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A two-co-ordinated gold(I) loop [Au(dpdo)]ClO_4 [dpdo = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane] as a luminescence light switch for substrate binding reactions

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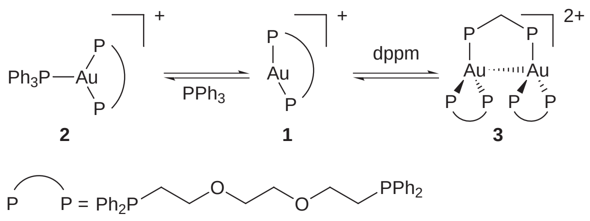
Reaction of [Au(tht)Cl] (tht = tetrahydrothiophene) with dpdo [dpdo = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane] afforded $[Au(dpdo)]^+$ **1** which was isolated as a perchlorate salt; binding of a phosphine moiety to **1** in solution triggered a strong photoluminescence.

A 'molecular light switch' effect, *i.e.* the conversion of a non-emissive metal complex to a strongly emissive one through substrate binding reactions, is of increasing importance in molecular recognition and sensory materials research. The notable examples in this area are $[Ru(bpy)_2(dppz)]^{2+}$ [bpy = 2,2′-bipyridine, dppz = dipyrido(3,2-*a*:2′,3′-*c*)phenazine] for DNA binding and a cyclodextrin derivative with a europium aza crown for incorporation of aromatic hydrocarbons.[1,2] In these two cases, the external substrates (DNA and aromatic hydrocarbons) bind to the molecular sensors through non-covalent hydrophobic interactions. Our attention has focused on mononuclear two-co-ordinate gold(I) complexes which are known to be non-emissive but display strong photoluminescence upon interaction with added nucleophiles.[3–6] In this context, the gold(I) loop [Au(dpdo)]ClO_4 [**1**]ClO_4 [dpdo = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane] (Scheme 1) is of interest. This complex is isostructural to $[Au(PPh_3)_2]^+$ but the chelating nature of the dpdo ligand imparts stability and disfavors phosphine ligand dissociation from the Au atom.[4] We herein report that photoluminescence is 'switched on' through substrate binding reactions to cation **1**. Among the nucleophiles studied, including SCN^- and CN^-, the light switching-on effect is unique to phosphine ligands, suggesting that **1** is a good sensor for phosphine detection even at 10^{-5} mol dm^{-3} concentration.

Reaction of [Au(tht)Cl] (tht = tetrahydrothiophene) with a stoichiometric amount of dpdo in dichloromethane at room temperature readily afforded **1**, which was isolated as the perchlorate salt.‡ The structure of [**1**]ClO_4 has been established by an X-ray crystal analysis.§ As shown in Fig. 1, the complex cation **1** displays a loop-like structure with the dpdo ligand adopting a *trans*-chelating geometry. The Au atom is two-co-ordinated and adopts a nearly linear configuration [P(1)–Au(1)–P(2) angle of 172.2(1)°]. The Au–O distances of 3.14 and 3.23 Å indicate insignificant interaction between the Au and oxygen atoms.

The ^{31}P NMR spectrum of **1** shows a singlet at δ 35.2 (CD_2Cl_2, room temperature). Addition of stoichiometric amounts of PPh_3 or dppm gradually shifts the phosphorus resonances to values closer to that of free PPh_3 or dppm. Cooling the solution to −70 °C leads to three singlets corresponding to **1**, species **2** or **3** and free PPh_3 or dppm (Scheme 1). Attempts to isolate the gold–phosphine species **2** by addition of diethyl



Scheme 1 Equilibria between cation **1** and PPh_3 or dppm in solution

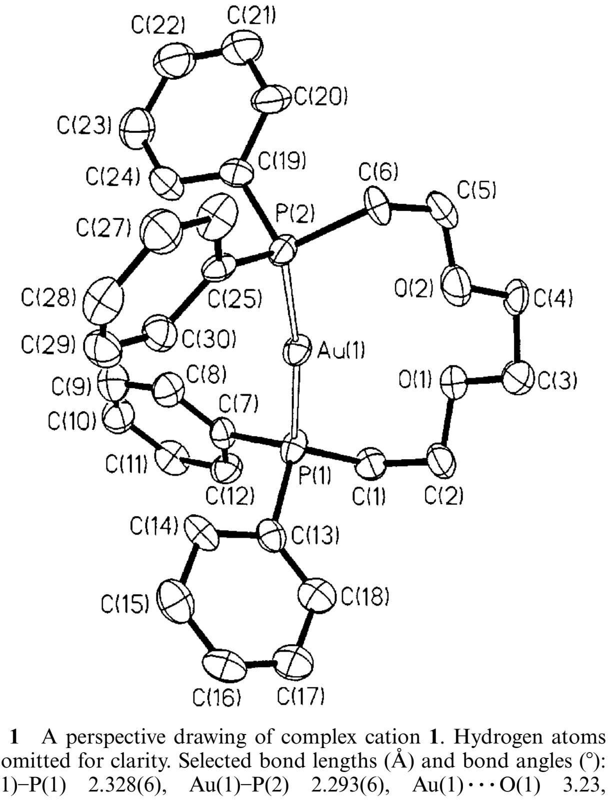


Fig. 1 A perspective drawing of complex cation **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Au(1)–P(1) 2.328(6), Au(1)–P(2) 2.293(6), Au(1)···O(1) 3.23, Au(1)···O(2) 3.14; P(1)–Au(1)–P(2) 172.2(1)

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‡ A mixture of [Au(tht)Cl] (0.32 g, 1.0 mmol) and dpdo (0.89 g, 1.0 mmol) in dichloromethane (50 ml) was stirred at room temperature for 2 h. The solvent was removed *in vacuo* leaving a white residue. Metathesis of the crude product with $LiClO_4$ (0.11 g, 1.0 mmol) in methanol (5 ml) afforded a colorless crystalline solid. Crystals of [**1**]ClO_4 were obtained by diffusion of diethyl ether into an acetonitrile solution (yield 0.51 g, 65%) (Found: C, 45.87; H, 4.15. Calc. for $C_{30}H_{32}AuClO_6P_2$: C, 46.02; H, 4.12%).

§ Crystal data for [**1**]ClO_4: $C_{30}H_{32}AuClO_6P_2$, $M = 782.9$, monoclinic, space group *Cc*, $a = 15.605(1)$, $b = 13.473(1)$, $c = 15.962(1)$ Å, $\beta = 117.12(1)°$, $U = 2987.0(2)$ Å^3, $Z = 4$, μ(Mo-Kα) = 5.164 mm^{-1}, no. of unique reflections = 3567, no. of reflections with $F > 4.0\sigma(F) = 2888$, $R = 0.033$, $R' = 0.038$, $T = 294$ K. CCDC reference number 186/1024.

Table 1 Photophysical data for degassed solutions of [**1**]ClO$_4$* in the presence of different substrates measured at room temperature

Substrate (concentration/ mol dm^{-3})	Solvent	$\lambda_{max}{}^{em}$/nm (excited at 328 nm)	τ/µs
—	CH$_3$CN	—	—
—	DMF	468	—
PPh$_3$ (10^{-5}–10^{-1})	CH$_3$CN	510	4.7
dppm (10^{-4})	CH$_3$CN	610	10.8
Et$_2$S ($\leq$10^{-2})	CH$_3$CN	—	—
NaSCN ($\leq$10^{-2})	CH$_3$CN	—	—
NaCN ($\leq$10^{-2})	DMF	474	—

* Concentration of [**1**]ClO$_4$ in acetonitrile ≈ 1 × 10^{-5} mol dm^{-3}.

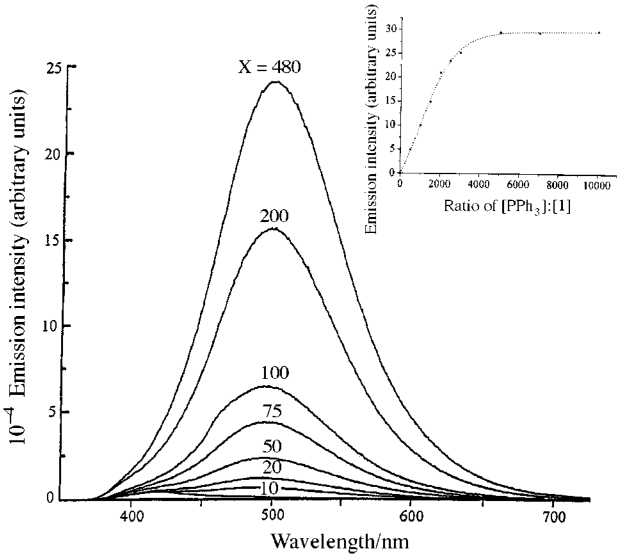

Fig. 2 Room temperature emission spectra of [**1**]ClO$_4$ in the presence of PPh$_3$ in degassed acetonitrile solution. Molar ratio of PPh$_3$: **1** = X : 1. Insert: the graph shows a plot of the emission intensity of **1** + PPh$_3$ *vs.* the molar concentration of PPh$_3$: **1** (concentration of [**1**]ClO$_4$ = 10^{-5} mol dm^{-3})

ether to an acetonitrile solution were unsuccessful and the starting complex [**1**]ClO$_4$ was recovered. Other nucleophiles such as Et$_2$S, SCN$^-$ and CN$^-$ with concentrations 100 times higher than that of PPh$_3$ do not show any notable effect on the ^{31}P NMR spectrum of [**1**]ClO$_4$ in acetonitrile.

The photophysical data of [**1**]ClO$_4$, and its solutions in the presence of different substrates, are listed in Table 1. The complex is non-emissive in the solid state and in degassed acetonitrile solution. However, addition of PPh$_3$ ($\geq$10^{-5} mol dm^{-3}) immediately triggers an intense yellow photoluminescence at 510 nm with a long lifetime (τ = 4.7 µs). We suggest that the emission comes from a three-co-ordinated gold–phosphine species **2** that is in equilibrium with **1** and PPh$_3$ (Scheme 1). As expected, the emission intensity increases with further addition of PPh$_3$ but reaches a plateau value at high PPh$_3$ concentrations (Fig. 2 and insert). The estimated equilibrium constant of the PPh$_3$-binding reaction is not large (32 ± 3 dm^3 mol^{-1}), and hence the dramatic photoluminescence enhancement is likely due to a high emission quantum yield of the three-co-ordinated gold(I) phosphine species. Enhancement of emission has also been observed with dppm (*ca.* 10 molar equivalents). However, the emission maximum is red-shifted to 610 nm (τ = 10.8 µs). Presumably, it is due to the bonding interaction between adjacent AuP$_3$ units (Scheme 1). Other nucleophiles X (X = Et$_2$S, SCN$^-$ or CN$^-$) (≈1000 molar equivalents), do not lead to any notable ‘molecular light switch’ effects. This may be attributed to low formation constants and/or low emission quantum yields of the three-co-ordinated AuP$_2$X species.

In this work, we have shown that photoluminescence is triggered through binding of phosphine substrates to the co-ordinatively unsaturated Au^I. Compared with [Au(PPh$_3$)$_2$]$^+$, the structure of **1** is more robust and hence the complex can be exploited as a sensitive spectroscopic probe for compounds with a phosphine moiety.

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