# Spectroscopy and Redox Properties of the Luminescent Excited State of $[Au_2(dppm)_2]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$)†

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The electronic absorption spectrum of $[Au_2(dppm)_2]^{2+}$ [dppm = bis(diphenylphosphino)methane] in acetonitrile exhibits an absorption band at 290 nm, attributable to a $p_\sigma \longleftarrow d_{\sigma^*}$ transition. A much weaker band in the region 300—370 nm is assigned to a $p_\sigma \longleftarrow d_{\delta^*}$ transition. Excitation of $[Au_2(dppm)_2]^{2+}$ in degassed acetonitrile at 310–390 nm at room temperature results in phosphorescence centred at 575 nm, which is most likely to be derived from the $^3B_{1u}$ $[(d_{\delta^*})^1(p_\sigma)^1]$ state. The phosphorescence of $[Au_2(dppm)_2]^{2+*}$ is found to be quenched by a number of electron acceptors and donors, as well as energy-transfer acceptors. The powerful reducing nature of $[Au_2(dppm)_2]^{2+*}$ is revealed by its excited-state redox potential $E°[Au_2(dppm)_2{}^{3+/2+*}]$ of −1.6(1) V *vs.* a saturated sodium chloride calomel electrode (s.s.c.e.) which was determined through studies of quenching by a series of pyridinium acceptors.

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There is much current interest in the photochemistry of binuclear metal–metal-bonded complexes.[1–7] Extensive studies on the photochemical properties and photochemistry of dimeric complexes of $Rh^I$, $Ir^I$, and $Pt^{II}$ with bridging di-isocyanide, diphosphine, or pyrophosphite ligands indicated that binuclear metal complexes possess unique photochemical reactivities.[3,4] For example, the $^3A_{2u}$ excited state of $[Pt_2(H_2P_2O_5)_4]^{4-}$, besides a better oxidant and reductant[3b] than its ground state, has been shown to undergo facile atom-transfer reactions[6] with a variety of organic substrates such as alkenes, alcohols, aromatic hydrocarbons, and halogenocarbons. Photodehydrogenation of alcohols catalysed by $[Pt_2(H_2P_2O_5)_4]^{4-}$ has also been reported.[6a–e]

In the search for new photocatalysts for C–X bond activation we have turned our attention to $d^{10}$–$d^{10}$ metal systems. Our interest in this area was inspired by a few reports on this class of compounds, which have been shown to exhibit photoluminescence and novel reactivities.[5,7–9] Binuclear gold(I) complexes are the main focus of our work because $Au^I$, which is usually two- or three-co-ordinated, is co-ordinatively unsaturated. Hence the metal centres in such systems are readily accessible towards substrate binding, which is essential for inner-sphere multielectron atom-transfer reactions. Here we report the spectroscopic properties and photochemistry of a diphosphine-bridged gold(I) complex, $[Au_2(dppm)_2]^{2+}$ [dppm = bis(diphenylphosphino)methane]. The photophysical properties of this complex have previously been communicated.[5a,9b]

## Experimental

*Materials.*—The salt $K[AuCl_4]$ (Johnson Matthey Chemicals) and dppm (Strem) were used without further purification. Complexes $[Au_2(dppm)_2]Y_2$ ($Y = ClO_4^-$ or $PF_6^-$) were prepared using a modification of a published procedure.[10] Thiodiglycol (2,2′-thiodiethanol) (Aldrich) (0.26, 2.12 mmol) was added with stirring to a methanolic solution of $K[AuCl_4]$ (0.4 g, 1.06 mmol in 40 cm$^3$ methanol). Solid dppm (0.4 g, 1.04 mmol) was then added. A pale yellow solid precipitated first which dissolved upon warming giving a colourless solution. Addition of excess of $LiClO_4$ or $NH_4PF_6$ to the mixture produced a white powder which was filtered off, washed with distilled water, diethyl ether, and purified by recrystallisation from acetonitrile–diethyl ether. After recrystallisation a white crystalline solid was obtained, characterised as $[Au_2(dppm)_2][ClO_4]_2$ by elemental analysis and $^{31}P$ n.m.r. spectroscopy (Found: C, 43.90; H, 3.15; Cl, 5.20. Calc. for $C_{50}H_{44}Au_2Cl_2O_8P_4$: C, 44.05; H, 3.25; Cl, 5.20%). $^{31}P$ N.m.r. (acetonitrile): δ 35.13(s) p.p.m.

*N,N′*-Dimethyl-4,4′-bipyridinium chloride (methyl viologen hydrate) was obtained from Aldrich. The $CF_3SO_3^-$ (triflate) salt was prepared by metathesis with $Ag(O_3SCF_3)$ in methanol, and after removal of AgCl by filtration was precipitated by addition of diethyl ether. 4-Methoxycarbonyl-*N*-methylpyridinium iodide was prepared by refluxing methyl iodide and 4-methoxycarbonylpyridine in acetone–ethanol (1:1 v/v) solution for 4 h. Metathesis of the iodide salt with ammonium hexafluorophosphate in water gave 4-methoxycarbonyl-*N*-methylpyridinium hexafluorophosphate, which was recrystallised from an acetonitrile–diethyl ether solution. All other pyridinium quenchers used in the experiment were prepared similarly to 4-methoxycarbonyl-*N*-methylpyridinium hexafluorophosphate by using the appropriate alkylating agent and pyridine. *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine (tmpd) from Aldrich was recrystallised several times from light petroleum, vacuum dried, and stored under vacuum in the dark.[11] *trans*-Stilbene (Aldrich, 96%) was recrystallised twice from absolute ethanol. *cis*-Stilbene (Aldrich, 97%) and styrene (Aldrich, 99%) were fractionally distilled under reduced pressure before use. Acetonitrile (Ajax AR) was distilled over $KMnO_4$ and $CaH_2$ under nitrogen. Solvents used in synthesis were of analytical quality and were used without further purification. All solutions for photochemical experiments were degassed with no less than three freeze–pump–thaw cycles.

*Physical Measurements and Instrumentation.*—The u.v.–visible spectra were recorded on a Shimadzu UV-240 spectrophotometer. Steady-state emission and excitation spectra were obtained with Corning filters on a Hitachi 650-60 fluorescence spectrophotometer. Corrected emission spectra were obtained using a Hitachi data processor 650-0178 accessory. The absolute luminescence quantum yield was measured by the method of Demas and Crosby[12] using quinine sulphate in 0.05

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† *Non-S.I. unit employed:* eV ≈ $1.60 \times 10^{-19}$ J.

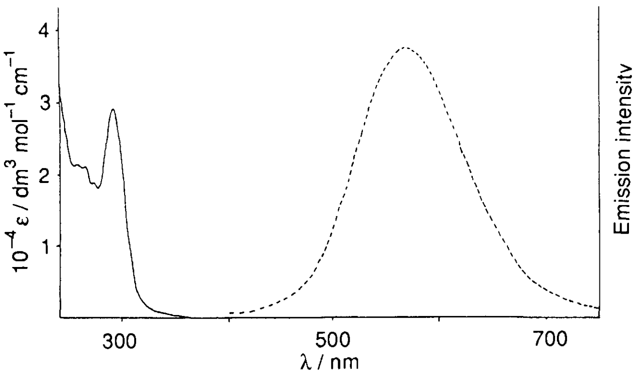

**Figure 1.** Electronic absorption (——) and emission (----) spectra of $[Au_2(dppm)_2][ClO_4]_2$ in acetonitrile at room temperature

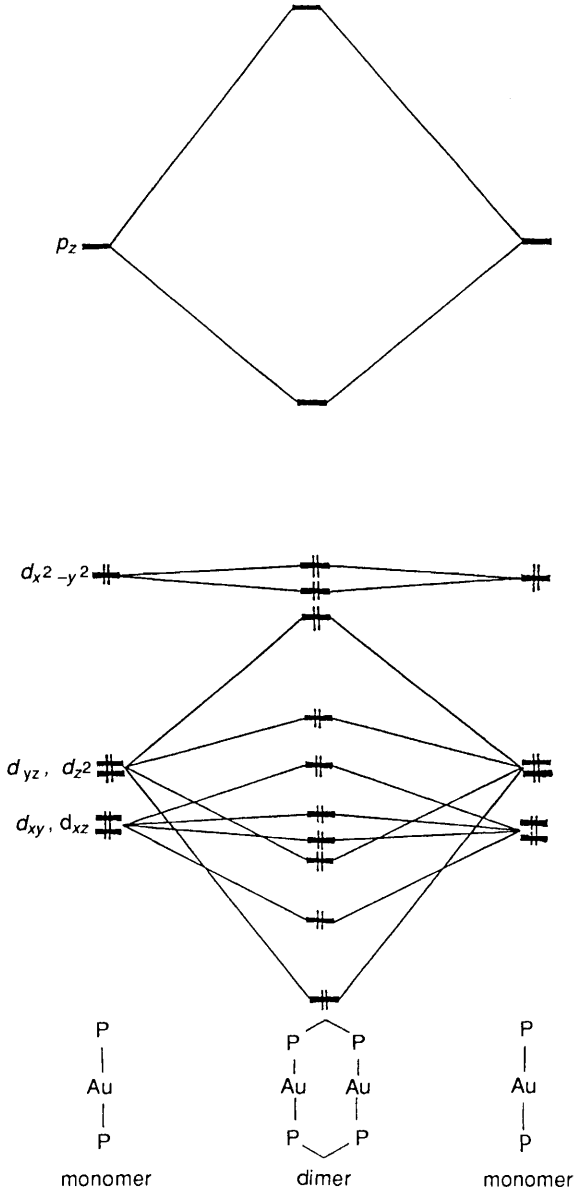

**Figure 2.** Molecular-orbital diagram for the interaction of two linear $d^{10}$ gold(I) ions complexed with phosphine ligands

mol dm$^{-3}$ sulphuric acid (less than $10^{-4}$ mol dm$^{-3}$) as a standard. The emission-lifetime and flash-photolysis experiments were performed using standard instrumentation where the excitation source was a Quanta Ray DCR-3 Nd-YAG laser system [full width at half maximum (fwhm) 8 ns, excitation at 355 nm]. The laser energy per pulse was 1—5 mJ cm$^{-2}$. Stern–Volmer quenching experiments were carried out with degassed acetonitrile solutions of $[Au_2(dppm)_2]^{2+}$ ($10^{-3}$ mol dm$^{-3}$) in the presence of a quencher (Q). In each case a linear plot of $\tau_0/\tau$ *versus* [Q] was obtained from which the bimolecular quenching rate constant ($k_q$) was deduced ($\tau_0$ and $\tau$ refer to emission lifetime in the absence and presence of quencher).

## Results and Discussion

*Spectroscopic and Ground-state Properties of* $(Au_2(dppm)_2)^{2+}$.—It was previously shown that $[Au_2(dppm)_2]^{2+}$ can be prepared by addition of dppm to an ethanolic solution of dibromoaurate(I).[13] In this work, a different synthetic route was adopted with tetrachloroaurate(III) as the starting material, which was subsequently reduced to $Au^I$ *in situ* by thiodiglycol. Both the $PF_6^-$ and $ClO_4^-$ salts have been isolated. The structure of $[Au_2(dppm)_2][ClO_4]_2$ has been confirmed by *X*-ray crystallography.[14]

The room-temperature u.v.–visible absorption spectrum of $[Au_2(dppm)_2]^{2+}$ in acetonitrile is shown in Figure 1. Intense absorption bands were observed at 290 nm ($\varepsilon_{max.}$ 30 000 dm$^3$ mol$^{-1}$ cm$^{-1}$), which is absent for related mononuclear gold(I) phosphine complexes, and at 267 nm ($\varepsilon_{max.}$ 19 800 dm$^3$ mol$^{-1}$ cm$^{-1}$), which is vibronically structured. Some low-energy weak absorptions are also observed in the region 300—370 nm. However no additional peak has been resolved even with a concentrated solution of the metal complex.

Figure 1 also shows the emission spectrum of $[Au_2(dppm)_2]^{2+}$ in degassed acetonitrile. Excitation of a degassed acetonitrile solution of $[Au_2(dppm)_2]^{2+}$ at 310—390 nm at room temperature results in photoluminescence centred at 570 nm. Exposure of the solution to air results in severe quenching of the luminescence, suggesting that the emissive state at 570 nm is a low-lying triplet excited state. This is in accordance with the measured long lifetime {$[Au_2(dppm)_2][PF_6]_2$ 21 $\pm$ 1 μs; $[Au_2(dppm)_2][ClO_4]_2$ 18 $\pm$ 2 μs} for the emission at 570 nm. Luminescence quantum yields of the triplet emission relative to quinine sulphate are 0.15(5) and 0.21(5) for the $ClO_4^-$ and $PF_6^-$ salts, respectively.

By analogy to the well established pattern for $d^8$–$d^8$ species,[3,4] the intense absorption band at 290 nm has been attributed to the spin-allowed $p_\sigma \longleftarrow d_{\sigma^*}$ transition. The low $p_\sigma \longleftarrow d_{\sigma^*}$ transition energy of $[Au_2(dppm)_2]^{2+}$ relative to mononuclear gold(I) species is in accordance with the measured Au–Au distance of 2.962(1) Å in $[Au_2(dppm)_2]Cl_2$,[15] suggesting the presence of a metal–metal interaction.

With reference to a related study on a $d^{10}$–$d^{10}$ dimer of platinum,[8] and gold(I),[16] and assuming that the relative orbital energies do not differ much, the molecular-orbital energy-level diagram for $d^{10}$ $AuL_2$ and $d^{10}$–$d^{10}$ $(AuL_2)_2$ complexes has been constructed (Figure 2). In the $D_{\infty h}$ $d^{10}$ $AuL_2$ complex the relative energies of the highest-occupied orbitals are $d_{xz},d_{xy} < d_{z^2},d_{yz} < d_{x^2-y^2}$, with the $d_{z^2}$ being mixed with the 6*s* orbital,[16] and the lowest unoccupied orbital is $p_z$. The $d^{10}$–$d^{10}$ $(AuL_2)_2$ system (of $D_{2h}$ symmetry) is constructed from two interacting $AuL_2$ fragments. In $d^{10}$–$d^{10}$ complexes, although the $d_\sigma$–$d_{\sigma^*}$ splitting is expected to be much greater than $d_\delta$–$d_{\delta^*}$, from the relative energies of the orbitals, we tentatively suggest that the highest occupied orbital in $(AuL_2)_2$ is $d_{\delta^*}$ rather than $d_{\sigma^*}$. This assignment, which is different from that of Mason and co-workers,[16d,e] is based on the very large Stokes' shift between the $p_\sigma \longleftarrow d_{\sigma^*}$ transition energy (290 nm) and the emission energy (570 nm). Thus, the emissive state is unlikely to be $d_{\sigma^*} \longleftarrow p_\sigma$ in origin. Possibly, the emission at 570 nm is derived from some

**Table 1.** Rate constants for the energy-transfer quenching of $^3[Au_2(dppm)_2]^{2+*}$ in degassed acetonitrile at 22 ± 2 °C

| Quencher | $E_t{}^a$/kJ mol$^{-1}$ | $k_q$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| Oxygen | 96 | $2.0 \times 10^9$ |
| *trans*-Stilbene | 205 | $1.1 \times 10^9$ |
| *cis*-Stilbene | 238 | $1.4 \times 10^8$ |
| Styrene | 259 | $1.5 \times 10^8$ |
| Hept-1-ene | >334 | $8.8 \times 10^4$ |
| Cyclohexene | >334 | $4.6 \times 10^4$ |

[a] From refs. 19 and 20.

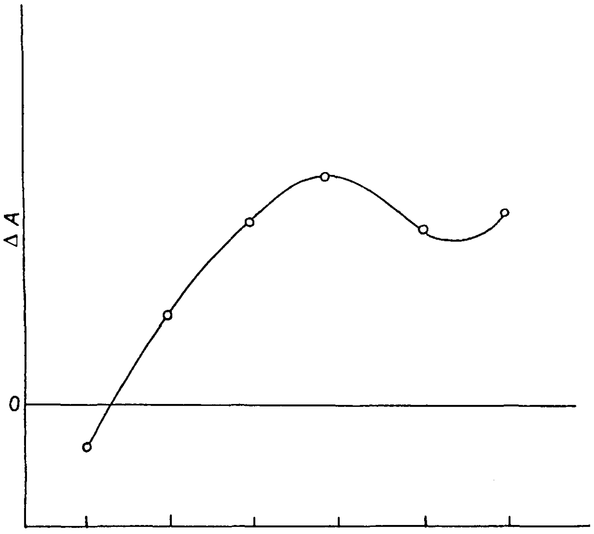

**Figure 3.** Transient absorption difference spectrum of $[Au_2(dppm)_2][ClO_4]_2$ (acetonitrile solution, 22 ± 2 °C, $[Au_2{}^{2+}] = 10^{-3}$ mol dm$^{-3}$, $\lambda_{ex.} = 355$ nm)

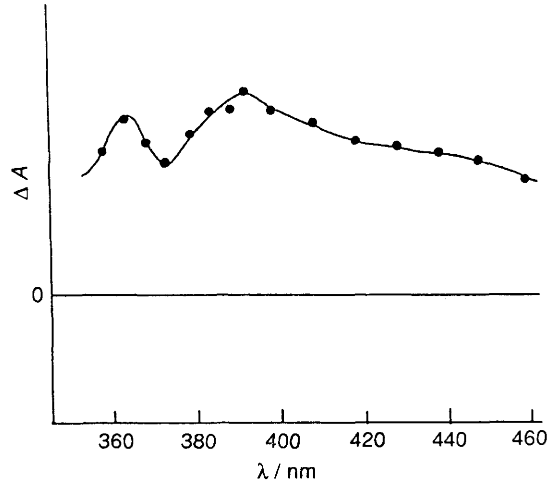

**Figure 4.** Transient absorption difference spectrum recorded 4 μs after a 355-nm pulse excitation of an acetonitrile solution of $[Au_2(dppm)_2][ClO_4]_2$ ($1 \times 10^{-4}$ mol dm$^{-3}$) and *trans*-stilbene ($1 \times 10^{-3}$ mol dm$^{-3}$)

low-lying phosphorescent state, either of $^2B_{1u}$ $[(d_{\delta*})^1(p_\sigma)^1]$ or metal-to-ligand charge transfer (m.l.c.t.) origin.

The co-ordinatively unsaturated nature of the 14-electron two-co-ordinated gold(I) system has been shown to exhibit substrate binding. Addition of LiCl to an acetonitrile solution of $[Au_2(dppm)_2][ClO_4]_2$ resulted in an upfield shift of the dppm resonance signal in the $^{31}$P n.m.r. spectrum: $[Au_2(dppm)_2][ClO_4]_2$, δ 35.134(s); in the presence of LiCl, 32.846(s) p.p.m. The ability of $[Au_2(dppm)_2]^{2+}$ to undergo substrate binding is further supported by the perturbation of its electronic absorption and emission spectra in the presence of LiCl. Upon addition of LiCl the band at 290 nm ($d_{\sigma*}$–$p_\sigma$) disappeared while a shoulder appeared at 317 nm, and the emission maximum shifted to lower energy ($\lambda_{em} \approx 640$ nm). The upfield shift of the $^{31}$P n.m.r. signal is consistent with the σ-donating property of $Cl^-$, which on binding to $Au^I$ increases the π back donation to phosphorus and causes shielding to occur. Binding products of the form $[Au_2(dppm)_2]X_2$ are suggested since the *X*-ray crystal structure of $[Au_2(dppm)_2]Cl_2$ is known.[15] Such binding ability is important for the design of inner-sphere multielectron atom-transfer rections.

*Triplet-state Absorption Spectrum.*—Figure 3 presents the transient difference spectrum of $[Au_2(dppm)_2]^{2+}$ in degassed acetonitrile following flash excitation at 355 nm. The assignment of the transient absorption due to the emissive triplet state has been confirmed by matching the decay of the transient absorption with that of the phosphorescence at 570 nm. The spectrum is characterised by an absorption maximum at around 380 nm. However, at wavelengths above 450 nm the intense phosphorescence ($\lambda_{max.}$ 570 nm) of the gold complex interferes strongly, and hence makes study of the transient absorption rather difficult.

*Quenching of Phosphorescence of* $[Au_2(dppm)_2]^{2+}$.—*Energy transfer.* Like the $^3A_{2u}$ excited state of $[Rh_2L_4]^{2+}$ (L = 1,3-di-isocyanopropane or 2,5-di-isocyano-2,5-dimethylhexane),[17] and $[Pt_2(H_2P_2O_5)_4]^{4-}$,[6e,18] the luminescence of $[Au_2(dppm)_2]^{2+}$ is quenched by energy transfer as shown in equation (1). The bimolecular energy-transfer rate constants

$$[Au_2(dppm)_2]^{2+*} + Q \longrightarrow [Au_2(dppm)_2]^{2+} + Q^* \quad (1)$$

determined by Stern–Volmer quenching experiments are given in Table 1. This pathway is feasible for these quenchers because of their low triplet energies.[19,20] Attempts accurately to determine the triplet energy of $[Au_2(dppm)_2]^{2+*}$ using an extensive series of triplet quenchers were unsuccessful due to the difficulty encountered in obtaining suitable quenchers which do not absorb in the excitation region. However, from the data obtained, the $E_t$ for $[Au_2(dppm)_2]^{2+*}$ in acetonitrile should be higher than 238 kJ mol$^{-1}$ (2.34 eV, 530 nm). From the emission spectrum of $[Au_2(dppm)_2]^{2+}$ the 0–0 energy of the excited state is estimated to be around 2.5 eV (500 nm), a value not inconsistent with the results of quenching.

Flash photolysis has also been used to study the energy-transfer process. Figure 4 shows the transient absorption difference spectrum recorded after the 355-nm laser-pulse excitation of a degassed acetonitrile solution of $[Au_2(dppm)_2]^{2+}$ and *trans*-stilbene. The spectrum is characterised by absorption bands at 365 and 390 nm, typical of the triplet excited state of *trans*-stilbene.[21] The observation of energy transfer to *trans*-stilbene under anaerobic conditions is interesting because it is well documented that the triplet state of *trans*-stilbene cannot be populated by direct irradiation of solutions of the compound at ambient temperature; therefore the triplet state must have been generated by photosensitisation from $[Au_2(dppm)_2]^{2+*}$.

*Electron transfer.* We have also investigated the photoredox properties of $[Au_2(dppm)_2]^{2+*}$ by using laser flash photolysis. For reductive quenching, tmpd was used as the electron donor. The quenching rate constant of tmpd is $6.6 \times 10^9$ dm$^3$ mol$^{-1}$s$^{-1}$ which is close to the diffusion limit of acetonitrile indicating that quenching is quite efficient. The transient absorption difference

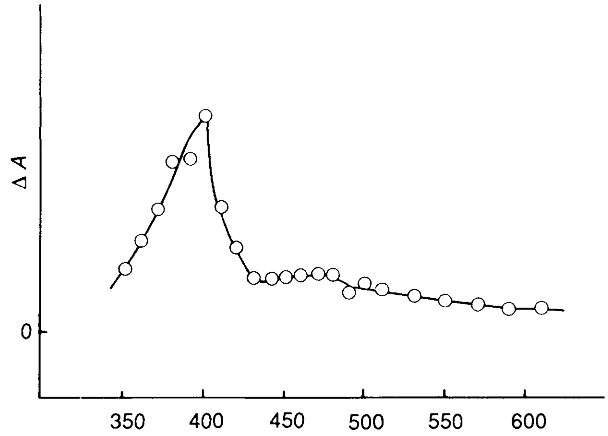

**Figure 5.** Transient absorption difference spectrum recorded 20 µs after a 355-nm pulse excitation of a degassed acetonitrile solution of $[Au_2(dppm)_2]^{2+}$ ($1 \times 10^{-4}$ mol dm$^{-3}$) and 4-methoxycarbonyl-*N*-methylpyridinium ($5 \times 10^{-3}$ mol dm$^{-3}$)

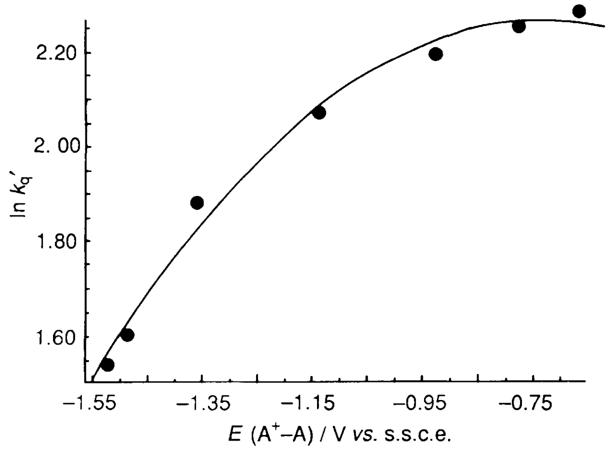

**Figure 6.** Plot of ln $k_q'$ *versus* $E(A^+–A)$ for the electron-transfer quenching of $[Au_2(dppm)_2]^{2+*}$ by pyridinium acceptors in degassed acetonitrile; (●) experimental, (—) theoretical

spectrum recorded 10 µs after the 355-nm laser-pulse excitation of a solution of $[Au_2(dppm)_2][ClO_4]_2$ containing tmpd in degassed acetonitrile shows a maximum at 600 nm, attributable to the tmpd$^+$ radical cation.[22] As tmpd is a one-electron donor it follows that $[Au_2(dppm)_2]^{2+*}$ is a one-electron acceptor. Therefore, the reaction between $[Au_2(dppm)_2]^{2+*}$ and tmpd is as in equation (2). The long-time decay behaviour of tmpd$^+$

$$[Au_2(dppm)_2]^{2+*} + \text{tmpd} \longrightarrow [Au_2(dppm)_2]^{+} + \text{tmpd}^{+} \quad (2)$$

shows that the reverse electron transfer between tmpd$^+$ and $[Au_2(dppm)_2]^+$ [reverse of reaction (2)] is not quantitative. Presumably one of the products {probably $[Au_2(dppm)_2]^+$} decays by an additional pathway. The irreversible nature of the cyclic voltammetric waves during electrochemical reduction is also indicative of the extreme chemical instability of $[Au_2(dppm)_2]^+$.[23]

For oxidative quenching the redox products of $[Au_2(dppm)_2]^{2+*}$ with methylviologen (*N*,*N*′-dimethyl-4,4′-bipyridinium, dmbipy) and 4-methoxycarbonyl-*N*-methylpyridinium salt have been investigated. With dmbipy$^{2+}$ the measured $k_q$ value is very high, $6.1 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. The electron-transfer nature of the reaction (3) is evident from the typical

$$[Au_2(dppm)_2]^{2+*} + \text{dmbipy}^{2+} \longrightarrow [Au_2(dppm)_2]^{3+} + \text{dmbipy}^{+} \quad (3)$$

transient absorption spectrum of the dmbipy$^+$ radical cation, peaking at 395 and 600 nm.[24] In the wavelength range 350—700 nm no absorption of $[Au_2(dppm)_2]^{3+}$ is observed. This may be due to the strong absorption of dmbipy$^+$ superimposed on the much weaker absorption of the oxidised gold dimer.

The decay of dmbipy$^+$ observed at 600 nm is attributed to the back electron-transfer reaction (4). The bimolecular nature

$$[Au_2(dppm)_2]^{3+} + \text{dmbipy}^{+} \longrightarrow [Au_2(dppm)_2]^{2+} + \text{dmbipy}^{2+} \quad (4)$$

of this has been established by a study of the laser energy dependence of the rate of back electron transfer. A faster decay rate for the dmbipy$^+$ signal is observed with higher laser excitation energy, which is consistent with the proposed mechanism where the rate follows second-order kinetics [equation (5)]. A second-order back-electron-transfer rate

$$-d[\text{dmbipy}^+]/dt = k[Au_2(dppm)_2{}^{3+}][\text{dmbipy}^+] \quad (5)$$

constant, $k_b$, of $1.5 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ has been obtained from a plot of $1/\Delta A$ *versus* time for the decay signal.* Since electron transfer between $[Au_2(dppm)_2]^{2+*}$ and dmbipy$^{2+}$ is reversible, net photochemistry, even after prolonged steady-state irradiation, is not observed.

With 4-methoxycarbonyl-*N*-methylpyridinium, the measured $k_q$ value is $4.47 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. Figure 5 shows the transient absorption spectrum recorded 20 µs after the 355-nm laser pulse. It is identical to that for the known reduced molecule of this pyridinium ion,[25] thereby establishing the powerful one-electron reducing ability of $[Au_2(dppm)_2]^{2+*}$.

*Excited-state Potential of* $[Au_2(dppm)_2]^{2+*}$ *in Acetonitrile.*—In order to understand more about the excited-state reactivities and photoredox properties of $[Au_2(dppm)_2]^{2+*}$, it is important to know the excited-state potential of $[Au_2(dppm)_2]^{2+*}$. Attempts to use the spectroscopic and electrochemical properties of $[Au_2(dppm)_2]^{2+}$ to establish $E^{\circ\prime}[Au_2(dppm)_2{}^{2+*/+}]$ and $E^{\circ\prime}[Au_2(dppm)_2{}^{3+/2+*}]$ were unsuccessful. The cyclic voltammogram of $[Au_2(dppm)_2]^{2+}$ in acetonitrile shows two irreversible reduction waves at *ca.* −1.70 and −1.90 V *vs.* Ag–AgNO$_3$.[23] No anodic wave is observed even up to 2.2 V *vs.* Ag–AgNO$_3$. Because of the irreversible nature of the cyclic voltammetric waves during electrochemical reduction and the absence of a couple during electrochemical oxidation, an estimation of the excited-state potential by this method is impossible. Therefore, quenching studies have been employed. A series of alkylated pyridinium acceptors [A$^+$] with widely varying reduction potentials has been chosen. The bimolecular quenching rate constants $k_q$ for the pyridinium salts are shown in Table 2. To correct for diffusional effects, the values were converted into $k_q'$ based on the relationship (6) where $k_D$ is

$$1/k_q = 1/k_q' + 1/k_D \quad (6)$$

the diffusion-limited rate constant in acetonitrile, taken to be

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* The rate constant $k_b$ has been calculated from the slope, $m$, of a plot of $1/\Delta A$ *versus* time, $k_b = l(\Delta\varepsilon)m$ where $l$ is the cell pathlength (1 cm) and $\Delta\varepsilon$ the absolute value of the difference between the sum of the absorption coefficients of the products and those of the reactants at 605 nm: $\Delta\varepsilon = |[\varepsilon(Au_2{}^{3+}) + \varepsilon(\text{dmbipy}^+)] - [\varepsilon(Au_2{}^{2+}) + \varepsilon(\text{dmbipy}^{2+})]|$. As the transient decay signal at 605 nm is dominated by the absorption of dmbipy$^+$, $\Delta\varepsilon$ is approximated as $\varepsilon(\text{dmbipy}^+)$, which is equal to 13 000 ± 600 dm$^3$ mol$^{-1}$ cm$^{-1}$ at 605 nm in acetonitrile (see ref. 25).

**Table 2.** Rate constants for the oxidative quenching of $^3[Au_2(dppm)_2]^{2+*}$ by pyridinium acceptors in degassed acetonitrile at 22 ± 2 °C

| Quencher[a] | $E(A^{+/0})$[b] (V *vs.* s.s.c.e.) | $k_q$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_q'$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| *N,N'*-Dimethyl-4,4'-bipyridinium | −0.45 | $6.1 \times 10^9$ | $1.6 \times 10^{10}$ |
| 4-Cyano-*N*-methylpyridinium | −0.67 | $5.6 \times 10^9$ | $1.3 \times 10^{10}$ |
| 4-Methoxycarbonyl-*N*-methylpyridinium | −0.78 | $4.5 \times 10^9$ | $8.2 \times 10^9$ |
| 4-Amido-*N*-ethylpyridinium | −0.93 | $2.9 \times 10^9$ | $4.1 \times 10^9$ |
| 3-Amido-*N*-methylpyridinium | −1.14 | $9.5 \times 10^8$ | $1.0 \times 10^9$ |
| *N*-Ethylpyridinium | −1.36 | $1.4 \times 10^8$ | $1.4 \times 10^8$ |
| 4-Methyl-*N*-methylpyridinium | −1.49 | $9.6 \times 10^6$ | $9.6 \times 10^6$ |
| 2,6-Dimethyl-*N*-methylpyridinium | −1.52 | $4.9 \times 10^6$ | $4.9 \times 10^6$ |

[a] All the compounds are hexafluorophosphate salts except for *N,N'*-dimethyl-4,4'-bipyridinium trifluoromethanesulphonate. [b] From ref. 4*f*.

$1.0 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$. A plot of $(RT/F)\ln k_q'$ *vs.* $E_{\frac{1}{2}}$ values for pyridinium salts is shown in Figure 6. A value of −1.6(1) V *vs.* s.s.c.e. [$RT\ln K\kappa\nu$ = 0.58(10) V *vs.* s.s.c.e., $\lambda$ = 0.90(10) eV] for $E^\circ[Au_2(dppm)_2{}^{3+/2+*}]$ has been obtained by three-parameter, non-linear least-squares fits by equation (7) where

$$(RT/F)\ln k_q' = (RT/F)\ln K\kappa\nu - [\lambda(1 + \Delta G/\lambda)^2/4] \quad (7)$$

$\Delta G = E^\circ[Au_2(dppm)_2{}^{3+/2+*}] - E^\circ(A^{+/0}) + \omega_p - \omega_r$ ($\omega_p$ and $\omega_r$ are coulombic work terms), $K = k_D/k_{-D}$, $\kappa$ is the transmission coefficient, $\nu$ is the nuclear frequency, and $\lambda$ the reorganisation energy for electron transfer. The equilibrium constant for association, *K*, calculated for $[Au_2(dppm)_2]^{2+*}$ and the pyridinium quenchers is approximately 1—2 dm$^3$ mol$^{-1}$. The work term associated with bringing $[Au_2(dppm)_2]^{2+*}$ and a pyridinium acceptor together is 0.01—0.03 eV.[26] This contribution is neglected in the analysis of the electron-transfer rate data. Attempts to use a series of amines to determine the reduction potential $E^\circ[Au_2(dppm)_2{}^{2+*/+}]$ were unsuccessful because of ground-state reaction (binding) between $Au_2$ and some amines.

## Conclusion

We have demonstrated an example of a class of binuclear $d^{10}$–$d^{10}$ gold(I) complexes, which like binuclear $d^8$–$d^8$ complexes, possesses a rich photochemistry. The triplet excited state of $[Au_2(dppm)_2]^{2+}$ is long-lived in fluid solution at room temperature. Photoinduced redox reactions with electron donors and acceptors have been observed. It has been found that this binuclear gold(I) complex is a powerful photoreductant with $E^\circ[Au_2(dppm)_2{}^{3+/2+*}]$ −1.6 ± 0.1 V *vs.* s.s.c.e.

## Acknowledgements

H-L. K. acknowledges the receipt of a Croucher studentship, administered by the Croucher Foundation. Financial support from the University of Hong Kong and Croucher Foundation is gratefully acknowledged.

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*Received 7th March 1990; Paper 0/01028F*