

# Organic Memory Devices Based on a Bis-Cyclometalated Alkynylgold(III) Complex

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**S** Supporting Information

**ABSTRACT:** A bis-cyclometalated alkynylgold(III) complex,  $[\text{Au}(\text{}^t\text{BuC}^{\wedge}\text{N}^{\wedge}\text{C}^t\text{Bu})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_5)_2\text{-}p)]$  ( $\text{}^t\text{BuHC}^{\wedge}\text{N}^{\wedge}\text{CH}^t\text{Bu} = 2,6\text{-bis}(4\text{-}tert\text{-butylphenyl})\text{pyridine}$ ), has been synthesized and characterized. The complex was found to exhibit rich photophysical and electrochemical properties. More interestingly, the complex has been employed in the fabrication of organic memory devices. The as-fabricated memory devices exhibited good performances with low operating voltage, high ON/OFF ratio, long retention time, and good stability.

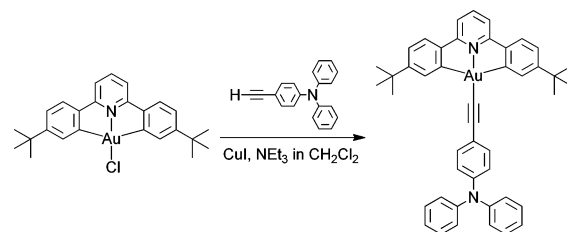
In contrast to the past, when the chemistry of gold was mainly focused on gold(I) systems,<sup>1–8</sup> the study of square planar gold(III) coordination complexes<sup>9–12</sup> has recently become an emerging field of interest owing to their potential applications as functional materials such as triplet emitters,<sup>9,10</sup> supramolecular assemblies,<sup>9e,12</sup> catalysts,<sup>8</sup> and anticancer drugs.<sup>13</sup> In particular, the preparation of room-temperature emissive gold(III) complexes via the incorporation of strong  $\sigma$ -donating ligands<sup>9a–c,h</sup> has successfully paved the way for the preparation of highly efficient organic light-emitting devices based on small-molecule alkynylgold(III) complexes and their dendritic derivatives,<sup>9d,f,10</sup> rendering them attractive candidates for optoelectronic applications.

On the other hand, organic memories represent another type of organic functional devices of topical interest.<sup>14,15</sup> The rapid burst in information technology at present has urged the development of new materials for data storage. To date, nonvolatile memory devices are mainly limited to those based on organic compounds and polymers;<sup>16,17</sup> those based on transition metal complexes have remained rather under-explored and are limited to only a few kinds of transition metal complex systems with nitrogen-donor ligands, such as copper(II)<sup>18</sup> and silver(I)<sup>19</sup> tetracyanoquinodimethane (TCNQ) and copper(II) phthalocyanine (CuPc) derivatives,<sup>20</sup> as well as a ruthenium(II) complex.<sup>21</sup> To the best of our knowledge, there has been no example of organic memory devices based on small-molecule organometallic complexes. Given the synthetic versatility and rich photophysical and optoelectronic properties,<sup>9b</sup> utilization of  $d^8$  transition metal complexes with charge-transfer properties for the fabrication of organic memory devices is anticipated to give rise to attractive device properties. The use of small-molecule transition metal complexes would allow ready structural modifications and would provide an alternative to conventional memory

devices.<sup>16</sup> The relatively nontoxic and environmentally benign nature of gold(III) complexes has rendered them attractive for material applications. In particular, alkynylgold(III) complexes have been observed to exhibit rich photophysical properties. In addition to room-temperature photoluminescence in various media, these complexes have also been observed to exhibit interesting electroluminescence<sup>9d,f,10</sup> as well as electrochemiluminescence properties.<sup>11a</sup> As an extension of our research interest in photoswitching<sup>22</sup> and optoelectronic materials,<sup>9a,d,f,10a–c,23,24</sup> a program has been launched to explore the possible utilization of gold(III) complexes for organic memory applications. Herein we report the synthesis, characterization, and photophysical and electrochemical properties of an electron-rich alkynyl-containing donor–acceptor bis-cyclometalated gold(III) complex,  $[\text{Au}(\text{}^t\text{BuC}^{\wedge}\text{N}^{\wedge}\text{C}^t\text{Bu})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_5)_2\text{-}p)]$  (**1**), and its applications in the fabrication of solution-processable organic memory devices, representing the first example of small-molecule organometallic complexes for memory applications.

The precursor compound,  $[\text{Au}(\text{}^t\text{BuC}^{\wedge}\text{N}^{\wedge}\text{C}^t\text{Bu})\text{Cl}]$ , was prepared according to modified literature procedures,<sup>9c,e</sup> while complex **1** was synthesized via a copper-catalyzed route according to modification of a reported procedure (Scheme 1).<sup>9</sup> The identity of **1** has been confirmed by <sup>1</sup>H NMR

## Scheme 1. Synthesis of Complex 1



spectroscopy, FAB mass spectrometry, and IR spectroscopy. The alkynylgold(III) complex was found to exhibit rich photophysical properties in various media at both ambient and low temperatures. The electronic absorption spectrum featured a higher-energy absorption band at 313 nm and a lower-energy vibronic-structured absorption band at 391–408 nm. The lower-energy absorption band was attributed to a metal-perturbed intraligand (IL)  $\pi-\pi^*$  transition of the

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Table 1. Photophysical and Electrochemical Data of Complex 1

absorption <sup>a</sup>	emission		$\Phi_{\text{lum}}^b$	oxidation $E_{\text{pa}}/\text{V}$ vs SCE <sup>c</sup>	reduction $E_{1/2}/\text{V}$ vs SCE <sup>c</sup> ( $\Delta E_p/\text{mV}$ )
	$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	medium ( $T/\text{K}$ )			
313 (37 770), 391 (15 000), 408 (13 060)	CH <sub>2</sub> Cl <sub>2</sub> (298)	600 (0.1)	0.078	+0.91	-1.60 (85)
	glass (77) <sup>d,e</sup>	484, 518, 553 (132)			

<sup>a</sup>In dichloromethane at 298 K. <sup>b</sup>The luminescence quantum yield, measured at 298 K using [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> as a standard. <sup>c</sup>In dichloromethane solution with 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte at room temperature; working electrode, glassy carbon; scan rate, 100 mV s<sup>-1</sup>.  $E_{\text{pa}}$  refers to the anodic peak potential for the irreversible oxidation waves, whereas  $E_{\text{pc}}$  refers to the cathodic peak potential for the irreversible reduction waves.  $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ ;  $E_{\text{pa}}$  and  $E_{\text{pc}}$  are peak anodic and peak cathodic potentials, respectively.  $\Delta E_p = |E_{\text{pa}} - E_{\text{pc}}|$ . <sup>d</sup>Vibronic-structured emission band. <sup>e</sup>In EtOH–MeOH–CH<sub>2</sub>Cl<sub>2</sub> (40:10:1 v/v).

tridentate <sup>t</sup>BuC<sup>^</sup>N<sup>^</sup>C<sup>t</sup>Bu ligand, with some charge-transfer character from the *tert*-butylphenyl moiety to the central pyridine unit.<sup>9</sup> An additional absorption tail that extended to ca. 475 nm was also observed, suggestive of the possibility of an admixture of IL  $\pi-\pi^*$  [<sup>t</sup>BuC<sup>^</sup>N<sup>^</sup>C<sup>t</sup>Bu and C $\equiv$ C–C<sub>6</sub>H<sub>4</sub>N–(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-*p*] and ligand-to-ligand charge-transfer (LLCT) [ $\pi(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_5)_2-p) \rightarrow \pi^*(^t\text{BuC}^{\wedge}\text{N}^{\wedge}\text{C}^t\text{Bu})$ ] transitions in the low-energy absorption bands due to the presence of the electron-rich –N(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> substituent on the alkynyl moiety.<sup>9d</sup> The photophysical properties are summarized in Table 1, and Figure 1a shows the UV–vis absorption spectrum.

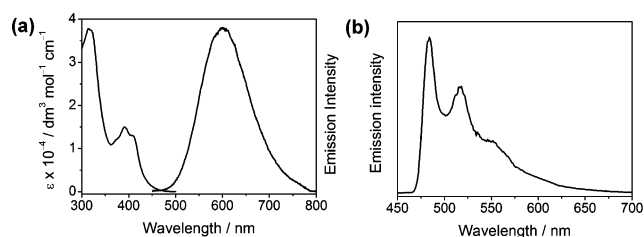


Figure 1. (a) UV–vis absorption and emission spectra in dichloromethane at 298 K. (b) Emission spectrum in ethanol–methanol–dichloromethane (40:10:1 v/v) glass at 77 K.

In dichloromethane solution at ambient temperature, complex 1 exhibited a broad structureless emission band centered at ca. 600 nm upon excitation at  $\lambda \geq 350$  nm. The solution emission spectrum is shown in Figure 1a. The emission decay was found to be in the sub-microsecond regime, suggestive of the triplet parentage of the emission. This low-energy emission band was assigned as originating from an excited state of <sup>3</sup>LLCT [ $\pi(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_5)_2-p) \rightarrow \pi^*(^t\text{BuC}^{\wedge}\text{N}^{\wedge}\text{C}^t\text{Bu})$ ] nature due to the presence of the electron-rich –N(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> substituent on the alkynyl moiety, which rendered the  $\pi(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_5)_2-p)$  orbital higher-lying in energy.<sup>9</sup> The emission was found to be blue-shifted when compared to the literature values for gold(III) complexes containing the same alkynyl ligand, because the electron-donating *tert*-butyl substituents on the bis-cyclometalating ligand in 1 has resulted in a higher-lying  $\pi^*(^t\text{BuC}^{\wedge}\text{N}^{\wedge}\text{C}^t\text{Bu})$  orbital and thus a wider HOMO–LUMO energy gap for the LLCT emission. On the other hand, the low-temperature alcoholic glass at 77 K was found to exhibit a vibronic-structured emission band at 484–553 nm, assignable to an emission from a <sup>3</sup>IL  $\pi-\pi^*$  (<sup>t</sup>BuC<sup>^</sup>N<sup>^</sup>C<sup>t</sup>Bu) excited state (Figure 1b).<sup>9</sup>

The electrochemical properties of the gold(III) complex have been studied by cyclic voltammetry. As shown in the cyclic voltammogram in Figure 2, complex 1 in dichloromethane (0.1 mol dm<sup>-3</sup> <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>) showed a quasi-reversible reduction

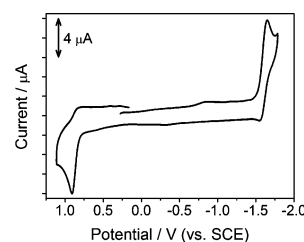


Figure 2. Cyclic voltammogram of complex 1 in dichloromethane (0.1 mol dm<sup>-3</sup> <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>) (scan rate = 100 mV s<sup>-1</sup>).

couple at –1.60 V and an irreversible oxidation wave at +0.91 V vs SCE. The reduction wave at –1.60 V vs SCE was assigned to the ligand-centered reduction of the <sup>t</sup>BuC<sup>^</sup>N<sup>^</sup>C<sup>t</sup>Bu ligand.<sup>9</sup> The oxidative wave at +0.91 V vs SCE, on the other hand, was assigned to the ligand-centered oxidation of the electron-rich ethynyltriphenylamine ligand.<sup>9</sup>

Given its air-stability and high decomposition temperature of ca. 365 °C, determined by thermogravimetric analysis (Figure S1), the gold(III) complex has been employed for the fabrication of organic memory devices. A schematic diagram of the memory device configuration is shown in Figure 3a,

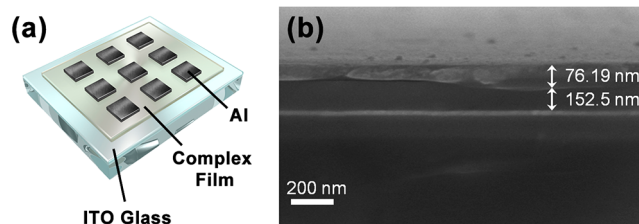
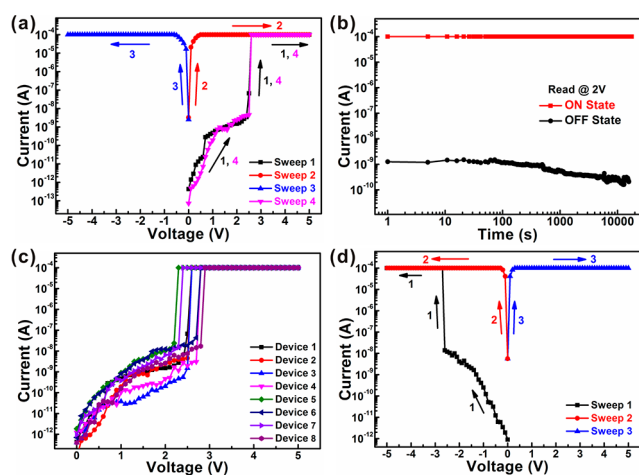


Figure 3. (a) Schematic diagram of the device configuration. (b) SEM image of the cross section of a memory device.

while the procedure for device fabrication is described in the Supporting Information. As depicted in the scanning electron microscopy (SEM) image of the device cross section in Figure 3b, the thicknesses of Al and the complex film were ca. 80 and 150 nm, respectively. Powder X-ray diffraction studies revealed the amorphous nature of the complex film with  $\pi-\pi$  stacking interactions between the molecules (Figure S2). The electrical characteristics of the memory devices with a compliance current of 10<sup>-4</sup> A are shown in Figure 4. The forward bias was defined as a positive bias applied to the ITO electrode. The current–voltage ( $I-V$ ) characteristics of the device are shown in Figure 4a. This device initially exhibited a high-resistance state (OFF state). When a voltage sweep from 0 to +5 V (Sweep 1) was applied on the device, the current showed a sharp increase from 10<sup>-9</sup> to 10<sup>-4</sup> A at switching threshold voltage ( $V_{\text{th}}$ ) of around 2.5 V, indicating that the memory



**Figure 4.** (a)  $I$ - $V$  curves of the memory device. (b) Retention time characteristics of the ON and OFF states of the memory device. (c)  $I$ - $V$  curves measured from eight memory cells. (d)  $I$ - $V$  curves with an initial reverse voltage sweep.

device was switched to a low-resistance state (ON state) from an OFF state. This process can be regarded as the “writing” process in a memory device. In addition, this memory could be kept at the ON state in subsequent sweep from 0 to +5 V (Sweep 2) and a reverse sweep from 0 to -5 V (Sweep 3). Sweep 4 was carried out after the power of the memory device was turned off. It was found that the ON state had been relaxed to the OFF state after the power was turned off, and then changed to the ON state again by Sweep 4. These processes could be repeated many times, which can be considered as a typical write-once read-many-times (WORM) behavior. This memory characteristic can be rationalized by the transfer of electron density located on the electron-donating diphenylamino substituent of the phenylalkynyl moiety to the  $\pi$ -accepting  ${}^t\text{BuC}^{\wedge}\text{N}^{\wedge}\text{C}^t\text{Bu}$  moiety under an electric field to form a permanent charge-separated state, giving rise to a WORM characteristic.<sup>25,26</sup>

Figure 4b shows the retention performance of the memory devices. A high ON/OFF current ratio of over  $10^5$  was obtained at a constant read voltage of +2 V. Such high ON/OFF current ratios could ensure a low misreading rate in memory devices. Moreover, a long retention time of over  $10^4$  s was obtained for both ON and OFF states by consecutive tests, and the ON/OFF current ratio remained over  $10^5$  without any degradation, indicating the good stability and reliability of the memory devices. Moreover, additional statistical data for the memory devices based on the gold(III) complex were further obtained by measurements on dozens of devices. Notably, these devices exhibited a similar electrical switching behavior. Figure 4c shows the  $I$ - $V$  curves measured from eight memory cells and reveals a relatively narrow  $V_{\text{th}}$  distribution at 2.2–2.8 V, indicating the excellent reproducibility of the devices. It is worth noting that these memory devices could retain their performance after storage in air for 4 months (Figure S3). The memory device was also observed to exhibit excellent electrical switching with an initial reverse voltage sweep. As shown in Figure 4d, the device was initially swept from 0 to -5 V. An abrupt increase in the current was observed at the switching threshold voltage of -2.6 V, which shows almost the same characteristics as the forward sweep. The results indicate that the gold(III)-based memory device could work both in positive and negative bias.

In conclusion, a donor–acceptor bis-cyclometalated alkynylgold(III) complex with an electron-rich alkynyl moiety,  $[\text{Au}({}^t\text{BuC}^{\wedge}\text{N}^{\wedge}\text{C}^t\text{Bu})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_5)_2-p)]$ , has been successfully prepared and characterized. The complex was found to exhibit absorption bands at 391–408 nm, assigned to the IL transition of the bis-cyclometalating ligand. Upon photoexcitation, the complex was observed to show a  ${}^3\text{LLCT}$  [ $\pi(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_5)_2-p) \rightarrow \pi^*({}^t\text{BuC}^{\wedge}\text{N}^{\wedge}\text{C}^t\text{Bu})$ ] emission at 600 nm. Electrochemical studies showed that the complex exhibited an alkynyl-centered oxidation wave at +0.91 V and a ligand-centered reduction at -1.60 V vs SCE from the tridentate  ${}^t\text{BuC}^{\wedge}\text{N}^{\wedge}\text{C}^t\text{Bu}$  ligand. It was remarkable that organic memory devices have been fabricated using the alkynylgold(III) complex. Satisfactory memory device performances have been demonstrated with low operating voltages of 2.2–2.8 V, high ON/OFF ratios of over  $10^5$ , long retention times of over  $10^4$  s, and good stability and reliability, representing the first example of organic memory devices based on small-molecule organometallic complexes. Extension of this work to organic memories based on organometallic gold(III) complexes and complexes of other transition metal centers is currently in progress, and it is anticipated that this will open up new opportunities in the development of organic electronic devices.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details; synthetic procedures; characterization data; TGA thermogram; X-ray diffraction patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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