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Self-assembly of Au₁₆ Ring via Metal-Metal Bonding Interactions

Ya-Qing Wang,^[a] Xuan-Feng Jiang*,^[b] and Shu-Yan Yu*^{[a],[b]}

Abstract: Metal-metal bonding interactions have been employed as an efficient strategy to generate a numerous of unique gold(I) metallomacrocycles with fascinating functions. The self-assembly, crystal structure and emission property of novel nest-like tetramer 1₄, namely, $\{[Au_4(\mu-dppm)_2(\mu-dctp^2)](BF_4)_2\}_4 \cdot (CH_3CN)_2$ (dppm = bis(diphenylphosphino)methane, dctp²⁻ = N,N'-bis(dicarbodithioate)-2,11-diaza[3.3]paracyclophane) was reported. The complex has been characterized by single-crystal X-ray diffraction analysis, ¹H NMR, ¹³C NMR, CSI-MS spectrometry. The aggregate demonstrates the sixteen gold(I) atoms array in the ring with the circumference of 50.011(68)Å generated by Au¹···Au¹ attractions. UV-visible and luminescence spectroscopies revealed that such novel Au¹···Au¹ bonding metallomacrocycle exhibited yellow phosphorescence.

The study of polynuclear Au(I) complexes has attracted a considerable current interest because of their unusual structures and catalytic, optical, photochemical and electronic properties ^[1-9]. The Au(I)...Au(I) bonding interactions, which are similar in strengths with hydrogen bonds, have emerged as structural motifs in the design and construction of metal-organic supramolecular aggregates. Such gold-containing assembles received particular attention because of not only their diverse structures, such as polynuclear metallomacrocycles^[10], cages^[11] and clusters^[12], but also owing to their intriguing spectroscopic properties^[2d,3a,13-16]. Until now, there are some reported small rings with Au(I)...Au(I) bonding interactions like Au₃ (triangle)^[17], Au₄ (square)^[2e,3a], Au₅ (pentagon)^[18], however, the self-assembly of well-defined large-ring aggregates containing continuous metal-metal bonds (M-M type) or bonding interactions (M····M type) remains a challenge. Very recently, our group has increased the number of Au(I) to construct the chiral giant gold rings from Au₁₂ to Au₁₆ and Au₃₆, the largest member of the gold ring family to date, which using the unique Au(I)...Au(I) bonding interactions-directed stepwise macrocyclization strategy^[10].

Based on previous work, we designed a new ligand to self-assembly a large size of crown-like Au₁₆ ring in this communication. Such large gold ring exhibited yellow phosphorescence and may serve as potential luminescent materials for chemical sensors and OLEDs.

A solution of the dicarbodithioate ligand (dctp) in methanol was added dropwise to a white suspending solution of (dppm)Au₂Cl₂ in methanol for 24 hrs at room temperature. Recrystallization by diffusion of diethyl ether into a MeCN solution afforded light yellow crystals. As shown in Figure S4, the ¹H-NMR spectrum of $1\cdot 2BF_4$ in CD₃CN exhibited broad signals in comparing with free organic ligand in the metal-organic macrocyclic architecture. All of signals in the spectra could be ascribed to four kinds of protons, phenyl (dctp²⁻)-H,

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phenyl (PPh₃)-H and methylene-H, respectively. For complex $1 \cdot 2BF_4^-$, the featured broad peaks ranged from 3.83 to 4.25 ppm were assigned to methylene-H from dctp²⁻ ligands and dppm di-gold motifs, while the upfield chemical shift at 6.65-6.78 ppm were corresponded to aromatic protons from dctp²⁻ ligand. The proton resonances of the triphenylphosphine appear as a set of overlap signal at δ 7.90-7.02 ppm. The formation of the monomer **1** was also supported by CSI-MS showing the mass to charge ratio (m / z) peak 971.8 for [(dppm)₂Au₄(dpt²⁻)]²⁺ (Fig. S6).



Monomer 1

Scheme 1. Synthetic route for gold(I) tetramer **1**₄. The yellow bands represent the [(dppm)Au₂]₄⁸⁺ half-rings, and the blue arch-bridges represent the dctp²⁻ ligands.



Figure 1. The perspective view of $\mathbf{1}_4$. The eight BF₄ anions located outside the cationic macrocycle, all the H atoms and Benzene rings are omitted for clarity (gold-Au, yellow-S, purple-P, gray-C).

omitted for clarity (gold-Au, yellow-S, purple-P, gray-C).

Single-crystal X-ray analysis has revealed that the molecular structure of the cation of tetramer 1_4 (see Fig. 1) consists of sixteen gold(I) atoms arranged in a slightly distorted ring including the half-ring 1 (Au1, Au2, Au3, Au4, Au4(A), Au3(A), Au2(A) and Au1(A)) and the half-ring 2 (Au8, Au7, Au6, Au5, Au5(A), Au6(A),Au7(A) and Au8(A)). Figure 1 shows the perspective view of the cation of 1_4 , with each monomer combined by two {(dppm)Au₂} units orientedly linked by a bridging dctp²⁻ ligand but two gaps because of the larger inducing group, phenyl. The average distance between intermolecular Au(I)...Au(I) bonding is 2.949Å (monomer to monomer) and the gap is 4.404Å (between eight-member half rings). The tetramer can be viewed as making up of two halves a dimer-to-dimer coupling. The two monomers, [(dppm)Au1···Au8-(dppm)] are linked

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together by two intermolecular Au(I)····Au(I) interactions (Au2····Au3 and Au6 ··· Au7), affording a dimer. Similarly, the other two monomers formed another dimer. The two dimers were coupled by two intermolecular Au(I)····Au(I) interactions(Au4····Au4(A)) and Au5 ····Au5(A)) to form a ring-like framework of 16 Au(I) centers. The average intramolecular Au(I)····Au(I) separation is 2.86 Å, which was about 0.18Å shorter than the intermolecular ones. It has proved that Au(I)····Au(I) interactions exist in the molecule for both are shorter than the sum of van der Waals radii for gold (3.32Å)^[19]. In addition, the 16 Au(I) centers are not in the same plane. The perimeter of the gold ring is about 50.011(68) Å. Inside of the gold ring are four cross-shaped dithiocarbamate linkers; outside of the ring are eight dppm units which are arranged in a distorted array.

Absorbtion(UV-Vis) and luminescence properties



Figure. 2 UV-vis spectral traces of $\mathbf{1}_4$ in MeCN solution. The insert shows the dimerization plot for a monomer-dimer equilibrium at various concentrations, top; Fluorescence emission spectrum (right) of $\mathbf{1}_4$ in MeCN solution, down.

Figure 2 shows the UV-visible absorption spectrum of solutions of **1** in MeCN at 298K. The electronic absorption spectra of **1**(Figure 2a) in MeCN at 298 K are dominated by high-energy absorption bands at 272 nm ($\epsilon_{max} = 149,207 \text{ M}^{-1} \text{ cm}^{-1}$), which is assigned as metal-perturbed intraligand transitions of the dppm and/or thiocarbamate ligands with reference to the previous studies on Au(I) thiolate complexes^[2,10]. There are additional low-energy shoulders at around 408 nm ($\epsilon_{max} = 6231 \text{ M}^{-1} \text{ cm}^{-1}$) that become more apparent with increasing concentration. The low-energy shoulders are tentatively assigned as ligand-to-metal charge transfer LMCT (thiocarbamate-to-gold) transitions.

Upon excited at 390nm, **1** emit at 500nm in deoxygenated acetonitrile solution at 298 K. With reference to the previous reports on the luminescence studies of Au(I) thiolate complexes, ^[2,10] the emission bands are tentatively assigned to be derived from triplet excited states of metal-centered (ds/dp) and ligand-to-metal charge transfer character that has been modified by Au^I...Au^I interactions.

In summary, we present a novel Au₁₆ ring with continuous $Au(I) \cdots Au(I)$ interactions self-assembled from bridging dithiocarbamate linkers and dinuclear terminal blocks. The Au(I)...Au(I) bonding interactions have provided the driving force to induce the self-assembly of a unique gold(I)-containing supramolecular metallo-macrocycle. NMR, CSI-TOF-MS, singlecrystal X-ray diffraction analysis, UV-Vis and luminescence spectroscopies were used to characterize the metallo-macrocycle. Such nest-like tetrameric gold (I) ring exhibit triplet yellow phosphorescence in solution, which could be exploited as potential phosphorescent sensor materials via host-guest and metal-metal bonding interaction.

Experimental Section

N,N'-bis(dicarbodithioate)-2,11-diaza[3.3]paracyclophane To a stirred suspension of NaH (60%, 3.8g, 95.0mmol) in DMF (180ml) was added a mixture of 1,4-bis(bromomethyl)benzene (11.9g, 45.2mmol) and p-toluenesulfonamide (7.6g, 45.2mmol) in DMF (180ml) over a period of 5hrs under nitrogen atmosphere, the temperature being kept at 50°C. After additional stirring and heating for 5hrs, the still hot yellow filtrate to give 10.8 g of a pale yellow precipitate. Separation by column chromatography (Wako-gel C-300, CH₂Cl₂/CH₃COOC₂H₅ = 40:1) afforded Ts₂N₂[3²]PC (660.8mg). The removal of the tosyl groups was achieved by treatment with a large excess of LiAlH₄ under mild conditions (40-50°C, THF, 18hrs) to yield the 2,11-diaza[3.3]paracyclophane (H₂N₂[3²]PC in 88% yield. Carbon disufide reacted with the aqueous solution of H₂N₂[3²]PC easily produced the ligand dctp, N,N'-bis(dicarbodithioate)-2,11-diaza[3.3]paracyclophane.

Au₁₆(μ -dppm)₈(μ - dctp²)₄](BF₄)₈(CH₃CN)₂ A solution of ligand (9.4 mg, 0.02 mmol) in methanol (3ml) was added dropwise to a white suspending solution of (dppm)Au₂Cl₂ (34 mg, 0.04mmol) in methanol (2ml) over 10 minutes. The reaction mixture turned yellow immediately and remained clear. After being stirred at room temperature for 24 hrs, an excess of NaBF₄ in methanol (2ml) was added to separate the product as light yellow powder. Upon removal of the solvent, the product was washed with methanol and dried in vacuum-desiccator, yield 49.0mg, 83.8%. Recrystallization by diffusion of diethyl ether into a MeCN solution afforded light yellow crystals.

Empirical formula $[C_{272}H_{240}N_8P_{16}S_{16}Au_{16}][BF_4]_8[CH_3CN]_2$, formula weight 8557.58, temperature 293(2)K, crystal system: monoclinic, space group *C* 2/c, *a* = 31.5257(66)Å, *b* = 44.6773(74)Å, *c* = 26.3487(41)Å, *β* = 101.164(9)°, *V* = 36409.43(6564)Å^3, and *Z* = 8. Data collections were performed at 293(2)K on a Bruker-AXS Smart CCD diffractometer (graphite-monochromated Mo K α

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radiation, $\lambda = 0.71073$ Å). The raw frame data for **1**₄ was integrated into SHELEX-format reflection files and corrected for Lorentz and polarization effects using SAINT. Corrections for incident and diffracted beam absorption effects were applied using SADABS. The structure was solved by a combination of the Patterson method using SHELXTL and the difference Fourier technique and refined by full matrix least squares on F². Crystallographic agreement factors for the refinement are as follows: R₁ = 6.28%, wR₂ = 13.11% for 14180 reflections with I > 2 σ (I) (R₁ = 18.28%, wR₂ = 19.43% and S = 1.025 for all data) and 1439 variable parameters. CCDC 280466.

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Keywords: self-assembly • macrocycle • aurophilicity • gold

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Gold ring: A novel metallo-macrocyle composing of 16 gold(I) atoms self-assembled *via* strong Au¹···Au¹ bonding interaction in the solid state

Ya-qing Wang, Xuan-feng Jiang* and Shu-yan Yu*

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