Photophysical properties, crystal structure, and host–guest interaction of a luminescent tetranuclear gold(I)–phenylacetylide complex with a supramolecular phosphine ligand

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A novel tetranuclear gold(I)–phenylacetylide complex containing a tetraazamacrocycle cavity is prepared by the reaction of [Au(C≡CPh)]∞ with the ligand 1,4,8,11-tetra(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane and its structure characterized by X-ray crystal analysis; this complex shows dramatic changes in absorption and emission properties upon complexation with alkali- and transition-metal ions.

The design of new luminescent supramolecules for study of induced photo-physical and -chemical changes upon cation complexation and host–guest photochemistry has received much attention in recent years.[1] Our approach to this area is to build supramolecular hosts by attaching luminescent d^{10} metal complexes to the peripheral appendages of polyazamacrocycles and crown ethers. Recent studies revealed that novel luminescent organometallic materials could be readily prepared from [Au(C≡CPh)]∞ and the pyridylphosphine[2a,b] or bridging phosphine ligands.[2c] Herein is described a novel tetranuclear gold(I)–phenylacetylide complex containing a tetraazamacrocycle cavity. This complex is reminiscent of anthraceno-crown ethers and cryptands[3] in that dramatic changes in absorption and emission properties occur upon cation complexation.

The reaction of [Au(C≡CPh)]∞ (100 mg) with the ligand 1,4,8,11-tetra(diphenylphosphinomethyl)-1,4,8,11-tetraazo-cyclotetradecane (L)[4] (120 mg) in CH_2Cl_2 (20 ml) for 20 min gave a clear yellow solution, from which the yellow product [{Au(C≡CPh)}$_4$L] was obtained in 65% yield. Its ^{31}P NMR spectrum recorded in $CDCl_3$ shows a singlet at δ 28.28.

Fig. 1 shows a perspective view of the molecule.† The structure features a tetraazamacrocycle with four bent appendages pointing away from each other, so that the four gold(I) atoms are well separated. A two-fold axis passes through the centre of the N_4 ring, and the bond distances and angles for each P–Au(C≡CPh) moiety are comparable to those of [(Ph₃P)Au(C≡CPh)],[2a] [Au₂(dp-pe)(C≡CPh)₂] [dppe = 1,2-bis-(diphenylphosphino)ethane],[2a] and [{Au₂(dppy)(C≡CPh)₂}∞] [dppy = 2,6-bis(diphenylphosphino)pyridine].[2c] As shown in Fig. 1, the phenylacetylides and the cavity of the tetraaza-macrocycle remain intact to allow binding interaction with other cations to occur at both or at either site.

As with [(Ph₃P)Au(C≡CPh)], the absorption spectrum of a dichloromethane solution of [{Au(C≡CPh)}$_4$L] (10^{-5} mol dm⁻³) is dominated by the intense intraligand transition of coordinated phenylacetylide at 260–310 nm. Increasing the concentration of the complex does not lead to a notable change of the absorption spectrum; presumably, the absorptions, if any, at λ > 300 nm are too weak to reflect any change.

The complex shows room-temperature emission upon photo-excitation at 300–400 nm. As shown in Fig. 2 it shows dual emissions with maxima at ca. 425 and 560 nm in degassed dichloromethane solution. Increasing the complex concentration leads to an increased intensity of the low-energy emission and a concomitant reduction of the high-energy emission

intensity. The high-energy emission is suggested to be due to an intraligand transition of phenylacetylide, and the complexes [(Ph₃P)Au(C≡CPh)]^{2a} and [Au(C≡CPh)₂]$^{-2a}$ show similar emission in this spectral range. The possibility that the Ph₂P–Au
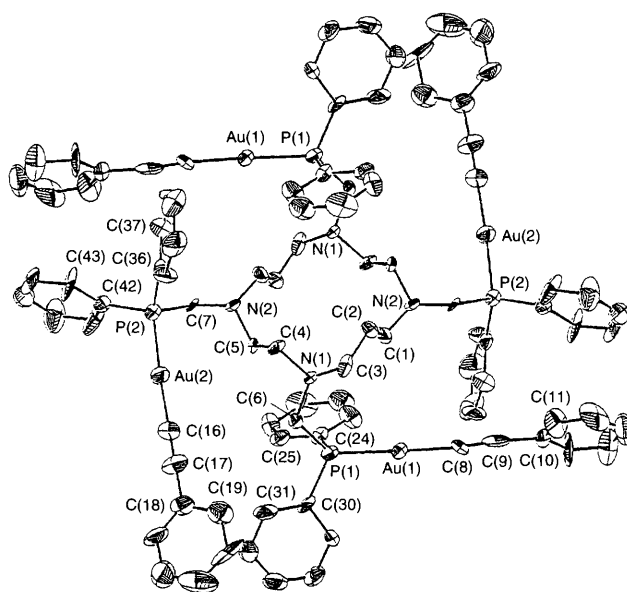
Fig. 1 A perspective view of [{Au(C≡CPh)}$_4$L] (bond lengths in Å, angles in °), Au(1)–P(1) 2.260(7), Au(1)–C(8) 1.990(23), Au(2)–P(2) 2.273(6), Au(2)–C(16) 2.013(23), P(1)–Au(1)–C(8) 177.9(7), P(2)–Au(2)–C(16) 177.1(6), Au(1)–P(1)–C(6) 114.8(7), Au(1)–P(1)–C(24) 111.3(8), Au(2)–P(2)–C(7) 111.3(6), Au(2)–P(2)–C(36) 115.9(8), Au(2)–P(2)–C(42) 114.0(7)
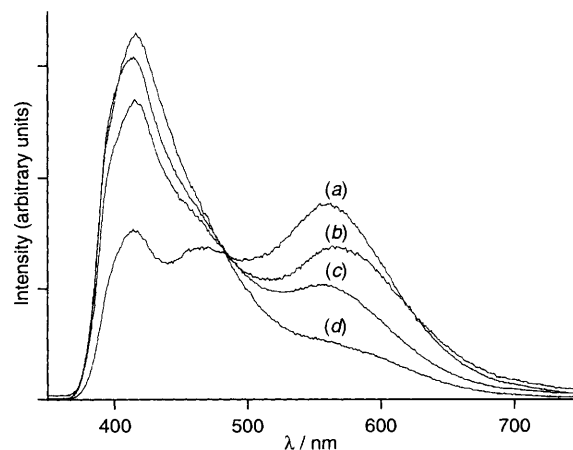

Fig. 2 The concentration dependence emission spectra of [{Au(C≡CPh)}$_4$L] in dichloromethane; (a) 5.1×10^{-4}, (b) 1.27×10^{-4}, (c) 6.35×10^{-5} and (d) 1.27×10^{-5} mol dm⁻³. Excitation at 350 nm.

portion contributed to the emission could not be excluded, since the complexes [(Ph₃P)AuX] (X = halide) also show photoluminescence in this spectral region.[5] The low-energy emission at *ca.* 560 nm is suggested to originate from the stacking of the Au(C≡CPh) units of [{Au(C≡CPh)}₄L] in solution. This suggestion is based on the finding that [{Au(C≡CPh)₂}(dppe)], which has an intermolecular Auᴵ···Auᴵ contact of 3.153(2) Å, shows similar emission in solid state.

Preliminary studies reveal that there is a distinct effect on the spectroscopic properties of the complex in the presence of transition-metal and alkali-metal cations. The results are listed in Table 1. Addition of alkali-metal ions does not have a notable effect on the absorption spectrum, but there is a significant change in the presence of Cu^+ or Ag^+. The spectral changes showing the effect of adding Ag^+ on the absorption spectrum is shown in the insert of Fig. 3. At an $[Ag^+]/[complex]$ ratio ≤1.5, isosbestic points at 251 and 300 nm are maintained, but start to deviate at larger ratios. We tentatively assign the spectral changes to complex formation between [{Au(C≡CPh)}₄L] and Ag^+. Similar results have also been found with Cu^+. Fig. 3 shows the emission spectra of [{Au(C≡CPh)}₄L] upon addition of metal cations. The high-energy emission is strongly enhanced in the presence of alkali-metal ions, increasing in the order $Li^+ < Na^+ < K^+$. On the other hand, addition of Cu^+ or

Ag^+ resulted in the enhancement of the emissions at 550–600 nm.

Although the reason for the effect of alkali-metal ions is not clear, the present finding is reminescent of the changes of emission properties of anthracenocryptands such as 6,9,17,20-tetraoxa-3,12-diaza[14.8](9,10)anthracenophane[3a,b] upon cation complexation. In that case, addition of alkali-metal cations was suggested to prohibit the formation of an intramolecular exciplex leading to enhancement of the fluorescence emission of the anthracene moiety. In the [{Au(C≡CPh)}₄L] complex, the high-energy emission is due to an intraligand transition of the coordinated phenylacetylide. Inter- and/or intra-molecular interactions between the Au(C≡CPh) moieties, which provide facile non-radiative decay pathways of the intraligand excited state of the coordinated phenylacetylides, are likely to be prohibited if an alkali-metal cation is trapped inside the cavity of the tetraazamacrocycle. The fact that Li^+ has the smallest effect is understandable since the small size of the Li^+ cation poorly matches the cavity. Interaction between [{Au(C≡CPh)}₄L] and Cu^+ or Ag^+ is likely to give a 1:1 complex, which is responsible for the emission at 550–600 nm. In this context, we have found that the solid-state emission of [{Au(C≡CPh)}₂(dppe)],[2a] and the emissions of the mixed-metal acetylide clusters of d^{10} metal ions such as $[Ag_6Cu(C≡CPh)_{14}]^{-6}$ are at similar energy.

Table 1 The photophysical properties of [{Au(C≡CPh)}₄L] $(10^{-4}$ mol dm⁻³) in degassed dichloromethane and in the presence of 10^{-3} mol dm⁻³ of alkali- or transition-metal ions at room temperature

Metal ion added	Emission (λ_{max}/nm)	Lifetime $(\tau/\mu s)$
None	418	0.33
	565	0.30
Li^+	470	0.84
Na^+	468	0.85
K^+	454	0.88
Cu^+	530	3.03
Ag^+	567	0.86
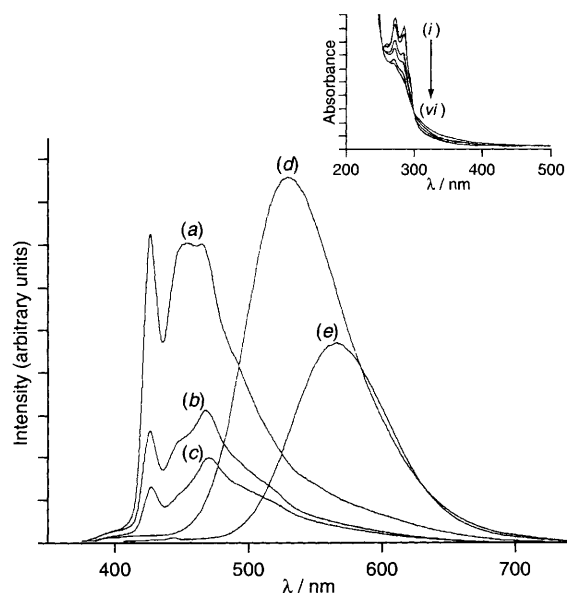
Fig. 3 The emission spectra of [{Au(C≡CPh)}₄L] $(10^{-4}$ mol dm⁻³) in dichloromethane in the presence of 10^{-3} mol dm⁻¹ of (a) KClO₄, (b) NaBF₄, (c) LiClO₄, (d) CuClO₄ and (e) AgClO₄ {insert is the spectral change showing the effect of adding Ag^+ on the absorption spectrum with [{Au(C≡CPh)}₄L]:[Ag⁺] = 1:0.15 (*i*), 1:0.25 (*ii*), 1:0.5 (*iii*), 1:0.75 (*iv*), 1:1 (*v*) and 1:1.5 (*vi*)}. Excitation at 350 nm.

Footnote

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