# An intensely and oxygen independent phosphorescent gold(I)–silver(I) complex: "trapping" an $Au_8Ag_{10}$ oligomer by two gold-alkynyl-diphosphine molecules†

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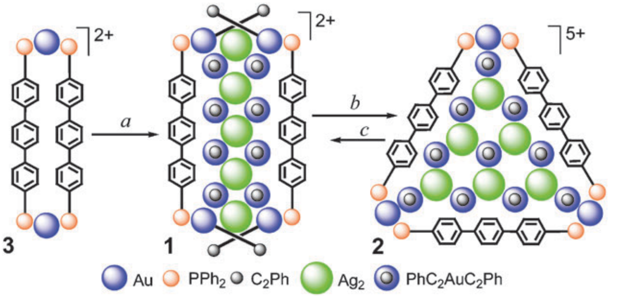
**The molecular heterometallic $[\{Au_8Ag_{10}(C_2Ph)_{16}\}\{(PhC_2Au)_2PPh_2(C_6H_4)_3PPh_2\}_2]^{2+}$ aggregate of unprecedented topology was obtained and structurally characterized; this compound demonstrates unusually effective phosphorescence, which displays negligible oxygen quenching due to shielding of emissive central cluster by the outer shell of the molecule.**

The chemistry of metal alkynyl complexes is an area of broad and extensive research that has significantly progressed during the past decade. These advances have been stimulated by the continuous discoveries of their intriguing physical properties, such as luminescence, optical non-linearity, liquid crystallinity and electrical conductivity.[1,2] However, polynuclear heterometallic alkynyl complexes have received much less attention in comparison to their homometallic analogues, in spite of the rich structural diversity and attractive emissive characteristics demonstrated by these compounds.[3–6]

Recently we reported a series of intensely luminescent $Au^I$–$Cu^I$ and $Au^I$–$Ag^I$ heterometallic alkynyl-diphosphine (diphosphine = $PPh_2$–$(C_6H_4)_n$–$PPh_2$, $n$ = 1, 2, 3) clusters,[5–7] which display similar structural patterns based on the heterometallic $(Au_xM_y(C_2Ph)_{2x})^{y-x}$ fragments "wrapped" by the $[Au_3(\text{diphosphine})_3]^{3+}$ "belts". One of the synthetic pathways leading to these species is treatment of digold $PhC_2Au$–diphosphine–$AuC_2Ph$ complexes with $Cu^+$ or $Ag^+$ ions. To gain a better insight into this type of self-assembly processes we then examined carefully the composition of the reaction mixtures. Serendipitously, in the case of $M^+ = Ag^+$ and the terphenyl-based diphosphine, we discovered and isolated a novel heterometallic complex—$[\{Au_8Ag_{10}(C_2Ph)_{16}\}\{(PhC_2Au)_2PPh_2(C_6H_4)_3PPh_2\}_2]^{2+}$ (**1**)—as an intermediate in the synthesis of the $[\{Au_{10}Ag_{12}(C_2Ph)_{20}\}Au_3(PPh_2(C_6H_4)_3PPh_2)_3]^{5+}$ cluster (**2**).[7] However, the original procedure gave a very low yield (<5%) and required tedious recrystallization. Fortunately, an alternative route (depolymerization of an equimolar mixture of $(AuC_2Ph)_n$ and $(AgC_2Ph)_n$ with 50% excess of $[Au_2(PPh_2(C_6H_4)_3PPh_2)_2]^{2+}$ (**3**)) gave **1** in good yield (Scheme 1).



**Scheme 1** Reaction conditions: (a) $10(AuC_2Ph)_n$, $10(AgC_2Ph)_n$, 1.5 **3**, *ca.* 60%; (b) 0.5 **3**, $2Ag^+$, >85%; (c) crystallization by gas-phase diffusion of diethyl ether into NCMe–MeOH (2 : 1 v/v) solution of **2** at room temperature, *ca.* 30%.

Bright-yellow complex $\mathbf{1}(PF_6)_2$ has been characterized by $^1H$, $^{31}P$ NMR and ESI-MS. Its structure in the solid state has been determined by an X-ray diffraction study‡ (Fig. 1). The ESI mass spectrum of **1** (Fig. S1, ESI†) displays the signal of a doubly charged cation at $m/z$ 3331, the isotopic pattern of which completely fits the stoichiometry of the $[\{Au_8Ag_{10}(C_2Ph)_{16}\}\{(PhC_2Au)_2PPh_2(C_6H_4)_3PPh_2\}_2]^{2+}$ molecular ion.

The molecule contains a linear-like heterometallic alkynyl cluster $[Au_8Ag_{10}(C_2Ph)_{16}]^{2+}$ that is enveloped by two neutral $Au_2(C{\equiv}CPh)_2(\mu\text{-}Ph_2P(C_6H_4)_3PPh_2)$ molecules anchored to the central part by the Au–Au, π–C≡C–Ag and weak Au–Ag bonds. The latter digold complex has been synthesized previously[6] as an individual compound. Structural parameters (bond lengths and angles) of these neutral species are similar to those found for their close relatives $Au_2(C{\equiv}CPh)_2(\mu\text{-}Ph_2P(C_6H_4)_nPPh_2)$ ($n$ = 1,[8] 2[5]). The Au–Au contacts between the central and external fragments (2.9522(6) and 3.1973(4) Å) in **1** fall in the range typical for aurophilic interactions.[4,6,9] The central alkynyl $[Au_8Ag_{10}(C_2Ph)_{16}]^{2+}$ cluster consists of eight slightly twisted $[PhC_2AuC_2Ph]^-$ rods held together by the Ag–Au and π–C≡C–Ag bonds. To the best of our knowledge, the nuclearity and the structural topology of this complex, where the metal Au–Ag core is enveloped and held together by two gold phosphino-alkynyl units, are unprecedented.

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† Electronic supplementary information (ESI) available: X-Ray crystallographic data in CIF format for **1**, experimental details, ESI MS spectra of **1** and **4**, selected NMR spectra of **1** and **4**, optimized Cartesian coordinates of the studied systems. CCDC 715007. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901893j

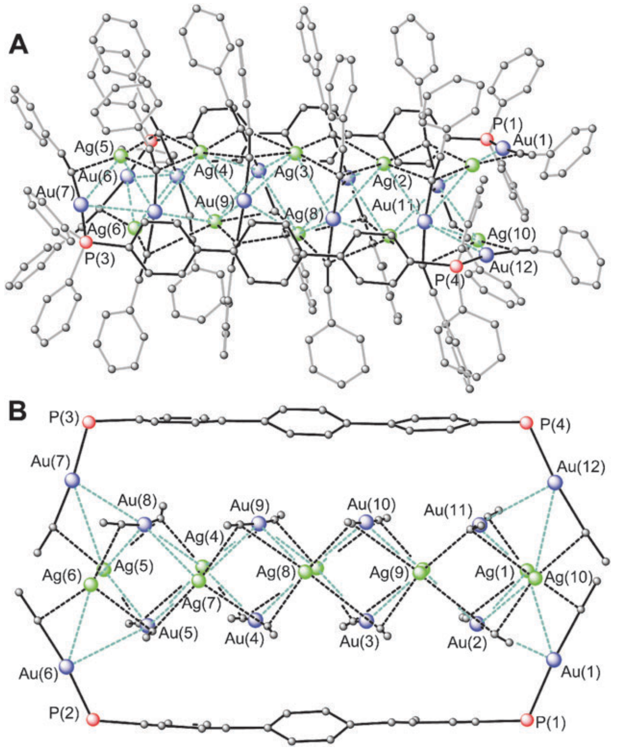

**Fig. 1** Two projections of the molecular structure of **1** (B—phenyl rings omitted for clarity).

The NMR data obtained for **1** are completely consistent with the solid state structure. In accord with the idealized $D_2$ symmetry group of **1** found in the solid state, its $^{31}P$ NMR spectrum displays single resonance at 38.5 ppm, whereas the proton spectrum shows three sets of signals generated by phenylene spacers, together with seven characteristic groups of phenyl protons (two groups of phenyl substituents at the phosphorus atoms and five groups of the alkynyl fragments; a detailed assignment is given in the ESI†). Relative intensities of the resonances, their multiplicity and specific long range $^1H$–$^1H$ and $^{31}P$–$^1H$ couplings fit the $D_2$ symmetry of **1** that points to retention of the solid state structure in solution.

**1** is moderately stable in concentrated solution at room temperature and its spontaneous decomposition results in slow formation of **2**, **3** and an unidentified, insoluble precipitate. Alternatively, **1** can be easily converted into **2** by treating with stoichiometric amounts of **3** and $Ag^+$ (Scheme 1). Interestingly, this transformation between two totally different structural topologies is reversible; upon slow precipitation of **2** from acetonitrile–methanol solution, crystals of **1** are obtained in *ca.* 30% yield.

Application of the synthetic method (Scheme 1) using $[Au_2(PPh_2(C_6H_4)_2PPh_2)_2]^{2+}$,[5] based on the diphosphine with biphenyl spacer, allowed for the isolation of the aggregate $[\{Au_6Ag_8(C_2Ph)_{12}\}\{(PhC_2Au)_2PPh_2(C_6H_4)_2PPh_2\}_2]^{2+}$ (**4**), which is similar to **1** and consists of a central heterometallic $[Au_6Ag_8(C_2Ph)_{12}]^{2+}$ cluster enveloped by two $Au_2(C{\equiv}CPh)_2(\mu\text{-}Ph_2P(C_6H_4)_2PPh_2)$ molecules. X-Ray crystallography confirmed this structural pattern but poor diffraction by the crystals prevented high-quality refinement. However, the ESI MS (Fig. S3†) and NMR spectroscopic studies (Fig. S4†) clearly support this geometrical arrangement of **4**. Unfortunately, **4** was obtained in a low yield (*ca.* 20%) with poor reproducibility and appeared to be unstable at room temperature both in solution and in the solid state to give an unidentified insoluble material and the $[\{Au_6Ag_6(C_2Ph)_{12}\}Au_3(PPh_2(C_6H_4)_2PPh_2)_3]^{3+}$ complex based on a triangular "rods-in-belt" motif analogous to **2**,[7] thus preventing detailed study of **4**. Expectedly, the shortest diphosphine, $Ph_2PC_6H_4PPh_2$, doesn't afford the aggregate structurally similar to **1** and **4**.

Detailed photophysical data for compounds **1** and **2** are presented in Table 1, while their steady state absorption and luminescence spectra in dichloromethane are depicted in Fig. S6.† Independent of excitation wavelength (350–500 nm), compound **1** shows intense luminescence ($\lambda_{em}$ = 560–580 nm) in solution at 298 K. In degassed $CH_2Cl_2$, the quantum yield (Q.Y.) was measured to be 0.71 ± 0.02. The observed lifetime of 4.62 μs and hence a deduced radiative lifetime of 6.48 μs ensures the origin of emission from the triplet manifold, *i.e.* the phosphorescence. To our surprise, upon aeration Q.Y. was 0.70 ± 0.02 with an observed lifetime of 4.54 μs. Within the experimental error, the phosphorescence shows negligible oxygen quenching effect. Based on the collisional type of energy transfer, the rate of $O_2$ quenching to the triplet state is approximately 1/9 of the ($CH_2Cl_2$) diffusion controlled rate. Accordingly, in aerated solution, the observed lifetime of phosphorescence is commonly of the order of tens to a few hundred nanoseconds.[10] The high phosphorescence yield with negligible $O_2$ quenching rate manifests the uniqueness of the framework built by compound **1**.

Quantum chemical studies on the supramolecular $Au^I$-$Ag^I$ complexes show the frontier orbitals of **1** to be located within the heterometallic core of the complex, which is protected by

**Table 1** Photophysical data for **1** and **2**, $CH_2Cl_2$, 298 K

| Complex | | $\lambda_{ab}$/nm ($10^{-3}$ $\varepsilon$/cm$^{-1}$M$^{-1}$) | $\lambda_{em}$/nm[a] | $\Phi_{em}$[b] | $\tau_{obs}$/μs | $k_r$/s$^{-1}$[c] | TPA cross section/GM[de] | TPA cross section/GM[df] |
|---|---|---|---|---|---|---|---|---|
| **1** | aerated | 256 (295.1), 319 (223.5) | 568 | 0.70 | 4.54 | $1.56 \times 10^5$ | 101.2 ± 10 | 104.9 ± 6 |
| | degassed | | | 0.71 | 4.62 | $1.54 \times 10^5$ | | |
| **2**[g] | degassed | 261 (258.7), 319 (247.4), 390 (67.0) | 571 | 0.023 | 4.90 | $4.69 \times 10^3$ | | |

[a] $\lambda_{excit}$ = 450 nm. [b] Measured in dichromethane solutions, coumarin 480 in methanol was used as a standard for the quantum yield measurements. [c] $k_r = k_{obs}\ (1/\tau_{obs}) \times$ quantum yield. [d] TPA cross-section in $10^{-50}$ cm$^4$ s photon$^{-1}$ (GM) measured at 800 nm. [e] Samples in dichloromethane and the reference dye, coumarin 480, in methanol were all prepared at a concentration of $1 \times 10^{-5}$ M. [f] Measured by open-aperture *Z*-scan method in dichloromethane. [g] Complex **2** is photochemically unstable, decomposing under steady state irradiation, therefore the emission characteristics given in the Table are restricted to the initial stage of irradiation of a freshly prepared solution.[7]

bulky ligands (Fig. S9, S10†). The frontier orbital characteristics of **1** suggest the observed phosphorescence originates from metal-centered [sp(Ag) → sd(Au),d(Ag)] triplet emission. The protected nature of the central chromophore of **1** is likely to be a significant contributing factor to the observed negligible oxygen quenching of the phosphorescence (see ESI for further details†).

In sharp contrast, the emission of compound **2** is much weaker and Q.Y. is only 0.023 in the degassed solution. This discrepancy may be rationalized by the short radiative lifetime (~6.5 μs in $CH_2Cl_2$) for **1** due to the efficient spin–orbit coupling involving metal frontier orbitals (*vide supra*) in the $T_1$ state. Conversely, according to the computational results (Fig. S9†), the $T_1$ state of complex **2** is mainly ascribed to the $^3\pi\pi^*$ transition lacking spin–orbit coupling. This viewpoint is also spectroscopically supported by the much longer radiative lifetime of ~213 μs for **2** (*cf.* ~6.5 μs for **1**), thus the $T_1$–$S_0$ relaxation is dominated by the radiationless deactivation.

In view of the latent application regarding this intense and oxygen quenching-free phosphorescence in *e.g.* imaging, we then investigated the two photon absorption cross section of **1** by two-photon induced fluorescence (TPIE) techniques in combination with the open-aperture *Z*-scan method (see ESI for the detailed experimental setup and data analyses†). The corresponding data summarized in Table 1 reveal that the value of the two-photon cross section for compound **1**, measured by TPIE technique at 800 nm, is 101.2 GM, which is consistent with that (104.9 GM) obtained *via* the *Z*-scan method. Although the transition metal acetylides and their derivatives have been reported to exhibit nonlinear optical properties,[2] including two-photon absorption of platinum complexes,[11] to the best of our knowledge, this demonstrates for the first time a remarkable two-photon phosphorescence property for the class of gold alkynyl compounds.

In conclusion, a novel supramolecular $Au^I$–$Ag^I$ cluster of an unprecedented structural topology has been synthesized. The photophysical studies revealed very intense room temperature luminescence with a negligible oxygen quenching effect. These results, together with two-photon phosphorescence properties, should spark a broad spectrum of interest in the field of two-photon time-resolved phosphorescence imaging.[12] The synthetic methodology described in this work is now being extended and will allow for the preparation of a series of related heterometallic complexes with variable luminescent and non-linear optical properties to be reported elsewhere.

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## Notes and references

‡ Crystal data for **1**: $C_{254.50}H_{189}Ag_{10}Au_{12}Cl_5F_{12}O_4P_6$, $M$ = 7344.43, yellow block, 0.47 × 0.15 × 0.11 mm, monoclinic, space group $P2_1/n$ (No. 14), $a$ = 25.1281(2), $b$ = 23.4103(2), $c$ = 39.8036(3) Å, $\beta$ = 99.6710(10)°, $V$ = 23082.0(3) Å$^3$, $Z$ = 4, $D_c$ = 2.113 g cm$^{-3}$, $F_{000}$ = 13796, Nonius KappaCCD, MoKα radiation, $\lambda$ = 0.71073 Å, $T$ = 90(2) K, $2\theta_{max}$ = 52.0°, 231 392 reflections collected, 44 603 unique ($R_{int}$ = 0.0488). Final $GooF$ = 1.008, $R1$ = 0.0387, $wR2$ = 0.0718, $R$ indices based on 32 359 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 2813 parameters, 65 restraints. Lp and absorption corrections applied, $\mu$ = 8.582 mm$^{-1}$. CCDC 715007.

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