Spectroscopic Properties and Redox Chemistry of the Phosphorescent Excited State of $[Au_2(dppm)_2]^{2+}$ [dppm = bis(diphenylphosphino)methane]

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The complex $[Au_2(dppm)_2]^{2+}$ [dppm = bis(diphenylphosphino)methane] exhibits a long-lived room temperature photoluminescence in fluid solutions (emission maximum, 565 nm; τ_0, 17.0 μs; ϕ_{em}, 0.15); the phosphorescent excited state of $[Au_2(dppm)_2]^{2+}$ undergoes oxidative and reductive quenching with methyl viologen and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, respectively, and can be quenched by organic halides.

Binuclear metal complexes of bridging di-isocyanides, diphosphines and diphosphites exhibit rich photophysical and photochemical properties.[1] An example is the intensely luminescent, phosphite-bridged binuclear d^8–d^8 species, $Pt_2(P_2O_5H_2)_4{}^{4-}$, which catalyses photochemical cleavage of C–H bonds under mild conditions.[1e,1f] In the search for new photocatalysts for C–H bond activation, we are inspired by the recent work on related d^{10}–d^{10} systems,[2] which are shown to exhibit luminescence and novel reactivities. We describe here the spectroscopic properties and redox chemistry of a co-ordinatively unsaturated d^{10}–d^{10} complex, $[Au_2(dppm)_2](ClO_4)_2$,[3] which shows novel photochemical behaviour [dppm = bis(diphenylphosphino)methane].

The electronic absorption spectrum of an acetonitrile solution of $[Au_2(dppm)_2](ClO_4)_2$ exhibits bands at 292 nm (ε_{max} 29210) and 267 nm (ε_{max} 19870 mol^{-1} dm^3 cm^{-1}), the latter of which is vibrational structured (Figure 1). The intense 292 nm band is attributable to the spin-allowed $d_{\sigma*}$–p_σ transition. The low d–p transition energy of $[Au_2(dppm)_2]^{2+}$,[4] is in accordance with the measured Au–Au distance of 2.962(1) Å in $[Au_2(dppm)_2Cl_2]$,[5] suggesting the presence of metal–metal interaction. Excitation of a degassed acetonitrile solution of $[Au_2(dppm)_2](ClO_4)_2$ at 290—320 nm at room temperature results in photoluminescence (Figure 2). The long-lived emission band at 565 nm (τ_o = 17.0 μs; ϕ_{lum} = 0.15) probably arises from a low-lying phosphorescent state as suggested by the large Stokes shift between excitation and emission energies.

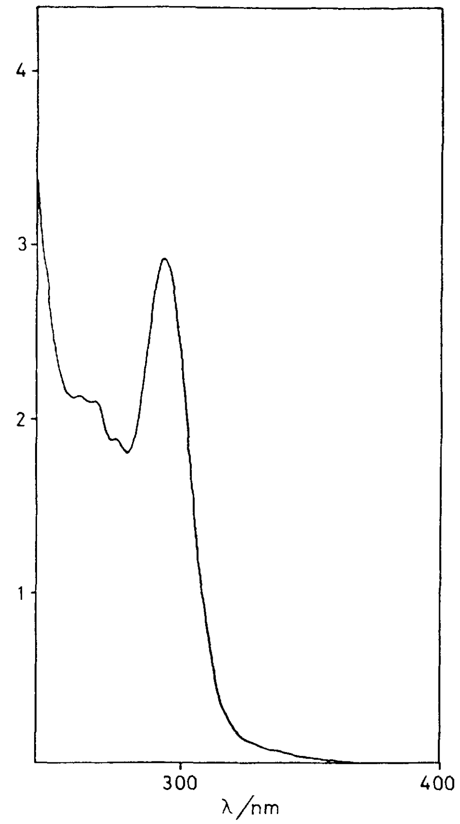


Figure 1. Electronic absorption spectrum of $[Au_2(dppm)_2](ClO_4)_2$ in acetonitrile.

The co-ordinatively unsaturated nature of the 14-electron two-co-ordinated Au^I system has also been shown to exhibit substrate binding. Addition of LiCl or LiBr resulted in an upfield shift of the dppm resonance signal in the ^{31}P n.m.r. spectrum of $[Au_2(dppm)_2](ClO_4)_2$ in acetonitrile {$[Au_2(dppm)_2](ClO_4)_2$ in MeCN: δ_P 35.134; $[Au_2(dppm)_2](ClO_4)_2$ in MeCN + LiCl: δ_P 32.745; $[Au_2(dppm)_2](ClO_4)_2$ in MeCN + LiBr: δ_P 31.078}. The upfield shift is consistent with the σ-donating property of Cl^- and Br^-, which on binding to Au^I increases the back π-donation to phosphorus and causes shielding to occur. Binding products of the form $[Au_2(dppm)_2X_2]$ are suggested since *X*-ray crystal structure of $[Au_2(dppm)_2Cl_2]$ is known.[5] The ability of $[Au_2(dppm)_2]^{2+}$ to undergo substrate binding is further supported by perturbations of its electronic absorption and emission spectra in the presence of LiCl. Upon addition of LiCl, the 292 nm band disappeared and the emission maximum shifted to 640 nm with a lifetime of only 1.7 μs. Similarly, in the presence of 0.5 M

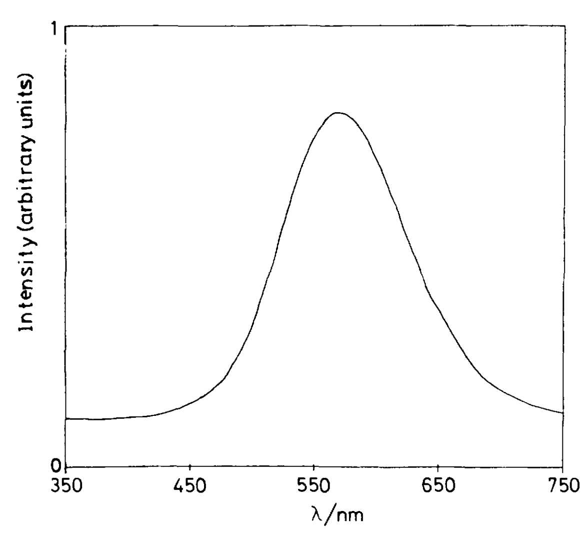
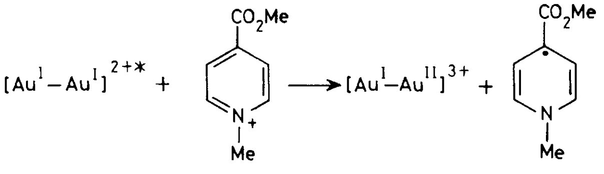


Figure 2. Emission spectrum of $[Au_2(dppm)_2](ClO_4)_2$ in acetonitrile.



Scheme 1

LiBr the electronic absorption and emission spectra are characterised, respectively, by the absence of the 292 nm band and the shifting of emission maximum to 640—645 nm with a lifetime of 2.68 μs. Such substrate binding capability is important for the design of inner-sphere multi-electron atom transfer reactions.

The phosphorescent state of $[Au_2(dppm)_2]^{2+}$ in acetonitrile undergoes electron-transfer reactions with both donors and acceptors. The quenching rate constants for TMPD (*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine) and MV^{2+} (methylviologen) are 6.6×10^9 and $6.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively, which are near diffusion-controlled. Transient absorption attributable to $TMPD^+$ (λ_{max} 600 nm)[6] is observed in laser flash kinetic spectroscopic studies of a degassed acetonitrile solution of $[Au_2(dppm)_2](ClO_4)_2$ and TMPD, thereby establishing an electron-transfer quenching mechanism:

$$[Au^I-Au^I]^{2+*} + TMPD \xrightarrow{k_q} [Au^I-Au^0]^+ + TMPD^+$$

Similarly, transient absorption attributable to MV^+ (λ_{max} 610 nm)[7] is also observed in the reaction of $[Au_2(dppm)_2](ClO_4)_2$ with MV^{2+} in acetonitrile:

$$[Au^I-Au^I]^{2+*} + MV^{2+} \xrightarrow{k_q} [Au^I-Au^{II}]^{3+} + MV^+$$

Both transient absorption spectra indicate that the $[Au^I-Au^0]^+$ and $[Au^I-Au^{II}]^{3+}$ species do not show appreciable absorption in the 330—700 nm region. The transient MV^+ signal is found to back decay *via* second-order kinetics with a bimolecular back-electron-transfer rate of *ca.* $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

$$[Au^I-Au^{II}]^{3+} + MV^+ \rightarrow [Au^I-Au^I]^{2+} + MV^{2+}$$

However, the back decay for $TMPD^+$ appears to be very complicated.

Preliminary experiments also show that the 1-methyl-4-(methoxycarbonyl)pyridinium ion [$E_{1/2} = -0.78$ *vs.* standard calomel electrode (SCE)] quenches the phosphorescence of $[Au_2(dppm)_2]^{2+*}$ *via* an electron transfer mechanism to give the pyridinyl radical species (λ_{max} ~400 nm),[8] thereby establishing the powerful one-electron reducing ability of $[Au^I-Au^I]^{2+*}$, see Scheme 1.

Table 1. Rate constants for the quenching of $[Au_2(dppm)_2]^{2+}$ by organic halides in degassed acetonitrile at 25 °C.

Quencher	$k_q(\text{M}^{-1}\text{ s}^{-1})^a$
Tetrabromomethane	8.90×10^9
Bromoform	8.70×10^9
Tetrachloromethane	3.37×10^9
Ethyl iodide	1.73×10^9
Methyl iodide	1.00×10^9
Allyl bromide	7.58×10^8
Chloroform	4.59×10^7
n-Butyl bromide	2.85×10^6
Benzyl chloride	1.85×10^6

[a] Obtained from Stern–Volmer analysis where $\tau_0/\tau = 1 + k_q\tau_0[Q]$.

A number of organic halides are also found to quench the phosphorescence of $[Au_2(dppm)_2]^{2+*}$ in acetonitrile (Table 1). The absence of perturbation on the electronic absorption and ^{31}P n.m.r. spectra indicates that ground state binding of organic halide to $[Au_2(dppm)_2]^{2+}$ is absent. The quenching rate constants seem to correlate well with the half-wave potentials for organic halides. From these and related experiments it is apparent that $[Au_2(dppm)_2]^{2+*}$ exhibits rich photoredox chemistry.

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