophilic interaction has been commonly observed for other gold(I) species containing a [Au₂(dppm)]²⁺ moiety.^[42,49] The preferable aurophilic interaction in [Au₂(dppm)]²⁺ causes the two {Au(D-pen-S)}⁻ coordination arms to point in the same direction, which may lead to the 'chelating' coordination mode of [1]²⁻. In the crystal packing, complex molecules are connected to each other through CH...π interactions, resulting in 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 water/ethanol molecules. Notably, [21] is the first crystallographically determined heterometallic structure consisting of chalcogen-bridged Au and Zn centers (Au–E–Zn).

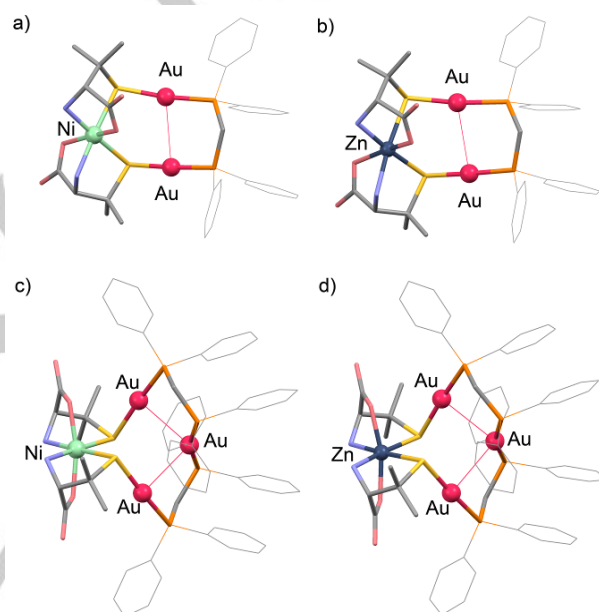
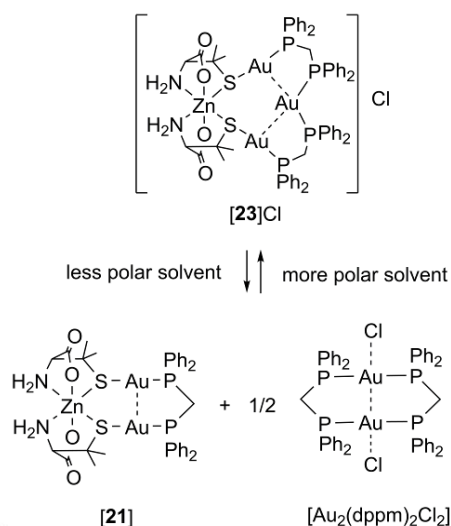


Figure 11. Molecular structures of (a) [20], (b) [21], (c) [22]Cl, and (d) [23]Cl.

As in the case of the parental metalloligand [1]²⁻, we demonstrated that the Au₂M complexes with a digold(I) moiety, [20] and [21], readily convert to new Au₃M complexes with a trigold(I) moiety, [Ni{Au₃(dppm)₂(D-pen)₂}]Cl ([22]Cl) and [Zn{Au₃(dppm)₂(D-pen)₂}]Cl ([23]Cl), respectively, upon the addition of 0.5 molar equiv of [Au₂(dppm)₂Cl₂] in ethanol (Scheme 1).^[16,17] X-ray analysis revealed that [22]Cl and [23]Cl are also isomorphous and isostructural with each other. Both [22]⁺ and [23]⁺ contain an octahedral [M(D-pen-N,O,S)₂]²⁻ unit with a trans(O) geometry, the structure of which is almost the same as that in [20] and [21] (Figure 11c,d). The two bridging S atoms in [22]⁺ and [23]⁺ adopt the *R* configuration as found in [20] and [21]. However, [22]⁺ and [23]⁺ possess a [Au₃(dppm)₂]³⁺ linker in place of [Au₂(dppm)]²⁺ in [20]/[21], resulting in an S-bridged MAu₃ tetranuclear structure with a 12-membered MAu₃S₂P₄C₂ metalloring, [M{Au₃(dppm)₂(D-pen)₂}]⁺. In these trigold(I) species, two intramolecular aurophilic interactions were observed (Au...Au = 2.9774(3) Å for [22]⁺ and 2.9929(3) Å for [23]⁺), which

maintain the unique 12-membered metalloring structure. No aggregation of the complex cations is observed in the crystal-packing structure of $[22]^+/[23]^+$, unlike the case of $[20]/[21]$, where aggregation of the complex molecules was observed. This may be attributed to the cationic nature of $[22]^+/[23]^+$, which preferentially interact with Cl^- anions through $\text{NH}\cdots\text{Cl}$ hydrogen bonds. Notably, the Au_3M complexes $[22]\text{Cl}$ and $[23]\text{Cl}$ can also be prepared by reacting a trigold(I) complex **19** with the M ion, which indicates that complex **19** can act as a chelating-type metalloligand, similar to the digold(I) metalloligand **1** (Scheme 1). The reverse conversion from tetranuclear $[22]^+/[23]^+$ to trinuclear $[20]/[21]$ is achieved by treating a 1:1 mixture of $[\text{Au}(\text{D-pen-S})_2]^{2+}$ and M^{2+} ($\text{M} = \text{Ni}, \text{Zn}$) ion within a few minutes. Therefore, quick and reversible expansion/contraction between the 8-membered $\text{MAu}_2\text{S}_2\text{P}_2\text{C}$ metalloring and the 12-membered $\text{MAu}_3\text{S}_2\text{P}_4\text{C}_2$ metalloring are achieved by simple treatment with $[\text{Au}_2(\text{dppe})_2]^{2+}$, while the coordination environment around the M center is retained.

Complexes **[21]** and $[23]^+$ contain only closed-shell atoms and are thus diamagnetic in nature. This property enabled the investigation of their structures in solution via nuclear magnetic resonance (NMR) spectroscopy. The ^1H NMR spectrum of $[23]^+$ in methanol- d_4 shows proton signals attributable to **[21]** and $[\text{Au}_2(\text{dppe})_2]^{2+}$, as well as signals assignable to $[23]^+$. The estimated ratio of **[21]** to $[23]^+$ is approximately 1:2. Thus, one third of $[23]^+$ is converted into **[21]** and $[\text{Au}_2(\text{dppe})_2]^{2+}$ in this solvent to reach equilibrium. The equilibrium was found to be highly dependent on the polarity of the solvent. In less-polar solvents, such as chloroform, the ionic species $[23]^+$ and Cl^- are not stabilized via solvation and are instead converted into neutral species of **[21]** and $[\text{Au}_2(\text{dppe})_2\text{Cl}_2]$. In contrast, a polar solvent, such as water, can effectively stabilize ionic species, preventing the dissociation of $[23]^+$ into **[21]** and $[\text{Au}_2(\text{dppe})_2]^{2+}$ (Scheme 2). In addition, the Au-Zn complexes **[21]** and $[23]\text{Cl}$ exhibited relatively strong yellow and green phosphorescence,

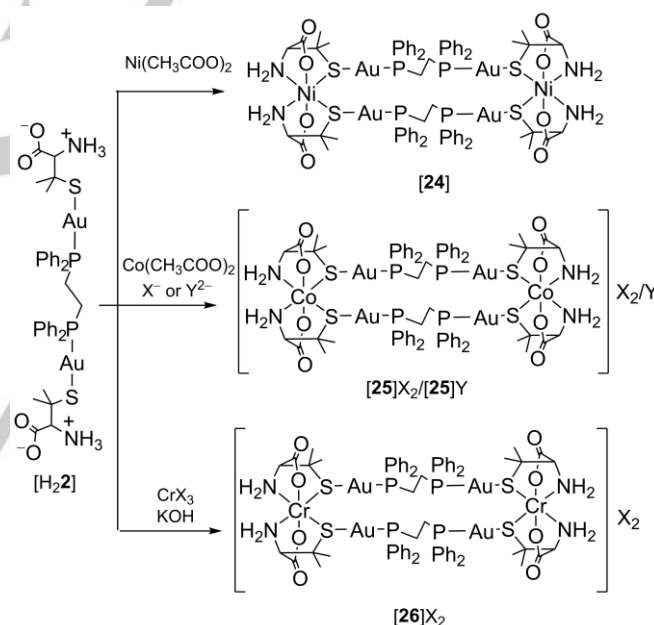


Scheme 2. Solvent-dependent equilibria among **[21]**, $[23]\text{Cl}$, and $[\text{Au}_2(\text{dppe})_2\text{Cl}_2]$, depending on solvent.

respectively, arising from a $^3\text{LMMCT}$ ($\text{S}\rightarrow\text{Au}\cdots\text{Au}$) transition. Interestingly, the emission quantum yield of $[23]\text{Cl}$ ($\Phi = 0.13$) is much higher than that of **[21]** ($\Phi = 0.03$). The larger quantum yield for $[23]\text{Cl}$ is compatible with its rigid $\text{Au}_3\text{Zn}^{\text{II}}$ tetranuclear structure with its two $\text{Au}\cdots\text{Au}$ contacts, which are shorter than the $\text{Au}\cdots\text{Au}$ contact found in the $\text{Au}_2\text{Zn}^{\text{II}}$ trinuclear structure in **[21]**. The interconvertible structures in **[21]** and $[23]\text{Cl}$, which show different emission colors and intensities, have potential as switchable luminescent sensors and probes.^[50]

3.2. Polynuclear and supramolecular structures constructed from $[\text{Au}_2(\text{dppe})(\text{D-pen-S})_2]^{2+}$.

Unlike the dppe-bridged digold(I) complex $[\text{H}_2\textbf{1}]$, which acts as a chelating-type metalloligand, the dppe-bridged digold(I) complex $[\text{H}_2\textbf{2}]$ coordinates to octahedral Ni^{II} , Co^{III} , and Cr^{III} ions in a closed-bridging mode to form discrete M_2Au_4 hexanuclear structures in $[\text{Ni}_2\{\text{Au}_2(\text{dppe})(\text{D-pen-S})_2\}_2]$ (**[24]**),^[20] $[\text{Co}_2\{\text{Au}_2(\text{dppe})(\text{D-pen-S})_2\}_2]^{2+}$ (**[25]**)^[21], and $[\text{Cr}_2\{\text{Au}_2(\text{dppe})(\text{D-pen-S})_2\}_2]^{2+}$ (**[26]**)^[18b] (Scheme 3).



Scheme 3. Synthetic routes to **[24]**, $[\text{25}]\text{X}_2$, $[\text{25}]\text{Y}$, and $[\text{26}]\text{X}_2$. X and Y represent monovalent anions and divalent anions, respectively.

The neutral $\text{Ni}^{\text{II}}_2\text{Au}^{\text{I}}_4$ complex **[24]** is prepared by the treatment of $[\text{H}_2\textbf{2}]$ with $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ in a 1:1 ratio in ethanol, and it is isolated as blue-green crystals ($[\text{24}]\cdot 0.5\text{EtOH}\cdot 0.5\text{Et}_2\text{O}\cdot 7.25\text{H}_2\text{O}$) by the vapor diffusion of diethyl ether.^[20] X-ray analysis revealed that these crystals consist of the hexanuclear complex-molecule **[24]** and ethanol, diethyl ether, and water molecules. In **[24]**, two $[\text{Au}_2(\text{dppe})(\text{D-pen-S})_2]^{2-}$ moieties adopt an anti-conformation, as found in the crystal structure of **2**. Therefore, two terminal $\{\text{Au}(\text{D-pen-S})\}^-$ coordination arms orient in the opposite directions, which prevents the chelating-type coordination mode of **2**. The

metalloligands each bind to two Ni^{II} atoms in a bis(tridentat-N,O,S) coordination mode to form a twisted $\text{Au}_4\text{Ni}_2\text{S}_4\text{P}_4\text{C}_4$ 18-membered metalloring (Figures 12a and 12b). Each Ni^{II} atom is situated in an $\text{N}_2\text{O}_2\text{S}_2$ octahedral geometry with a trans(O) configuration, as found in [20] and [22]⁺. In [24], the four bridging S atoms are all asymmetric and have the *R* chiral configuration. Thus, only a single optically active isomer with molecular D_2 symmetry exists in its crystal. In the crystal, the Au_4Ni_2 molecules are connected to each other through mutual hydrogen bonds between amine and carboxylato groups (av $\text{N}\cdots\text{O} = 3.04 \text{ \AA}$), resulting in a 1D straight-chain structure (Figure 12c). The 1D chains are arranged parallel to each other, and ethanol, diethyl ether, and water molecules, which do not show strong mutual interactions, are accommodated between the chains. Interestingly, blue-green crystals of [24]·0.5EtOH·0.5Et₂O·7.25H₂O were converted to blue crystals including only water molecules as solvating molecules ([24]·16H₂O) after soaking in water through a single-crystal-to-single-crystal process. In [24]·16H₂O, the hexanuclear complex molecules [24] are hydrogen bonded to each other through amine and carboxylato groups (av $\text{N}\cdots\text{O} = 3.16 \text{ \AA}$) to form a right-handed 4₁ helix structure (Figure 12d). The helix chains are arranged parallel in the crystal, and water molecules are accommodated between the chains. The presence of the water molecules seems to be responsible for the helix arrangement of the Au_4Ni_2 hexanuclear molecules in [24]·16H₂O.

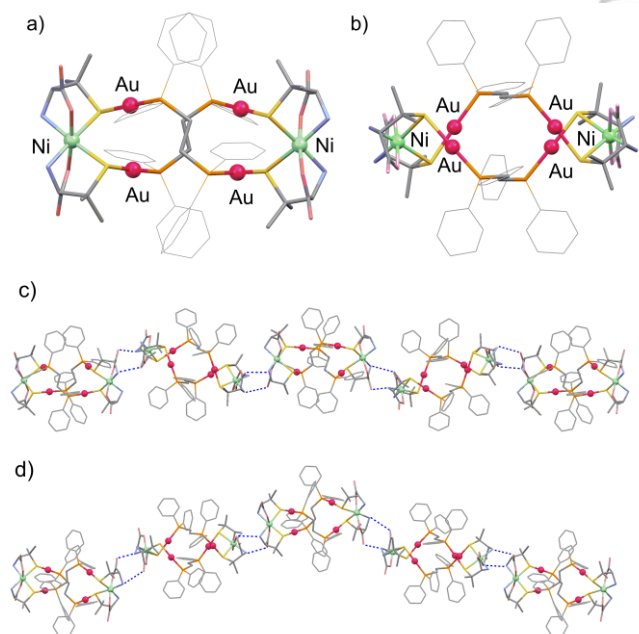


Figure 12. (a) Top and (b) side views of molecular structure and (c) straight-chain structure in [24]·0.5EtOH·0.5Et₂O·7.25H₂O. (d) Helix structure in [24]·16H₂O. Dotted lines indicate hydrogen bonds.

The $\text{Au}_2\text{Co}^{\text{III}}$ hexanuclear complex [25]²⁺ was prepared from the 1:1 reaction of **2** and $\text{Co}(\text{CH}_3\text{COO})_2$ in ethanol/water under aerobic conditions.^[18] The resulting +2-charged product is readily crystallized as a perchlorate salt ([25](ClO₄)₂) after the

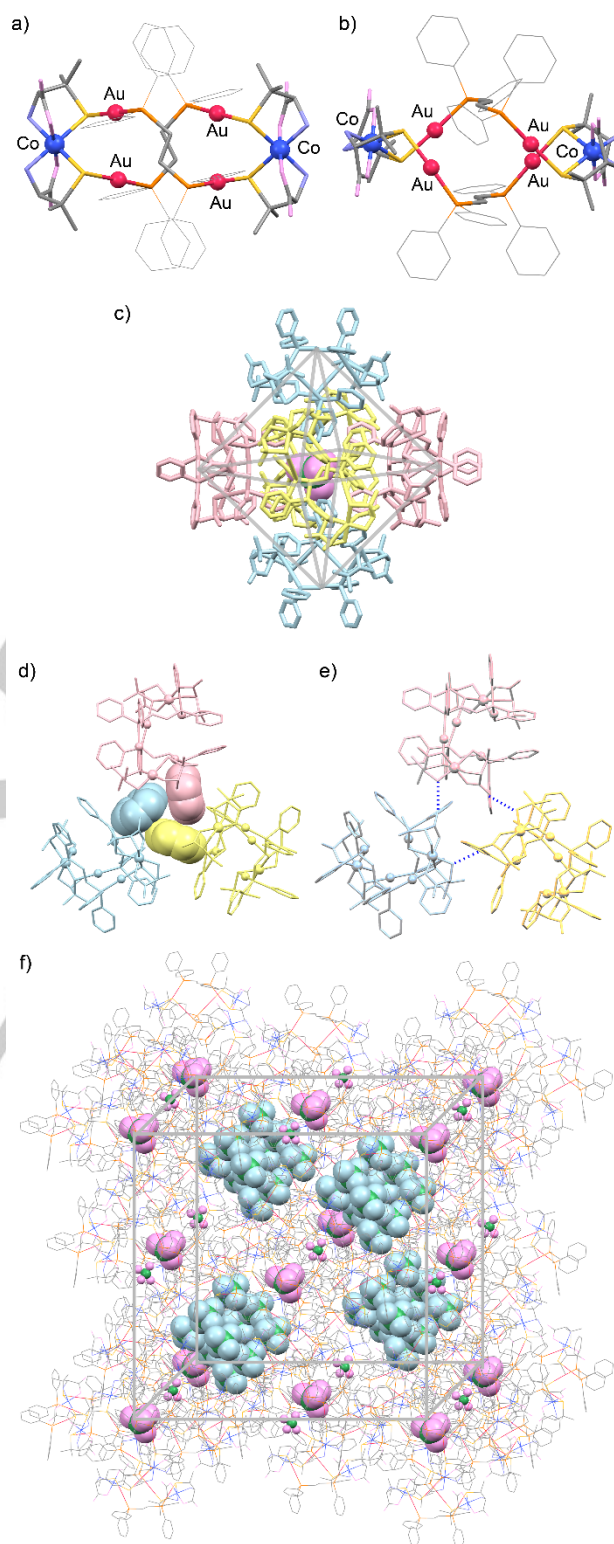


Figure 13. (a) Top and (b) side views of molecular structure of [25]²⁺, (c) octahedron-shaped ([25]²⁺)₆ supramolecular structure, (d) CH... π interactions, and (e) NH...OOC hydrogen bonds in [25](ClO₄)₂. (f) Packing structure of [25](ClO₄)₂.

addition of NaClO_4 . Single-crystal X-ray analysis revealed that $[\mathbf{25}]^{2+}$ consists of two $[\text{Au}_2(\text{dppe})(\text{D-pen-S})_2]^{2-}$ moieties that span two Co^{III} atoms to form an S-bridged $\text{Au}_4\text{Co}^{\text{III}}_2$ hexanuclear structure in $[\text{Au}_4\text{Co}_2(\text{dppe})_2(\text{D-pen})_4]^{2+}$, which is analogous to that in $[\mathbf{24}]$ (Figures 13a and 13b). A twisted $\text{Au}_4\text{Co}_2\text{S}_4\text{P}_4\text{C}_4$ 18-membered ring and the *R* configurational asymmetric bridging S atoms were also observed. In crystal form, interestingly, $[\mathbf{25}]^{2+}$ is aggregated into an octahedron-shaped supramolecular hexameric structure with a diameter of ca. 32 Å, $\{[\mathbf{25}]^{2+}\}_6$, which accommodates a ClO_4^- ion in the center (Figure 13c). In $\{[\mathbf{25}]^{2+}\}_6$, a total of 24 $\text{CH}\cdots\pi$ interactions (Figure 13d) and a total of 12 $\text{NH}\cdots\text{OOC}$ hydrogen bonds (Figure 13e) support the supramolecular octahedron structure. In the crystal, $\{[\mathbf{25}]^{2+}\}_6$ are closely packed in a face-centered cubic (fcc) structure (Figure 13f) with intermolecular $\text{CH}\cdots\pi$ contacts between supramolecular octahedrons. In this fcc structure, there is a single type of smaller octahedral interstice (81 Å³) and two types of larger tetrahedral interstices: hydrophilic surrounded by amine groups (1184 Å³) and hydrophobic surrounded by phenyl and methyl groups (1861 Å³). Whereas one ClO_4^- ion is accommodated in each of the octahedral interstices, 10 ClO_4^- ions are accommodated in each of the hydrophilic tetrahedral interstices in an adamantane-like arrangement (Figure 14). The closest $\text{O}\cdots\text{O}$ distance between adjacent ClO_4^- anions in the $\{\text{ClO}_4^-\}_{10}$ cluster is 3.13(2) Å without the mediation of water molecules. The $\{\text{ClO}_4^-\}_{10}$ cluster is surrounded by four $\{[\mathbf{25}]^{2+}\}_6$ supramolecular octahedrons to form multiple $\text{NH}\cdots\text{OClO}_3$ hydrogen bonds between the amine groups of D-pen and ClO_4^- ions. While no ClO_4^- ions are found in the hydrophobic tetrahedral interstices, the presence of a number of disordered water molecules in this interstice is implied.

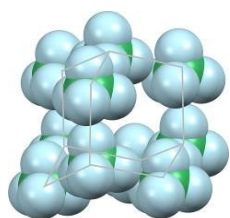


Figure 14. Structure of the $(\text{ClO}_4^-)_{10}$ cluster in $[\mathbf{25}](\text{ClO}_4)_2$.

One of the most fundamental laws of nature is that cationic and anionic species are alternately arranged in crystals to avoid Coulombic repulsion and promote Coulombic attraction (Figure 15a). However, amazingly, complex-cation $[\mathbf{25}]^{2+}$ and ClO_4^- anions are separately aggregated into $\{[\mathbf{25}]^{2+}\}_6$ and $\{\text{ClO}_4^-\}_{10}$, respectively, forming a unique non-alternate arrangement of cations and anions in $[\mathbf{25}](\text{ClO}_4)_2$. Such ionic crystals that consist of both cationic aggregates and anionic aggregates appear to be previously unknown (Figure 15b). Large repulsive Coulombic interactions are expected to exist in the cation octahedron and the anion cluster. We propose that the presence of multiple non-Coulombic interactions between the complex cations, such as hydrogen bonds and $\text{CH}\cdots\pi$ interactions, compensates for the Coulombic repulsion energy and stabilizes the unique cation-anion separate aggregate structure.

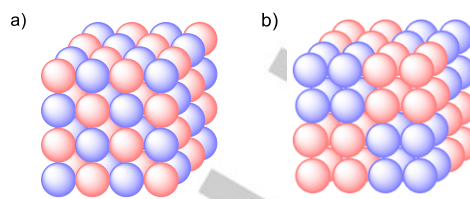


Figure 15. Schematic representation of (a) regular and (b) anomalous structures of ionic crystals. Red and blue balls represent cationic and anionic species, respectively.

When other monovalent anions with tetrahedral, trigonal planar, linear, or spherical geometries ($\text{X}^- = \text{BF}_4^-, \text{NO}_3^-, \text{Cl}^-, \text{Br}^-, \text{N}_3^-$) were used as counter anions, ionic crystals of $[\mathbf{25}](\text{X})_2$ were created (Figure 16a-e).^[18b] However, inorganic anions with a high affinity toward Co^{III} or Au^{I} centers, such as SCN^- and I^- , cannot be used as they lead to the decomposition of the $\text{Au}_4\text{Co}^{\text{III}}_2$ hexanuclear structure in $[\mathbf{25}]^{2+}$. Furthermore, the use of inorganic anions that appear to be too large to be accommodated in the hydrophilic tetrahedral interstice, such as octahedral PF_6^- or tetrahedral ReO_4^- , also failed to produce this class of ionic crystals. Notably, we were able to incorporate PF_6^- ions into this class of ionic crystals by mixing them with spherical Br^- ions in a 1:1 ratio. In $[\mathbf{25}](\text{PF}_6)(\text{Br})$, PF_6^- ions were found to selectively occupy the tetrahedral sites of each adamantane-like anionic cluster and the center of each cationic supramolecular octahedron and each octahedral interstice, whereas the octahedral site of each adamantane-like anionic cluster was occupied by Br^- ions (Figure 16f). This is also the case for $[\mathbf{25}](\text{BF}_4)(\text{Br})$ and $[\mathbf{25}](\text{NO}_3)\text{Br}$, which show site-selective distributions of two different inorganic anions (Figure 16g,h).

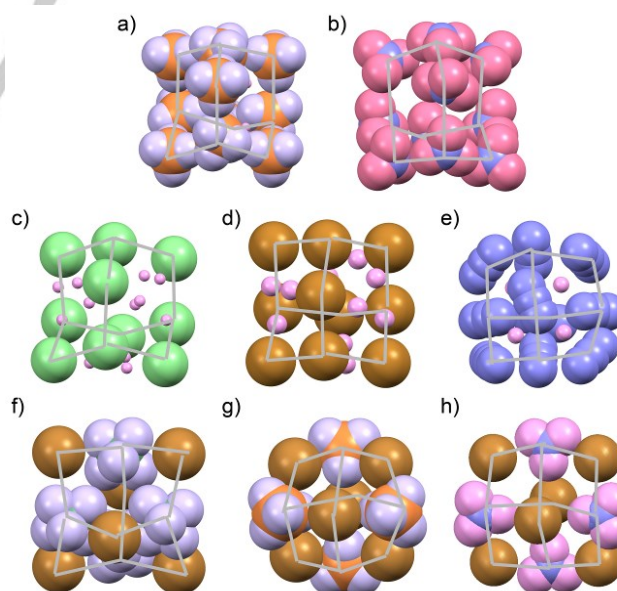


Figure 16. Structures of the (a) $(\text{BF}_4^-)_{10}$, (b) $(\text{NO}_3^-)_{10}$, (c) $(\text{Cl}^-)_{10}$, (d) $(\text{Br}^-)_{10}$, (e) $(\text{I}_3^-)_{10}$, (f) $(\text{PF}_6)_4(\text{Br}^-)_6$, (g) $(\text{BF}_4)_4(\text{Br}^-)_6$, and (h) $(\text{NO}_3)_4(\text{Br}^-)_6$ in $[\mathbf{25}]\text{X}_2$. Pink small balls in (a), (c), (d), (e) represent water molecules.

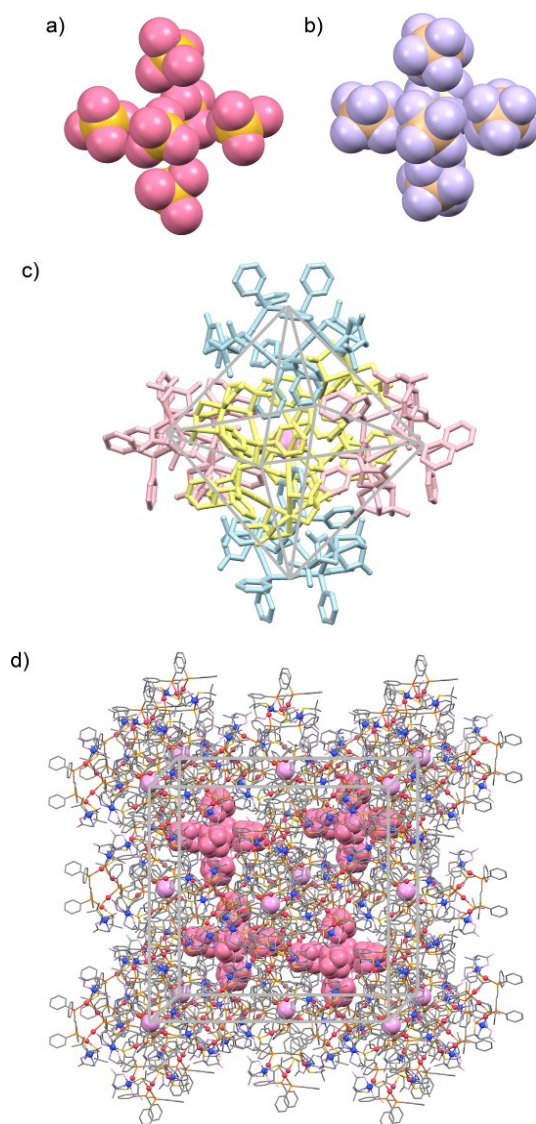


Figure 17. Structures of (a) $(\text{SO}_4^{2-})_6$ and (b) $(\text{SiF}_6^{2-})_6$ in $[\text{25}]\text{Y}_2$. (c) Hexameric $([\text{25}]^{2+})_6$ octahedron that accommodates water molecules and (d) packing structure in $[\text{25}]\text{SO}_4$.

When divalent anions ($\text{Y}^{2-} = \text{SO}_4^{2-}$, SiF_6^{2-}) were employed for crystallization instead of monovalent anions, isomorphous ionic crystals showing the aggregation of cationic and anionic species ($[\text{25}]\text{Y}$) are formed. In $[\text{25}]\text{Y}$, all of the structural features involving the cationic parts of $[\text{25}]^{2+}$ are the same as those found in $[\text{25}](\text{ClO}_4)_2$. However, Y^{2-} anions exist only in each of the hydrophilic tetrahedral interstices and form an octahedral $\{\text{SO}_4^{2-}\}_6/\{\text{SiF}_6^{2-}\}_6$ cluster, which balances the charge of the cationic $\{[\text{25}]^{2+}\}_6$ supramolecular octahedron (Figure 17a,b). The center of each $\{[\text{25}]^{2+}\}_6$ supramolecular octahedron and each octahedral interstice is occupied by a water molecule in $[\text{25}]\text{Y}$ (Figure 17c). Thus, all of the cations and anions in $[\text{25}]\text{Y}$ are separately aggregated into the +12-charged $\{[\text{25}]^{2+}\}_6$ octahedrons and the -12-charged $\{\text{Y}^{2-}\}_6$ octahedrons, respectively, which behave very similarly to Zn^{2+} and S^{2-} ions in

zinc-blende, resulting in a giant zinc-blende lattice structure (Figure 17d).^[51]

Additionally, it was found that the $\text{Au}_4\text{Cr}^{\text{III}}_2$ hexanuclear complex $[\text{26}]^{2+}$ produces ionic crystals ($[\text{26}]\text{X}_2$) using monovalent anions ($\text{X}^- = \text{Cl}^-$, NO_3^-).^[18b] X-ray analyses established that $[\text{26}]\text{X}_2$ is isomorphous with $[\text{25}]\text{X}_2$ and contains an S-bridged $\text{Au}_4\text{Cr}^{\text{III}}_2$ hexanuclear complex cation $[\text{Au}_4\text{Cr}_2(\text{dppe})_2(\text{D-pen})_4]^{2+}$, which forms a hexameric octahedron $\{[\text{26}]^{2+}\}_6$ incorporating an X^- ion, as found in the case of $[\text{25}]^{2+}$ (Figure 18). In the crystal, the octahedrons arrange in a fcc structure, which accommodates another X^- ion and a $(\text{X}^-)_{10}$ cluster in its octahedral and tetrahedral interstices, respectively.

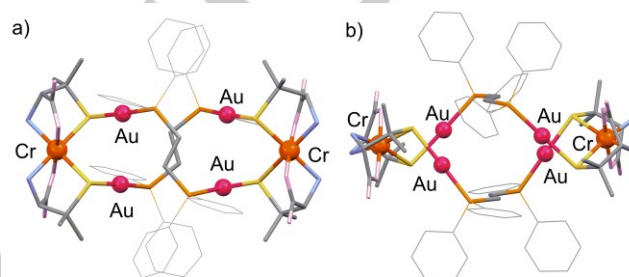
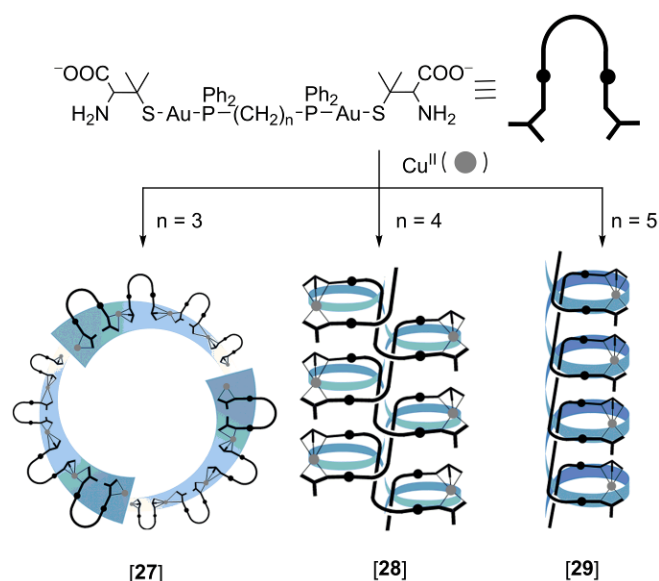


Figure 18. (a) Top and (b) side views of molecular structure of $[\text{26}]^{2+}$.

3.3. Polymeric structures constructed from $[\text{Au}_2(\text{dppp})(\text{D-pen-S})_2]^{2-}$, $[\text{Au}_2(\text{dppb})(\text{D-pen-S})_2]^{2-}$, and $[\text{Au}_2(\text{dpppe})(\text{D-pen-S})_2]^{2-}$.

As shown in the previous chapters, dppm-bridged $[\text{H}_2\text{1}]$ and dppe-bridged $[\text{H}_2\text{2}]$ adopt the chelating (Figure 3a) and closed-bridging (Figure 3b) coordination modes, respectively, to form discrete metallocyclic structures. In contrast, we found that metalloligands with a longer alkyl chain ($[\text{H}_2\text{3}]-[\text{H}_2\text{5}]$) can adopt the remaining extended-bridging mode to the Cu^{2+} ion, forming infinite $(\text{Au}_2\text{Cu}^{\text{II}})_\infty$ structures in $[\text{Cu}\{\text{Au}_2(\text{dppp})(\text{D-pen})\}]_\infty$ ($[\text{27}]$), $[\text{Cu}\{\text{Au}_2(\text{dppb})(\text{D-pen})\}]_\infty$ ($[\text{28}]$), and $[\text{Cu}\{\text{Au}_2(\text{dpppe})(\text{D-pen})\}]_\infty$ ($[\text{29}]$) (Scheme 4).^[19] The three polymeric $(\text{Au}_2\text{Cu}^{\text{II}})_\infty$ structures were obtained as blue plate-shaped crystals from a 1:1 mixture of dppx-bridged digold(I) metalloligand $[\text{H}_2\text{3}]-[\text{H}_2\text{5}]$ with $\text{Cu}(\text{OAc})_2$ in a 1:1 ratio in $\text{EtOH}/\text{H}_2\text{O}$.

Single-crystal X-ray analysis of $[\text{27}]$ revealed that the dppp-bridged metalloligand assumes an all-trans conformation for the alkyl chain backbone and a syn orientation for the two-terminal $\{\text{Au}(\text{D-pen-S})\}^-$ coordination arms. Every metalloligand binds to two Cu^{II} ions using two D-pen moieties through S, N, and O atoms from the $\{\text{Au}(\text{D-pen-S})\}^-$ coordination arms to form an infinite 1D chain structure. Each Cu^{II} center also has a distorted square-pyramidal geometry (coordinated by two nitrogen and two sulfur atoms, which form a *cis*- N_2S_2 square plane, and one oxygen atom, which occupies an axial position) in a $[\text{Cu}(\text{D-pen-N,S})(\text{D-pen-N,O,S})]^{2-}$ unit (Figure 19a). Remarkably, the 1D chain is not straight but instead is gently wavy and forms a



Scheme 4. Synthetic routes to **[27]**, **[28]**, and **[29]**.

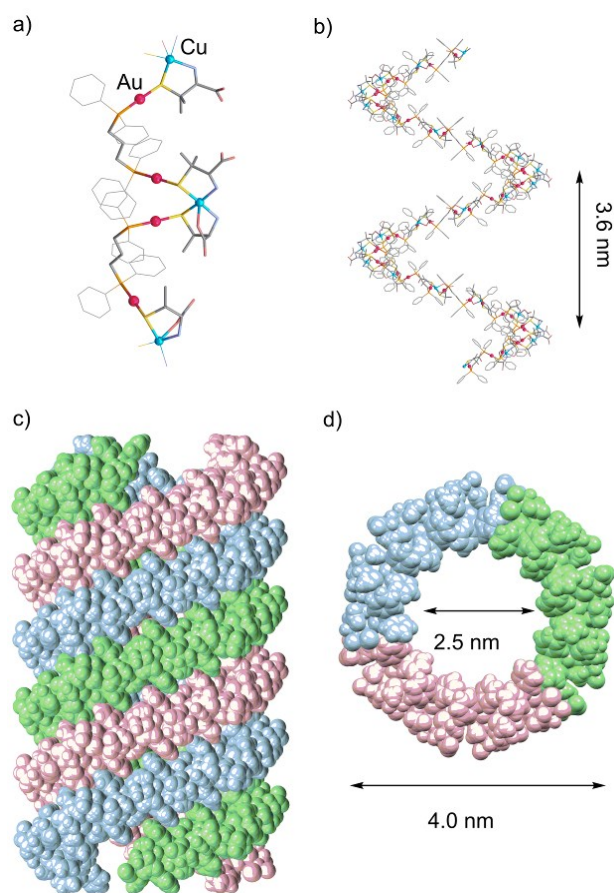


Figure 19. (a) The Cu^{II} ions coordinated by $[3]^{2-}$, (b) the 1D helix structure, and (c) top and (d) side views of the triple-helix structure in **[27]**.

large-scale right-handed helix consisting of 12 $[\text{Cu}\{\text{Au}_2(\text{dppp})(\text{D-pen})_2\}]$ repeating units with a pitch length of approximately 3.6 nm (Figure 19b). In this 1D helix structure, all bridging S atoms are asymmetric and have *R* chiral configurations. This unified chiral configuration, together with the wavy helix structure, allows the square-pyramidal $\{\text{Cu}(\text{D-pen})_2\}^{2-}$ units that are located on the same side of the 1D chain to avoid mutual steric interactions in the chain. More remarkably, this 1D helix is not a single strand, but instead, three right-handed helical chains are intertwined through $\pi \cdots \pi$ and $\text{CH} \cdots \pi$ interactions, constructing a huge, tubular, triple-stranded helix with inner and outer diameters of approximately 2.5 nm and 4.0 nm, respectively (Figure 19c,d).

As in the case of **[27]**, the metalloligands $[4]^{2-}$ are each connected by Cu^{II} atoms to form an infinite 1D chain structure composed of square-pyramidal $[\text{Cu}(\text{D-pen-}N,S)(\text{D-pen-}N,O,S)]^{2-}$ and bridging $\{\text{Au}_2(\text{dppb})\}^{2+}$ units in **[28]** (Figure 20a). However, in **[28]**, each metalloligand has an anti-orientation with respect to the two $\{\text{Au}(\text{D-pen-S})\}^-$ coordination arms, which is enforced by the even number of methylene groups with the all-trans conformation, as found in the parental **[H₂4]**. Although the 1D chain of **[28]** has a non-wavy, straight topology, it possesses a helical chirality because of P-Au-S-Cu-S-Au-P linkage loops (Figure 20b). Interestingly, the helicity of the loops in one chain is not homochiral, but instead, right- and left-handed helical loops are alternately arranged to create a rare meso-helix structure, despite the presence of the homochiral D-pen. Either left- or right-handedness is generally selected when a homochiral ligand is employed to construct a helix structure,^[52] and examples of coordination polymers with a meso-helix structure have been obtained from achiral ligands or racemic pairs of ligands.^[53] A detailed structural inspection of **[28]** indicated that the two bridging sulfur atoms of each left-handed helical loop adopt the *R* configuration, whereas those of each right-handed helical loop have the *R* and *S* configurations. These unsymmetrical chiral configurations contribute to the formation of the 1D meso-helix structure in **[28]**, combined with the anti-configuration of the two D-pen moieties in $[4]^{2-}$.

The dpppe-bridged metalloligand $[5]^{2-}$ also adopts the all-trans conformation, such that the two-terminal $\{\text{Au}(\text{D-pen-S})\}^-$ coordination arms are oriented in the syn direction in **[29]** (Figure 20c). The overall structure of **[29]** resembles that of **[28]**, rather than that of **[27]**; its 1D chain has a non-wavy, straight form (Figure 20d). This is explained by the absence of intrachain interactions between the square-pyramidal $\{\text{Cu}(\text{D-pen})_2\}^{2-}$ moieties because of dpppe's longer alkyl chain. However, all P-Au-S-Cu-S-Au-P linkages in **[29]** uniformly adopt left-handedness with *R* configurational S atoms, constructing a single-stranded homochiral helix. The syn directionality of the two D-pen moieties in **[29]**, which is regulated by the odd number of methylene groups, is responsible for the formation of the molecular topology of **[28]**.

To summarize these results, a close correlation between the alkyl chain length in dppx and the topology of the obtained helix is observed. In particular, the fact that the parity of alkyl chains in dppx (odd vs. even) controls the chirality of the helix

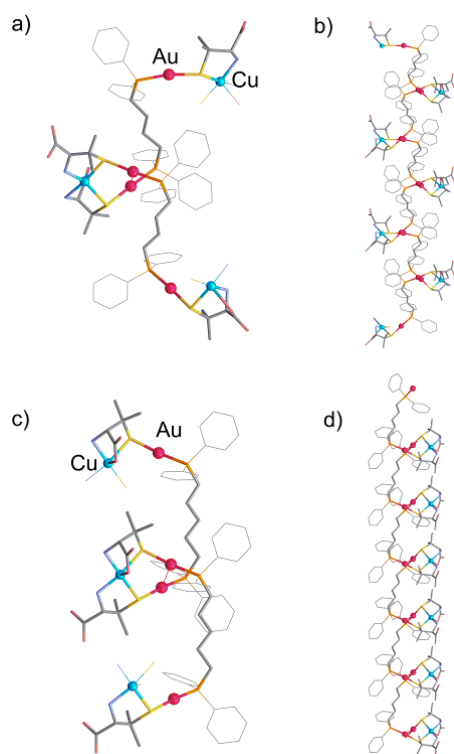


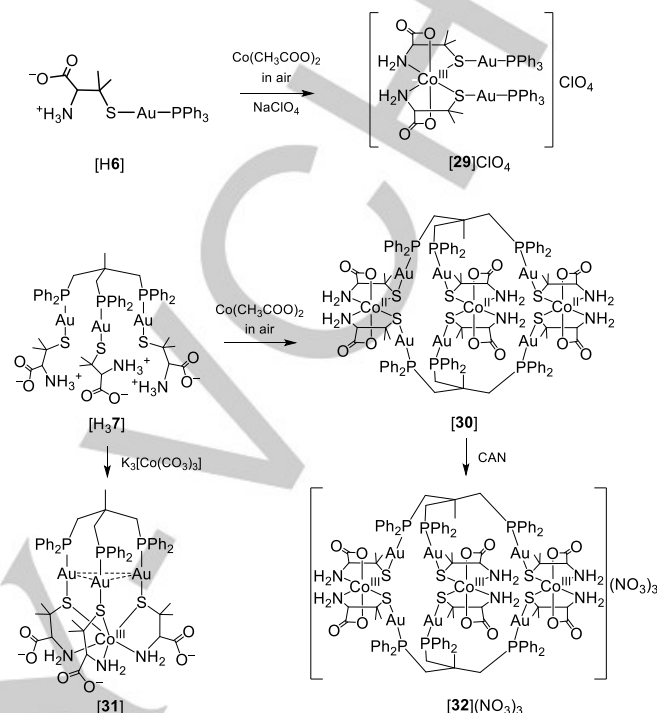
Figure 20. (a) The Cu^{II} ions coordinated by $[4]^{2-}$ and (b) the meso-helix structure in $[28]$. (c) The Cu^{II} ions coordinated by $[5]^{2-}$ and (d) the left-handed helix structure in $[29]$.

(homochiral helix and meso-helix) is remarkable. In 2000, Albrecht proposed the odd–even rule that dominates the helicate and mesocate molecular structures for a discrete coordination system based on the systematic study of a series of dinuclear complexes: $[\text{Ti}_2(\text{O}^-\text{O}(\text{CH}_2)_n\text{O}^-\text{O})_3]$ ($\text{O}^-\text{O}(\text{CH}_2)_n\text{O}^-\text{O} = \alpha, \omega$ -bis(2,3-dihydroxyphenyl)alkane).^[54] The $\text{Au}^{\text{I}}\text{-Cu}^{\text{II}}$ coordination system is the first coordination system in which the odd–even rule has been applied to obtain infinite homochiral helix and meso-helix structures. By applying this odd–even rule in a polymeric system, a number of unique meso-helices with a long methylene chain backbone can be systematically prepared.

4. Coordination Behavior of Gold(I) Metalloligands with Monophosphine or Triphosphine.

To increase or reduce the number of phosphorus donors in a phosphine ligand from diphosphine, a new class of metalloligands possessing a different number of $\{\text{Au}(\text{D-pen-S})\}^-$ coordination arms was designed. This strategy is a straightforward improvement regarding the diversity of metalloligands. In this chapter, we will briefly describe our very recent study on the coordination behavior of a simple monogold(I) metalloligand $[\text{Au}(\text{PPh}_3)(\text{D-Hpen-S})]$ ($[\text{H6}]$) and a tripod-type trigold(I) metalloligand, $[\text{Au}_3(\text{tme})(\text{D-Hpen-S})_3]$

($[\text{H37}]$; $\text{tme} = 1,1,1$ -tris(diphenylphosphinomethyl)ethane) to a cobalt(II) ion (Scheme 5).^[21,22]



Scheme 5. Synthetic routes to $[29]\text{ClO}_4$, $[30]$, $[31]$ and $[32](\text{NO}_3)_3$.

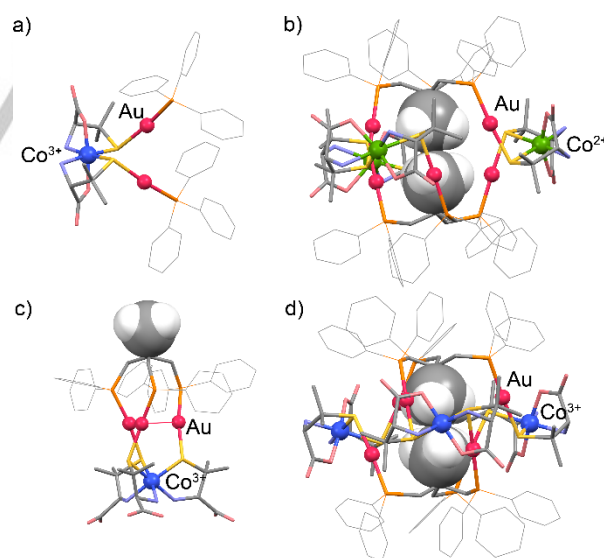


Figure 21. Molecular structures of (a) $[29]$, (b) $[30]$, (c) $[31]^{3+}$, and (d) $[32]^+$.

Treatment of $[\text{H6}]$ with Co^{2+} ions under aerobic conditions produced a $\text{Co}^{\text{III}}\text{Au}_2^{\text{I}}$ trinuclear complex, $[\text{Co}\{\text{Au}(\text{PPh}_3)(\text{D-pen})\}_2]^+$ ($[29]^+$), in which the cobalt center was oxidized to the +III oxidation state (Figure 21a). Complex $[29]^+$ consists of an octahedral $[\text{Co}(\text{D-pen})_2]^-$ unit bounded by two $\{\text{Au}(\text{PPh}_3)\}^+$ moieties through S atoms. Of the three geometrical

configurations (trans(N), trans(O), and trans(S)) possible for the $[M(D\text{-pen-}N,O,S)_2]^{n-}$ octahedron,^[10] **[29]⁺** adopts the trans(O) configuration in the crystalline and solution states, as found in the dppe-bridged cyclic $Au_4M^{III}_2$ hexanuclear complex **[25]²⁺**. This implies that the trans(O) configuration is the most thermodynamically stable for the $[M(D\text{-pen-}N,O,S)_2]^-$ unit bound by two $\{Au(PPh_2R)\}^+$ moieties through S atoms. Note that **[29]ClO₄** adopts a normal alternate arrangement of cations and anions in the crystal.

The reaction of neutralized **[H₃7]** with Co^{2+} ions under aerobic conditions afforded a $Co^II_3Au^I_6$ nonanuclear complex with a ball-like shape, $[Co_3\{Au_3(tdme)(D\text{-pen-}N,O,S)_3\}_2]$ (**[30]**), in which two **[7]³⁻** sandwich three high-spin Co^{II} ions (Figure 21b). The two methyl groups from the two tdme ligands are directed toward the interior of the complex-ball and come into contact with one another with a C⋯C distance of 3.24 Å. When the metalloligand **[H₃7]** was reacted with the Co^{3+} ion instead of the Co^{2+} ion, a $Co^{III}Au_3$ tetranuclear complex $[Co\{Au_3(tdme)(D\text{-pen-}N,S)_3\}]$ (**[31]**) was selectively formed. In **[31]**, one **[7]³⁻** metalloligand chelates to a Co^{3+} ion in a hexadentate- N_3S_3 mode through three $\{Au(D\text{-pen-S})\}^-$ coordination arms, such that the tdme methyl group is directed to the exterior of the structure (Figure 21c). The independent formation of the $Co^II_3Au^I_6$ nonanuclear structure in **[30]** and the $Co^{III}Au_3$ tetranuclear structure in **[31]** from the same metalloligand **[7]³⁻** can be explained by the difference in the electronic states of the cobalt centers. In the nonanuclear structure in **[30]**, each cobalt center is loosely sandwiched between two tridentate- N,O,S D-pen moieties; this looseness is ascribed to the steric repulsion between the two methyl groups in the center of the structure. In such a loose octahedral coordination environment with an $N_2O_2S_2$ donor set, which provides relatively weak ligand field, the larger, high-spin Co^{II} ion is preferred. Conversely, the cobalt center in **[31]** is chelated by three bidentate- N,S D-pen moieties from one metalloligand, forming a tight octahedral environment supported by intramolecular aurophilic interactions. Such a tight octahedral environment with an N_3S_3 donor set affords a stronger ligand field, and it is thus suitable for the smaller, low-spin Co^{III} ion.

Although a few octahedral cobalt(II) species with aliphatic thiolato donor groups have been prepared,^[55] all of them have been shown to be air-sensitive. In contrast, the $Au^I_6Co^{II}_3$ complex **[30]** is air-stable and was not oxidized by a typical oxidizing reagent (PbO_2). The oxidized $Au^I_6Co^{III}_3$ complex, $[Co_3\{Au_3(tdme)(D\text{-pen})_3\}_2]^{3+}$ (**[32]³⁺**), was finally obtained as a nitrate salt after treatment with ceric ammonium nitrate (CAN), which is one of the strongest oxidizing agents available (Figure 21d). X-ray analysis revealed an unusually large structural distortion around the cobalt(III) center present in **[32]³⁺** relative to the dppe-containing $Au^I_4Co^{III}_2$ complex **[25]²⁺** and a simple trinuclear $Au^I_3Co^{III}$ complex, $[Co\{Au(PPh_3)(D\text{-pen})\}_2]^+$ (**[29]⁺**), which is derived from the monogold(I) metalloligand **[H6]**.^[22] We noted that the averaged Co–S bond distances increased in the order **[29]⁺** < **[25]²⁺** < **[32]³⁺**, which parallels the order of their nuclearities. Moreover, the averaged Co–S–Au bridging angle in **[32]³⁺** is quite small compared with those in **[29]⁺** and **[25]²⁺**. Thus, it is reasonable to suggest that the steric crowdedness in

the nonanuclear structure resulting from the methyl...methyl repulsion creates the longer Co–S bonds and the smaller Co–S–Au angles, thereby weakening the ligand field and destabilizing the +III oxidation state of the cobalt centers.

5. Summary and Future Outlook.

In this report, we described our recent study addressing the rational creation of chiral heterobimetallic multinuclear structures based on a series of heteroleptic digold(I) metalloligands with a diphosphine (dppx) and two D-penicillamine (D-pen) moieties. This class of metalloligands showed high affinity to 3d metal ions, such as chromium(III), cobalt(II/III), nickel(II), copper(II), and zinc(II), because of the strong binding ability of $[Au(D\text{-pen-S})]^-$ coordination arms, which can chelate second metal ions through N, O, and S atoms. In contrast, the bridging dppx moiety was found to control the orientation of the $[Au(D\text{-pen-S})]^-$ coordination arms, leading to three classes of coordination modes (chelating, closed-bridging, and extended-bridging) by changing the alkyl chain lengths in dppx. Notably, the presence of both hydrophilic D-pen and hydrophilic dppx in the metalloligands results in excellent self-assembling ability through the formation of hydrogen bonding and $CH\cdots\pi$ interactions among the heterobimetallic structures.

It was also shown that the structural motif of this class of digold(I) metalloligands can be expanded to a trigold(I) structure by using triphosphine ligands instead of dppx. In principle, any organic phosphines could be employed instead of dppx, which guarantees the further development of coordination systems based on heteroleptic gold(I) metalloligands. In addition, it is also possible for the D-pen ligands to be chemically modified to control the coordination behavior of the $[Au(D\text{-pen-S})]^-$ coordination arms. Efforts in this direction have already begun and involve an *N*-substituted D-penicillamine^[56] or an *L*-configurational penicillamine.^[57]

Currently, we are focusing on the unique cation-anion separate-aggregation behavior observed in the ionic crystals composed of the hexameric octahedrons of the cationic hexanuclear $Co^{III}_2Au^I_4$ complex and the decameric adamantanes or hexameric octahedrons of the inorganic anions. These crystals are constructed by introducing multiple non-Coulombic interactions (hydrogen bonding and $CH\cdots\pi$ interactions) to overcome the Coulombic interactions and exhibit a unique non-alternating arrangement of cations and anions. Therefore, we have named this new class of ionic solids 'non-Coulombic ionic solids (NCIS)'. This new category of compounds, NCIS, is expected to show specific reactivity and/or physical properties based on the non-alternating arrangement of ionic species; such properties are currently being investigated by our group and our collaborators.

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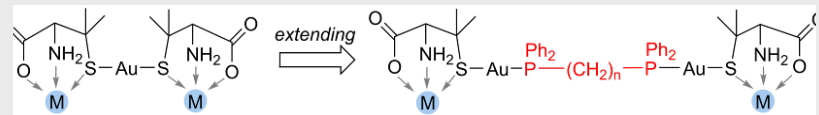
Layout 2:

PERSONAL ACCOUNT

Nobuto Yoshinari, Takumi Konno*

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**Metallosupramolecular Structures
Derived from a Series of
Diphosphine-bridged Digold(I)
Metalloligands with Terminal D-
Penicillamine**



A new family of chiral heteroleptic digold(I) metalloligands with mixed diphosphine and D-penicillamine (D-pen), $[\text{Au}_2(\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2)(\text{D-pen-S})_2]^{2-}$ and their application for the construction of chiral multinuclear and metallosupramolecular structures is described.