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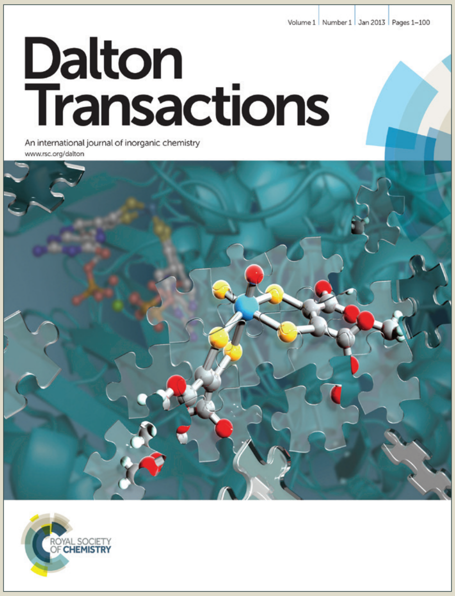

ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Novel Electrochemi- / Photo-Luminescence of Ag_3Cu_5 Heterometallic Alkynyl Clusters

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Two windmill-like Ag_3Cu_5 alkynyl clusters were synthesized and characterized. They display novel PL and ECL properties, which could be modified by changing of the substituent on the alkynyl ligands. According to the study of electrochemical behaviours, ECL behaviours and ECL emission spectra of the Ag_3Cu_5 clusters, a possible ECL mechanism was proposed.

Electrochemiluminescence (ECL) has become a powerful analytical technique during the past decades due to its high versatility, simplified optical setup, good temporal and spatial control, and fast sample analysis.[1] Among the various materials investigated in ECL study, an important branch is metal complexes due to their thermal and photochemical stability and high photoluminescence (PL) efficiency, and most of the ECL studies on metal complexes have focused on tris(2,2'-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$)[2-3]. With the increasing application of ECL, it is considerable interest to develop new and efficient ECL labels that can be easily modified for different samples analysis.[4-5]

Coinage-metal alkynyl complexes have attracted considerable attention of both rich structural diversity and remarkable photoluminescent (PL) properties over the last few decades.[6] With respect to the very large number of homometallic M(I) (M = Cu, Ag, Au) alkynyl complexes, heterometallic coinage-metal alkynyl complexes have been much less explored because of the difficulty in controlling the heterometallic arrays and the tendency to form homo metallic arrays.[6-15] To the best of our knowledge, the number of Ag(I)−Cu(I) heterometallic alkynyl arrays is extremely scarce and only a few papers[12-15] have reported the synthesis and PL properties of these complexes. Moreover, survey and analysis of the literatures showed that the ECL properties of coinage-metal alkynyl complexes were completely unexplored. It is known to all that the PL of coinage-metal alkynyl complexes could be modified via changing of the alkynyl ligands,[6] suggesting that they may also be functioned as controllable ECL luminophores. This inspired us to extend the corresponding chemical research for the preparative routes to the Ag(I)–Cu(I) compounds, followed by the photophysical and ECL studies of the novel objects, thus opening up a new class of controllable ECL systems for analytical application.

Compounds $[Ag_3Cu_5(C{\equiv}CC_6H_4R\text{-}4)_6(\mu\text{-dpppy})_3](ClO_4)_2$ (R = H (**1**), CH_3 (**2**); dpppy = 2, 6-bis(diphenylphosphino)pyridine) were prepared by reaction of $[Cu_2(\mu\text{-dpppy})_3](ClO_4)_2$ with 3 equiv of $[Ag(C{\equiv}CC_6H_4R\text{-}4)]_n$ (R = H, CH_3) and satisfactorily characterized† by ESI-MS, ^1H NMR, $^{31}P\{^1H\}$ NMR, elemental analyses, IR spectroscopy, and by X-ray crystallography[16] (Detailed data in Table S1-S2 †).

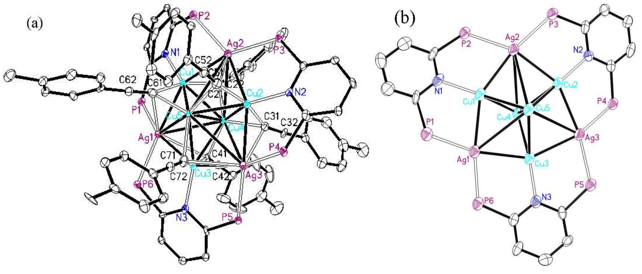

Fig. 1 (a) ORTEP drawing of the cation of complex **2** with atom labelling scheme showing 30% thermal ellipsoids, (b) dpppy-stabilized Ag_3Cu_5 cluster core. Phenyl rings on the phosphorus atoms and hydrogen atoms are omitted for clarity.

As depicted in Fig. 1 and Fig. S1†, the $\mathbf{Ag_3Cu_5}$ heterometallic clusters show a windmill-like structure that can be regarded as a hexagonal bipyramidal rotational axis (Ag_3Cu_5) and three sails of the windmill consisting of three dpppy ligands. The hexagonal bipyramidal apices are occupied by two copper(I) centres (Cu4 and Cu5) with a C_3 axis through the two copper(I) atoms, and the hexagon (Ag_3Cu_3) is made of three silver(I) and three copper(I) centres. It is obvious that the $\mathbf{Ag_3Cu_5}$ cluster structure is stabilized by three auxiliary tridentate diphosphine ligands (dpppy) and six alkynyl C (C1, C11, C21, C31, C41, and C51) donors (Figure 1). The dpppy ligand adopts a tridentate bridging mode, with two P donors bound to two silver(I) atoms, respectively, and the N donor bound to one copper(I) atom (Cu−N, 2.057(12)-2.088(7) Å), forming two five-membered coordination rings, which is different from our reported $[Ag_2Au_2(C{\equiv}CC_6H_4R\text{-}4)_2(\mu\text{-dpppy})_3](ClO_4)_2$ complexes[8a]. The alkynyl ligand adopts a very asymmetric μ_3-bonding mode, in which it coordinates to two copper(I) atoms and one silver(I) atom, to form six tetrahedrons ($CAgCu_2$) and lie on the pyramid ($AgCu_2$) of the hexagonal bipyramid (Ag_3Cu_5). The Cu–C lengths (1.916(16)–2.135(12) Å) are always much shorter than those of Ag–C (2.490(9)–2.689(10) Å). The copper(I) atom is surrounded by two C and one N donor to give a T geometry for the Cu1−Cu3, and by three C donors to afford a distorted trigonal-planar environment for the Cu4 and Cu5, respectively. The silver(I) centre displays distorted tetrahedral surroundings with one P and three acetylide C donors. The Ag···Cu (2.615(2)−3.216(2) Å), and Cu···Cu (2.531(2)−2.740(2) Å) distances fall in the range of closed d^{10} shell interactions typical for coinage metals.[12-15]

The UV−Vis absorption spectra of **1** and **2** (Fig. S2†) are characterized by two absorption regions at < 350 and 417–436 nm. The higher-energy absorptions below 350 nm are typical for ligand-centered [$\pi \rightarrow \pi^*$] (dpppy ligand)[8a] absorption and the intraligand [$\pi \rightarrow \pi^*$] ($C{\equiv}CC_6H_4R$-4) transitions of the alkynyl-phenyl moieties.[6–15] The lower-energy absorption bands of 417–436 nm, are likely to from metal-centered (^{1}MC) [d/Cu→p/Cu] transition, mixed with some LMMCT [$C{\equiv}CC_6H_4R\text{-}4 \rightarrow Ag_3Cu_5$] transition, based on a slight red-shift in energy from the phenylacetylide complex **1** to 4-methyl-phenylacetylide **2** counterparts.

Both complexes **1** and **2** display orange luminescence with a microsecond range of luminescent lifetime (Table S3†). Comparing the emissions of **1** and **2** both in solid state and in fluid solution, a slight red-shift in energy is observed on going from the phenylacetylide complex **1** to 4-methyl-phenylacetylide counterpart **2** (Fig. S3†). Interestingly, the emissions of **1** and **2** (590−609 nm) are considerably red-shifted compared to those of Ag_4Cu_2, Ag_6Cu_2, and Ag_8Cu_2 alkynyl clusters (450−522 nm) in solutions.[12-14] The emissions of **1** and **2** are free of oxygen quenching effect and similar to a few recently reported Ag(I)–M(I) (M = Cu, Ag) complexes[7, 10, 13], for which the Ag_3Cu_5 core is well protected by the surrounded dpppy ligands. Therefore, the emission of the Ag_3Cu_5 complex is likely derived from a ^{3}LMMCT ^{3}[$C{\equiv}CC_6H_4R$-4 and dpppy→Ag_3Cu_5] transition, mixed with an Ag_3Cu_5 cluster-centered triplet excited state modified by metal−metal interactions, in view of the short Cu−Cu and Cu−Ag contacts.[7-14]

It is noteworthy that the emission intensities of **1** and **2** in CH_3CN/H_2O solution are dramatically increasing with the increasing of the ratio of water, and the emission energies are both slightly blue-shifted (Fig. 2). The quantum yields of **1** and **2** both follow the order in CH_3CN/H_2O (10:90, v/v) ($\Phi = 0.062$ for **1** and 0.058 for **2**) > CH_2Cl_2 ($\Phi = 0.015$ for **1** and 0.013 for **2**) > CH_3CN ($\Phi = 0.004$ for **1** and 0.007 for **2**). The remarkably enhanced emission of **1** and **2** in CH_3CN/H_2O may be ascribed to the aggregation-induced emission (AIE) as reported by our and other groups,[17] since complexes **1** and **2** are soluble in CH_3CN, but poor water solubility. This could prove valuable for application as potential luminescent probes particularly for those demanding in water.

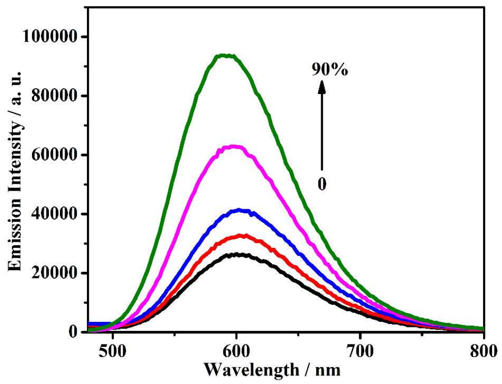

Fig. 2 Emission responds of complex **1** in various CH_3CN/H_2O mixtures. From the bottom to the top the ratio of water: 0, 25%, 50%, 75%, and 90%.

The redox behaviors of **1**, **2** (0.1 mM) and dpppy ligand (1 mM) for comparison in CH_3CN (0.1 M TBAP) were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) at a scan rate of 100 mV s^{-1} (Fig. S4†). Both **1** and **2** undergo three irreversible oxidation processes in the potential range of + 0.80 to + 0.84 V, + 1.42 V, and + 1.70 to + 1.84 V, respectively. Based on the similar oxidation potentials observed in the dpppy ligand, the irreversible oxidation waves for **1** and **2** are ascribed to the oxidation of the dpppy ligand.

Much to our surprise, both **1** and **2** in solutions exhibit excellent ECL activity, although their quantum yields of PL are not high. To the best of our knowledge, this is the first case that alkynyl metal complex exhibits ECL emission without amine or peroxydisulfate as coreactants, which is distinctly different from those found in alkynylgold(III)[4b], $[Pt_2Ag_4(C{\equiv}CC_6H_4R)_8]$ (R = H, CH_3)[4a] and alkynylplatinum complexes[4c].

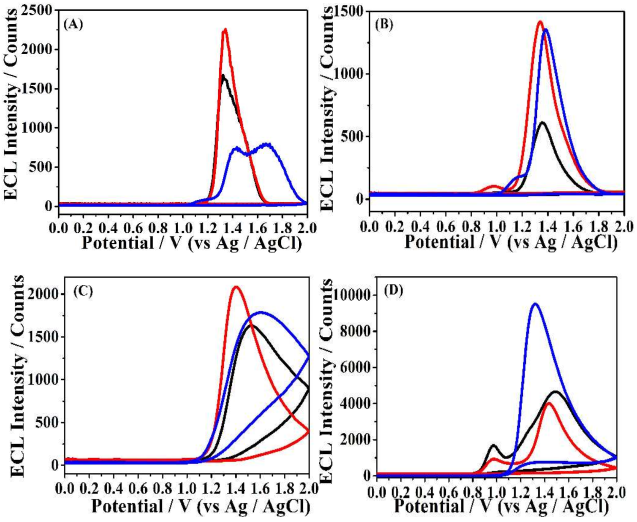

Fig. 3 ECL curves of 10 μM **1** (black), **2** (red) and $[Ru(bpy)_3]Cl_2$ (blue) on a GC working electrode in a CH_3CN (5%) solution (pH 9.0) containing 0.05 M (A) PBS (95%), (B) BBS (95%), and (C) Tris-HCl (95%) in the absence of TPrA; (D) Tris-HCl (95%) in the presence of 1 mM TPrA.

Fig. 3A-3C shows the ECL emissions of compounds **1** and **2** in different media solutions, when the potential is swept from 0 to +2.0 V. It is found that the ECL response of **1** and **2** is most sensitive in Tris-HCl/CH_3CN. Therefore, the effects of the other experimental conditions, such as the ratio of CH_3CN solvent and pH in Tris-HCl/CH_3CN solution, and electrode materials were further investigated. It is found from Fig. S5A that the ECL intensities of **1** and **2** are pronouncedly increasing with the increasing of the ratio of Tris-HCl buffer solution. The ECL intensities are increasing with the increasing of pH at the range of pH 7.5–9.0 in Tris-HCl/CH_3CN solution, but they are decreasing sharply (Fig. S5B†) upon further increasing of pH, which may be ascribed to the instability of **1** and **2** in strongly alkaline solutions (pH > 9.0). Additionally, it was observed that the electrode materials greatly affected the ECL of **1** and **2** in the solution containing 0.05 M pH 9.0 Tris-HCl (95%) and CH_3CN (5%) solution. Among Pt, Au, and GC working electrodes, the ECL intensities of **1** and **2** both follow the order: GC electrode > Au electrode > Pt electrode. It is noted that the potential of the maximum ECL intensity of complex **2** is shifted toward more negative potential by about 10-50 mV and 40-330 mV than that of **1** and $[Ru(bpy)_3]Cl_2$, respectively, under the same experimental conditions. Furthermore, ECL quantum efficiency of **2** is slightly higher than that of **1**, and is on the same order of magnitude as that of $[Ru(bpy)_3]Cl_2$. These indicate that the ECL of the current $\mathbf{Ag_3Cu_5}$ clusters could be modified only via changing of the substituents on the alkynyl ligands, opening up a new strategy for the design of other heterometallic alkynyl clusters with novel ECL properties for different samples analysis.

To further investigate the ECL mechanism, we measured the ECL spectra of **1** and **2** with a series of optical filters and compared them with their PL spectra, respectively. The ECL spectra of **1** and **2** are almost identical to their PL spectra, respectively (Fig. S6†), indicating formation of the same emissive states generated both in ECL and PL.[1,2,4] Moreover, it is evident from above experimental results that the ECL intensities of **1** and **2** are pH-dependent: the higher pH is used, the stronger ECL intensity is observed. This indicated the ECL responses of the current $\mathbf{Ag_3Cu_5}$ clusters result from that OH^- anion in the media reacts with electrogenerated $[\mathbf{Ag_3Cu_5}]^{4+}$ to produce the excited sate $[\mathbf{Ag_3Cu_5}]^{4+}*$. This result suggests that the hydroxyl ion acts as a co-reactant in the ECL process of the current $\mathbf{Ag_3Cu_5}$ clusters.

Tri-n-propylamine (TPrA) has been used as a popular coreactant to enhance the ECL intensity in the ECL system due to its solubility in both organic and aqueous solutions.[1-5] Fig. 3D show the coreactant ECL emission of the current $\mathbf{Ag_3Cu_5}$ clusters in the presence of TPrA as coreactant on a GC working electrode. When the potential was scanned positively, a weak ECL signal of **1** in the presence of 1 mM TPrA was first observed at 0.97 V at GC working electrode, and then a strong ECL signal at the potential of 1.48 V was obtained. In analogy with the known $[Ru(bpy)_3]^{2+}$ / TPrA system[1, 2], the ECL generation from $\mathbf{Ag_3Cu_5}$ clusters could be explained by the following reaction:

$$[\mathbf{Ag_3Cu_5}]^{2+} - 2e^- \rightarrow [\mathbf{Ag_3Cu_5}]^{4+} \quad (1)$$

$$\text{TPrA} - e^- \rightarrow \text{TPrA}\bullet + H^+ \quad (2)$$

$$[\mathbf{Ag_3Cu_5}]^{4+} + \text{TPrA}\bullet \rightarrow [\mathbf{Ag_3Cu_5}]^{4+}* + \text{P1} \quad (3)$$

$$[\mathbf{Ag_3Cu_5}]^{4+}* \rightarrow [\mathbf{Ag_3Cu_5}]^{4+} + h\nu \quad (4)$$

where TPrA• is $(CH_3CH_2CH_2)_2NC\bullet HCH_2CH_3$, and P1 is $Pr_2N^+{=}CHCH_2CH_3$. Under the same experimental conditions, the potential of the maximum ECL intensity of **1** is shifted by about 50 mV toward more positive potential than that of **2**. ECL quantum efficiencies of **1**/TPrA system ($\varphi°_{ECL}$= 0.68) are higher than that of **2**/TPrA system ($\varphi°_{ECL}$= 0.44), measured using $[Ru(bpy)_3]Cl_2$/TPrA system as a standard.[4]

Conclusions

In conclusion, we have demonstrated an effective self-assembly preparative methodology of $\mathbf{Ag_3Cu_5}$ heterometallic alkynyl clusters. The current $\mathbf{Ag_3Cu_5}$ heterometallic alkynyl clusters display novel PL and ECL properties, which could be modified by changing of the substituent on the alkynyl ligands. Although a few PL heterometallic silver(I)-M (M = Cu(I) or Au(I)) alkynyl clusters have been reported in the literatures, the current $\mathbf{Ag_3Cu_5}$ heterometallic alkynyl clusters, to the best of our knowledge, are the first case that shows ECL emission. The present work provides a new strategy for the design of other heterometallic alkynyl clusters with novel ECL properties and could be expected to extend the applications of heterometallic alkynyl clusters in ECL analysis.

This work is funded by Key Science Project (type A) of the Fujian Provincial Department of Education, China (Grant JA12021), the Science Foundation of the Fujian Province, China (Grant 2014J01046), and the National Basic Research Program of China (Grant 2010CB732403).

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† Electronic Supplementary Information (ESI) available: Experimental details; Crystallographic parameters and the details for data collections and refinements of the two Ag_3Cu_5 clusters, and Fig. S1–S6. See DOI: 10.1039/b000000x/

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Graphic Abstract for Contents

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