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Dinuclear organogold(I) complexes bearing uracil moieties: chirality of Au(I)-Au(I) axis and self-assembling

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The conjugation of the dinuclear organogold(I) complexes with a bridging diphosphine ligand as an organometallic compound and the uracil derivative as a nucleobase was demonstrated to afford the bioorganometallic conjugates. The single-crystal X-ray structure determination of the dinuclear organogold(I)-uracil conjugates revealed the assembly properties of the gold(I) and the uracil moieties in a solid state. The crystal structure of **(U6Au)$_2$(μ-Xantphos)** (**U6** = 6-ethynyl-1-octyluracil) with Xantphos as a bridging diphosphine ligand revealed an intramolecular aurophilic Au(I)-Au(I) interaction. *R*- and *S*-enantiomers based on Au(I)-Au(I) axis are exist in the unit cell, which are connected alternately to form the hydrogen-bonded assembly through intermolecular hydrogen bonds between the uracil moieties. In the case of the dinuclear organogold(I) complex **(U5Au)$_2$(μ-Xantphos)** (**U5** = 5-ethynyl-1-octyluracil), both enantiomers were found to form homochiral *RR* and *SS* dimers, respectively, through the π-π interaction between 5-ethynyl-uracil moieties. In the crystal packing each dimers are assembled alternately to form the hydrogen-bonded assembly through intermolecular hydrogen bonds between the uracil moieties. As expected, the utilization of (*R*)-BINAP as a bridging diphosphine ligand with axial chirality was performed to induce the chirality of Au(I)-Au(I) axis. The crystal structure of the dinuclear organogold(I) complex with (*R*)-BINAP **(U6Au)$_2$(μ-*R*-BINAP)** confirmed the axial chirality in Au(I)-Au(I) axis to form *R*,*R*-enantiomer, wherein each molecule is arranged through intermolecular hydrogen bonds between the uracil moieties to form a helical molecular arrangement.

Introduction

Gold(I) alkynyl compounds have attracted much attention in a variety of areas such as luminescent materials and metallodrugs.[1] A number of gold(I) alkynyl complexes are characterized to possess the luminescent properties, which show long emission lifetimes and emissive excited states derived from alkynyl moieties.[2] Several gold(I) alkynyl complexes are also reported to exhibit cytotoxicity for cancer cells.[3] Gold(I) complexes are known to aggregate through d^{10}–d^{10} closed shell aurophilic bonding interaction, which plays an important role in aggregated structures and physical properties.[4] The emission properties of the gold(I) complexes are influenced by the aurophilic interaction, which often expresses specific emission properties. Some gold(I) complexes show mechanochromic luminescence by the switching of the aurophilic interaction through mechanical stimuli such as grinding in a solid state.[5] The design of aggregation in the gold(I) complexes is important for control of the aurophilic interaction. The dinuclear gold(I) complex with a bridging ligand is considered to be a convenient approach for the rearrangement of the Au(I) centers. In particular, the semirigid bridging diphosphine ligand is expected to arrange Au(I) centers in the same side of the ligand and facilitate induction of the aurophilic interaction.[6] On the other hand, biomolecules such as nucleobases, peptide, and sugars play the important role in the formation of the highly-organized structures like DNA, proteins, and enzymes. The utilization of non-covalent bonds is a convenient strategy for construction of the designed assembly structure. The complementary hydrogen bond of nucleobases is regarded as a powerful tool for building up of various self-assembly systems based on its directionality and specificity.[7] The reversibility and tunability of hydrogen bonding also plays an important factor for the chemical and/or physical properties of molecular assemblies.[8] The combination of functional organometallic compounds with biomolecules such as

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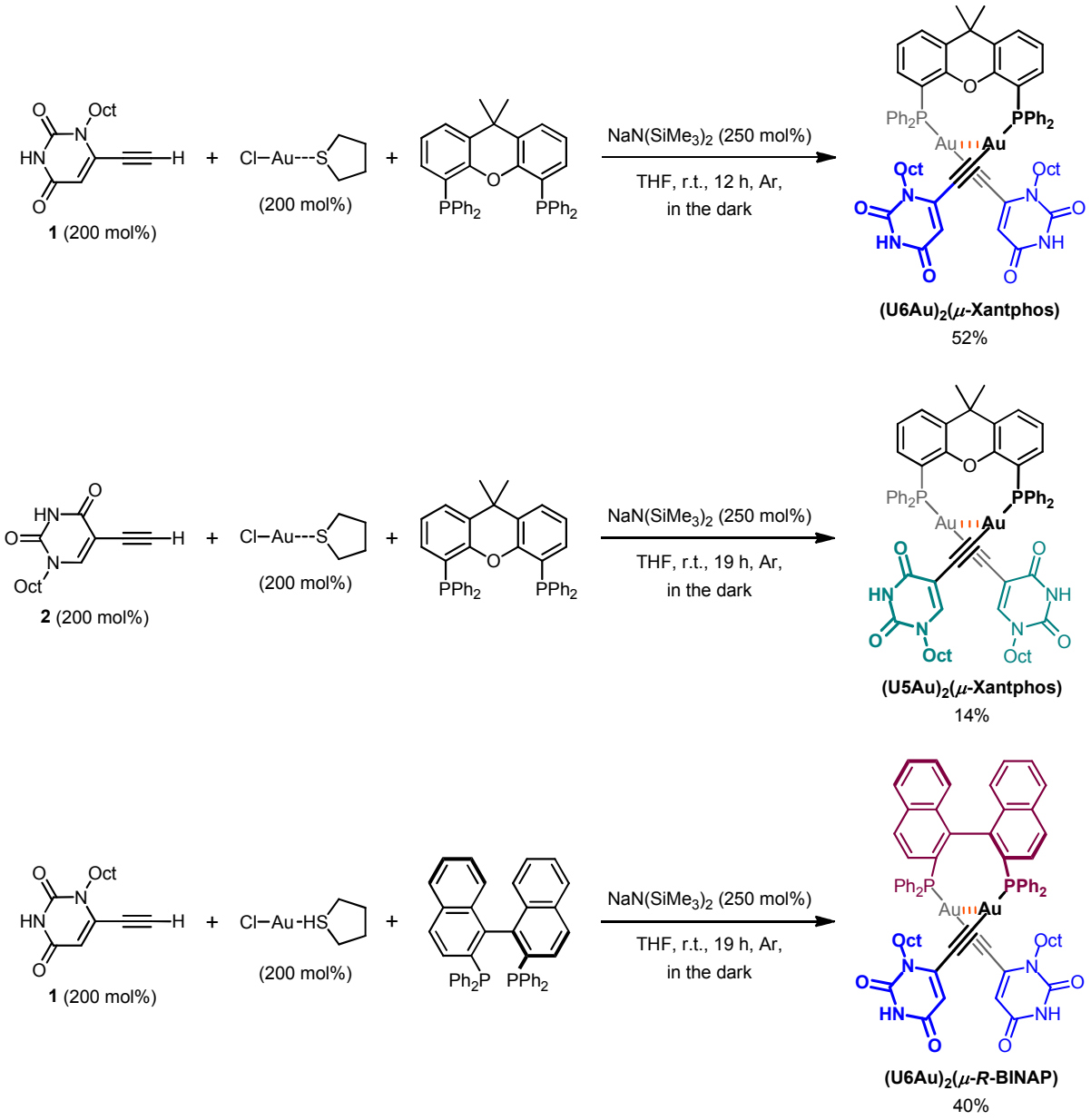
nucleobases and peptides is envisioned to afford bioorganometallic compound.[9] We have already reported the emergence of emission based on metallophilic interaction of the aggregated structures of the organoplatinum(II)-uracil and organogold(I)-guanine conjugates.[10] From these points of view we herein designed and synthesized the dinuclear organogold(I)-uracil conjugates with the bridging diphosphine ligands in order to control the arrangement of Au(I) centers and self-assembly properties of the uracil moieties in a crystal structure.

Results and discussion

Xantphos and (*R*)-BINAP were focused on as the bridging diphosphine ligand. The advantage in the use of Xantphos and (*R*)-BINAP depends on their semirigid backbone to arrange the phosphorus atoms on the same side. The dinuclear organogold(I)-uracil conjugates with the bridging diphosphine ligands were designed by the introduction of Xantphos and (*R*)-BINAP to induce an intramolecular aurophilic Au(I)-Au(I) interaction. The dinuclear organogold(I)-uracil conjugates **(U6Au)$_2$(μ-Xantphos)**, **(U5Au)$_2$(μ-Xantphos)** and **(U6Au)$_2$(μ-*R*-BINAP)** were prepared by the reaction of 6-ethynyl-1-octyluracil (**1**) or 5-ethynyl-1-octyluracil (**2**) with (ClAu)$_2$(μ-diphosphine) (diphosphine = Xantphos or (*R*)-BINAP), which were obtained by the treatment of chloro(tetrahydrothiophene)gold(I) [ClAu(tht)] with the



Scheme 1. Synthesis of the dinuclear organogold(I)-uracil conjugates **(U6Au)$_2$(μ-Xantphos)**, **(U5Au)$_2$(μ-Xantphos)** and **(U6Au)$_2$(μ-*R*-BINAP)**.

corresponding diphosphine *in situ*, in the presence of sodium bis(trimethylsilyl)amide ($NaN(SiMe_3)_2$) (Scheme 1). Thus obtained dinuclear organogold(I)-uracil conjugates were fully characterized by ^1H NMR, ^{13}C NMR, ^{31}P NMR, IR, HRMS and elemental analysis. In the ^1H NMR spectra, the signal for the ethynyl proton disappeared and the upfield shift of the uracil proton was observed after the introduction of the Au(I) center. The ^{31}P NMR spectra of **(U6Au)$_2$(μ-Xantphos)**, **(U5Au)$_2$(μ-Xantphos)** and **(U6Au)$_2$(μ-*R*-BINAP)** showed only one kind of resonance at around 30 ppm in CD_2Cl_2, indicating that two phosphorus atoms of the dinuclear organogold(I)-uracil conjugates are equivalent in NMR time scale.

X-ray crystallographic analyses were performed in order to clarify the coordination environment of Au(I) centers and self-assembly properties of the dinuclear organogold(I)-uracil conjugates (Table 1). Diffraction-quality single crystals of **(U6Au)$_2$(μ-Xantphos)** and **(U5Au)$_2$(μ-Xantphos)** were grown by diffusion of methanol into dichloromethane solution of **(U6Au)$_2$(μ-Xantphos)** and diffusion of hexane into dichloromethane solution of **(U5Au)$_2$(μ-Xantphos)**. The dinuclear structure of **(U6Au)$_2$(μ-Xantphos)** composed of 6-ethynyl-1-octyluracil was confirmed by single-crystal X-ray structure determination (Fig. 1). Selected bond distances and angles are listed in Table 2. The crystal structure revealed a linear coordination geometry of the Au(I) centers bridged by the Xantphos ligand. It should be noted that an intramolecular aurophilic Au(I)-Au(I) interaction was observed with Au(1)-Au(2) distance of 2.9994(8) Å. The semirigid xanthene backbone was found to play an important role in the arrangement of the phosphorus atoms on the same side to induce intramolecular Au(I)-Au(I) interaction. The conformational enantiomers based on the torsional twist about the Au(I)-Au(I) axis are possible in the dinuclear gold(I)-uracil conjugates as depicted in Fig 2. The dinuclear organogold(I) complex **(U6Au)$_2$(μ-Xantphos)** crystallized in the space group *P*-1 with *R*- and *S*- enantiomers based on the Au(I)-Au(I) axis

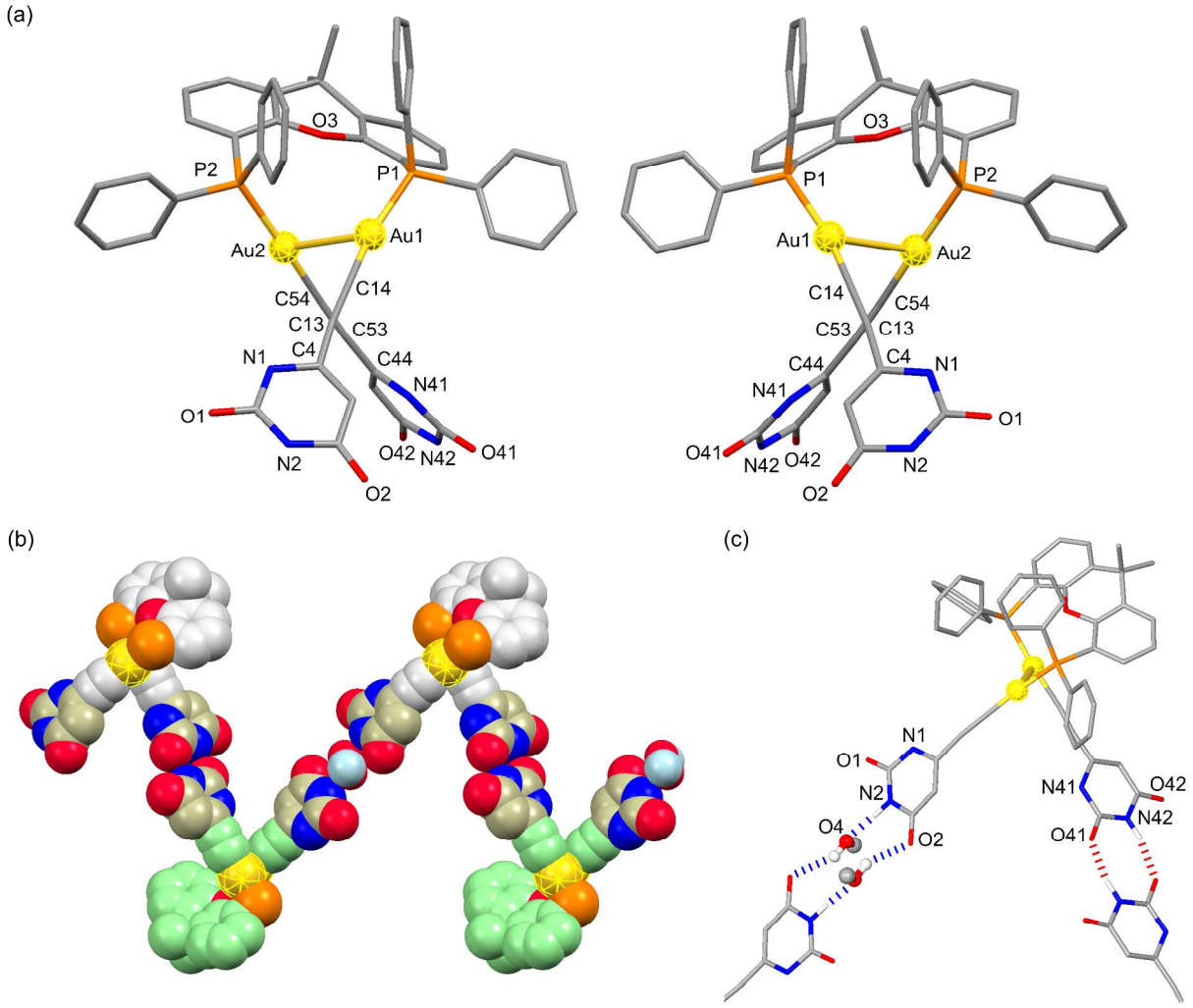


Fig. 1 (a) Molecular structures of the *R*- and *S*-enantiomers, (b) the heterochiral hydrogen-bonded assembly through intermolecular hydrogen bonds between the uracil moieties of the dinuclear organogold(I)-uracil conjugates **(U6Au)$_2$(μ-Xantphos)** and (c) a portion of the crystal structure showing two types of the hydrogen bonding pattern in the heterochiral hydrogen-bonded assembly (hydrogen atoms and octyl moieties are omitted for clarity).

Table 1.
Crystallographic date for **(U6Au)$_2$(μ-Xantphos)**, **(U5Au)$_2$(μ-Xantphos)** and **(U6Au)$_2$(μ-*R*-BINAP)**

	(U6Au)$_2$(μ-Xantphos)	(U5Au)$_2$(μ-Xantphos)	(U6Au)$_2$(μ-*R*-BINAP)
Empirical formula	$C_{67}H_{70}N_4O_5P_2Au_2$• CH_2Cl_2 • CH_3OH	$C_{67}H_{70}N_4O_5P_2Au_2$• CH_2Cl_2	$C_{72}H_{70}N_4O_4P_2Au_2$• $CHCl_3$
Formula weight	1584.17	1552.13	1630.63
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	*P*-1 (No. 2)	*C*2/*c* (No. 15)	$P2_12_12_1$ (No. 19)
a (Å)	10.6798(6)	30.3688(18)	11.0678(16)
b (Å)	14.2920(7)	26.6704(15)	23.228(4)
c (Å)	22.3083(13)	21.7986(12)	27.246(4)
α (°)	97.4663(16)		
β (°)	90.7906(16)	109.0564(16)	
γ (°)	91.1556(14)		
V (Å^3)	3375.0(3)	16688.2(16)	7004.5(18)
Z	2	8	4
D_{calcd} (g cm^{-3})	1.559	1.235	1.546
μ (Mo Kα) (cm^{-1})	45.360	36.672	44.086
T (°C)	4.0	4.0	-150
λ (Mo Kα) (Å)	0.71075	0.71075	0.71075
*R*1 [a]	0.083	0.054	0.078
*wR*2 [b]	0.232	0.179	0.211

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2.
Selected bond distances (Å) and angles (º) for **(U6Au)$_2$(μ-Xantphos)**, **(U5Au)$_2$(μ-Xantphos)** and **(U6Au)$_2$(μ-*R*-BINAP)**

	(U6Au)$_2$(μ-Xantphos)	(U5Au)$_2$(μ-Xantphos)	(U6Au)$_2$(μ-*R*-BINAP)
Bond distances			
Au(1)–Au(2)	2.9994(8)	2.9286(5)	3.0021(9)
Au(1)–P(1)	2.283(4)	2.281(3)	2.281(4)
Au(2)–P(2)	2.275(3)	2.253(4)	2.290(4)
Au(1)–C(14)	2.009(14)	1.976(10)	2.066(14)
Au(2)–C(54)	2.002(17)	1.926(11)	2.003(17)
C(13)–C(14)	1.16(2)	1.230(13)	1.14(2)
C(53)–C(54)	1.18(2)	1.188(17)	1.16(2)
Bond angles			
P(1)–Au(1)–C(14)	168.1(4)	166.9(3)	172.2(5)
P(2)–Au(2)–C(54)	174.5(5)	176.1(3)	176.5(4)
Au(1)–C(14)–C(13)	180.0(13)	175.1(11)	175.8(14)
Au(2)–C(54)–C(53)	173.1(16)	170.5(8)	175.6(14)
C(14)–C(13)–C(4)	173.3(17)		168.7(18)
C(54)–C(53)–C(44)	173(2)		175.3(18)
C(14)–C(13)–C(3)		171.6(13)	
C(54)–C(53)–C(43)		175.9(10)	

in the unit cell (Fig 1a). The Au(I)-Au(I) interaction was found to induce the deviation from the linearity of the coordination structures of the Au centers with P-Au-C angles of 168.1(4)° and 174.5(5)°. The torsion angle of P(1)-Au(1)-Au(2)-P(2) of 82° indicates that the P-Au-C moieties are almost perpendicular to each other. Furthermore, each enantiomer is connected alternately to form the heterochiral hydrogen-bonded assembly through intermolecular hydrogen bonds between the uracil moieties (Fig. 1b and Table 3). There are two types of the hydrogen bonding pattern in the heterochiral hydrogen-bonded assembly, wherein one uracil moiety is connected by the hydrogen-bonded bridges of methanol solvent molecules and another uracil moiety is hydrogen-bonded to the uracil moiety of another molecule directly (Fig. 1c).

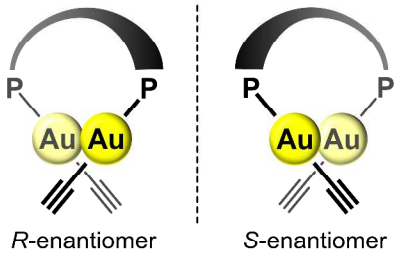


Fig. 2 Enantiomorphous conformations of the dinuclear organogold(I)-uracil conjugates with the bridging diphosphine ligands. The enantiomorphs are related by the mirror plane.

Table 3.
Intermolecular hydrogen bonds for **(U6Au)$_2$(μ-Xantphos)**, **(U5Au)$_2$(μ-Xantphos)** and **(U6Au)$_2$(μ-*R*-BINAP)**

Compound	Donor	Acceptor	D•••A (Å)	D–H•••A (°)
(U6Au)$_2$(μ-Xantphos)	O(4)[a]	O(2)[b]	2.73(2)	147(10)
	N(2)	O(4)[a]	2.78(2)	172(5)
	N(42)	O(41)[c]	2.798(15)	167(4)
(U5Au)$_2$(μ-Xantphos)	N(2)	O(42)[d]	2.816(13)	166(4)
	N(42)	O(1)[e]	2.924(13)	169(3)
(U6Au)$_2$(μ-*R*-BINAP)	N(2)	O(41)[f]	2.816(17)	158(4)
	N(42)	O(2)[g]	2.789(18)	176(4)

[a] Oxygen atom of methanol. [b] -X+2, -Y+1, -Z+2. [c] -X+2, -Y+1, -Z+1. [d] X, -Y, Z+1/2. [e] X, -Y, Z+1/2-1. [f] -X+2, Y+1/2-1, -Z+1/2. [g] -X+2, Y+1/2, -Z+1/2.

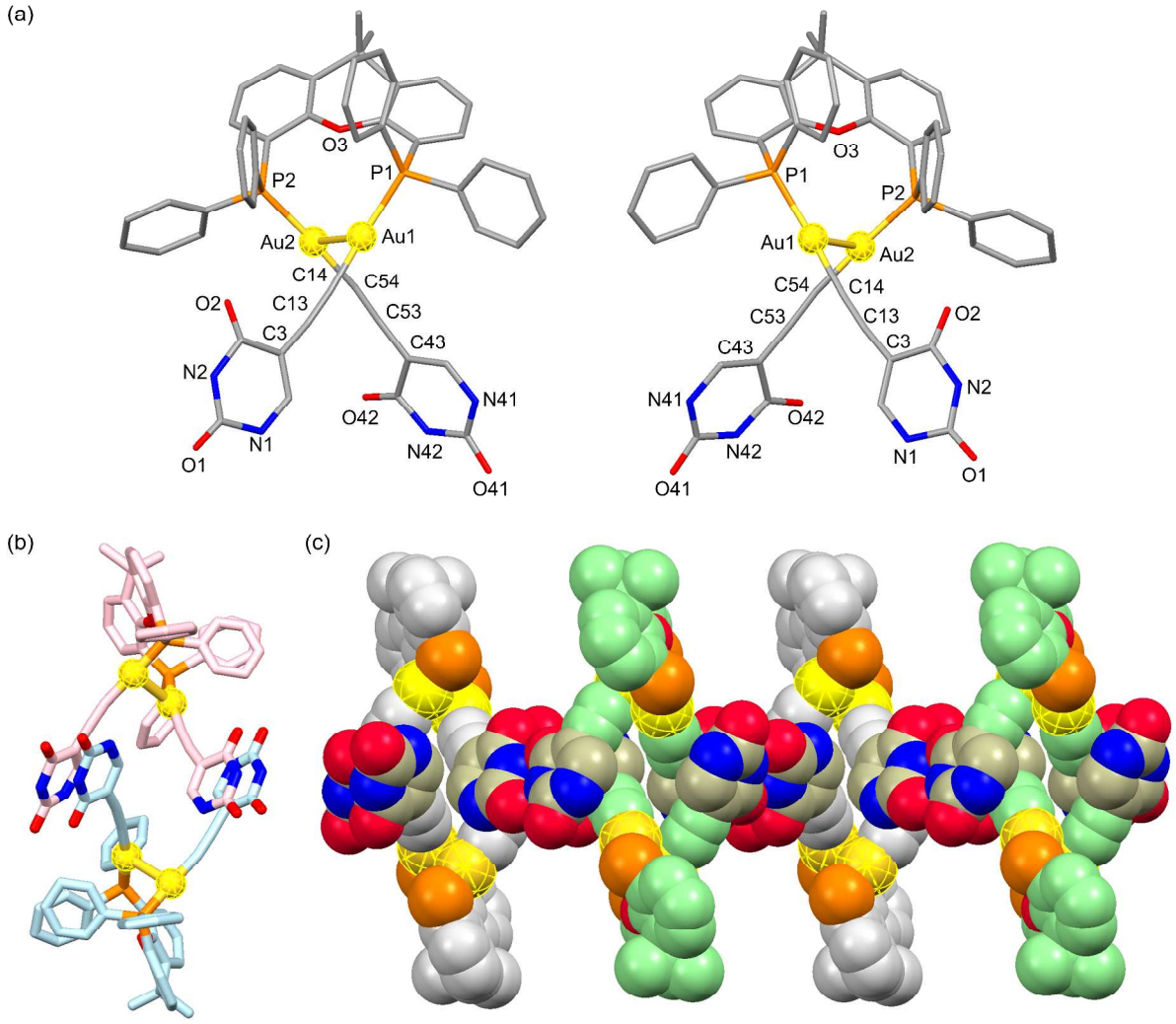


Fig. 3 (a) Molecular structures of the *R*- and *S*-enantiomers, (b) the homochiral π stacked dimer and (c) the heterochiral hydrogen-bonded assembly through intermolecular hydrogen bonds between the uracil moieties of the dinuclear organogold(I)-uracil conjugate **(U5Au)$_2$(μ-Xantphos)** (hydrogen atoms and octyl moieties are omitted for clarity).

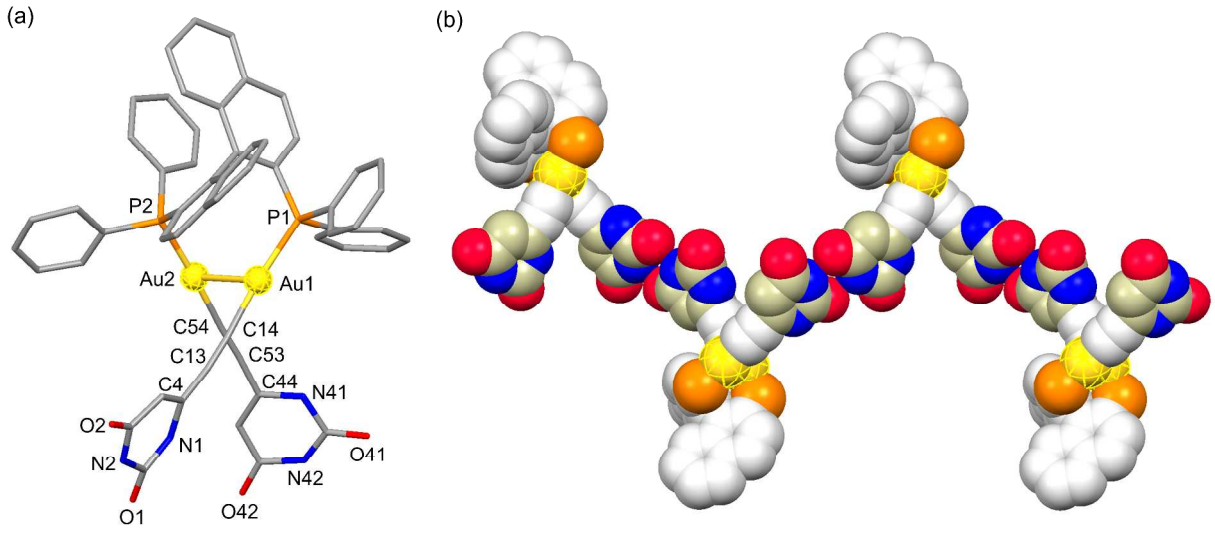


Fig. 4 (a) Molecular structure of the *R*-enantiomer and (b) the homochiral hydrogen-bonded assembly through intermolecular hydrogen bonds between the uracil moieties of the dinuclear organogold(I)-uracil conjugate **(U6Au)$_2$(μ-*R*-BINAP)** (hydrogen atoms and octyl moieties are omitted for clarity).

An intramolecular aurophilic Au(I)-Au(I) interaction with Au(1)-Au(2) distance of 2.9286(5) Å in the crystal structure of **(U5Au)$_2$(μ-Xantphos)** composed of 5-ethynyl-1-octyluracil, wherein the direction of hydrogen bonding sites of the uracil moieties is different from **(U6Au)$_2$(μ-Xantphos)**, was also confirmed by single-crystal X-ray structure determination (Fig. 3). *R*- and *S*-enantiomers based on Au(I)-Au(I) axis observed in **(U5Au)$_2$(μ-Xantphos)** are present as depicted in Fig. 3a. The distortion of the linear coordination geometry of the Au centers based on the Au(I)-Au(I) interaction was also observed resulting in P-Au-C angles of 166.9(3)° and 176.1(3)° (Table 2). Compared with **(U6Au)$_2$(μ-Xantphos)**, the P(1)-Au(1)-Au(2)-P(2) torsion angle of 78.96(10)° was slightly small. The Au-C bond of **(U5Au)$_2$(μ-Xantphos)** was a little shorter than that of **(U6Au)$_2$(μ-Xantphos)**. The position of the introduced ethynyl moiety of the uracil is likely to influence the electronic environment of the Au centers. Interestingly, both enantiomer form homochiral *RR* and *SS* dimers, respectively, through π–π interactions between the uracil moieties (Fig. 3b). Furthermore, each homochiral π stacked dimer is connected alternately to form the hydrogen-bonded assembly through intermolecular hydrogen bonds between the uracil moieties (Fig. 3c and Table 3). Self-assembly patterns were found to depend on the direction of hydrogen bonding sites.

Based on the above-mentioned intriguing results, we embarked upon the chirality induction in Au(I)-Au(I) axis by using the bridging diphosphine ligand with axial chirality. Diffraction-quality single crystal of **(U6Au)$_2$(μ-*R*-BINAP)** was grown by diffusion of hexane into chloroform solution of **(U6Au)$_2$(μ-*R*-BINAP)**. The dinuclear organogold(I)-uracil conjugate **(U6Au)$_2$(μ-*R*-BINAP)** crystallized in the space group $P2_12_12_1$; the molecular structure shows an intramolecular Au(I)-Au(I) interaction based on the aurophilic interaction (Fig. 4). The deviation from the linear coordination structure of the Au centers with P-Au-C angles of 172.2(5)° and 176.5(4)° based on the Au(I)-Au(I) interaction was also observed (Table 2). The crystal structure of **(U6Au)$_2$(μ-*R*-BINAP)** showed the P(1)-Au(1)-Au(2)-P(2) torsion angle of 71.97(8)°, which is smaller than that of the gold(I)-uracil conjugates with Xantphos probably due to the difference for rigidity of the diphosphine frameworks. Gratifyingly, **(U6Au)$_2$(μ-*R*-BINAP)** adopts *R,R*-configuration through the chirality induction in Au(I)-Au(I) axis by the axial chirality of BINAP moiety as shown in Fig. 4a. Although Au(I)-Au(I) aurophilic interactions have been studied by using the bridging diphosphine ligand,[6] to the best of our knowledge, the chirality induction in Au(I)-Au(I) axis has not been reported so far. In the crystal packing, each molecule is assembled through intermolecular hydrogen bonds between the uracil moieties to form a helical molecular arrangement (Fig. 4b and Table 3).

Conclusions

In conclusion, the bioorganometallic compounds were designed and synthesized by the conjugation of the dinuclear organogold(I) complexes with a bridging diphosphine ligand as an organometallic compound and the uracil derivative as a nucleobase. The single-crystal X-ray structure determination of the dinuclear organogold(I)-uracil conjugates was demonstrated to reveal the assembly properties of the gold(I) and the uracil moieties in a solid state. The semirigid bridging diphosphine ligand was found to play an important role in the arrangement of the phosphorus atoms on the same side to induce intramolecular aurophilic Au(I)-Au(I) interaction, wherein *R*- and *S*-enantiomers based on Au(I)-Au(I) axis exist. It is noteworthy that the chirality of Au(I)-Au(I) axis was induced by the utilization of (*R*)-BINAP as the bridging diphosphine ligand with axial chirality. Interesting feature of the dinuclear organogold(I)-uracil conjugates is their strong tendency to self-

assemble through intermolecular hydrogen bonds between the uracil moieties, wherein hydrogen bonding patterns were found to depend on the direction of hydrogen bonding sites. Further investigation of the application and dynamic control of the assembly of the bioconjugates including functional materials and catalysts is now in progress.

Experimetal

General Methods.

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. All manipulations were carried out under Ar. Infrared spectra were obtained with a JASCO FT/IR-6200 spectrometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a JNM-ECS 400 (400, 100 and 160 MHz, respectively) spectrometer. For ^{1}H and ^{31}P NMR spectra, chemical shifts were determined by using of tetramethylsilane and 85% H_3PO_4 aq. as standard samples, respectively. Chemical shifts of ^{13}C NMR spectra were determined relative to the solvent residual peaks. Mass spectra were run on a JEOL JMS-700 mass spectrometer.

6-Ethynyl-1-octyluracil,[11] 5-ethynyl-1-octyluracil[12] and chloro(tetrahydrothiophene)gold(I) [ClAu(tht)][13] were prepared by the literature methods.

Synthesis of the dinuclear organogold(I)-uracil conjugate (U6Au)$_2$(μ-Xantphos)

A mixture of Xantphos (0.12 g, 0.21 mmol), chloro(tetrahydrothiophene)gold(I) (0.13 g, 0.41 mmol) and 6-ethynyl-1-octyluracil (**1**) (0.10 g, 0.40 mmol) was stirred in THF (20 mL) at room temperature for 10 minutes under Ar. To the solution was added sodium bis(trimethylsilyl)amide (93 mg, 0.51 mmol) and the resulting solution was stirred at room temperature under Ar for 12 h. The mixture was diluted with dichloromethane, washed with water, brine, and then dried over Na_2SO_4. The solvent was evaporated and the residue was washed with ethyl acetate. The crude product was purified by recrystallization from dichloromethane and methanol to afford the desired dinuclear organogold(I)-uracil conjugate **(U6Au)$_2$(μ-Xantphos)** (0.15 g, 0.10 mmol) as a colorless crystal.

(U6Au)$_2$(μ-Xantphos): yield 50%; IR (KBr) 3172, 3047, 2925, 2854, 2119, 1677, 1579, 1435, 1403, 1363, 1227 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M): δ 8.22 (br, 2H), 7.69 (dd, 2H, J = 7.8, 1.4 Hz), 7.48-7.44 (m, 4H), 7.34-7.23 (m, 16H), 7.11 (td, 2H, J = 7.8 Hz, $^{4}J_{H-P}$ = 1.2 Hz), 6.48 (ddd, 2H, J = 7.8, 1.4 Hz, $^{3}J_{H-P}$ = 12.1 Hz), 5.67 (s, 2H), 4.01 (t, 4H, J = 7.2 Hz), 1.69 (s, 6H), 1.67-1.60 (m, 4H), 1.29-1.12 (m, 20H), 0.81 (t, 6H, J = 6.8 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M): 163, 153 (d, $^{2}J_{c-p}$ = 4.0 Hz), 151.3, 150.2 (d, $^{2}J_{c-p}$ = 140.9 Hz),140.8, 134.6 (d, $^{2}J_{c-p}$ = 14.9 Hz), 133.4, 132, 130, 129.8 (d, $^{1}J_{c-p}$ = 51.8 Hz), 129.5 (d, $^{3}J_{c-p}$ = 12 Hz), 124.9 (d, $^{3}J_{c-p}$ = 9.1 Hz), 117 (d, $^{1}J_{c-p}$ = 52.2 Hz), 104.8, 95.5 (d, $^{3}J_{c-p}$ = 26.8 Hz), 46.6, 35.1, 32.2, 31.6, 29.8, 29.6, 29.2, 27.1, 23, 14.2 ppm; ^{31}P NMR (160 MHz, CD_2Cl_2, 5.0 x 10^{-3} M): 31.2 ppm; HRMS (FAB) m/z calcd for $C_{67}H_{71}N_4O_5P_2Au_2$ (M+H$^+$), 1467.4225; found, 1467.4215; Anal. Calcd. for $C_{67}H_{70}N_4O_5P_2Au_2$: C, 54.85; H, 4.81; N, 3.82. Found: C, 54.85; H, 4.94; N, 3.82.

Synthesis of the dinuclear organogold(I)-uracil conjugate (U5Au)$_2$(μ-Xantphos)

A mixture of Xantphos (58 mg, 0.10 mmol), chloro(tetrahydrothiophene)gold(I) (64 mg, 0.20 mmol) and 5-ethynyl-1-octyluracil (**2**) (50 mg, 0.20 mmol) was stirred in THF (10 mL) at room temperature for 10 minutes under Ar. To the solution was added sodium bis(trimethylsilyl)amide (47 mg, 0.26 mmol) and the resulting solution was stirred at room temperature under Ar for 19 h. The mixture was diluted with dichloromethane, washed with water, brine, and then dried over Na_2SO_4. The solvent was evaporated and purification of the crude product by preparative thin-layer chromatography using dichloromethane/methanol (93:7 v/v) as mobile phase gave the desired dinuclear organogold(I)-uracil conjugate **(U5Au)$_2$(μ-Xantphos)** (20 mg, 0.014 mmol). Recrystallization from dichloromethane and hexane produced a pale yellow crystal.

(U5Au)$_2$(μ-Xantphos): yield 14%; IR (KBr) 3178, 3053, 2925, 2854, 2116, 1682, 1435, 1403, 1343, 1221 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M): δ 8.15 (br, 2H), 7.66 (d, 2H, J = 7.7 Hz), 7.45-7.41 (m, 6H), 7.36-7.27 (m, 16H), 7.09 (t, 2H, J = 7.7 Hz), 6.49 (dd, 2H, J = 7.7 Hz, $^{2}J_{H-P}$ = 11.4 Hz), 3.66 (t, 4H, J = 7.3 Hz), 1.69-1.60 (m, 10H), 1.33-1.22 (m, 20H), 0.87 (t, 6H, J = 6.8 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M): 162.8, 153.1 (d, $^{2}J_{c-p}$ = 2.0 Hz), 151.1, 146.1, 137.5 (d, $^{2}J_{c-p}$ = 141.6 Hz), 134.8 (d, $^{2}J_{c-p}$ = 14.5 Hz), 133.3, 132, 131.5, 130.7(d, $^{1}J_{c-p}$ = 55.8 Hz), 129.6, 129.3 (d, $^{3}J_{c-p}$ =11.4 Hz), 124.6 (d, $^{3}J_{c-p}$ = 8.1 Hz) 117.8 (d, $^{1}J_{c-p}$ = 50.5 Hz), 102.3, 94.6 (d, $^{3}J_{c-p}$ = 28.6 Hz), 49.1, 35, 32.1, 31.4, 29.5, 29.4, 26.7, 23, 14.2 ppm; ^{31}P NMR (160 MHz, CD_2Cl_2, 5.0 x 10^{-3} M): 31.8 ppm; HRMS (FAB) m/z calcd for $C_{67}H_{71}N_4O_5P_2Au_2$ (M+H$^+$), 1467.4225; found, 1467.4171.

Synthesis of the dinuclear organogold(I)-uracil conjugate (U6Au)$_2$(μ-*R*-BINAP)

A mixture of (*R*)-BINAP (0.13 g, 0.21 mmol), chloro(tetrahydrothiophene)gold(I) (0.13 g, 0.41 mmol) and 6-ethynyl-1-octyluracil (**1**) (99 mg, 0.40 mmol) was stirred in THF (20 mL) at room temperature for 20 minutes under Ar. To the solution was added sodium bis(trimethylsilyl)amide (93 mg, 0.51 mmol) and the resulting solution was stirred at room temperature under Ar for 19 h. The mixture was diluted with dichloromethane, washed with water, brine, and then dried over Na_2SO_4. The solvent was evaporated and purification of the crude product by preparative thin-layer chromatography using dichloromethane/methanol (93:7 v/v) as mobile phase gave the desired dinuclear organogold(I)-uracil conjugate **(U6Au)$_2$(μ-*R*-BINAP)** (0.12 g, 0.079 mmol). Recrystallization from chloroform, diethyl ether and hexane produced a pale yellow crystal.

(U6Au)$_2$(μ-*R*-BINAP): yield 40%; IR (KBr) 3165, 3049, 2925, 2853, 2118, 1683, 1582, 1456, 1407, 1367 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M): δ 8.69 (br, 2H), 8.11 (d, 2H, J = 8.8 Hz), 7.93 (d, 2H, J = 8.2 Hz), 7.76-7.71 (m, 4H), 7.59 (t, 2H, J = 8.8 Hz, $^3J_{H-P}$ = 8.8 Hz), 7.49-7.36 (m, 10H), 7.25-7.17 (m, 8H), 6.87-6.83 (m, 2H), 6.60 (d, 2H, J = 8.5 Hz), 5.65 (s, 2H), 4.01-3.90 (m, 4H), 1.68-1.60 (m, 4H), 1.34-1.14 (m, 20H), 0.83 (t, 6H, J = 6.8 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M): 163.3, 152.1 (d, $^2J_{c-p}$ = 141.9 Hz), 151.4, 143.3 (dd, $^2J_{c-p}$ = 16 Hz, $^3J_{c-p}$ = 7.2 Hz), 140.7 (d, $^4J_{c-p}$ = 2.6 Hz), 135.3 (d, $^2J_{c-p}$ = 14 Hz), 135, 134.8 (d, $^2J_{c-p}$ = 14.6 Hz), 134.1 (d, $^3J_{c-p}$ = 10 Hz), 131.8, 130.5 (d, $^3J_{c-p}$ = 4.8 Hz), 130.4 (d, $^1J_{c-p}$ = 56.6 Hz), 130.2 (d, $^2J_{c-p}$ = 8.4 Hz), 129.5 (d, $^3J_{c-p}$ = 11.5 Hz), 129.3 (d, $^3J_{c-p}$ = 11.7 Hz), 128.9 (d, $^1J_{c-p}$ = 56.6 Hz), 128.8, 128.6, 128.2 (d, $^1J_{c-p}$ = 56.2 Hz), 127.4, 127.3, 105.1, 93.2 (d, $^3J_{c-p}$ = 25.9 Hz), 46.6, 32.2, 29.8, 29.7, 29.1, 27.1, 23, 14.2 ppm; ^{31}P NMR (160 MHz, CD_2Cl_2, 1.0 x 10^{-2} M): 33.5 ppm; HRMS (FAB) m/z calcd for $C_{72}H_{71}N_4O_4P_2Au_2$ (M+H$^+$), 1511.4276; found, 1511.4257; Anal. Calcd. for $C_{72}H_{70}Au_2N_4O_4P_2\cdot CHCl_3$: C, 53.77; H, 4.39; N, 3.44. Found: C, 53.78; H, 4.45; N, 3.42.

X-ray Structure Analysis

All measurements for **(U6Au)$_2$(μ-Xantphos)**, **(U5Au)$_2$(μ-Xantphos)** and **(U6Au)$_2$(μ-*R*-BINAP)** were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated MoKα radiation. The structures of **(U6Au)$_2$(μ-Xantphos)**, **(U5Au)$_2$(μ-Xantphos)** and **(U6Au)$_2$(μ-*R*-BINAP)** were solved by direct methods[14] and expanded using Fourier techniques. All calculations were performed using the CrystalStructure crystallographic software package[15] except for the refinement, which was performed using SHELXL-97.[16] The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1033826 for **(U6Au)$_2$(μ-Xantphos)**, CCDC-1033825 for **(U5Au)$_2$(μ-Xantphos)** and CCDC-1033824 for **(U6Au)$_2$(μ-*R*-BINAP)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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