

# A two-co-ordinated gold(I) loop [Au(dpdo)]ClO<sub>4</sub> [dpdo = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane] as a luminescence light switch for substrate binding reactions

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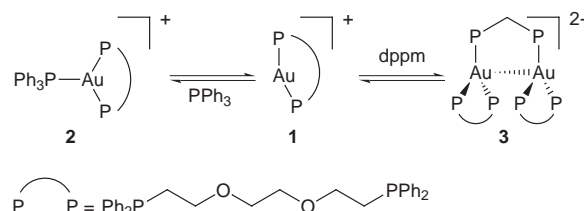
Reaction of [Au(tht)Cl] (tht = tetrahydrothiophene) with dpdo [dpdo = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane] afforded [Au(dpdo)]<sup>+</sup> **1** which was isolated as a perchlorate salt; binding of a phosphine moiety to **1** in solution triggered a strong photoluminescence.

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)<sub>2</sub>(dppz)]<sup>2+</sup> [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.<sup>1,2</sup> 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.<sup>3-6</sup> In this context, the gold(I) loop [Au(dpdo)]ClO<sub>4</sub> [**1**]ClO<sub>4</sub> [dpdo = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane] (Scheme 1) is of interest. This complex is isostructural to [Au(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> but the chelating nature of the dpdo ligand imparts stability and disfavors phosphine ligand dissociation from the Au atom.<sup>4</sup> We herein report that photoluminescence is 'switched on' through substrate binding reactions to cation **1**. Among the nucleophiles studied, including SCN<sup>-</sup> and CN<sup>-</sup>, the light switching-on effect is unique to phosphine ligands, suggesting that **1** is a good sensor for phosphine detection even at 10<sup>-5</sup> mol dm<sup>-3</sup> 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<sub>4</sub> 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 <sup>31</sup>P NMR spectrum of **1** shows a singlet at δ 35.2 (CD<sub>2</sub>Cl<sub>2</sub>, room temperature). Addition of stoichiometric amounts of PPh<sub>3</sub> or dppm gradually shifts the phosphorus resonances to values closer to that of free PPh<sub>3</sub> or dppm. Cooling the solution to –70 °C leads to three singlets corresponding to **1**, species **2** or **3** and free PPh<sub>3</sub> or dppm (Scheme 1). Attempts to isolate the gold–phosphine species **2** by addition of diethyl



Scheme 1 Equilibria between cation **1** and PPh<sub>3</sub> or dppm in solution

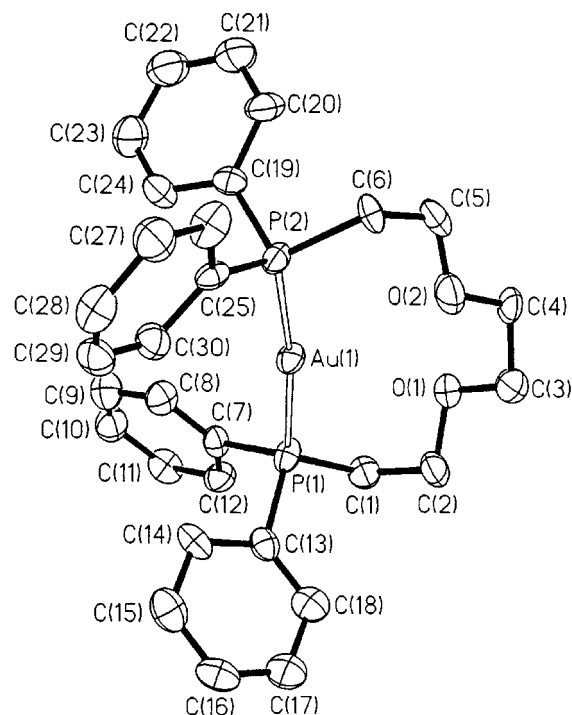


Fig. 1 A perspective drawing of complex cation **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Au(1)–P(1) 2.328(6), Au(1)–P(2) 2.293(6), Au(1)···O(1) 3.23, Au(1)···O(2) 3.14; P(1)–Au(1)–P(2) 172.2(1)

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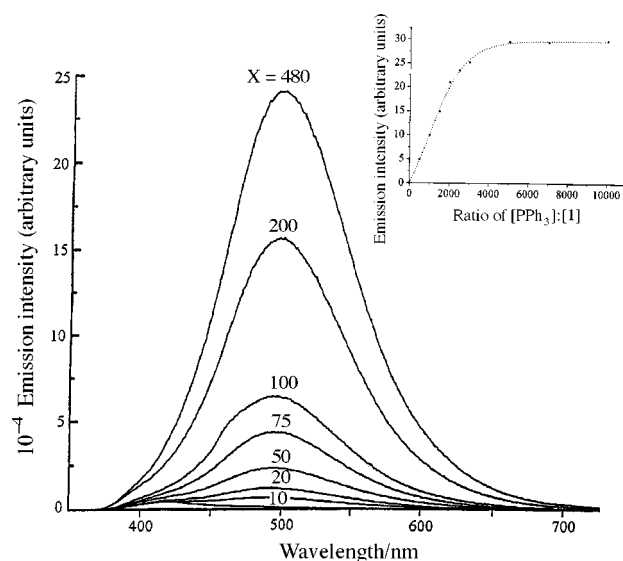
‡ A mixture of [Au(tht)Cl] (0.32 g, 1.0 mmol) and dpdo (0.89 g, 1.0 mmol) in dichloromethane (50 ml) was stirred at room temperature for 2 h. The solvent was removed *in vacuo* leaving a white residue. Metathesis of the crude product with LiClO<sub>4</sub> (0.11 g, 1.0 mmol) in methanol (5 ml) afforded a colorless crystalline solid. Crystals of [**1**]ClO<sub>4</sub> 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<sub>30</sub>H<sub>32</sub>AuClO<sub>6</sub>P<sub>2</sub>: C, 46.02; H, 4.12%).

§ Crystal data for [**1**]ClO<sub>4</sub>: C<sub>30</sub>H<sub>32</sub>AuClO<sub>6</sub>P<sub>2</sub>, *M* = 782.9, monoclinic, space group *Cc*, *a* = 15.605(1), *b* = 13.473(1), *c* = 15.962(1) Å, β = 117.12(1)°, *U* = 2987.0(2) Å<sup>3</sup>, *Z* = 4, μ(Mo-Kα) = 5.164 mm<sup>-1</sup>, no. of unique reflections = 3567, no. of reflections with *F* > 4.0σ(*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<sub>4</sub>\* in the presence of different substrates measured at room temperature

Substrate (concentration/ mol dm <sup>-3</sup> )	Solvent	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$ (excited at 328 nm)	$\tau/\mu\text{s}$
—	CH <sub>3</sub> CN	—	—
—	DMF	468	—
PPh <sub>3</sub> (10 <sup>-5</sup> –10 <sup>-1</sup> )	CH <sub>3</sub> CN	510	4.7
dppm (10 <sup>-4</sup> )	CH <sub>3</sub> CN	610	10.8
Et <sub>2</sub> S ( $\leq 10^{-2}$ )	CH <sub>3</sub> CN	—	—
NaSCN ( $\leq 10^{-2}$ )	CH <sub>3</sub> CN	—	—
NaCN ( $\leq 10^{-2}$ )	DMF	474	—

\* Concentration of **[1]**ClO<sub>4</sub> in acetonitrile  $\approx 1 \times 10^{-5}$  mol dm<sup>-3</sup>.



**Fig. 2** Room temperature emission spectra of **[1]**ClO<sub>4</sub> in the presence of PPh<sub>3</sub> in degassed acetonitrile solution. Molar ratio of PPh<sub>3</sub>:**1** = X:1. Insert: the graph shows a plot of the emission intensity of **1** + PPh<sub>3</sub> vs. the molar concentration of PPh<sub>3</sub>:**1** (concentration of **[1]**ClO<sub>4</sub> = 10<sup>-5</sup> mol dm<sup>-3</sup>)

ether to an acetonitrile solution were unsuccessful and the starting complex **[1]**ClO<sub>4</sub> was recovered. Other nucleophiles such as Et<sub>2</sub>S, SCN<sup>-</sup> and CN<sup>-</sup> with concentrations 100 times higher than that of PPh<sub>3</sub> do not show any notable effect on the <sup>31</sup>P NMR spectrum of **[1]**ClO<sub>4</sub> in acetonitrile.

The photophysical data of **[1]**ClO<sub>4</sub>, 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<sub>3</sub> ( $\geq 10^{-5}$  mol dm<sup>-3</sup>) immediately triggers an intense yellow photoluminescence at 510 nm with a long lifetime ( $\tau = 4.7 \mu\text{s}$ ). We

suggest that the emission comes from a three-co-ordinated gold–phosphine species **2** that is in equilibrium with **1** and PPh<sub>3</sub> (Scheme 1). As expected, the emission intensity increases with further addition of PPh<sub>3</sub> but reaches a plateau value at high PPh<sub>3</sub> concentrations (Fig. 2 and insert). The estimated equilibrium constant of the PPh<sub>3</sub>-binding reaction is not large ( $32 \pm 3 \text{ dm}^3 \text{ mol}^{-1}$ ), 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 ( $\tau = 10.8 \mu\text{s}$ ). Presumably, it is due to the bonding interaction between adjacent AuP<sub>3</sub> units (Scheme 1). Other nucleophiles X (X = Et<sub>2</sub>S, SCN<sup>-</sup> or CN<sup>-</sup>) ( $\approx 1000$  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<sub>2</sub>X species.

In this work, we have shown that photoluminescence is triggered through binding of phosphine substrates to the coordinatively unsaturated Au<sup>I</sup>. Compared with **[Au(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>**, 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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