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Synthesis, Characterization, Structure, and Selective Cu^{2+} Sensing Studies of an Alkynylgold(I) Complex Containing the Dipicolylamine Receptor

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Summary: A novel DPA-containing alkynylgold(I) complex has been successfully synthesized and structurally characterized. The complex has been shown to exhibit rich photoluminescence property and to function as a selective sensor for Cu^{2+}, as revealed by the large UV−vis change and significant emission quenching. The recognition event was also found to show complete reversibility, with the revival of the luminescence signal upon addition of EDTA.

The development of gold(I) chemistry has attracted growing interest in the past two decades, due to the attractive Au$\cdots$Au interactions.[1,2] Gold(I) alkynyl compounds are of particular interest, not only due to their stability and ease of preparation, but also because of their rich photophysical properties, such as photoluminescence[2−6] and optical nonlinearity.[7] Introduction of gold(I) to the π-conjugated unsaturated alkynyl ligand has recently been shown to induce long-lived phosphorescence, which allows the time-resolved discrimination of key luminescent processes, as a result of the heavy metal atom effect, which enhances the spin−orbital coupling.[5c,5d] In addition, the d^{10} closed-shell electronic configuration of gold(I) does not allow the existence of low-lying d−d excited states, and hence the lifetime and luminescent triplet excited states would not be affected by an internal quenching mechanism. Due to its linear geometry and rigidity, together with the aurophilic nature of gold, a number of supramolecular structures based on gold(I) alkynyl complexes have been designed and reported by us[2−4] and others,[5,6] many of which show unique luminescence properties that are strongly influenced by the presence of Au$\cdots$Au interactions.

In the field of supramolecular and host−guest chemistry, there has been a growing interest in the search for host molecules that can selectively recognize specific guest molecules through measurable photophysical changes. The sensing receptor for Cu^{2+} is of particular interest due to the fact that this metal ion is not only a commonly found metal pollutant but also an essential trace element in the biological system, particularly as one of the major sources of oxidative stress that is closely related to the neurogenerative diseases.[8] However, the development of a selective sensor for Cu^{2+} is rather rare,[9a−9c] when compared to other biologically relevant metal ions, including alkali ions (Na^{+}, K^{+}),[9d] alkaline earth metal ions (Mg^{2+} and Ca^{2+}),[9e] and other d-block ions, such as Zn^{2+}.[9f,9g] Effective signal transduction plays an important role in the design of ion-specific chemosensors, and luminescence technology has been widely used due to its high sensitivity and the simplicity of its equipment requirement.[10] Most studies in the past on ion-controlled luminescent probes were focused on organic receptors that are based

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on polyaromatic luminophores.[9,11] It was only quite recently that metalloreceptors based on various transition metal complexes, especially those that show metal-to-ligand charge transfer (MLCT) excited state properties, have attracted growing interest, with rhenium(I) and ruthenium(II) systems being most extensively studied.[12] To the best of our knowledge, the employment of the intriguing photophysical properties of the gold(I) alkynyl complexes, with the advantages of their simple, linear, and rigid structure, together with the presence of a π-conjugated system, which is usually involved in the origin of luminescence, in the design of luminescent chemosensors is very rare. Very recently, we reported a series of di- and tetranuclear gold(I) alkynylcrown and alkynylcalixcrown complexes, which have been shown to exhibit interesting photophysical and cation-binding properties.[4]

As an extension of our previous work in host−guest chemistry, herein we report the synthesis of a novel luminescent alkynylgold(I) complex, $[PPh_3AuC{\equiv}CC_6H_4SO_2N(CH_2\text{-py-}2)_2]$ (**1**), with the dipicolyamine (DPA) receptor, which is well-known to show remarkable binding ability to transition metal ions and has been widely used in the design of sensors for molecular recognition.[9f,9g,13] The ion-binding properties of the complex with various metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, and Ni^{2+} have been studied by UV−vis and luminescence spectroscopy, and the complex was found to be highly sensitive and selective toward Cu^{2+} ion, in which the luminescence is switched off upon Cu^{2+} binding. The recognition event was also found to show complete reversibility, with the revival of the luminescence signal upon addition of EDTA (Scheme 1).

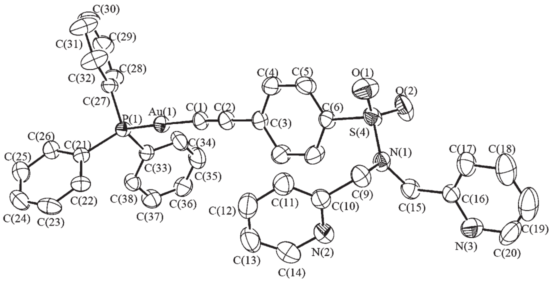
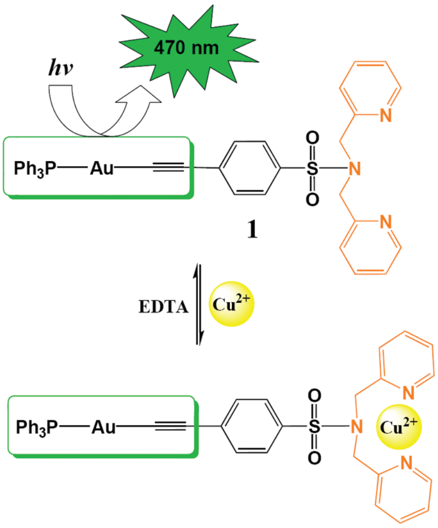


Figure 1. Perspective drawing of complex **1** with atomic numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Scheme 1. Schematic Representation of the Photophysical Change of 1 upon Binding Cu^{2+}



Complex **1** was synthesized by reacting $HC{\equiv}CC_6H_4SO_2N(CH_2\text{-py-}2)_2$ ($HC{\equiv}CC_6H_4SO_2DPA$) with 1 equiv of PPh_3AuCl in the presence of an excess of triethylamine in dichloromethane. Subsequent layering of hexane onto a dichloromethane solution of the complex gave the product as white crystals. The identity has been confirmed by ^1H NMR, $^{31}P\{^1H\}$ NMR, FAB-MS, and satisfactory elemental analysis. The structure of the complex has also been determined by X-ray crystallography.

The perspective drawing of the complex is shown in Figure 1. The P−Au (2.274 Å) and C≡C (1.185 Å) bond lengths are comparable to those observed in other alkynylgold(I) phosphine complexes.[2−6] The P−Au−C angle of 174.9° is close to linear geometry and is typical of sp hybridization found in Au(I) alkynyl complexes. The shortest intermolecular Au···Au contact is 9.650 Å, which indicates the absence of Au···Au interactions.

The photophysical data of complex **1** are tabulated in Table 1. The UV−vis spectrum exhibits an intense high-energy band at 270−302 nm, with a tail extending to ca. 400 nm. The close resemblance of the high-energy absorption band to that observed in $[Au(PPh_3)Cl]$[5a] and $[Au(PPh_3)(C{\equiv}CPh)]$[5a] is suggestive of their similar origin and is tentatively assigned as the intraligand transition characteristic of triphenylphosphine. The low-energy tail that is absent in $[Au(PPh_3)Cl]$ may be characteristic of the alkynylgold(I) com-

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Table 1. Photophysical Data of Complex 1

absorption λ/nm($\varepsilon \times 10^{-4}$/dm^3 mol^{-1} cm^{-1})	medium (T/K)	emission λ_{em}/nm (τ_0/μs)
270 (2.72), 286 (3.00), 302 (3.35)	DCM (298)	444, 470 (0.20)
	solid (298)	468 (193)
	solid (77)	468 (32.9)
	glass (77)^a	447, 472 (26.0)

^{a} In EtOH−MeOH−CH_2Cl_2 (4:1:1 v/v).

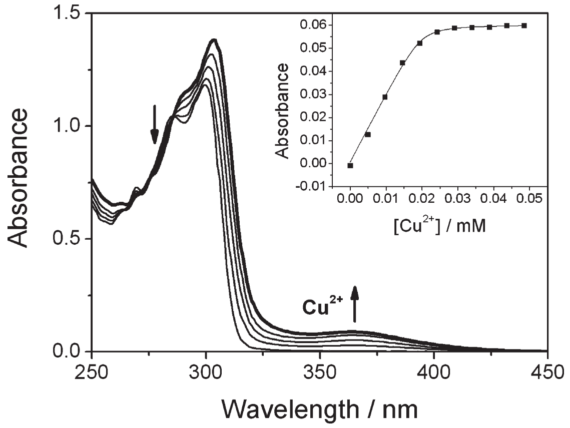

Figure 2. UV−vis spectral changes of complex **1** (2.0×10^{-5} M) in CH_2Cl_2−MeOH (1:1 v/v; 0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of Cu(ClO$_4$)$_2$. Inset: Plot of absorbance at 366 nm as a function of Cu^{2+} concentration and its theoretical fit for the 1:1 binding of complex **1** with Cu^{2+}.

plex. Excitation of **1** in CH_2Cl_2 and 77 K glass both gave a structured emission band at ca. 444 and 472 nm with vibrational progressional spacings of ca. 1336 cm^{-1}, corresponding to the C$\overset{\dots}{-}$C vibrational modes of the aromatic rings, while the emission was centered at ca. 468 nm in the solid state at both 298 and 77 K, typical of ligand-centered emission. The absence of low-energy emission bands is indicative of the absence of short Au···Au contacts in the solid states. The luminescence lifetimes in the microsecond range are suggestive of an excited state of triplet parentage.

Addition of Cu^{2+} to a CH_2Cl_2−MeOH (1:1 v/v) solution of **1** produced observable UV−vis spectral changes. A new low-energy absorption band at 366 nm was formed, with a well-defined isosbestic point at 286 nm, suggesting a clean reaction that involved two absorbing species. Figure 2 shows the electronic absorption spectral changes of **1** upon addition of the Cu^{2+} ion in CH_2Cl_2−MeOH (1:1 v/v; 0.1 ^{n}Bu$_4$NPF$_6$). The new band at ca. 366 nm upon addition of Cu^{2+} is tentatively assigned as the ligand-to-metal charge transfer (LMCT), arising from the transfer of an electron from the lone pair of the amine group to the metal-centered orbital. A 1:1 binding mode is proposed and confirmed by the method of continuous variation.[14] As can be seen from the Job's plot in Figure 3, a plot of absorbance at 366 nm versus X_M (= $[Cu^{2+}]/([Cu^{2+}] + [\mathbf{1}])$) shows a break point at a molar ratio of ca. 0.5, indicative of a 1:1 stoichiometry. A log K_s of 6.2 ± 0.1 of **1** for Cu^{2+} at 298 K was obtained from a nonlinear least-squares fit for 1:1 binding. The inset of Figure 2 shows a close agreement of the experimental data to the theoretical fit, further supportive of the 1:1 binding.

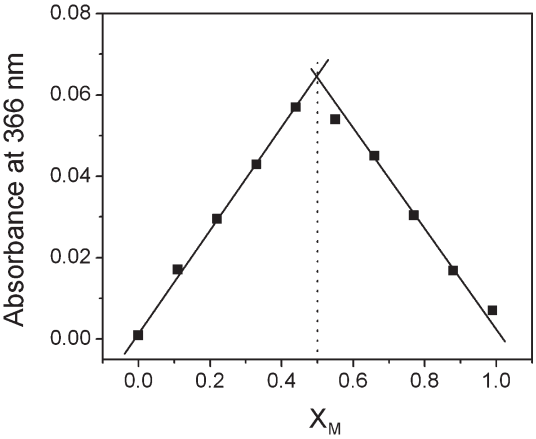

Figure 3. Job's plot for the binding of complex **1** with Cu^{2+}, showing 1:1 stiochiometry. The absorbance at 366 nm was measured as a function of the molar ratio X_M, where X_M = ($[Cu^{2+}]/([Cu^{2+}] + [\mathbf{1}])$).

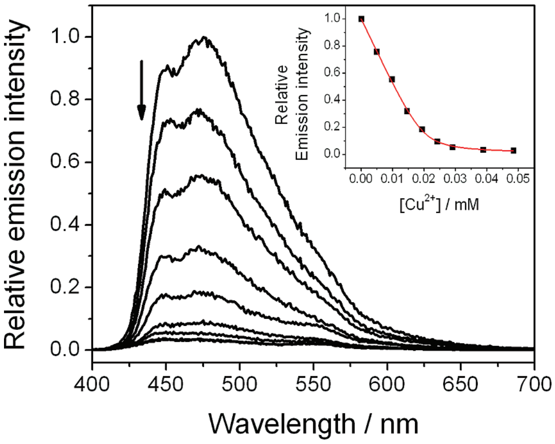

Figure 4. Emission spectral traces of **1** (2.0×10^{-5} M) in CH_2Cl_2−MeOH (1:1 v/v; 0.1 M ^{n}Bu$_4$NPF$_6$) upon treatment of Cu(ClO$_4$)$_2$. Excitation at the isosbestic wavelength of 286 nm. Inset: Plot of emission intensity at 475 nm as a function of Cu^{2+} concentration and its theoretical fit for the 1:1 binding of complex **1** with Cu^{2+}.

When Cu^{2+} was added to the solution of **1**, emission quenching was observed, which is due to the energy or electron transfer process because of the d^9 electronic configuration. The stability constant was also determined from the change of the emission intensity at 475 nm as a funcion of the concentration of Cu^{2+} ion added using nonlinear least-squares fit. A log K_s of 6.4 ± 0.1 was obtained, which is in good agreement with that determined by the UV−vis spectrophotometric method. Figure 4 shows the changes in the luminescence response of **1** toward Cu^{2+} in CH_2Cl_2−MeOH (1:1 v/v; 0.1 M ^{n}Bu$_4$NPF$_6$), excited at the isosbestic wavelength of 286 nm. The inset of Figure 4 also shows a good agreement of the experimental data to the theoretical fit based on 1:1 binding stoichiometry.

The binding of Cu^{2+} to **1** was found to be reversible. When an aqueous solution of EDTA disodium salt was added to a solution of **1** (2.0×10^{-5} M) and Cu^{2+} (4.0×10^{-5} M) in CH_2Cl_2−MeOH (1:1 v/v; 0.1 M ^{n}Bu$_4$NPF$_6$), the emission intensity at 475 nm was completely revived and the absorbance at 366 nm in the UV−vis spectrum was found to

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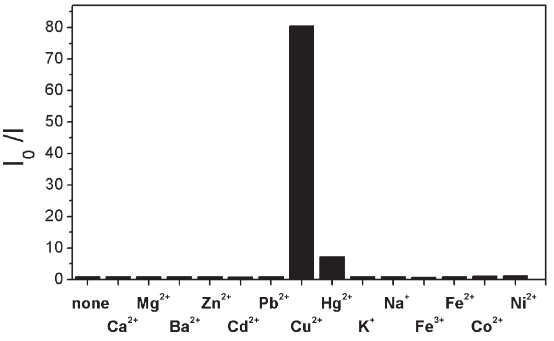

Figure 5. Responses of **1** (2.0×10^{-5} M) in CH_2Cl_2−MeOH (1:1 v/v; 0.1 M $^{n}Bu_4NPF_6$) upon addition of 5 equiv of different metal ions. Excitation was at 286 nm, and the emission was monitored at 475 nm.

diminish, suggesting that Cu^{2+} has been extracted out of the DPA unit, confirming the complete reversibility of the Cu^{2+} binding process.

To examine the selectivity of complex **1** toward various metal ions, the luminescence response upon addition of metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, and Ni^{2+} has been investigated. As shown in Figure 5, a drastic spectral change is shown by Cu^{2+} binding, indicating the high selectivity of **1** toward Cu^{2+}.[15] While Hg^{2+} shows a similar phenomenon of emission quenching, the change is to a lesser extent. For all other metal ions, including some transition metal ions that have a partially filled d-orbital, such as Co^{2+}, Ni^{2+}, and Fe^{2+}, very small to negligible changes were observed under identical conditions. However, addition of Fe^{3+} would cause a modest increase of the emission intensity by ca. 1.4-fold. The reason has been ascribed to the increased acidity as a result of the strong hydrolyzing ability of Fe^{3+}.[16] Although DPA is also well-known to readily bind Zn^{2+} ion, no spectral changes were observed upon addition of Zn^{2+} ions, probably due to the lack of a quenching pathway.

Since Cu^{2+} is a paramagnetic metal ion, not suitable for the NMR experiment, the ^{1}H NMR titration study of **1** with Zn^{2+} was carried out instead (Figure 6). The ^{1}H NMR titration experiment in $CDCl_3$−CD_3OD (1:1 v/v) showed that the proton resonances on the pyridine and phenyl rings were shifted downfield and became broader upon Zn^{2+} addition, indicating the coordination of Zn^{2+} ion to **1**. Upon complexation of zinc ions to the DPA moiety, a decrease in the electron density on the DPA unit and the conjugated phenyl ring would cause a downfield shift of the signal. The experimental data were found to be in good agreement with the theoretical fit obtained from the EQNMR program using a 1:1 binding model.[17] The binding constant log K_s for Zn^{2+} was determined to be 2.20 ± 0.05, which is much smaller than that for Cu^{2+}, suggesting the higher selectivity for Cu^{2+}. In addition, the 1:1 stoichiometry between **1** and Zn^{2+} was further confirmed by the Job's method of continuous variation.

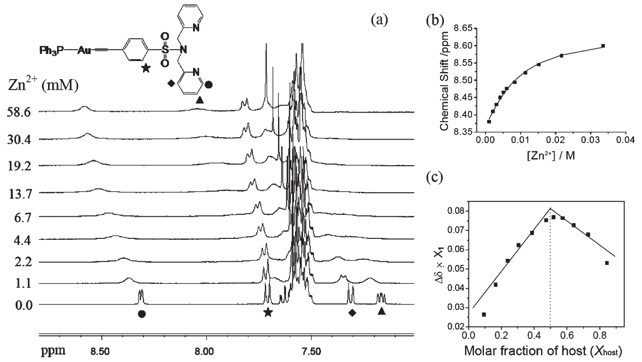

Figure 6. (a) ^{1}H NMR spectral changes of **1** (5.86 mM) upon addition of $Zn(ClO_4)_2$ in $CDCl_3$−CD_3OD (1:1 v/v). (b) Plot of proton chemical shifts of N═CH (labled as ●) as a function of the concentration of Zn^{2+} added. (c) Job's plots for 1:1 binding of **1** with Zn^{2+} ions showing a 1:1 stoichiometry. The changes of proton chemical shift of N═CH (labled as ●) were followed, where X_1 = ([**1**]/([Zn^{2+}] + [**1**])).

In summary, a novel DPA-containing alkynylgold(I) complex has been successfully synthesized and structurally characterized. The complex has been shown to exhibit a rich photoluminescence property and to function as a selective sensor for Cu^{2+}, as revealed by the large UV−vis change and significant emission quenching.

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Supporting Information Available: Synthesis and characterization of the ligand and complex **1** and the X-ray crystallographic determination data of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) A competitive ion-binding experiment was also studied. Addition of Cu^{2+} (1.0×10^{-4} M) to a CH_2Cl_2−MeOH (1:1 v/v) solution of **1** (1.9×10^{-5} M) containing an excess of Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, and Ni^{2+} (ca. 1.0×10^{-4} M, respectively) led to immediate quenching of the emission intensity (though the emission change is only about half that in the absence of other metal ions), suggesting that Cu^{2+} could displace other metal ions from binding with complex **1**.

(16) This has been verified by performing the measurements under buffered conditions in HEPES buffer (pH 7.2), where quenching of the emission intensity was observed but to a much lesser extent than that of Cu^{2+} under the same buffered conditions.

(17) Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.