# The First Luminescent Anionic Bis(ethynylphenanthroline)gold(I) Complex

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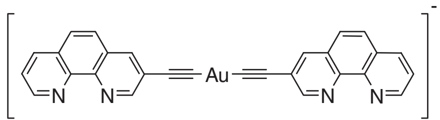
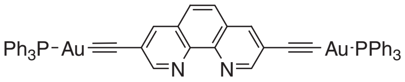
First anionic bis(ethynylphenanthroline)gold(I) complex and neutral diethynylphenanthroline–digold(I) complex have demonstrated an intense phosphorescence which is assignable to $^3\pi$–$\pi^*$(C≡C) emission even at room temperature. It is appropriate to highlight the role of gold(I) coordination which enables the spin–orbit coupling and facilitates the observation of triplet emissions.

Current research of luminescent gold(I) complexes[1] has gained great importance with respect to their potential applications to the burgeoning field of photonic devices and nano-materials, because particularly interesting properties as photoenergy storage[2] and nonlinear optical response[3,4] have been discovered from recent studies on gold(I) organometallics. Structural and photophysical studies on neutral gold(I) ethynylarene complexes have been extensively explored by Puddephatt et al.[5] and Yam's groups[6] in the past decade. These compounds are especially attractive for usefulness as a photoactive nano-wire; these compounds should be utilized as scaffolding to construct a rigid-rod upon coordination with strictly linear bridging diethynylarene ligands through the Au–C $\sigma$-bonding. Most studies on gold(I) ethynyl complexes have so far been made for gold(I) ethynylarene complexes.[5–7] In contrast to these compounds, gold(I) ethynyldiimine complexes should have a high potential ability of further coordination to other metal ions. However, no precedent has been reported to the best of our knowledge. The first synthetic report of anionic gold(I) arenediethynyl complexes was recently made by Vicente et al.[8] for the purpose of finding some peculiar structural features. In addition to the structural idiosyncrasy, the luminescent property of anionic gold(I) bis(ethynylarene) complexes is intriguing and significant studies have been undertaken in connection with neutral alkynylgold(I) complexes. Anionic gold(I) ethynyldiimine complex is further advantageous for the construction of heterometallic system because of Coulomb's law; the diimine ligand such as a bipyridine and phenanthroline is generally coordinated to cationic metal center. However, only one photophysical study on the anionic gold(I) bis(ethynylbenzene) complex has so far been reported to our knowlegde[7] and their result has encouraged us to extend the chemistry. Herein, we report the synthesis and photophysical study of the luminescent anionic gold(I) bis(ethynyldiimine) complex $[(i\text{-}C_3H_7)_2NH_2]$[Phen–≡–Au–≡–Phen] (**1**) for the first time and the neutral gold(I) diethynyl- and ethynyl-diimine complexes (PPh$_3$)Au–≡–phen–≡–Au(PPh$_3$) (**2**) and phen–≡–Au(PPh$_3$) (**3**) with ethynyl- or diethynyl-phenanthroline ligands which coordinate to gold(I) ion through the Au–C $\sigma$-bonding.

The anionic complex **1** was synthesised from Au(tht)Cl (tht = tetrahydrothiophene) and 3-ethynyl-1,10-phenanthroline (**4**) (1/2 ratio, with an excess diisopropylamine as a base), while complex **2** and **3** were prepared by reacting Au(PPh$_3$)Cl (PPh$_3$ = triphenylphosphine) with 3,8-bis(ethynyl)-1,10-phenanthroline (**5**) and **4**, respectively (2/1 and 1/1 ratio respectively, with an excess KOH or NaOMe). These complexes were characterised by ESIMS, $^1$H NMR, IR, UV–vis, emission spectroscopy, and elemental analysis.



**1**



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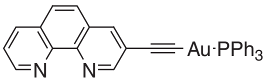

**3**

IR spectral data of these novel three complexes indicate that the metal–carbon bond between Au(I) and ethynylphenanthrolines is of $\sigma$-bonding. The characteristic $\nu$(C≡C) bands are observed at 2094 cm$^{-1}$(**1**), 2109 cm$^{-1}$(**2**), 2108 cm$^{-1}$(**3**), respectively and the $\nu$(CC–H) bands at 3146 cm$^{-1}$(**4**), 3175 cm$^{-1}$(**5**) are disappeared in these gold(I) complexes.[9] The formation of this type of Au–C≡C bond is further supported by the $^1$H NMR measurement; no assignable signal to ethynyl proton was detected and all observed signals for **1**–**3** correspond to the protons of the phenanthroline and/or the triphenylphosphine, respectively. Furthermore, the negative ESIMS spectrum for **1** predominantly shows one signal set that is compatible with the simulated pattern for mono anion [Phen–≡–Au–≡–Phen]$^-$.

Figure 1 displays the absorption and emission spectra of complex **1** in MeOH. The absorption bands at 345 nm are primarily assigned to $\pi$–$\pi^*$(C≡C) absorption for **1**. **2** and **3** show similar absorption spectra in CH$_2$Cl$_2$ (Figure 2). Molar extinction coefficients for $\pi$–$\pi^*$ absorptions (337 and 357 nm) in **2** are twice as those (315 and 328 nm) of **3**. As the absorption coefficient is proportional to the number of the Au(I)-ethynyl unit, this finding lends further support to interpretation that the intense absorptions are due to $\pi$–$\pi^*$(C≡C) transitions. The red shift of the $\pi$–$\pi^*$ absorptions (337 and 349 nm in CH$_2$Cl$_2$) in **1** compared with those (315 and 328 nm) in **3** should be attributed to more electron delocalization between two ethynylphenanthoroline ligands via a gold(I) ion.

The emission spectrum of the complex **1** displays an intense emission band in the visible region and a weak band in the UV area, which are so called dual emission in deoxygenated methanol at room temperature upon excitation at 328 nm (Figure 1). The former intense luminescence is formally assignable to the $^3\pi$–$\pi^*$ phosphorescence, because the luminescence excitation

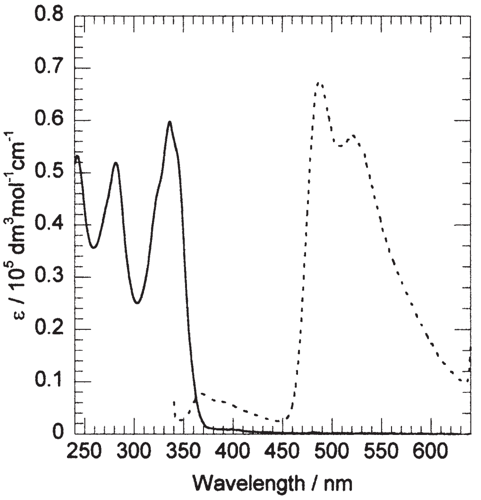

**Figure 1.** Absorption (—) and Emission (- - - -) spectra of **1** in MeOH purged $N_2$ at room temperature. Emission spectrum was detected upon excitation at 328 nm.

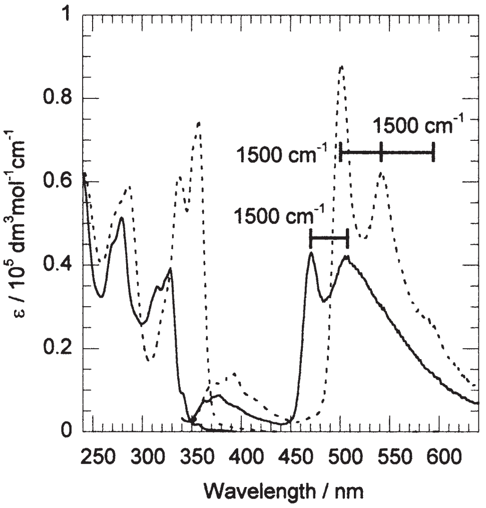

**Figure 2.** Absorption (left) and Emission (right) spectra of **2** (——) and **3** (- - - -) in $CH_2Cl_2$ purged $N_2$ at room temperature. Emission spectrum was detected upon excitation at 328 nm.

spectrum monitored at 488 nm of **1** between 250 and 450 nm is approximately in accord with the absorption spectrum in this region. Under an aerobic condition, the emission spectrum of **1** exhibits a quite weak phosphorescent band between 450 and 600 nm owing to $^3O_2$ quenching. On the contrary, the weak fluorescent band[10] between 350 and 450 nm is left intact. Entirely similar spectral changes are observed for **2** and **3** under aerobic and anaerobic conditions. Thus, these novel gold(I) complexes exhibit an intense phosphorescence only under an anaerobic condition at room temperature.

Another interesting finding is that these gold(I) complexes show a vibronic structure of the emission spectra even at an ambient temperature. The emission spectrum of 2 (Figure 2) displays vibronic progressions and the vibrational spacing of the main progression ($\nu = 1500\,\text{cm}^{-1}$) is in accord with aromatic C–C stretching region (1300 to 1700 cm$^{-1}$). The latest photophysical study on gold(I) ethynylarene complexes reported by Che et al.[11] lends support to this interpretation of the emission spectra for these complexes.

In summary, the gold(I) ethynyldiimine complexes have been prepared for the first time and shown the obvious luminescence assignable to $^3\pi$–$\pi^*$(C≡C) phosphorescence at room temperature. It is appropriate to highlight the role of gold(I) coordination which enables the spin–orbit coupling and facilitates the observation of triplet emissions. We are currently extending the synthetic work of novel rhenium(I)–gold(I) complexes in which these gold(I) complexes coordinate to the rhenium center in a rhenium(I) diimine complex and an exploration for the mechanism of photoinduced energy transfer process is continuing for hetero organometallics.

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