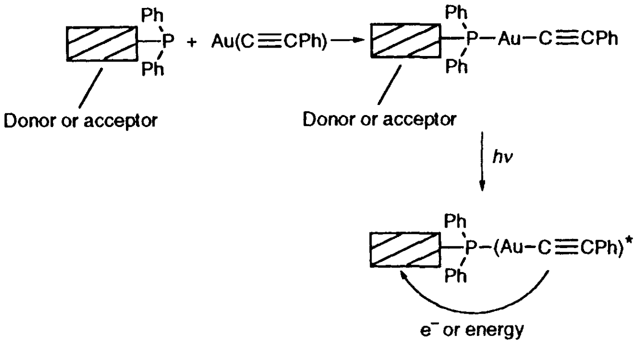
Luminescent Gold(I) Acetylide Complexes. Photophysical and Photoredox Properties and Crystal Structure of $[\{Au(C\equiv CPh)\}_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)]$†

Dan Li,[a] **Xiao Hong,**[a] **Chi-Ming Che,***[,a,b] **Wei-Chung Lo**[b] **and Shie-Ming Peng**[b]
[a] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*
[b] *Department of Chemistry, National Taiwan University, Taipei, Taiwan*

The spectroscopic and photophysical properties of three gold(I)–acetylide complexes $[N(PPh_3)_2][Au(C\equiv CPh)_2]$, $[Au(PPh_3)(C\equiv CPh)]$ and $[\{Au(C\equiv CPh)\}_2(\mu\text{-dppe})]$ [dppe = 1,2-bis(diphenylphosphino)ethane] are described. X-Ray crystal analysis of the latter showed a weak metal–metal interaction in the solid state with the shortest Au···Au separation being 3.153(2) Å. The gold(I)–acetylide complexes have long-lived and emissive $^3(\pi,\pi^*)$ excited states in solutions at room temperature. The photoreaction of $[Au(PPh_3)(C\equiv CPh)]$ with methyl viologen has been investigated by Stern–Volmer quenching and flash-photolysis experiments.

The photophysics and photochemistry of d^{10} metal complexes have received considerable attention in our laboratory,[1] mainly because such complexes usually possess long-lived and emissive electronic excited states. We have recently found that the phosphorescence of certain organic molecules would be enhanced through co-ordination to the strongly aurating reagent $Au(PPh_3)^+$.[2] This finding prompts us to construct new co-ordinatively unsaturated gold(I) complexes for photochemical studies.

Herein we show that gold(I)–acetylide complexes belong to a new class of luminophores with interesting photophysical and photochemical properties. Photochemical studies on these complexes are also of interest in the context of developing linear donor–acceptor systems (*via* Scheme 1) for photoinduced electron- and energy-transfer processes. The crystal structure of $[\{Au(C\equiv CPh)\}_2(\mu\text{-dppe})]$ [dppe = 1,2-bis(diphenylphosphino)ethane] has also been determined.



Scheme 1

Experimental

Materials.—The salt $K[AuCl_4]$ (Johnson Matthey Chemicals), 2,2′-thiodiethanol (Strem Chemicals), phenylacetylene, sodium acetate and dppe (all Aldrich) were used as received. Solvents for emission studies and lifetime measurements were of spectroscopic grade. The complexes $[\{Au(C\equiv CPh)\}_\infty]$,[3] $[Au(PPh_3)(C\equiv CPh)]$[3] and $[N(PPh_3)_2][Au(C\equiv CPh)_2]$[4] were prepared by literature methods.

Synthesis of $[\{Au(C\equiv CPh)\}_2(\mu\text{-dppe})]$.—A suspension of $[\{Au(C\equiv CPh)\}_\infty]$ (0.1 g, 0.33 mmol) and an excess of dppe (0.1 g, 0.25 mmol) in dichloromethane (20 cm^3) was stirred at room temperature until a clear solution was obtained. This usually took less than 20 min. The volume of the solution was reduced to 5 cm^3. Pale yellow crystals were obtained by diffusion of diethyl ether into the solution. The IR and UV/VIS spectral data are given in Table 3.

Instrumentation.—The UV/VIS absorption spectra were recorded on a Milton Roy Spectronic 3000 diode-array spectrophotometer and steady-state emission spectra on a SPEX Fluorolog-2 spectrofluorometer. Lifetime measurements were performed with a Quanta Ray DCR-3 Nd-YAG laser (pulse output 355 nm, 8 ns). Transient difference absorption spectra were measured with a 100 W tungsten lamp as the monitoring light source. The absolute emission quantum yield was measured by the method of Demas and Crosby[5] using quinine sulfate in 0.05 mol dm^{-3} sulfuric acid as standard. Solutions for photochemical experiments were degassed by at least four freeze–pump–thaw cycles.

X-Ray Crystallography for $[\{Au(C\equiv CPh)\}_2(\mu\text{-dppe})]$.—X-Ray diffraction data were collected on a Nonius CAD 4 diffractometer using the θ–2θ scan mode [$2\theta_{max} = 44.9°$, scan speed (16.48/2)–(16.48/7)° min^{-1}] at National Taiwan University. The unit-cell dimensions were obtained from 25 reflections in the range $18.48 < 2\theta < 24.14°$.

Crystal data. $(C_{42}H_{34}Au_2P_2)_2$, $M = 1028.22$, Triclinic, space group $P\bar{1}$, $a = 12.654(4)$, $b = 12.850(4)$, $c = 13.97(3)$ Å, $\alpha = 67.31(2)$, $\beta = 68.78(2)$, $\gamma = 69.52(3)°$, $U = 1894.5(9)$ Å^3, $\lambda = 0.710\,69$ Å, $Z = 1$, $D_c = 1.744$ g cm^{-3}, crystal dimensions $0.30 \times 0.25 \times 0.30$ mm, μ(Mo-Kα) = 39.8 cm^{-1}, $F(000) = 948$.

The last least-squares cycle was calculated with 80 atoms, 385 parameters and 3265 reflections ($|I_o| > 2\sigma|I_o|$) out of 4936 unique reflections. The residuals are as follows: for the significant reflections, $R = 0.058$, $R' = 0.057$ and goodness of fit = 3.97. The weighting scheme used was $w^{-1} = \sigma^2(F)$. All the data reduction and structural refinement was performed using the NRCC-SDP-VAX packages.[6]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Atomic coordinates for non-hydrogen atoms of [{Au(C≡CPh)}$_2$(μ-dppe)]

Atom	*x*	*y*	*z*
Au(1)	0.006 48(10)	0.172 15(11)	0.200 45(8)
Au(2)	−0.171 57(10)	0.002 43(11)	−0.068 09(8)
P(1)	−0.174 9(7)	0.143 6(6)	0.253 8(5)
P(2)	−0.167 3(7)	−0.109 0(6)	0.101 4(5)
C(1)	−0.208 0(23)	0.086 0(20)	0.169 5(17)
C(2)	−0.126 6(23)	−0.039 4(23)	0.171 3(18)
C(11A)	−0.216 3(21)	0.047 4(20)	0.393 3(17)
C(12A)	−0.298(3)	−0.015(3)	0.424 5(18)
C(13A)	−0.320(3)	−0.090(3)	0.529 6(20)
C(14A)	−0.264(3)	−0.098(3)	0.598 6(19)
C(15A)	−0.189 2(23)	−0.032(3)	0.569 2(19)
C(16A)	−0.162 0(23)	0.037 9(25)	0.467 0(19)
C(11B)	−0.280 3(22)	0.282 4(22)	0.244 8(17)
C(12B)	−0.391(3)	0.292(3)	0.324 5(20)
C(13B)	−0.466(3)	0.409(3)	0.308 0(24)
C(14B)	−0.437(3)	0.496(3)	0.227(3)
C(15B)	−0.331(3)	0.482(3)	0.154 8(22)
C(16B)	−0.255(3)	0.377 6(22)	0.164 4(20)
C(21A)	−0.312 5(21)	−0.128 5(22)	0.186 9(18)
C(22A)	−0.410 1(22)	−0.056(3)	0.160 2(22)
C(23A)	−0.516(3)	−0.066(3)	0.223 5(23)
C(24A)	−0.523 7(24)	−0.149(3)	0.316(3)
C(25A)	−0.432(3)	−0.225(3)	0.250 2(21)
C(26A)	−0.317 3(23)	−0.216 9(24)	0.284 5(20)
C(21B)	−0.067 6(21)	−0.246 0(21)	0.116 6(17)
C(22B)	−0.089 2(24)	−0.331 7(25)	0.095 4(19)
C(23B)	−0.012(3)	−0.443 1(25)	0.111 3(20)
C(24B)	0.089(3)	−0.466(3)	0.142 1(24)
C(25B)	0.111(3)	−0.386(3)	0.164(3)
C(26B)	0.029(3)	−0.278 6(25)	0.150 8(24)
C(3)	0.162 8(24)	0.207 2(22)	0.153 4(18)
C(4)	0.258 1(23)	0.228 0(23)	0.120 1(19)
C(41)	0.369 4(21)	0.252 8(23)	0.080 4(18)
C(42)	0.410(3)	0.308(3)	0.123 0(23)
C(43)	0.526(3)	0.333(3)	0.068(3)
C(44)	0.581(3)	0.285(3)	−0.020 4(25)
C(45)	0.548(3)	0.231(4)	−0.056(3)
C(46)	0.443 5(24)	0.214(3)	−0.009 1(23)
C(5)	−0.187(3)	0.113 2(23)	−0.200(3)
C(6)	−0.1767(23)	0.175 3(24)	−0.287 1(21)
C(61)	−0.170(3)	0.255(3)	−0.396 1(23)
C(62)	−0.069(3)	0.254(3)	−0.484(3)
C(63)	−0.058(4)	0.336(4)	−0.588(3)
C(64)	−0.170(3)	0.401(3)	−0.604(3)
C(65)	−0.280(3)	0.418(3)	−0.529(3)
C(66)	−0.261(3)	0.333(3)	−0.427(3)

Table 2 Selected bond distances (Å) and angles (°) for [{Au(C≡CPh)}$_2$(μ-dppe)]

Au(1)···Au(2)	3.153(2)	P(2)–C(2)	1.84(3)
Au(1)–P(1)	2.258(8)	C(1)–C(2)	1.58(4)
Au(2)–P(2)	2.255(7)	C(3)–C(4)	1.21(4)
Au(1)–C(3)	2.00(3)	C(4)–C(41)	1.42(4)
Au(2)–C(5)	1.87(3)	C(5)–C(6)	1.16(4)
P(1)–C(1)	1.83(2)	C(6)–C(61)	1.46(4)
Au(2)–Au(1)–P(1)	107.2(2)	Au(2)–Au(1)–C(3)	75.9(7)
P(1)–Au(1)–C(3)	176.6(7)	P(2)–Au(2)–C(5)	172(1)
Au(1)–C(3)–C(4)	177(2)	C(3)–C(4)–C(41)	180(2)
Au(2)–C(5)–C(6)	168(3)	C(5)–C(6)–C(61)	177(3)

Table 1 lists the atomic coordinates of the non-hydrogen atoms. Selected bond distances and angles are given in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The synthesis of [{Au(C≡CPh)}$_2$(μ-dppe)] had been reported by Coates and Parkin.[3] In this work the same complex was prepared by the reaction of [{Au(C≡CPh)}$_\infty$] with dppe in dichloromethane. It is an air-stable pale yellow solid.

Fig. 1 shows a perspective view of each asymmetric unit of [{Au(C≡CPh)}$_2$(μ-dppe)]. Two weakly interacting molecules of [{Au(C≡CPh)}$_2$(μ-dppe)] are *anti* to each other. The measured Au(1)···Au(2) and Au(2)···Au(2′) separations are 3.153(2) and 5.308(3) Å respectively. The former value is slightly longer than the intramolecular Au···Au distances in [Au$_2$(μ-dppm)$_2$]$^{2+}$ [2.982(2) Å][7] [dppm = bis(diphenylphosphino)methane] and [Au$_3$(μ-dpmp)$_2$]$^{3+}$ [3.0137(8) and 3.0049(8) Å][1a] [dpmp = bis(diphenylphosphinomethyl)phenylphosphine], but shorter than the intermolecular Au···Au separation in [Au(PPh$_3$)(C≡CPh)] [3.379(1) Å][8] and in [Au(C≡CPh)(NH$_2$Pr^i)] [3.274 Å],[9] suggesting weak gold(I)–gold(I) interaction in the solid state. The molecule can be described as bridging two non-interacting Au(C≡CPh) units, in the *syn* configuration, by the dppe ligand (see Fig. 1 and Scheme 2).

The P–Au–C≡C–C chain is nearly linear [P–Au–C 176.6(7) and 172(1), Au–C≡C 177(2) and 168(3); C≡C–C 179.6(24) and 177(3)°] as in the case of [Au(PPh$_3$)C≡CPh)][8] [P–Au–C 173.5(5) and 177.6(6); Au–C≡C 175.7(16) and 170.8(19); C≡C–C 176.5(18) and 174.0(20)°] and [Au(PPh$_3$)(C≡CC$_6$F$_5$)][10] [P–Au–C 177.9(3), Au–C≡C 175.4(10), C≡C–C 178.4(12)°]. The Au–C and Au–P distances are normal.[8]

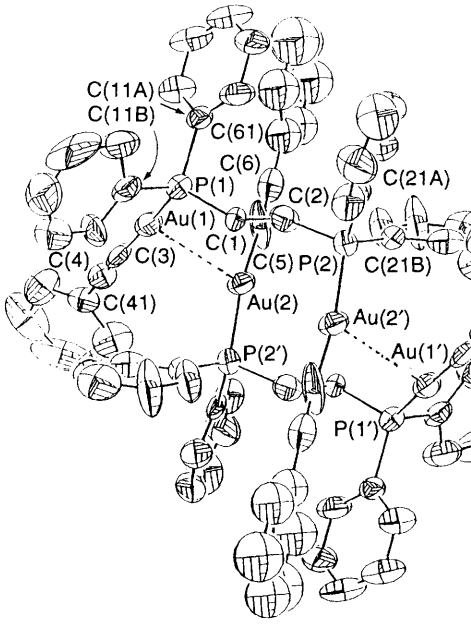
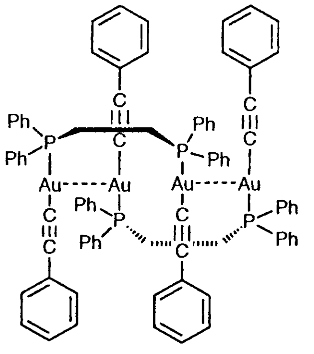


Fig. 1 Perspective view of [{Au(C≡CPh)}$_2$(μ-dppe)]

Spectroscopic Properties.—The spectroscopic and photophysical data of the three gold(I)–acetylide complexes are summarised in Table 3. Fig. 2 depicts the UV/VIS absorption spectra of [N(PPh$_3$)$_2$][Au(C≡CPh)$_2$], [Au(PPh$_3$)(C≡CPh)] and [{Au(C≡CPh)}$_2$(μ-dppe)] in dichloromethane at room temperature. The three spectra are similar suggesting that [{Au(C≡CPh)]$_2$(μ-dppe)] can be viewed as two non-interacting Au(C≡CPh) units, bridged by the dppe ligand. The intense absorption from 260 to 310 nm in each case arises from the intraligand π ——→ π* transition of phenylacetylide. We do not rule out the possibility that the lower-energy absorption of [Au(C≡CPh)$_2$]$^-$ at round 320 nm contains some metal-to-ligand charge-transfer (m.l.c.t.) Au→π* character.

Table 3 Spectroscopic and photophysical data of the gold(I)–acetylide complexes ($\approx 3.6 \times 10^{-4}$ mol dm^{-3}) at room temperature

Complex	IR, $\nu(C\equiv C)$/cm^{-1} (Nujol)	λ_{max}^{abs}/nm ($10^{-4}\varepsilon_{max}$/dm^3 mol^{-1} cm^{-1})	λ_{max}^{em}/nm	τ/μs(φ^{em})	Solvent
$[N(PPh_3)_2][Au(C\equiv CPh)_2]$	2098	269 (1.99)	450	1.2 (1.3×10^{-2})	CH_2Cl_2
$[Au(PPh_3)(C\equiv CPh)]$	2119	284 (3.1)	419	6.0 (1.0×10^{-2})	CH_2Cl_2
			421	1.9 (3.5×10^{-3})	MeCN
			419	1.3 (2.4×10^{-3})	EtOH
$[\{Au(C\equiv CPh)\}_2(\mu\text{-dppe})]$	2098	284 (4.9)	420	4.2 (2.0×10^{-2})	CH_2Cl_2



Scheme 2

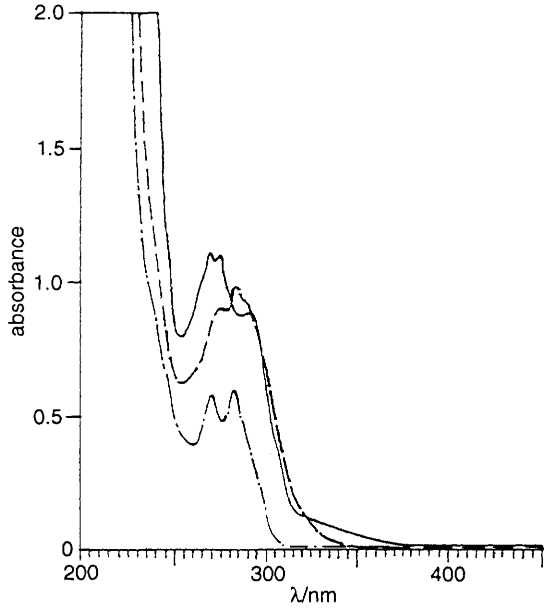


Fig. 2 The UV/VIS absorption spectra of $[N(PPh_3)_2][Au(C\equiv CPh)_2]$ (——), $[Au(PPh_3)(C\equiv CPh)]$ (— · —) and $[\{Au(C\equiv CPh)\}_2(\mu\text{-dppe})]$ (— — —) in dichloromethane at room temperature

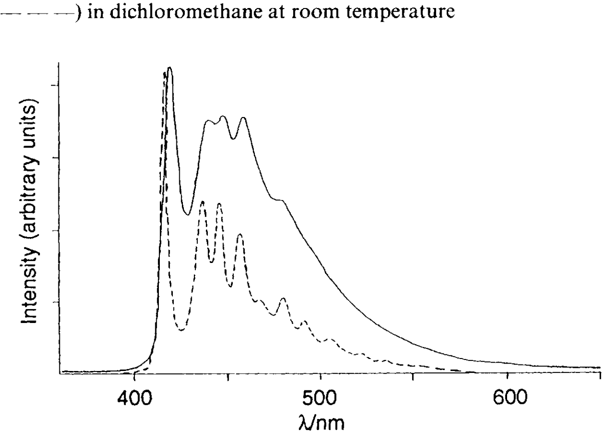


Fig. 3 Emission spectra of $[Au(PPh_3)(C\equiv CPh)]$ in dichloromethane at room temperature (———) and in an ethanol–methanol (4:1 v/v) glass at 77 K (– – – –)

Upon excitation at 280–350 nm, the gold(I)–acetylide complexes display intense emission. The spectra of $[N(PPh_3)_2][Au(C\equiv CPh)_2]$, $[Au(PPh_3)(C\equiv CPh)]$ and $[\{Au(C\equiv CPh)\}_2(\mu\text{-dppe})]$ are similar in solution at room temperature. Fig. 3 shows the spectra of $[Au(PPh_3)(C\equiv CPh)]$ in dichloromethane at room temperature and in ethanol–methanol (4:1 v/v) glass at 77 K. The well resolved vibrational fine structure displayed, which is due to a combination of the vibrations of the C≡C and phenyl groups, is similar to that of the $^3(\pi,\pi^*)$ emission of co-ordinated phenylacetylide in $[Pt(PEt_3)_2(C\equiv CPh)_2]$.[11] Self-quenching of the emission of $[Au(PPh_3)(C\equiv CPh)]$ was observed. A plot of the reciprocal of the lifetime *versus* the concentration of the gold(I) complex gave a straight line with the self-quenching rate constant and lifetime at infinite dilution being $(1.75 \pm 0.06) \times 10^8$ dm^3 mol^{-1} s^{-1} and 10 ± 0.5 μs respectively.

In the solid state the emission maximum of $[\{Au(C\equiv CPh)\}_2(\mu\text{-dppe})]$ is dramatically red-shifted to 550 nm (Fig. 4). This emission energy is close to that of $[Au_2(\mu\text{-dppm})_2]^{2+}$ (λ_{max} = 570 nm)[12a,b] which has an intramolecular Au···Au separation of 2.982(2) Å. From X-ray crystal analysis, two $[\{Au(C\equiv CPh)\}_2(\mu\text{-dppe})]$ molecules are packed in the solid state with weak gold–gold interaction. With reference to previous works,[1a,12,13] such interaction would give rise to p_σ as the lowest unoccupied molecular orbital and $d\delta^*$ as the highest occupied molecular orbital. Thus, in the solid state, the lowest electronic excited state is $(d\delta^*p_\sigma)$ in nature. In fluid solution the two $[\{Au(C\equiv CPh)\}_2(\mu\text{-dppe})]$ molecules separate and the intraligand phosphorescence becomes dominant. Cooling the solid sample to 77 K only leads to an increase in emission intensity. No vibrational fine structure was observed.

Photoredox Properties.—With long emission lifetimes, it is not surprising to find that the excited state of the gold(I)–acetylide complexes can participate in bimolecular redox reactions. The emissions are found to be quenched efficiently by methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dichloride, $[dmbipy]Cl_2$) in acetonitrile at room temperature. The corresponding quenching rate constant (k_q) for $[Au(PPh_3)(C\equiv CPh)]$ [$E°$ = −0.45 V *vs.* sodium chloride saturated calomel electrode (SSCE)] has been measured to be 5.1×10^8 dm^3 mol^{-1} s^{-1} from a Stern–Volmer plot ($\tau_0/\tau = 1 + k_q\tau_0[dmbipy^{2+}]$; τ_0 and τ are the lifetimes in the absence and presence of $dmbipy^{2+}$). The quenching mechanism is electron transfer in nature, as represented by equation (1).

$$[Au^I(PPh_3)(C\equiv CPh)]^* + dmbipy^{2+} \longrightarrow [Au^{II}(PPh_3)(C\equiv CPh)]^+ + dmbipy^+ \quad (1)$$

Evidence for the electron-transfer mechanism has been obtained from flash-photolysis experiments. The transient different absorption spectrum recorded 5 μs after flashing a degassed acetonitrile solution of $[Au(PPh_3)(C\equiv CPh)]$ in the presence of methyl viologen is given in Fig. 5. The spectrum matches well the characteristic absorption of $dmbipy^+$[14]

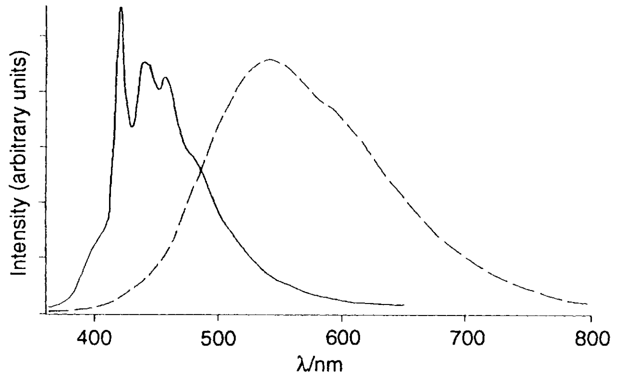


Fig. 4 Emission spectra of $[\{Au(C{\equiv}CPh)\}_2(\mu\text{-dppe})]$ in dichloromethane (——) and the solid state (— — —) at room temperature

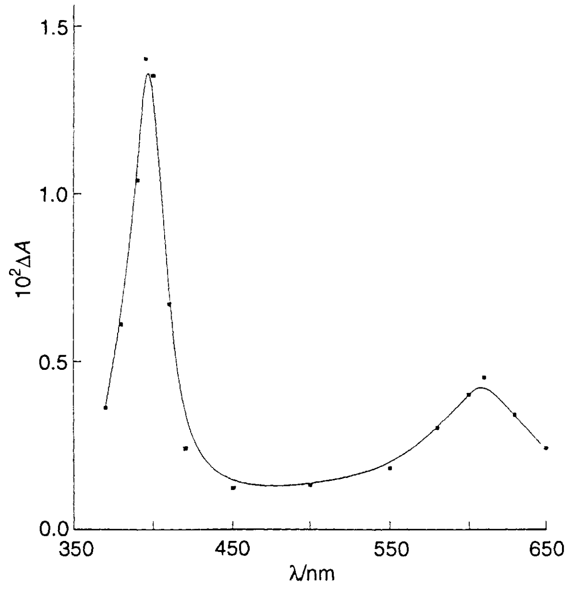


Fig. 5 Transient difference absorption spectrum recorded 5 μs after flashing a degassed acetonitrile solution of $[Au(PPh_3)(C{\equiv}CPh)]$ (10^{-4} mol dm^{-3}) with methyl viologen (10^{-3} mol dm^{-3}) at room temperature

which is so intense that the absorption of $[Au^{II}(PPh_3)(C{\equiv}CPh)]^+$ is obscured and could not be located in the spectrum.

Conclusion

The work described together with previous studies on gold(I) complexes of 2,2′-bibenzimidazolate[2a] and 7-azaindolate[2b] clearly suggests that co-ordination of organic molecules to Au^I provides a new entry to a new class of emissive materials with long-lived electronic excited states. This may be of importance in the design of new photosensitizers for electron- and energy-transfer reactions.

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References

1 (*a*) D. Li, C. M. Che, S. M. Peng, S. T. Liu, Z. Y. Zhou and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1993, 189; (*b*) S. J. Shieh, D. Li, S. M. Peng and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 195; (*c*) C. F. Lee, K. F. Chin, S. M. Peng and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 467.
2 (*a*) B. C. Tzeng, D. Li, C. M. Che and S. M. Peng, *J. Chem. Soc., Dalton Trans.*, 1993, 2365; (*b*) D. Li, K. K. Cheung and C. M. Che, unpublished work.
3 G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1962, 3220.
4 O. M. Abu-Salah and A. R. A. Al-Ohaly, *J. Chem. Soc., Dalton Trans.*, 1988, 2297.
5 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 99.
6 E. J. Cabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.
7 L. C. Porter, N. I. Md. Khan, C. King and J. P. Fackler, jun., *Acta Crystallogr., Sect. C*, 1989, **45**, 947.
8 M. I. Bruce and D. N. Duffy, *Aust. J. Chem.*, 1986, **39**, 1697.
9 P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, 1967, **23**, 156.
10 M. I. Bruce, E. Horn, J. G. Matisons and M. R. Snow, *Aust. J. Chem.*, 1984, **37**, 1163.
11 L. Sacksteder, E. Baralt, B. A. DeGraff, C. M. Lukehart and J. N. Demas, *Inorg. Chem.*, 1991, **30**, 2468.
12 (*a*) C. M. Che, H. L. Kwong, V. W. W. Yam and K. C. Cho, *J. Chem. Soc., Chem. Commun.*, 1989, 885; (*b*) C. M. Che, H. L. Kwong, C. K. Poon and V. W. W. Yam, *J. Chem. Soc., Dalton Trans.*, 1990, 3215; (*c*) V. W. W. Yam, T. F. Lai and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1991, 3747; (*d*) C. M. Che, H. K. Yip, V. W. W. Yam, P. Y. Cheung, T. F. Lai, S. J. Shieh and S. M. Peng, *J. Chem. Soc., Dalton Trans.*, 1992, 427.
13 C. King, J. C. Wang, N. I. Md. Khan and J. P. Fackler, jun., *Inorg. Chem.*, 1989, **28**, 2145.
14 T. Watanabe and K. Honda, *J. Phys. Chem.*, 1982, **86**, 2617.

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