

# Development of Au-based Multinuclear Complexes with *N*-Heterocyclic Carbene Ligands

(*N*-ヘテロ環状カルベン (NHC) を支持配位子とする多核金錯体の開発)

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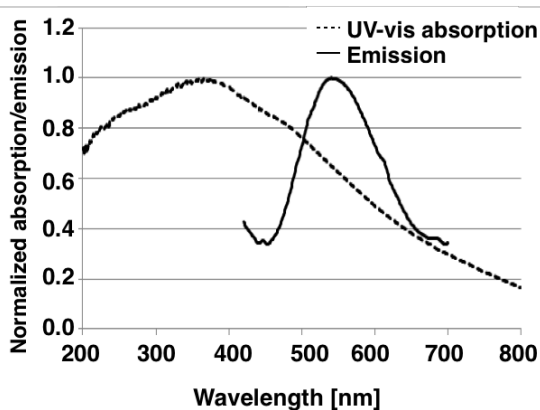
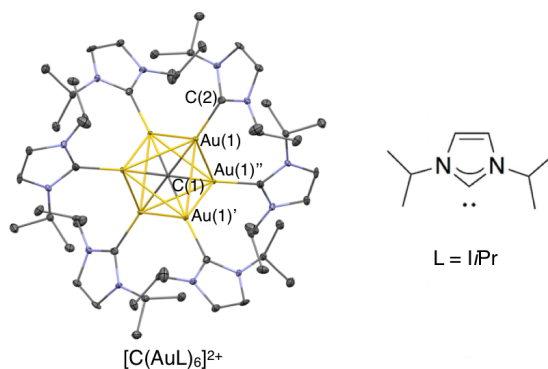
## 1. Introduction

Gold compounds have shown promise as catalysts for molecular transformation and luminescence materials. In particular, Au<sup>I</sup> compounds have unique characteristics such as carbophilic  $\pi$ -acidity, redox activity, and aurophilicity due to the d<sup>10</sup> closed shell electron configuration of Au<sup>I</sup> ions in a linear two-coordinate geometry. Among them, multinuclear Au<sup>I</sup> compounds, in which two or more Au<sup>I</sup> ions are bonded or located close to each other, have been extensively investigated to gain knowledge about the influence of aurophilic interactions on the structure-specific electronic properties leading to multi-electron redox catalysts and photoluminescence. Over the last two decades, there has been a steep rise in research related to Au<sup>I</sup> complexes ligated by *N*-heterocyclic carbene (NHC) ligands. Compared to traditional phosphine ligands, NHC ligands have a stronger  $\sigma$ -donating property, and manipulation of the electronic and steric characters of NHC ligands can be more easily achieved by *N*-functionalization. In this study, I focused on the construction of multinuclear Au<sup>I</sup> complexes with NHC ligands. Specifically, a carbon-centered CAu<sub>6</sub> cluster and a macrocyclic dinuclear Au<sup>I</sup> compound based on bis-NHC ligands have been developed for Au-based multinuclear complexes with structure-specific properties.

## 2. Synthesis and characterization of carbon-centered Au<sup>I</sup> complexes supported by NHC ligands

In my master course study, I constructed a carbon-centered Au<sup>I</sup> cluster, [C(Au<sup>I</sup>L)<sub>6</sub>]<sup>2+</sup>, supported by 1,3-diisopropylimidazol-2-ylidene (L = IiPr) ligands by the reaction of [(IiPrAu)<sub>3</sub>O](BF<sub>4</sub>) with (trimethylsilyl)diazomethane in CH<sub>2</sub>Cl<sub>2</sub> in the presence of triethylamine to produce chemically stable dark-brown solid. Based on this, detailed characterization of the product and comparison with those of phosphine ligand supporting counterparts were conducted based on <sup>1</sup>H and <sup>13</sup>C NMR, ESI-MS, absorption/emission, and XRD analyses in this study.

A single crystal of [C(AuIiPr)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> suitable for XRD measurement was obtained by slow evaporation from a CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane solution as a yellow block crystal. The Au<sup>I</sup> cluster has an antiprism structure with D<sub>3h</sub> symmetry, and the bond lengths of Au(1)–Au(1)′ and Au(1)–Au(1)″ are 3.0548(3) and 2.9282(3) Å, respectively. This result suggests strong Au–Au interactions in the cluster. The Au–



**Figure 1.** Upper: X-ray crystal structure of [C(AuIiPr)<sub>6</sub>]<sup>2+</sup>, bottom: UV-vis absorption (dash line) and emission spectra (bold line) of [C(AuIiPr)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> in the solid state.

Au distances are comparable to those of a triphenylphosphine supported counterparts (2.887(1)–3.226(1) Å). Notably, the whole crystal structure is not highly symmetrical due to the packing force arising from the bulky *i*Pr ligands.

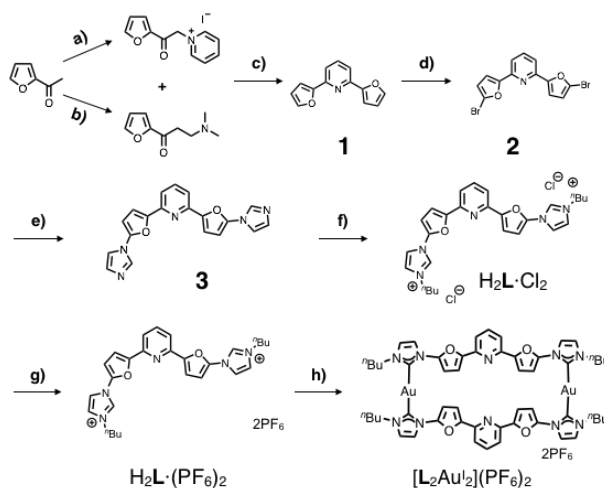
Photoluminescence measurement of [C(AuI*i*Pr)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> cluster in the solid state revealed that it is luminescent with green emission under irradiation of UV light ( $\lambda_{\text{ex}} = 370$  nm). The emission had a longer wavelength ( $\lambda_{\text{em}} = 547$  nm) compared with that of a triphenylphosphine supported carbon-centered cluster ( $\lambda_{\text{em}} = 537$  nm). This difference may come from the stronger  $\sigma$ -coordination ability of NHC ligands (Figure 1). On the other hand, no emission was observed for [C(AuI*i*Pr)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> in solution at room temperature.

### 3. Au-mediated macrocycle with bis-NHC ligands

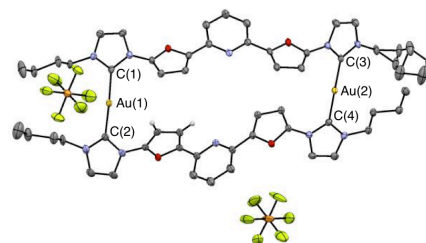
NHCs can be easily modified with many types of organic ligand donors at the nitrogen atoms directing toward metal array. In this study, aiming at linearly arranging heterometallic coinage metal ions with a close distance to study the influence of metallophilic interactions on metal array-specific properties, I developed a bis-NHC ligand **L** with a pyridine-centered heterocycle-coupled spacer. Since NHC ligands have a higher affinity to Au<sup>I</sup> ions than pyridine and furan, which prefer Ag<sup>I</sup> or Cu<sup>II</sup>, ligand **L** was expected to produce a linear heterometallic Au<sup>I</sup>–M–Au<sup>I</sup> (M = Ag<sup>I</sup> or Cu<sup>II</sup>) complex in a ladder or helical double-stranded structure.

Ligand **L** was synthesized from 2-acetylfuran in 6 steps (Scheme 1). Firstly, 2,6-difuryl pyridine **1** was prepared by a coupling reaction of two 2-acetyl furan derivatives, and then brominated by *N*-bromosuccinimide (NBS) to afford **2**. Compound **2** was reacted with imidazole using a Cu<sup>I</sup> catalyst to produce a bis-imidazole **3**, followed by alkylation at the terminal nitrogen atoms by *n*-butyl chloride to obtain a bis-imidazolium salt, H<sub>2</sub>L·Cl<sub>2</sub>. The counter anion was then replaced using AgPF<sub>6</sub> to obtain H<sub>2</sub>L·(PF<sub>6</sub>)<sub>2</sub>. Complexation of H<sub>2</sub>L·(PF<sub>6</sub>)<sub>2</sub> with equimolar amount of thtAuCl (tht = SC<sub>4</sub>H<sub>8</sub>) in the presence of base formed a macrocyclic dinuclear Au<sup>I</sup> complex, [L<sub>2</sub>Au<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> in 60% yield, which is air- and light-stable at room temperature. Its NMR spectra in CDCl<sub>3</sub> well established a high symmetrical structure in solution. The <sup>13</sup>C signals assignable to C<sub>carbene</sub> atoms were observed at 182.2 ppm, in the range for cationic two-coordinate NHC–Au–NHC compounds. The molecular structure of [L<sub>2</sub>Au<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was determined by single-crystal X-ray analysis (Figure 2). The intramolecular Au–Au distance is *ca.* 13.5 Å, which is too far for intramolecular aurophilic interactions. Notably, as the macrocyclic cavity is very narrow and there is steric hindrance between the proton atoms on the furan rings, the Au<sup>I</sup>-mediated macrocycle is distorted to adapt a helical structure while the single crystal is a racemic mixture.

H<sub>2</sub>L·(PF<sub>6</sub>)<sub>2</sub> and [L<sub>2</sub>Au<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> were investigated with respect to their photoluminescence properties (Figure 3). At room temperature, H<sub>2</sub>L·(PF<sub>6</sub>)<sub>2</sub> produced intense blue-purple luminescence both in solution and solid state. [L<sub>2</sub>Au<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> showed a photoluminescence behavior similarly to that of H<sub>2</sub>L·(PF<sub>6</sub>)<sub>2</sub>, except that the intensity both in solution and solid state were much decreased. This result indicates that the emission mainly comes from the linked heteroaromatic rings, while significant quenching takes place in [L<sub>2</sub>Au<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> due to the steric and electronic changes caused by the complexation with Au<sup>I</sup> ions.

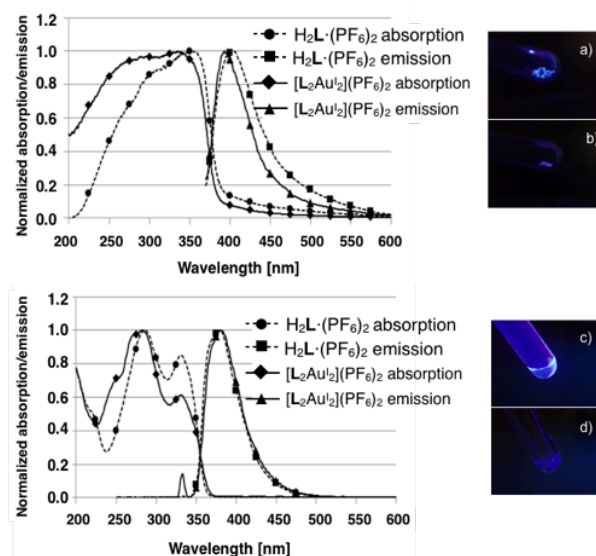


**Scheme 1.** a) I<sub>2</sub>, Pyridine, reflux, 3 h, 98%; b) conc. HCl, (CH<sub>2</sub>O)<sub>nb</sub>, (CH<sub>3</sub>)<sub>2</sub>NH·HCl, EtOH, reflux, 16 h, then K<sub>2</sub>CO<sub>3</sub>, 90%; c) NH<sub>4</sub>OAc, EtOH, reflux, 16 h, 21%; d) NBS, TsOH, benzene, 80 °C, 45 min, 67%; e) imidazole, *cat.* CuI, Cs<sub>2</sub>CO<sub>3</sub>, DMF, 120 °C, 60 h, 58%; f) *n*-BuCl, neat, 150 °C, 9 days; g) KPF<sub>6</sub>, H<sub>2</sub>O, rt, 98%; h) thtAuCl (1 eq), K<sub>2</sub>CO<sub>3</sub>, MeCN/DCM, rt, 8 h, 60%.

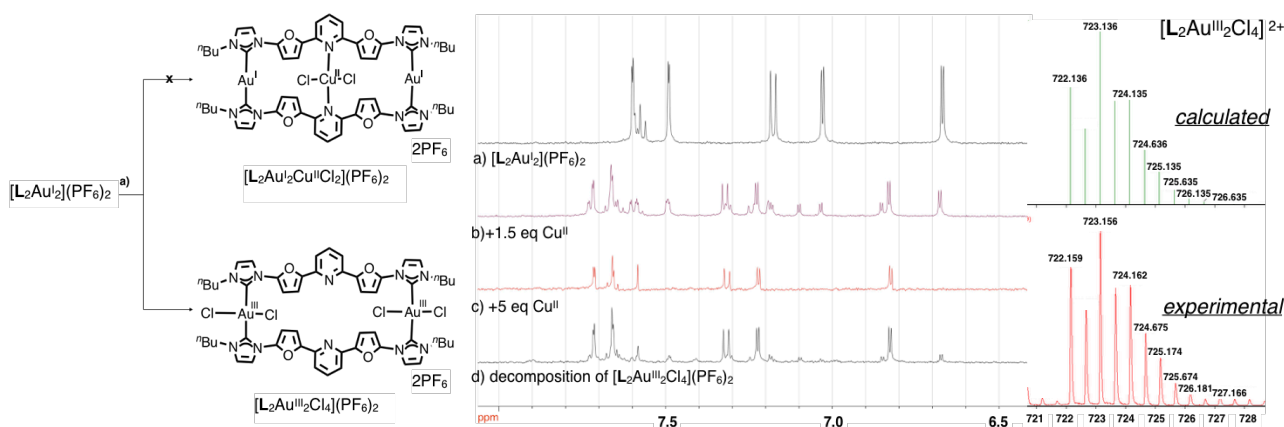


**Figure 2.** Single crystal X-ray structure ORTEP diagram of [L<sub>2</sub>Au<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> with 50% probability (H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): C(1)–Au(1) 2.020(6), C(2)–Au(1) 2.019(6), C(3)–Au(2) 2.015(6), C(4)–Au(2) 2.025(6), Au(1)–Au(2) 13.541, C(1)–Au(1)–C(2) 177.8(2), C(3)–Au(2)–C(4) 175.1(2).

The central pyridine moiety of the ligand **L** in  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$  can possibly coordinate to other metal ions to enable linear heterometallic arrangement. In expectation that a  $\text{Cu}^{\text{II}}$  ion would bridge two pyridine ligands in the macrocycle, 1.5 eq of  $\text{Cu}^{\text{II}}$  was added to a solution of  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$  in  $\text{CH}_3\text{CN}$ . However, instead of generation of  $[\text{L}_2\text{Au}_2\text{Cu}^{\text{II}}\text{Cl}_2](\text{PF}_6)_2$ , oxidation of  $\text{Au}^{\text{I}}$  to  $\text{Au}^{\text{III}}$  was observed, as the signals for  $\text{L}_2\text{Au}_2^{\text{I}}$ ,  $\text{L}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}$  and  $\text{L}_2\text{Au}_2^{\text{III}}$  were confirmed by NMR measurement (Figure 4). Further addition of  $\text{Cu}^{\text{II}}$  to the solution resulted in conversion from  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$  to a dinuclear  $\text{Au}^{\text{III}}$  macrocyclic compound  $[\text{L}_2\text{Au}_2^{\text{III}}\text{Cl}_4](\text{PF}_6)_2$ . Unfortunately, the isolation of  $[\text{L}_2\text{Au}_2^{\text{III}}\text{Cl}_4](\text{PF}_6)_2$  was not successful because of its decomposition, as  $\text{L}_2\text{Au}_2^{\text{I}}$  and  $\text{L}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}$  species were observed again after purification probably due to their disproportionation. In order to fully study the redox behaviors of dinuclear macrocyclic compound  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$  and to achieve redox-induced helicity switching in the solid state, later, freshly prepared dichloriodobenzene as an oxidant was added to a solution of  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$  in  $\text{CH}_3\text{CN}$  to generate fully oxidized dinuclear  $\text{Au}^{\text{III}}$  macrocyclic compound  $[\text{L}_2\text{Au}_2^{\text{III}}\text{Cl}_4](\text{PF}_6)_2$ , which was obtained as a stable white solid. Further study of the redox behavior and introduction of other heterometallic ions into macrocyclic  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$  is on going.



**Figure 3.** Upper: UV-vis absorption (dash line) and emission spectra (bold line) of  $\text{H}_2\text{L}\cdot(\text{PF}_6)_2$  and  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$  in the solid state upon excitation at 298 K. Bottom: UV-vis absorption (dash line) and emission spectra (bold line) of  $\text{H}_2\text{L}\cdot(\text{PF}_6)_2$  and  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$ , in  $\text{CH}_3\text{CN}$  at a concentration of 10  $\mu\text{M}$ , under aerobic condition at 298 K. Photographs: Luminescence of a)  $\text{H}_2\text{L}\cdot(\text{PF}_6)_2$  and b)  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$  in the solid state, c)  $\text{H}_2\text{L}\cdot(\text{PF}_6)_2$  and d)  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$  in  $\text{CH}_3\text{CN}$  at 5 mM, under aerobic condition at 298 K (365 nm).



**Figure 4.** Left:  $\text{Au}^{\text{I}}$  centers oxidized by  $\text{Cu}^{\text{II}}$ , a) 5 eq of  $\text{CuCl}_2$ ,  $\text{CH}_3\text{CN}$ , rt, 6 h; Middle: NMR spectrum of a)  $[\text{L}_2\text{Au}_2](\text{PF}_6)_2$ , b) a mixture of  $\text{L}_2\text{Au}_2^{\text{I}}$ ,  $\text{L}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}$  and  $\text{L}_2\text{Au}_2^{\text{III}}$  species; c)  $[\text{L}_2\text{Au}_2^{\text{III}}\text{Cl}_4](\text{PF}_6)_2$  and d) decomposition of  $[\text{L}_2\text{Au}_2^{\text{III}}\text{Cl}_4](\text{PF}_6)_2$  during purification steps (500 MHz, 300 K,  $\text{CD}_3\text{CN}$ ); Right: An ESI-TOF MS spectrum of  $[\text{L}_2\text{Au}_2^{\text{III}}\text{Cl}_4](\text{PF}_6)_2$  (positive,  $\text{CH}_3\text{CN}$ , 3000/30 V).

## 4. Conclusion

In this study, I have examined Au-based multinuclear complexes with *N*-heterocyclic carbene ligands using a carbon atom center or a linearly linking bis-monodentate ligand as the template, with a focus on the influence of carbene coordination and aurophilic interactions on the structure and electronic properties of the resultant complexes. Consequently, a carbon-centered  $\text{CAu}_6$  cluster with antiprism arrangement as well as a macrocyclic dinuclear  $\text{Au}^{\text{I}}$  compound based on bis-NHC ligands were obtained and their luminescent properties and redox behaviors have been clarified. Further studies on their photochemical and electronic properties and multi-electron-based catalytic activities are now underway.