

Tetranuclear Macrocyclic Gold(I) Alkynyl Phosphine Complex Containing Azobenzene Functionalities: A Dual-Input Molecular Logic with Photoswitching Behavior Controllable via Silver(I) Coordination/Decoordination

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Summary: Photoisomerization studies on a tetranuclear macrocyclic gold(I) alkynyl phosphine complex demonstrate the generation of a dual-input molecular logic with photoswitching behavior that can be controlled by addition or removal of silver(I) ions.

Azobenzene and its derivatives are well-known to undergo reversible trans–cis isomerization upon irradiation of UV light.¹ Because of the difference in the chemical and physical properties of the trans and cis isomers, the reversible optically induced isomerizable unit has been widely utilized as the photoresponsive component in optical switching, molecular logics, and devices.² Azo-containing transition-metal complexes present an intriguing system because of the combination of optical, redox, and magnetic properties of metal complexes with the photoisomerization properties of the azo moieties.³ Recent works have shown that a number of gold(I) phosphine complexes were capable of forming macrocyclic rings, catenanes, or polymers depending on the flexibility and geometry of the bridging ligands used, some of which underwent supramolecular self-assembly driven by the aurophilic attraction commonly found in gold(I)

compounds.^{4–6} With our recent interest in the study of conformational changes induced by photo- and ion-responsive processes⁷ and our longstanding interest in luminescent polynuclear gold(I) systems,^{6,8} we became interested in the utilization of the photoresponsive azobenzene moiety as a linker in the synthesis of gold(I) macrocycles with photoswitchable functions. Although a related azobenzene-containing mononuclear gold(I) alkynyl complex has been reported previously and its NLO properties studied,⁹ relatively little is known of their photoisomerization behavior. Herein we report the synthesis, X-ray crystal structure, and photoisomerization behavior of a tetranuclear macrocyclic gold(I) alkynyl phosphine complex, the photoswitching behavior of which could be locked or unlocked with a second input brought about by the addition or removal of silver(I) ions. A related dinuclear gold(I) molecular rod with photoswitchable capability has also been synthesized and studied.

Dinuclear and tetranuclear macrocyclic gold(I) alkynyl phosphine complexes containing azobenzene functionalities, $[\{\text{Au}(\text{PPh}_3)_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})\}]$ (1) and $[\text{Au}_4(\text{dppm})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})_2]$ (2), were synthesized by the reaction of 4,4'-

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diethynylazobenzene ($\text{HC}\equiv\text{C}-\text{L}-\text{C}\equiv\text{CH}$) with 2 equiv of $[\text{Au}(\text{PPh}_3)\text{Cl}]$ and with 1 equiv of $[\text{Au}_2(\text{dppm})\text{Cl}_2]$ (dppm = bis(diphenylphosphine)methane) in dichloromethane, respectively ($\text{L} = \text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4$).¹⁰ Subsequent recrystallization from layering of *n*-hexane onto concentrated dichloromethane solutions of **1** and **2** yielded the desired complexes as orange crystals. Reaction of **2** with 2 equiv of $[\text{Ag}(\text{MeCN})_4]\text{PF}_6$ in acetone at room temperature, followed by recrystallization from diffusion of diethyl ether into an acetone solution, gave $[\{\text{Au}_4(\text{dppm})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})_2\}\text{Ag}_2](\text{PF}_6)_2$ (**3**) as a deep orange solid.¹¹ All of the complexes have been characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, FT-Raman spectroscopy, and positive FAB mass spectrometry and gave satisfactory elemental analyses. A shift of the $\nu(\text{C}\equiv\text{C})$ stretch from 2113 cm^{-1} in **2** to 2043 cm^{-1} in **3** was observed, supporting the π coordination of the alkynyl units to the Ag(I) ions in **3**.

An X-ray crystal structure determination of **2** confirmed the trans conformation of the two azobenzene moieties in the tetranuclear macrocyclic gold(I) alkynyl complex (Figure 1a). The $\text{Au}\cdots\text{Au}$ distances were found to be 3.221(18) and 3.131(2) Å, indicative of the presence of intramolecular $\text{Au}\cdots\text{Au}$ interaction. The two $\text{Au}\cdots\text{Au}$ units in each molecule of **2** were twisted against each other with a dihedral angle of 26.9° (see Figure 1b). The dihedral angles of $\text{C}(7)-\text{C}(6)-\text{N}(1)-\text{N}(2)$, $\text{C}(6)-\text{N}(1)-\text{N}(2)-\text{C}(14)$, $\text{N}(1)-\text{N}(2)-\text{C}(14)-\text{C}(13)$, $\text{C}(23)-\text{C}(22)-\text{N}(3)-\text{N}(4)$, $\text{C}(22)-\text{N}(3)-\text{N}(4)-\text{C}(30)$, and $\text{N}(3)-\text{N}(4)-\text{C}(30)-\text{C}(29)$ were close to 180° , where the benzene rings in each of the two azobenzenes were roughly parallel to each other. Intermolecular weak $\pi-\pi$ stacking interactions exist between the azobenzene moieties of adjacent molecules to give discrete dimeric structures of **2** in the crystal-packing diagram (Figure 1b). The lack of an extended π -stacked oligomeric structure is probably due to the steric hindrance exerted by the neighboring dppm ligands, which prevents the close approach of the molecules.

The X-ray crystal structure suggested that **2** attained a macrocyclic structure. Although the formation of oligomers or

(10) A mixture of $\text{HC}\equiv\text{C}-\text{L}-\text{C}\equiv\text{CH}$ (18 mg, 0.077 mmol) and triethylamine (2 mL) in THF (5 mL) was added dropwise to a solution of $[\text{Au}(\text{PPh}_3)\text{Cl}]$ (80 mg, 0.162 mmol) in THF (5 mL). An orange suspension appeared rapidly, and the mixture was stirred for 20 h at room temperature, after which the orange precipitate was filtered and washed with deionized water, methanol, and diethyl ether. Subsequent recrystallization by vapor diffusion of diethyl ether into a concentrated dichloromethane solution of the product gave **1** as orange crystals (yield 68 %). Complex **2** was synthesized in a way similar to that for **1**, except $[\text{Au}_2(\text{dppm})\text{Cl}_2]$ (84 mg, 0.10 mmol) was used in place of $[\text{Au}(\text{PPh}_3)\text{Cl}]$ (yield 70 %). **1**: ^1H NMR (400 MHz, CDCl_3 , 298 K, relative to Me_4Si) δ 7.54–7.65 (m, 34H, PPh_3 and aryl H ortho to N), 7.85 (d, 4H, $J = 8.5$ Hz, aryl H meta to N); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K, relative to 85 % H_3PO_4) δ 43.4, s; positive FAB-MS m/z 1148 $[\text{M} + \text{H}]^+$; FT-Raman (solid with KBr, cm^{-1}) 2111 (m) $\nu(\text{C}\equiv\text{C})$. Anal. Found: C, 54.34; H, 3.50; N, 2.51. Calcd for $\text{Au}_2\text{C}_{68}\text{H}_{46}\text{P}_2\text{N}_2$: C, 54.50; H, 3.32; N, 2.45. **2**: ^1H NMR (400 MHz, CDCl_3 , 298 K, relative to Me_4Si) δ 3.59 (t, 4H, $J = 11$ Hz, CH_2), 7.30–7.44 (m, 40H, PPh_2), 7.61 (d, 8H, $J = 7.0$ Hz, aryl H ortho to N), 7.65 (d, 8H, $J = 7.0$ Hz, aryl H meta to N); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K, relative to 85 % H_3PO_4) δ 32.7, s; positive FAB-MS m/z 2014 $[\text{M} + \text{H}]^+$; FT-Raman (solid with KBr, cm^{-1}) 2113 (m) $\nu(\text{C}\equiv\text{C})$. Anal. Found: C, 47.80; H, 3.15; N, 2.56. Calcd for $\text{Au}_4\text{C}_{82}\text{H}_{60}\text{P}_4\text{N}_4\cdot\text{CH}_2\text{Cl}_2$: C, 47.50; H, 3.08; N, 2.67.

(11) To an orange suspension of **2** (20 mg, 0.01 mmol) in acetone (5 mL) was added dropwise $[\text{Ag}(\text{MeCN})_4]\text{PF}_6$ (8.3 mg, 0.02 mmol) in acetone (5 mL). The reaction mixture immediately turned clear reddish orange and was stirred for 30 min at room temperature. Recrystallization by vapor diffusion of diethyl ether into an acetone solution of the product yielded **3** as a reddish orange solid (yield 63%): ^1H NMR (400 MHz, CDCl_3 , 298 K, relative to Me_4Si) δ 3.60 (m, 4H, CH_2), 7.31–7.48 (m, 40H, PPh_2), 7.60 (d, 8H, $J = 7.0$ Hz, aryl H ortho to N), 7.69 (d, 8H, $J = 7.0$ Hz, aryl H meta to N); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K, relative to 85 % H_3PO_4) δ 32.7, s; positive ESI-MS m/z 1114 $[\text{M}]^{2+}$; FT-Raman (solid with KBr, cm^{-1}): 2043 (w) $\nu(\text{C}\equiv\text{C})$. Anal. Found: C, 39.46; H, 2.51; N, 2.28. Calcd for $\text{Au}_4\text{C}_{82}\text{H}_{60}\text{P}_6\text{N}_4\text{Ag}_2\text{F}_{12}\cdot\text{CH}_3\text{COCH}_3$: C, 39.60; H, 2.56; N, 2.17.

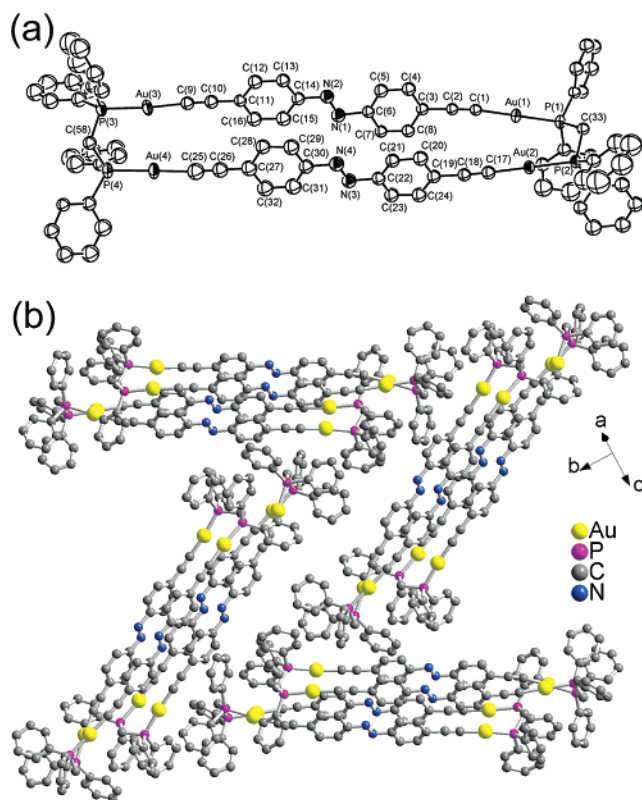


Figure 1. (a) Perspective drawing of $[\text{Au}_4(\text{dppm})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})_2]$ (**2**) with the atomic numbering scheme. Thermal ellipsoids are shown at the 30% probability level. (b) Crystal packing of $[\text{Au}_4(\text{dppm})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})_2]$ (**2**) showing the dimeric structure. Hydrogen atoms and solvent molecules have been omitted for clarity.

chains is possible upon dissolution of the complexes, the ^{31}P NMR spectra of **2** showed only a sharp singlet, suggestive of effective equivalence of all phosphorus atoms and probably the presence of one chemical species, though one cannot completely exclude the possibility of a dynamic process that occurs at a rate faster than that of the NMR time scale. However, it is believed that the macrocyclic structure is favored in the present system, given the syn conformation of the diphosphine ligand (dppm) and the possibility of the presence of intramolecular $\text{Au}\cdots\text{Au}$ interactions in the metallamacrocycle, although zigzag oligomers are also known to be formed with a syn conformation of the dppm ligand and $\text{Au}\cdots\text{Au}$ interactions. Similar suggestions have also been made for $\text{Au}_2(\text{dppm})\text{Cl}_2$ ¹² and for other related systems.⁴ Given the size, the conformation, and the flexibility of the linkers, it is believed that the 2:4:2 (ligand:metal:ligand) metallamacrocycle remains intact in solution, as thermodynamic control is also an important factor in governing the size of the macrocycles. Since the 1:2:1 metallamacrocycle is not possible in our system, the 2:4:2 metallamacrocycle is the smallest possible macrocycle, which is thought to be favored over larger macrocycles for entropic reasons.¹³

The electronic absorption spectra of complexes **1–3** in dichloromethane show moderately intense absorption shoulders at ca. 250–280 nm and an intense band at ca. 380–390 nm, with a tail extending to ca. 500 nm. The absence of the moderately intense absorption at the high-energy region in $\text{HC}\equiv\text{C}-\text{L}-\text{C}\equiv\text{CH}$ is suggestive of its assignment as an

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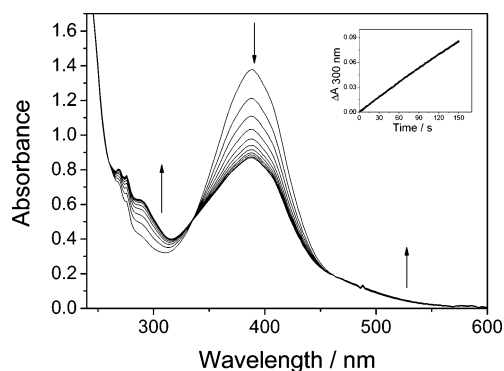


Figure 2. UV-vis spectral changes of $[\{\text{Au}(\text{PPh}_3)_2\}_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})]$ (**1**) in dichloromethane upon irradiation at 360 nm. The inset shows the absorbance change at 300 nm with irradiation time and its theoretical fit.

intraligand transition of the phosphine ligands. The intense absorption band at 380–390 nm, which also occurs in the azobenzene ligand, is assigned as a $\pi \rightarrow \pi^*$ intraligand transition of the azo moiety, while the tail to 500 nm is assigned as an $n \rightarrow \pi^*$ intraligand transition of the azo moiety.

Upon irradiation of a dichloromethane solution of **1** at 360 nm into the IL azo ($\pi \rightarrow \pi^*$) transition, trans-cis photoisomerization occurred, while irradiation of visible light into the IL ($n \rightarrow \pi^*$) transition at 486 nm caused a cis-to-trans photoisomerization (Figure 2). In order to obtain a quantitative measure of the photoinduced isomerization processes of **1**, the photochemical quantum yield for the trans-cis isomerization process of **1** was determined using chemical actinometry. The photoreactions were monitored by both UV-vis spectrophotometry and ^1H NMR spectroscopy. Upon irradiation at 360 nm, two new doublets appeared in the ^1H NMR spectrum, corresponding to the aryl protons meta and ortho to the $\text{N}=\text{N}$ moiety of the cis isomer formed, from which determination of the trans/cis integral ratio would give rise to the extinction coefficients of the trans and cis isomers. Subsequent monitoring of the photoreactions by UV-vis spectrophotometry gave a quantum yield of 0.1 for the trans-to-cis photoisomerization of **1**. A control experiment to correct for the presence of any thermal trans-cis isomerization reaction was performed, in which an equal amount of **1** was dissolved in the same amount of dichloromethane and placed in the dark. The thermal reaction was similarly monitored by UV-vis spectrophotometry, in which no observable cis isomer was detected in the absence of light.

The photoisomerization behavior of the tetranuclear macrocyclic gold(I) complex **2** was studied, in which similar UV-vis absorption changes were observed (Figure 3a). Interestingly, introduction of Ag^+ ions to **2** inhibited the trans-cis photoisomerization process (Figure 3b), probably due to the locking up of the photoresponsive moiety via π coordination of adjacent pairs of alkynyls to the Ag^+ ions in a sandwich binding fashion to give $[\{\text{Au}_4(\text{dppm})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})\}_2\text{Ag}_2]^{2+}$, as revealed from the FT-Raman studies,¹⁴ which resulted in the suppression

(14) It should be noted that there was a report on the silver(I) perturbation of trans-cis isomerization of azobenzene in the literature, in which the $\pi-\pi^*$ absorption band of the azo moiety for the azobenzene-silver adduct was shifted by ca. 1100 cm^{-1} to lower energy.¹⁵ However, in the present study, we believed that the silver(I) ions were bound to the alkyne units because of the absence of a red-shifted $\pi-\pi^*$ absorption band, and more importantly, a lowering of the frequency of the $\nu(\text{C}\equiv\text{C})$ stretch from 2113 cm^{-1} in $[\text{Au}_4(\text{dppm})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})]$ to 2043 cm^{-1} in $[\{\text{Au}_4(\text{dppm})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})\}_2\text{Ag}_2]^{2+}$ was observed, which was indicative of the π coordination mode of the alkyne ligands to the $\text{d}^{10}\text{Ag}(\text{I})$ centers.¹⁶

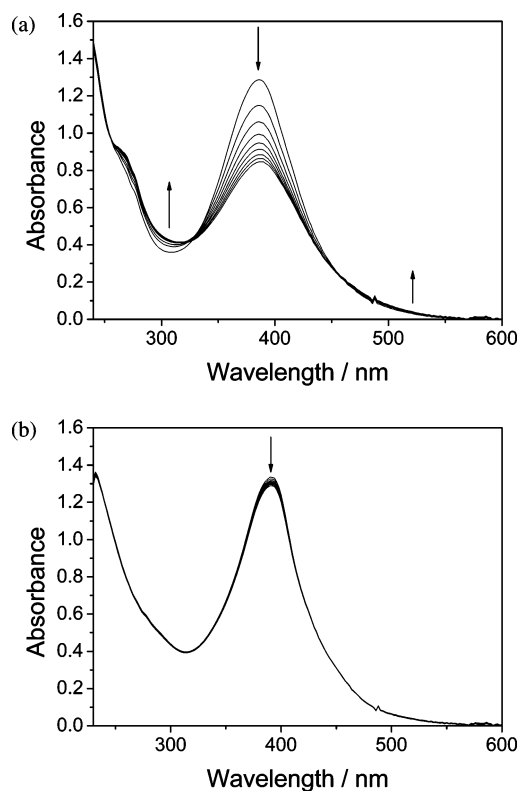
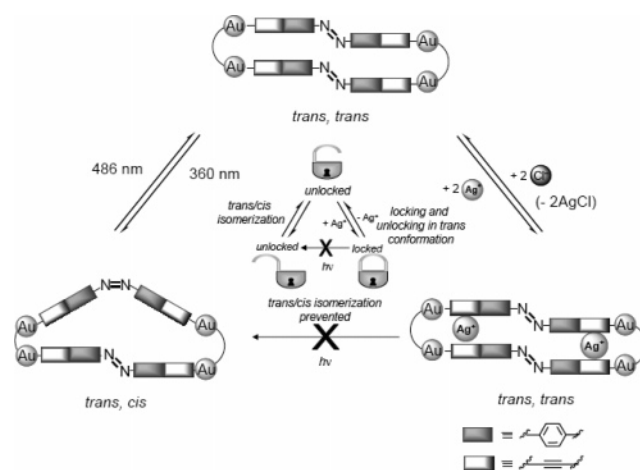


Figure 3. (a) UV-vis spectral changes of $[\text{Au}_4(\text{dppm})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})_2]$ (**2**; $1.34 \times 10^{-5}\text{ M}$) in dichloromethane upon irradiation at 360 nm for 240 s. (b) UV-vis spectral traces of $[\{\text{Au}_4(\text{dppm})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})_2\}_2\text{Ag}_2](\text{PF}_6)_2$ (**3**; $1.53 \times 10^{-5}\text{ M}$) in dichloromethane upon irradiation at 360 nm for 360 s.

Scheme 1. Schematic Diagram Demonstrating the “Locking” and “Unlocking” Mechanism Brought About by the Addition and Removal of Ag^+ Ions in Preventing and Facilitating Trans-Cis Isomerization in $[\text{Au}_4(\text{P}^i\text{P})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})_2]$



of the isomerization process. In contrast, addition of $n\text{Bu}_4\text{NCl}$ to $[\{\text{Au}_4(\text{dppm})_2(\text{C}\equiv\text{C}-\text{L}-\text{C}\equiv\text{C})\}_2\text{Ag}_2]^{2+}$ resulted in the abstraction of the Ag^+ ions, restoring the conformational flexibility

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within the gold(I) macrocycle. Scheme 1 shows the hypothesized schematic diagram of the “locking” and “unlocking” of the trans conformation on addition and elimination of Ag^+ to prevent and facilitate trans–cis photoisomerization in **2**. Since the UV–vis spectral change in **2** is similar to that observed in **1** and the conversion is relatively low and comparable to that of **1**, it is believed that photoisomerization of **2** would give rise to a trans–cis product. Assuming only the trans,cis product is formed, a photoisomerization quantum yield of 0.07 is determined on the basis of the photoreactions monitored by both UV–vis spectrophotometry and ^1H NMR spectroscopy. Interestingly, addition of Ag^+ salts to the trans,cis product of **2** did not have an effect on its reverse photoisomerization back to the trans,trans isomer of **2**, further confirming the sandwich binding mode of Ag^+ to the trans,trans metallamacrocycle, which becomes impossible in the trans,cis form.

In conclusion, photoisomerization studies showed that upon UV irradiation into the IL ($\pi \rightarrow \pi^*$) transition at 360 nm, trans-to-cis photoisomerization occurred, while irradiation with visible light at 486 nm promoted the reverse isomerization process. Interestingly, addition of Ag^+ ions to the macrocyclic gold(I) alkynyl complex affected the flexibility within the gold(I) macrocycle, inhibiting the photoisomerization reactions, while

addition of $n\text{Bu}_4\text{NCl}$ restored the ability of the azobenzene moiety to undergo photoisomerization. The present work serves as a proof of principle in demonstrating the versatility of molecular design in generating a dual-input lockable molecular logic photoswitch.

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Supporting Information Available: Text giving the details of experimental procedures for the synthesis and photoisomerization study of **1–3** and crystal data and refinement details for **2** and a CIF file giving crystal data for **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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