

Synthesis, characterisation, electrochemistry and luminescence studies of 9-anthrylgold(I) complexes†

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Received 13th July 2004, Accepted 27th October 2004

First published as an Advance Article on the web 22nd November 2004

Reaction of mono- and dinuclear gold(I) phosphine chloride precursors with an excess of organolithium reagent $C_{14}H_9Li$ in dry diethyl ether or THF gave mononuclear $[(PPh_3)Au(C_9H_{14})]$ and dinuclear $[(P^*P)Au_2(C_{14}H_9)_2]$ ($P^*P = dppm, dcpm$) and $[(dcpm)Au_2Br(C_{14}H_9)]$, respectively. These complexes were found to be emissive both in the solid state and in fluid solutions.

Introduction

A number of metal complexes of d^{10} electronic configuration have been shown to exhibit rich photoluminescence properties.¹ By introducing mono-, bi-, and polydentate phosphines as stabilizing ancillary ligands, the nuclearity of the metal complexes can be varied and the spectroscopic properties tuned. Most of the luminescence studies on organogold(I) systems were concentrated on the alkynylgold(I) phosphines,² with corresponding studies on the arylgold(I) phosphines relatively less explored. Earlier reports showed that $[(PPh_3)AuPh]$ and $[(dppm)Au_2R_2]$ ($R = Me, Ph$) display luminescence properties.³ We reported a series of organogold(I) complexes showing interesting luminescence properties.⁴ Reaction of $[(dmpm)Au_2Cl_2]$ or $[(dmmp)Au_3Cl_3]$ with an excess of organolithium reagent LiR in diethyl ether gave $[(dmpm)Au_2R_2]$ or $[(dmmp)Au_3R_3]$ in high yield ($R = Me$ or C_6H_4OMe-p).^{4a} These complexes were shown to be emissive both in the solid state and in fluid solutions. The complex, $[(dmmp)Au_3(C_6H_4OMe-p)_3]$, was found to show an excited-state reduction potential of $-2.0(1)$ V vs. sodium chloride saturated calomel electrode (SCE). Another series of luminescent organometallic complexes, $[(dppf)Au_2R_2]$ ($R = Me, Ph, 1-naphthyl, 9-anthryl, pyren-1-yl$), has also been reported by us, and their photophysical and electrochemical properties have been studied.^{4b} As an extension of our recent interest in d^{10} metal complexes, herein we report the synthesis, characterisation and photophysical studies of a series of organometallic 9-anthrylgold(I) phosphine complexes, $[(PPh_3)Au(C_9H_{14})]$ (**1**), $[(P^*P)Au_2(C_{14}H_9)_2]$ ($P^*P = dppm$ (**2**), $dcpm$ (**3**)), and $[(dcpm)Au_2Br(C_{14}H_9)]$ (**4**). The crystal structures of **2** and **4** are also described.

Experimental

Materials and reagents

Potassium tetrachloroaurate(III), bis(diphenylphosphino)methane (dppm), and bis(dicyclohexylphosphino)methane (dcpm) were obtained from Strem Chemicals Inc. Triphenylphosphine, 2,2'-thiodiethanol, methylolithium-lithium bromide (1.4 M in diethyl ether) and *n*-butyllithium (2.5 M in THF) were obtained from Aldrich Chemical Company. 9-Bromoanthracene was obtained from Lancaster Synthesis Ltd. The aryllithium reagents were prepared from *n*-butyllithium and the respective aryl bromide according to literature procedures.⁵ Dichloromethane

(Lab Scan, AR) and tetrahydrofuran (Lab Scan, AR) were purified and distilled using standard procedures before use.⁶ All other solvents and reagents were of analytical grade and were used as received.

Synthesis of gold(I) complexes

All reactions were performed under anaerobic and anhydrous conditions using standard Schlenk techniques under an inert atmosphere of nitrogen.

[(PPh₃)Au(C₉H₁₄)] (1). A solution of 9-anthryllithium (1.2 M, 1.0 ml, 1.18 mmol) was added to a suspension of $[(PPh_3)AuCl]$ (0.20 g, 0.4 mmol) in freshly distilled diethyl ether (20 ml) with stirring at -78 °C. The mixture was allowed to warm to room temperature slowly and during the warming process, the yellow suspension turned clear and then turbid again shortly. After stirring overnight, it was reduced in volume to ca. 5 ml and CH_2Cl_2 (20 ml) was added. Filtration followed by removal of solvent and subsequent recrystallization from slow evaporation of CH_2Cl_2 -*n*-hexane mixture gave **1** as yellow crystals. Yield: 182 mg, 71%. ¹H NMR (300 MHz, $CDCl_3$): δ 7.39 (t, 4H, $J = 6.3$ Hz, anthryl protons), 7.49–7.55 (m, 10H, PPh_3), 7.67–7.77 (m, 4H, PPh_3), 7.98 (t, 2H, $J = 6.3$ Hz, anthryl protons), 8.25 (s, 1H, anthryl proton), 8.82 (d, 2H, $J = 7.5$ Hz, anthryl protons). Positive-ion FAB-MS: m/z 636 $\{M\}^+$. Found: C, 60.06; H, 3.63%. $C_{32}H_{24}AuP$ requires: C, 60.38; H, 3.80%.

[(dppm)Au₂(C₁₄H₉)₂] (2). The procedure was similar to that for $[(PPh_3)Au(C_{14}H_9)]$ except $[(dppm)Au_2Cl_2]$ (170 mg, 0.2 mmol) was used in place of $[(PPh_3)AuCl]$ and freshly distilled THF in place of diethyl ether to give light yellow crystals of **2**. Yield: 134 mg, 60%. ¹H NMR (300 MHz, $CDCl_3$): δ 3.89 (t, 2H, $J = 10.5$ Hz, PCH_2P), 6.73 (t, 4H, $J = 6.3$ Hz, anthryl protons), 7.11 (t, 4H, $J = 6.3$ Hz, anthryl protons) 7.42 (m, 12H, $-PPh_2$), 7.68 (d, 4H, $J = 7.2$ Hz, anthryl protons), 7.80 (s, 2H, anthryl protons), 7.90–7.99 (m, 8H, $-PPh_2$), 8.19 (d, 4H, $J = 7.2$ Hz, anthryl protons). Positive-ion FAB-MS: m/z 1132 $\{M\}^+$. Found: C, 50.32; H, 3.14%. $C_{53}H_{40}Au_2P_2 \cdot 2CH_2Cl_2$ requires: C, 50.71; H 3.40%.

[(dcpm)Au₂(C₁₄H₉)₂] (3). The procedure was similar to that for $[(PPh_3)Au(C_{14}H_9)]$ except $[(dcpm)Au_2Cl_2]$ (175 mg, 0.2 mmol) was used in place of $[(PPh_3)AuCl]$ and freshly distilled THF in place of diethyl ether to give light yellow crystals of **3**. Yield: 130 mg, 56%. ¹H NMR (300 MHz, $CDCl_3$): δ 1.20–2.45 (m, 44H, C_6H_{11} ; 2H, PCH_2P), 6.68 (t, 4H, $J = 6.3$ Hz, anthryl protons), 7.06 (t, 4H, $J = 6.3$ Hz, anthryl protons), 7.66 (d, 4H, $J = 7.2$ Hz, anthryl protons), 7.77 (s, 2H, anthryl protons), 8.29

† Dedicated to Professor Hiroshi Masuhara on the occasion of his 60th birthday.

(d, 4H, $J = 7.2$ Hz, anthryl protons). Positive-ion FAB-MS: m/z 1353 $\{M + Au\}^+$. Found: C, 55.31; H, 6.69%. $C_{53}H_{74}Au_2P_2 \cdot 1/2n$ -hexane requires: C, 55.58; H, 6.74%.

[(dcpm)Au₂Br(C₁₄H₉)] (4). The procedure was similar to that for [(PPh₃)Au(C₁₄H₉)] except [(dcpm)Au₂Cl₂] (175 mg, 0.2 mmol) was used in place of [(PPh₃)AuCl] to give light yellow crystals of **4**. Yield: 137 mg, 65%. ¹H NMR (300 MHz, CDCl₃): δ 1.32–2.48 (m, 44H, C₆H₁₁; 2H, PCH₂P), 6.64 (t, 2H, $J = 6.5$ Hz, anthryl protons), 6.96 (t, 2H, $J = 6.5$ Hz, anthryl protons), 7.61 (d, 2H, $J = 7.4$ Hz, anthryl protons), 7.73 (s, 1H, anthryl proton), 8.21 (d, 2H, $J = 7.4$ Hz, anthryl protons). Positive-ion FAB-MS: m/z 1059 $\{M\}^+$. Found: C, 43.64; H, 6.01%. $C_{39}H_{55}Au_2P_2Br$ requires: C, 43.79; H, 6.13%.

Physical measurements and instrumentation

¹H NMR spectra were recorded on a 300 MHz Bruker DPX300 FT-NMR spectrometer. Chemical shifts (δ) were reported relative to tetramethylsilane (Me₄Si). Positive ion FAB mass spectra were collected on a Finnigan MAT95 mass spectrometer. UV-visible spectra were obtained on a Hewlett Packard 8452A diode array spectrophotometer. Steady-state excitation and emission spectra were recorded on a Spex Fluorolog 111 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. Elemental analyses of the new complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

All solutions for photophysical studies were prepared under vacuum in a 10 cm³ round-bottom flask equipped with a side-arm 1 cm fluorescence cuvette and sealed from the atmosphere by a Bibby RotaFlo HP6 Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

Cyclic voltammetric measurements were performed using a CH Instruments, Inc. Model CHI 620 electrochemical analyzer interfaced with a personal computer. The electrolytic cell used was a conventional two-compartment cell. The salt bridge of the reference electrode was separated from the working electrode compartment by a Vycor glass. A Ag/AgNO₃ (0.1 M in CH₃CN) reference electrode was used. The ferrocenium–ferrocene couple was used as the internal standard in the electrochemical measurements in acetonitrile (0.1 M ⁿBu₄NPF₆).⁷ The working electrode was a glassy-carbon (Atomergic Chemetals V25) electrode with a platinum foil acting as the counter electrode.

Crystal structure determination

Single crystals of **2** and **4** were obtained by slow evaporation of CH₂Cl₂–*n*-hexane solutions of the respective complexes. All the experimental details are given in Table 1. Selected bond distances and angles are summarized in Table 2. The crystals of **2** and **4** of dimensions 0.35 × 0.10 × 0.07 mm, and 0.25 × 0.15 × 0.10 mm, respectively, mounted in a glass capillary were used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å).

The space group of **2** was uniquely determined based on systematic absences and the structure was solved by Patterson methods and expanded by Fourier methods (*PATSY*)⁸ and refinement by full-matrix least squares using the software package *TeXsan*⁹ on a Silicon Graphics Indy computer. In the least-squares refinement, all 60 non-H atoms of the complex molecule were refined anisotropically, and 40 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms, were not refined. The space group of **4** was uniquely determined based on systematic absences and the structure was solved by direct method (*SIR92*)¹⁰, it was expanded by Fourier methods and refined by full-matrix

Table 1 Crystal and structure determination data for **2** and **4**

| Complex | 2 | 4 |
|--------------------------------|---|---|
| Molecular formula | C ₅₃ H ₄₀ Au ₂ P ₂ ·CH ₂ Cl ₂ | C ₃₉ H ₅₅ Au ₂ P ₂ Br·2H ₂ O |
| M_w | 1217.71 | 1095.68 |
| Crystal system | <i>P2₁/n</i> | <i>P2₁/a</i> |
| $a/\text{Å}$ | 12.258(2) | 17.211(3) |
| $b/\text{Å}$ | 16.047(3) | 12.442(2) |
| $c/\text{Å}$ | 23.166(3) | 22.955(3) |
| $\alpha/^\circ$ | 90 | 90 |
| $\beta/^\circ$ | 98.75(2) | 105.75(2) |
| $\gamma/^\circ$ | 90 | 90 |
| $V/\text{Å}^3$ | 4503(1) | 4731(1) |
| Z | 4 | 4 |
| $F(000)$ | 2352 | 2128 |
| μ/cm^{-1} | 67.75 | 71.58 |
| T/K | 301(2) | 301(2) |
| No. of reflections collected | 35310 | 37078 |
| No. of independent reflections | 7921 | 4867 |
| R_{int} | 0.072 | 0.071 |
| R_1^a | 0.050 | 0.057 |
| wR_2^a | 0.061 | 0.084 |

^a $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.035F_o^2)^2]$ with $I > 3\sigma(I)$.

Table 2 Selected bond distances (Å) and bond angles (°) for **2** and **4**

| 2 | | | |
|-------------|-----------|------------------|-----------|
| Au(1)–Au(2) | 3.0121(7) | P(1)–Au(1)–C(1) | 175.7(3) |
| Au(1)–C(1) | 2.098(10) | P(2)–Au(2)–C(15) | 176.4(4) |
| Au(2)–C(15) | 2.09(1) | | |
| Au(1)–P(1) | 2.309(3) | | |
| Au(2)–P(2) | 2.290(3) | | |
| 4 | | | |
| Au(1)–P(1) | 2.294(3) | P(1)–Au(1)–C(1) | 170.2(4) |
| Au(1)–C(1) | 2.12(1) | Br(1)–Au(2)–P(2) | 176.97(9) |
| Au(2)–Br(1) | 2.409(1) | | |
| Au(2)–P(2) | 2.259(3) | | |

least-squares using the software package *TeXsan*⁹ on a Silicon Graphics Indy computer. In the final least-squares refinement, C atoms of anthracene were refined isotropically, other non-H atoms anisotropically, and 55 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms, were not refined. Other four H atoms of the water solvent molecules were not included in the calculation.

CCDC reference numbers 245400 for **4**, 245401 for **2**.

See <http://www.rsc.org/suppdata/pp/b4/b410667a/> for crystallographic data in CIF or other electronic format.

Results and discussion

All the 9-anthrylgold(I) complexes were prepared by the reaction of [(PPh₃)AuCl], [(dppm)Au₂Cl₂] or [(dcpm)Au₂Cl₂] with an excess of the organolithium reagent in diethyl ether or THF under strictly anaerobic anhydrous conditions. All the newly synthesized complexes gave satisfactory elemental analyses and have been characterised by ¹H NMR and positive FAB mass spectrometry. The crystal structures of **2** and **4** have been determined.

Fig. 1 depicts the perspective drawings of **2** and **4**, with atomic numbering scheme. The observed Au–P bond distances of 2.309(3) and 2.290(3), 2.409(1) and 2.259(3) Å, Au–C bond distances of 2.098(10) and 2.09(1), 2.12(1) Å, for **2** and **4** respectively, are comparable to those observed in other alkynyl-gold(I) phosphine systems.² The observed Au–Br bond distance is 2.409(1), which is similar to those found in other related bromogold(I) phosphine complexes.¹¹ Short intra-molecular Au···Au contacts of 3.0121(7) Å are found between adjacent Au units for **2**. Such distances are shorter than the sum of van der Waals radii for Au and are comparable to Au···Au distances in

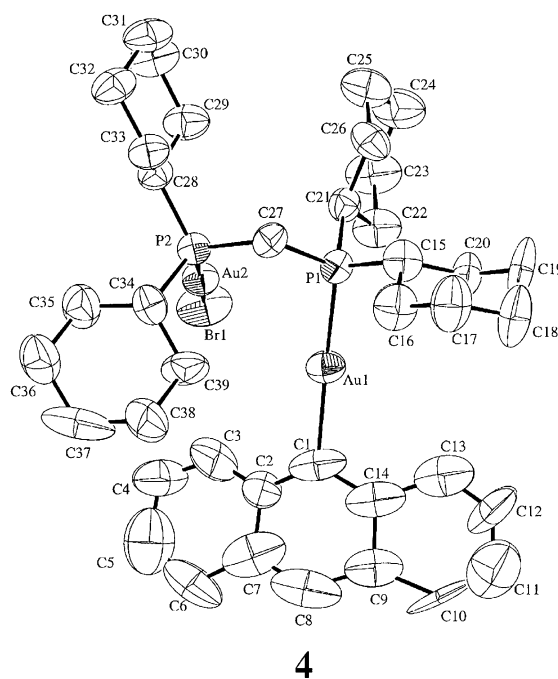
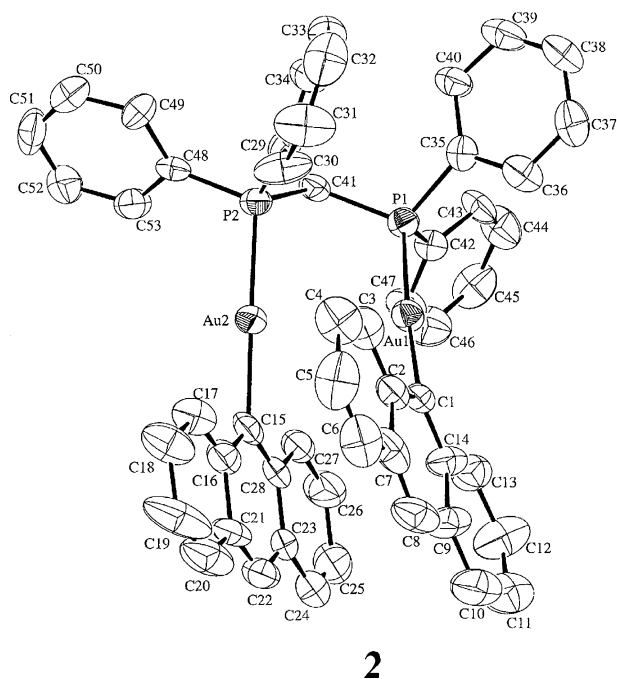


Fig. 1 Perspective views of **2** and **4** with atomic numbering scheme. Thermal ellipsoids are shown at the 40% probability level.

other Au(I) phosphine complexes,²⁻⁴ indicative of the presence of weak Au...Au interactions in the solid state. The dihedral angle between the two anthracene units in **2** is 6.61°, with the two anthracene units nearly parallel. It appears that the $\pi \cdots \pi$ interaction between the two anthracene units together with the Au...Au interaction would render the solid state structure to adopt preferentially a *syn* configuration rather than an *anti*-structure.

The 9-anthrylgold(I) complexes **1-4** showed irreversible anodic waves from +0.92 to +1.78 V vs. SCE. The electrochemical data are collected in Table 3 and a typical cyclic voltammogram is shown in Fig. 2.

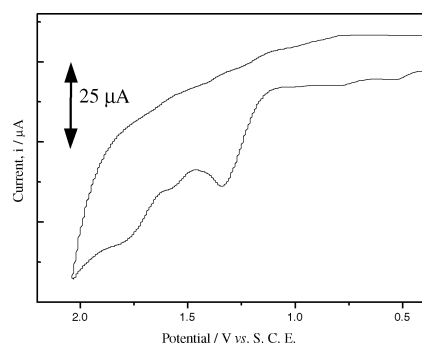


Fig. 2 Cyclic voltammogram of **2** in dichloromethane (0.1 mol dm⁻³ ⁿBu₄NPF₆). Scan rate = 100 mV s⁻¹.

Table 3 Electrochemical data for **1-4** in dichloromethane solution (0.1 mol dm⁻³ ⁿBu₄NPF₆) at 298 K^a

| Complex | Oxidation E_{pa}^b /V vs. SCE | Complex | Oxidation E_{pa}^b /V vs. SCE |
|----------|---------------------------------|----------|---------------------------------|
| 1 | +0.92 | 3 | +1.32 |
| | +1.38 | | +1.59 |
| 2 | +1.67 | 4 | +1.35 |
| | +1.34 | | +1.78 |
| | +1.57 | | |
| | +1.77 | | |

^a Working electrode, glassy carbon; scan rate, 100 mV s⁻¹. ^b E_{pa} is the anodic peak potential of the irreversible oxidation wave.

The anthracene ligand is known to exhibit an oxidation wave at *ca.* +1.36 V vs. SCE.¹² The close resemblance of the potential for anthracene oxidation to that of the first oxidation wave of the Au(I) aryl complexes lends support to its assignment as a ligand-centered oxidation. Further assignments of the other oxidation waves which occur at more positive potentials are not possible due to their irreversible nature.

The electronic absorption spectra of **1-4** are dominated by vibronic-structured bands at *ca.* 342–402 nm, with vibrational progression spacings of 1300–1560 cm⁻¹, typical of $\nu(C\cdots C)$ stretches of the aromatic rings. The electronic absorption data are collected in Table 4. The electronic absorption spectrum of **2** in dichloromethane at 298 K is shown in Fig. 3. A comparison of the absorption pattern to that of free anthracene shows that they are essentially similar with only a slight red shift in energy upon complexation to the gold(I) centre. The transition is therefore assigned as intraligand $\pi \rightarrow \pi^*$ transition in the anthryl unit, probably with some perturbation by the presence of the metal centre.

Upon photoexcitation, the anthracene-containing complexes show emission maxima at *ca.* 400–490 nm with vibrational progression spacings of *ca.* 1200 cm⁻¹. The photophysical data are collected in Table 4. The emission spectrum of **2** in

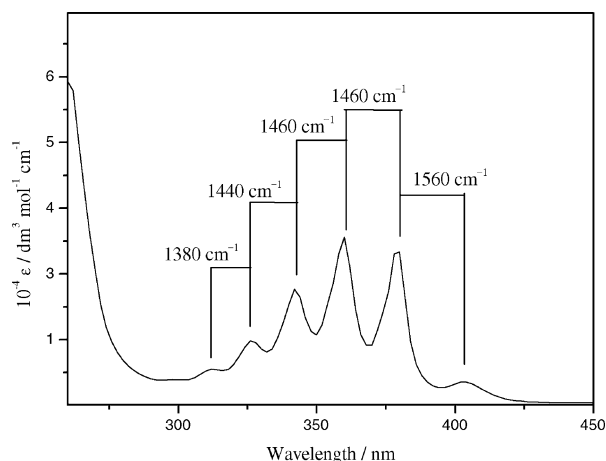
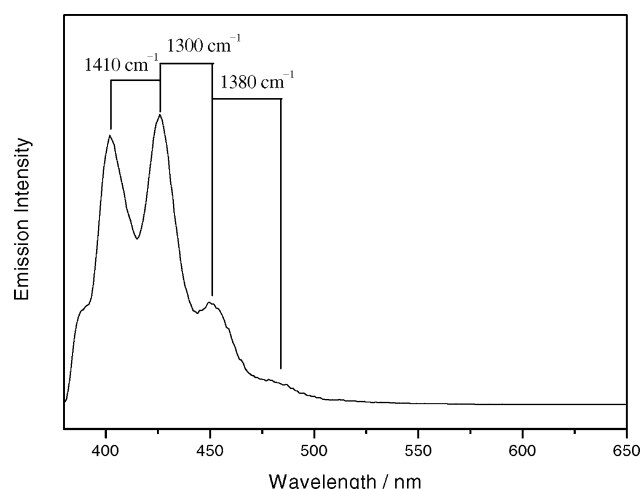


Fig. 3 Electronic absorption spectrum of **2** in dichloromethane at 298 K.

Table 4 Photophysical data for complexes 1–4

| Complex | Medium (T/K) | $\lambda_{\text{abs}}/\text{nm}(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$ | $\lambda_{\text{em}}/\text{nm}$ |
|---|---------------------------------------|--|---------------------------------|
| [(PPh ₃)Au(C ₉ H ₁₄)] (1) | CH ₂ Cl ₂ (298) | 280 (5880), 344 (3060), 360 (5590), 378 (8430), 400 (7600) | 385, 408, 427, 451sh |
| | Solid (298) | | 390, 440, 466 |
| [(dppm)Au ₂ (C ₉ H ₁₄) ₂] (2) | CH ₂ Cl ₂ (298) | 280 (8650), 312 (6430), 326 (12380), 342 (22220), 360 (35160), 380 (32300), 404 (4030) | 388sh, 402, 426, 451, 484sh |
| | Solid (298) | | 419, 442, 466 |
| [(dcpm)Au ₂ (C ₉ H ₁₄) ₂] (3) | CH ₂ Cl ₂ (298) | 270 (28330), 310 (11360), 326 (8040), 344 (9370), 360 (18760), 380 (15400), 402 (7450) | 383sh, 403, 426, 452, 483sh |
| | Solid (298) | | 419, 449, 466 |
| [(dcpm)Au ₂ Br(C ₉ H ₁₄)] (4) | Solid (77) | | 413, 438, 466 |
| | CH ₂ Cl ₂ (298) | 270 (19260), 310 (5680), 326 (5090), 344 (7210), 360 (12330), 380 (17070), 402 (11830) | 383sh, 403, 426, 452, 483 |
| | Solid (298) | | 449, 466, 481 |
| | Solid (77) | | 402, 426, 452 |

**Fig. 4** Emission spectrum of **2** in dichloromethane at 298 K.

dichloromethane at 298 K is shown in Fig. 4. The observation of vibronic structures in the emission band indicates that they are probably $\pi \rightarrow \pi^*$ intraligand in origin, which is characteristic of the anthracene moiety. The close resemblance of the emission to that of the free ligand with a slight red shift in energy in the gold(I) complexes is suggestive of an emission origin of metal-perturbed intraligand $\pi \rightarrow \pi^*$ character. The strong overlap of monomer and excimer emission in anthracene¹³ renders the assignment difficult. However, it is likely that the emission is dominated by monomeric emission, since complexes **2** and **3** emit at similar energies as that of **1** and **4** where only one anthryl unit is present. It is likely that the π - π interaction that appears in the solid state of **2** would not exist in solution.

Acknowledgements

V. W.-W. Y. acknowledges support from the University Development Fund of the University of Hong Kong and the University of Hong Kong Foundation for Educational Development and Research Limited. The work described in this paper has been supported by the Research Grants Council of the Hong Kong Special Administration Region, China (Project No. HKU7097/01P). We thank Dr K. K. Cheung for his help in crystal data collection and the preliminary structure determination. K.-L. C. and S.-K. Y. acknowledge the receipt of a postgraduate studentship administered by the University of Hong Kong.

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