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The Intrinsic $^3[d\sigma^*p\sigma]$ Emission of Binuclear Gold(I) Complexes with Two Bridging Diphosphane Ligands Lies in the Near UV; Emissions in the Visible Region Are Due to Exciplexes**

Wen-Fu Fu, Kwok-Chu Chan, Vincent M. Miskowski, and Chi-Ming Che*

Since the first report on the photoluminescence of $[Au_2(dppm)_2]^{2+}$ (dppm = bis(diphenylphosphanyl)methane),[1, 2] luminescent gold(I) compounds, particularly those involving Au–Au interactions, have received considerable attention.[3] Polynuclear gold(I) phosphane complexes generally display long-lived emissions in the visible region, and this was usually attributed to excited states involving Au–Au bonding.[1–11] The Au–Au interaction is expected to lower the energy of the $5d\sigma^* \rightarrow 6p\sigma$ transition, where $5d\sigma^*$ and $6p\sigma$ refer to the antibonding combination of the $5d_{z^2}$ and to the bonding combination of the $6s/6p_z$ orbitals, respectively, and the Au–Au axis is defined as the z axis. $[Au_2(dppm)_2](ClO_4)_2$ displays luminescence with λ_{max} at 575 nm in solution in acetonitrile.[1, 2] Importantly, this emission, which was assigned to the $^3[d\sigma^*p\sigma]$ excited state, is substantially red-shifted relative to the spin- and dipole-allowed $^1(d\sigma^* \rightarrow p\sigma)$ electronic absorption transition at 290 nm, an apparent Stokes shift of 17100 cm^{-1} (2.1 eV). This is an extraordinarily large Stokes shift, particularly when compared to the Stokes shifts of 6000 – 8000 cm^{-1} reported for the phosphorescence of d^8-d^8 binuclear compounds from their $^1(d\sigma^* \rightarrow p\sigma)$ absorptions.[12] The emissive state for these latter compounds is well established as $^3[d\sigma^*p\sigma]$ and hence should be nominally analogous to the emissive state of the $d^{10}-d^{10}$ Au^I complexes. Our recent ab initio calculations on $[Au_2(H_2PCH_2PH_2)_2]^{2+}$ predicted that its $^3[d\sigma^*p\sigma]$ excited state emits at 331 nm, that is, much higher in energy than reported in the literature, but readily forms an exciplex with acetonitrile molecules that is predicted to emit at 557 nm at room temperature.[13] Herein we describe experimental evidence for an intrinsic high-energy $^3[d\sigma^*p\sigma]$ state and visible-region emissions of solvent or anion exciplexes for binuclear gold(I) phosphane complexes.

We synthesized complexes of the type $[Au_2(dcpm)_2]Y_2$ [dcpm = bis(dicyclohexylphosphanyl)methane, $Y = ClO_4^-$ (**1**), PF_6^- (**2**), $CF_3SO_3^-$ (**3**), $[Au(CN)_2]^-$ (**4**), Cl^- (**5**), and I^- (**6**); see Figure 1], and **1**, **4**, and **6** were characterized by single-crystal X-ray structure determination.[14] The ligand conformations and Au–Au distances (2.9263(9), 2.9876(5), and 3.0132(6) Å for **1**, **4**, and **6**, respectively) are typical for bis(diphosphane)-bridged binuclear Au^I complexes.[15, 16] The structure of **6** features short Au···I contacts (3.069(1) Å) that result in a T-shaped AuP_2I geometry at the Au atoms. This is also typical; Mason et al.[15] reported a number of structures of halide (Cl^-, Br^-, I^-) salts of $[Au_2(diphosphane)_2]^{2+}$ cations [diphosphane = bis(dimethylphosphanyl)methane (dmpm) or bis(dimethylphosphanyl)ethane (dmpe)] that feature similar cation···anion interactions. Importantly for our present considerations, the closest Au···anion contacts in **1** (Au···$OClO_3$ 3.36[2] Å) and **4** (Au···NCAuCN 3.33(1) Å) are significantly longer than those of **6**.

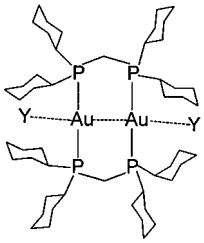

Figure 1. The structure of $[Au_2(dcpm)_2]Y_2$. $Y = ClO_4^-$, PF_6^-, $CF_3SO_3^-$, $[Au(CN)_2]^-$, Cl^-, I^-.

The UV/Vis spectroscopic data of the compounds are summarized in Table 1. For the compounds with weakly interacting counterions (ClO_4^-, PF_6^-, and $CF_3SO_3^-$) the absorption spectra feature an intense absorption band at 277 nm ($\varepsilon = 2.6-2.9 \times 10^4$ $mol^{-1}\,dm^3\,cm^{-1}$) and a weak shoulder at about 315 nm ($\varepsilon = 400$ $mol^{-1}\,dm^3\,cm^{-1}$) (Figure 2), which are respectively assigned to the $^1(d\sigma^* \rightarrow p\sigma)$ and $^3(d\sigma^* \rightarrow p\sigma)$ transitions. These assignments are based on previous studies of binuclear gold(I) complexes[15] and are strongly supported by recent resonance Raman measurements that revealed

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Table 1. Spectroscopic and photophysical properties of **1**–**6**.

Complex	Medium (T [K])	λ_{abs} [nm] (ε [dm^{3}mol^{-1}cm^{-1}])	λ_{em} [nm]/τ [μs][c]	ϕ_{em}
$[Au_2(dcpm)_2](ClO_4)_2$ (**1**)	CH_3CN (298)[a]	243 (8846), 278 (28920), 317(sh) (389)	370(w)/0.74, 510(s)/4.96	0.048 ± 0.007
	glass (77)[b]		362(s)/2.67, 410(w)/6.44	
	solid (298)		368(s)/4.88, 564(w)/4.73	
$[Au_2(dcpm)_2](PF_6)_2$ (**2**)	CH_3CN (298)[a]	243 (7676), 277 (25922), 315(sh) (414)	370(w)/0.85, 490(s)/5.12	0.025 ± 0.001
	glass (77)[b]		360(s)/2.54, 405(w)/6.49	
	solid (298)		368(s)/1.71, 505(w)/6.39	
$[Au_2(dcpm)_2](SO_3CF_3)_2$ (**3**)	CH_3CN (298)[a]	243 (8679), 277 (29185), 320(sh) (386)	370(w)/0.83, 500(s)/5.54	0.027 ± 0.002
	glass (77)[b]		360(s)/2.14, 411(w)/5.36	
	solid (298)		363(s)/1.17	
$[Au_2(dcpm)_2][Au(CN)_2]_2$ (**4**)	CH_3CN (298)[a]	240 (15110), 277 (24913), 314(sh) (376)	370(w)/0.33, 495(s)/3.57	0.013 ± 0.001
	glass (77)[b]		360(s)/2.41, 417(s)/3.68	
	solid (298)		368(s)/3.78, 515(w)/5.43	
$[Au_2(dcpm)_2]Cl_2$ (**5**)	CH_3CN (298)[a]	243 (6420), 277 (18379), 310 (1974)	513/5.74	0.065 ± 0.004
	glass (77)[b]		370(s)/2.04, 481(m)/7.31	
	solid (298)		513/(6.68)	
$[Au_2(dcpm)_2]I_2$ (**6**)	CH_3CN (298)[a]	246 (37377), 275 (20783), 323 (6136), 365(sh)(1344)	530/1.61	0.085 ± 0.002
	glass (77)[b]		460/8.02	
	solid (298)		473/1.87	
	solid (77)		475/2.74	

[a] Concentration: 6.0×10^{-5} M. [b] Solvent: EtOH/MeOH (1/4). [c] For emission spectra measurements, excitation wavelength: 280 nm. For luminescence lifetime measurements: excitation at 266 nm for high-energy emissions (360–417 nm); excitation at 355 nm for low-energy emissions (460–564 nm).

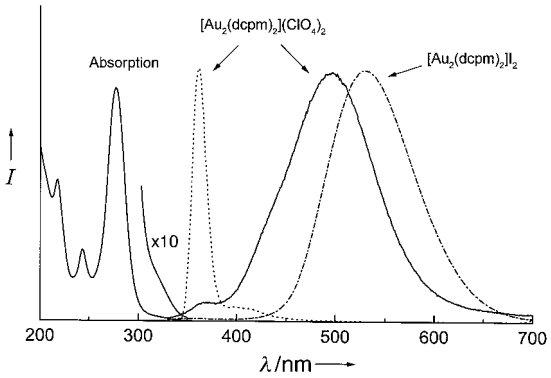

Figure 2. Electronic absorption (——) and emission spectra of $[Au_2(dcpm)_2](ClO_4)_2$ in degassed acetonitrile at room temperature (——) and in EtOH/MeOH (1/4) at 77 K (- - - -), and emission spectrum of $[Au_2(dcpm)_2I_2]$ (•–•–) in degassed acetonitrile at room temperature. I = intensity.

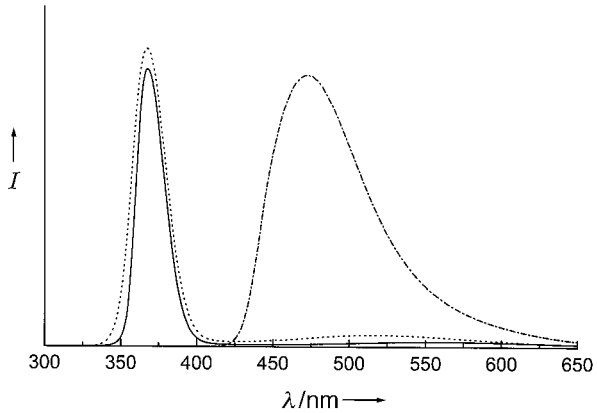

Figure 3. Room-temperature solid-state emission spectra of $[Au_2(dcpm)_2](ClO_4)_2$ (——), $[Au_2(dcpm)_2][Au(CN)_2]_2$ (- - - -), and $[Au_2(dcpm)_2I_2]$ (•–•–) with excitation at 280 nm. I = intensity.

major enhancement of the $\nu(Au_2)$ band for excitation resonant with the band at 277 nm.[17] Compound **6** (6.0×10^{-5} M in acetonitrile) exhibits additional bands with λ_{max} at 323 nm ($\varepsilon = 6136$ mol^{-1}dm^{3}cm^{-1}) and 365 nm ($\varepsilon = 1344$ mol^{-1}dm^{3}cm^{-1}, sh); these features are presumably attributable to ground-state Au···I interactions. Indeed, **1**–**4** have similar ^{31}P NMR chemical shifts ($\delta \approx 54.1$), but the ^{31}P NMR signal of **6** (2.0×10^{-4} M) is at $\delta = 48.5$, and this indicates significant perturbation of $[Au_2(dcpm)_2]^{2+}$ by complexation of I^-. Halide (Cl^-, Br^-, I^-) adducts of $[Au_2(diphosphane)_2]^{2+}$ (diphosphane = dmpm or dmpe) were previously shown to exhibit similarly perturbed electronic absorption spectra, and the first association constants for complexation in solution in acetonitrile were on the order of 10^4–10^5 M^{-1}.[15]

Upon excitation at 280 nm, **1**–**4**, both in the solid state at room temperature and as glassy solutions in MeOH/EtOH at 77 K, exhibit intense phosphorescence with λ_{max} at 360–368 nm (Figures 2 and 3). In contrast, crystalline **5** and **6** show only an intense low-energy emission with λ_{max} at 513 and 473 nm at room temperature, respectively (Table 1, Figure 3). The near-UV emission is also observed for **5** ($\lambda_{max} = 370$ nm) in a MeOH/EtOH glassy solution at 77 K, but is not observable for **6** (2×10^{-5} M) under the same experimental conditions. Time-resolved emission measurements revealed that the emission of solid $[Au_2(dcpm)_2](ClO_4)_2$ at 368 nm follows a single-exponential decay (Figure 4). Lifetime measurements revealed that both the high- (360–370 nm) and low-energy (460–550 nm) emissions have lifetimes on the microsecond timescale (Table 1), consistent with assignment to triplet excited states. A high-energy (near-UV) emission has not been previously reported for binuclear Au^I complexes. It is, however, completely consistent with expectations for emission from the $^3[d\sigma^*p\sigma]$ state. The Stokes shifts of the room-temperature solid-state emission of **1** at 368 nm from the 278 nm $^1(d\sigma^* \rightarrow p\sigma)$ and 317 nm $^3[d\sigma^* \rightarrow p\sigma]$ absorption bands are 8930 and 4570 cm^{-1}, respectively, in excellent agreement with values for the analogous transitions of d^8–d^8 complexes.[12] We conclude that this near-UV emission is the "intrinsic" emission of the $^3[d\sigma^*p\sigma]$ excited state of

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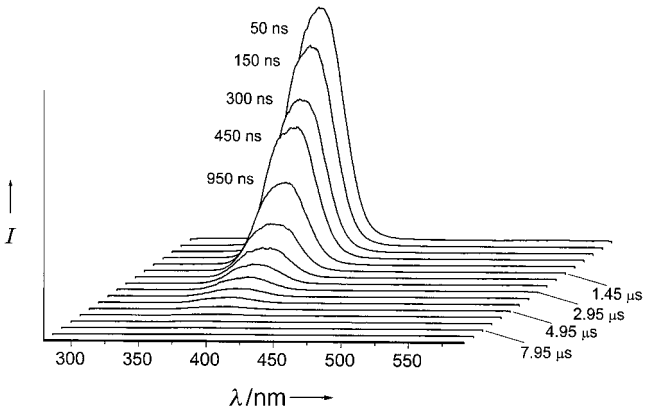

Figure 4. Room-temperature time-resolved emission spectra of solid $[Au_2(dcpm)_2](ClO_4)_2$ (excitation at 266 nm). I = intensity.

$[Au_2(dcpm)_2]^{2+}$, with an energy, width, and Stokes shift representative of the internal distortions that are characteristic for this excitation.

We assign the visible-region emissions to adducts of the excited state with solvent or counterions. In the case of halide as counterion, clear evidence exists for complexation of the ground state, and it seems reasonable to assign the absorption band observed for **6** at 365 nm (Table 1) to the spin- and dipole-allowed counterpart of the emission in solution at 530 nm; this assignment results in a reasonable Stokes shift of 8500 cm^{-1}. For **1**–**4**, emission from degassed acetonitrile solutions at room temperature is observed at about 500 nm. We attribute these emissions to an adduct of the excited state with the solvent, that is, an exciplex, since there is no evidence for complexation of the ground state. There is evidence for distortion of the excited state along coordinates other than Au–Au for the visible-emissive states, since the emission full widths at half height of 3200–3600 cm^{-1} are much larger than that of the near-UV emission (1500–1850 cm^{-1}).

We infer a large proclivity of the $d\sigma^* \rightarrow p\sigma$ excited states of these d^{10}-d^{10} binuclear complexes towards an increased coordination number of the Au^I centers. A key difference between d^{10}–d^{10} M_2L_4 and d^8–d^8 M_2L_8 complexes[12] is that the z^2 and x^2-y^2 $d\sigma^*$ orbitals of M_2L_4 can mix. A limiting case for the involvement of x^2-y^2 is represented by the planar three-coordinate Au^I tris(phosphane) complex characterized by McCleskey and Gray,[18] which, probably not coincidentally, displays emission at an energy very similar to that of the visible emissions of the binuclear Au^I compounds of this study. The distortion of the excited state in this case consists exclusively of shortening of the Au–L bonds, and we suggest that this type of excited-state distortion makes a significant contribution to the visible-emitting states of the binuclear complexes.

In view of the results presented here, we suggest that the interpretation of literature data on the luminescence of polynuclear d^{10} complexes may need revision in many cases.

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