Photoluminescent properties and molecular structures of [NaphAu(PPh_3)] and [μ-Naph {Au(PPh_3)}$_2$] ClO_4 (Naph = 2-naphthyl)†

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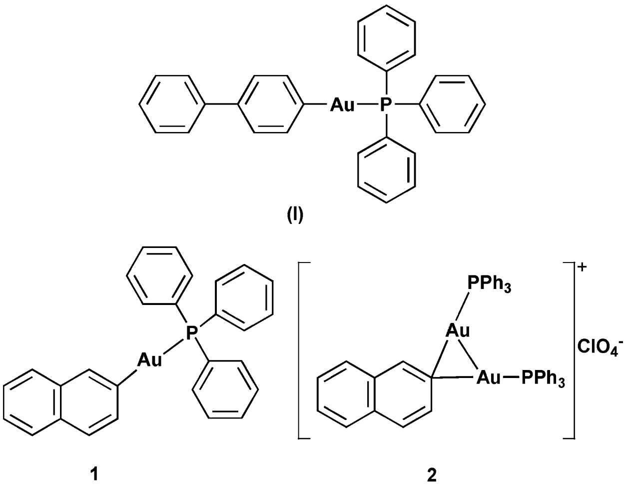
The complexes [NaphAu(PPh_3)], **1** and [μ-Naph{Au(PPh_3)}$_2$]ClO_4, **2** having the Au–C (aromatic) bond have been synthesized and characterized. The unique structure of **2** with two gold atoms bridged by a naphthyl group has been determined by X-ray crystallography. The intramolecular Au–Au separation in **2** is 2.7731(4) Å. Upon excitation at 266 nm, both complexes display intraligand phosphorescence at room temperature in solution and in solid state.

Introduction

There is growing interest in the synthesis of phosphorescent materials because of their potential application as luminescent dopants in OLED's and optsensing chemicals in biological systems, and various optelectronic devices.[1] According to a number of reports on the spectroscopic and photochemical studies of such materials, heavy atom effects[2] are often utilized for realizing room-temperature phosphorescence of aromatic molecules. The effects cause an increase in the rate constant of spin-forbidden processes, S→T and T→S, due to spin–orbit coupling induced by the internal[3] and/or external[4] heavy atoms. The merit to use heavy atom effects is an easy color determination by making choice of an organic chromophore with the desirable local triplet level.[4c]

Recently, we have reported the Au(I) complex which exhibits room-temperature phosphorescence from the locally excited triplet state of its polyaromatic ligand,^{3}LE (I in Scheme 1).[5c] The phosphorescence from this complex was clearly explained by the heavy atom effect of Au(I) attached to the polyaromatic unit through Au–C bond. During the course of this study,[5] an introduction of a triphenylphosphine gold(I) unit into an aromatic, making the metal–carbon bond, has a dramatic effect on the triplet state properties. The complex (I) was found to exhibit intense blue room temperature phosphorescence ($\Phi_p = 0.24$ and $\tau_T = 117$ μs) originated from the locally excited triplet of the biphenyl moiety (^{3}LE) in a degassed 2-methyltetrahydrofuran solution. On the assumption that $\Phi_{ST} = 1.0$ for I, the radiative rate constant (k_r) in the triplet state is calculated to be 2.06×10^3 s^{-1}.[5c] We envisaged that if two Au(I) units directly attach to the one carbon of the polyaromatic ligand, the more internal heavy atom effect may be attained, resulting in the higher yield of phosphorescence from the polyaromatic moiety at room temperature. The present paper reports the photophysics and photochemistry of the two type complexes[6] [2-naphthylAu(PPh_3)] and [μ-2-naphthyl(AuPPh_3)$_2$]ClO_4 (**1**, **2** in Scheme 1) composed of the naphthyl moiety and one or two triphenylphosphine gold(I) units.



Scheme 1

Experimental

General information

All reactions were carried out under the atmosphere of Ar, unless otherwise indicated. All solvents used for spectroscopic measurement, 2-methyltetrahydrofuran (2-MeTHF), tetrahydrofuran (THF), and dichloromethane were distilled prior to use. ^{1}H NMR, and ^{31}P NMR ware recorded using a JEOL EX-400 and a JEOL EX-500, respectively. ESI-MS spectra were recorded on a ThermoQuest Finnigan LCQ Duo mass spectrometer. Steady-state absorption and emission spectra were recorded by a Shimadzu UV-3100 and a RF-5300, respectively. The light-intensity distribution of a Xenon lamp has been corrected with the use of Rodamine B in ethyleneglycole and the wavelength-dependent characteristics of photomultiplier have been calibrated by $BaSO_4$ powder in the 300–600 nm. UV-vis absorption spectra of solid sample were measured on a SIS-50 optical waveguide spectrometer (System Instruments). For emission studies, dissolved dioxygen was removed by repeated freeze-pump-thaw cycles. The

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fluorescence quantum yields were determined by standard methods with quinine sulfate in 1 N H_2SO_4 ($\Phi_F = 0.546$) as references.[7] The O.D. of measured samples were adjusted to 0.06 (**1**; 3.7×10^{-6} M) at the excited wavelength, 266 nm. Solid-state phosphorescence quantum yields were determined with an absolute PL quantum yield mesurement system, C-9920-02 (HAMAMATSU). Laser photolysis studies were carried out with the use of a Nd:YAG laser (Sure Light 400 from Hoya Continuam Ltd.) equipped with second, third, and forth harmonic generators. Excitation light for lifetime measurements of phosphorescence was forth harmonics (266 nm): the duration and the energy of the laser pulse are 5 ns and 30 mJ/pulse, respectively. The monitoring system for the decay of phosphorescence as well as transient absorption spectra has already been reported elsewhere.[8]

Preparations

[2-naphthylAu(PPh$_3$)], 1. The synthetic method for **1** is analogous to that previously reported.[5c] Au(PPh$_3$)Cl was synthesized according to literature.[9] To a solution of 2-bromonaphthalene (100 mg, 0.48 mmol) in THF (5 ml) cooled below −70 °C, *n*-BuLi (0.31 ml, 1.63 M in hexane) was added *via* micro-syringe. After 10 min, a solution of Au(PPh$_3$)Cl (201 mg, 0.41 mmol) in THF (12 ml) was added slowly. After stirring for 30 min at −70 °C, the reaction mixture was allowed to warm to room temperature. Then, the solvent was removed under vacuum. Recrystallization of the crude product from the diethylether solution afforded analytical pure complex **1** as colorless crystals.

1. Yield: 168 mg, 70%; ^1H NMR (400 MHz, $CDCl_3$): δ 8.053 (d, J(P, H) = 5.87 Hz, 1H, H_1), 7.755–7.744 (m, 4H, $H_{3,4,5,8}$), 7.668–7.597 (m, 6H, H_{ph}), 7.536–7.439 (m, 9H, H_{ph}), 7.402–7.297 (m, 2H, $H_{6,7}$); $^{31}P\{^1H\}$ NMR (160 MHz): δ 43.77(s) in CD_2Cl_2, δ 43.80(s) in d_8-THF; Anal. Calcd for $C_{28}H_{22}Au_1P_1$: C, 57.35; H, 3.78; P, 5.28. Found C, 57.51; H, 3.87; P, 5.11.

[μ-2-naphthyl(AuPPh$_3$)$_2$]ClO$_4$, 2. The synthetic methodology for **2** is analogous to the reference.[6c] To a solution of the complex **1** (150 mg, 0.25mmol) in ether (30 ml) at −50 °C, neat $HClO_4$ (176 μl) was added *via* micro-syringe. After 10 min stirring the white precipitate was filtered off and washed with cold ether. Recrystallization of the crude product from THF solution gave pure complex **2** as light yellow crystals.

2. Yields: 95 mg, 66%; ESI-MS: *m/z* 1045.8 $[M\text{-}ClO_4]^+$; $^1P\{^1H\}$ NMR (160 MHz): δ 36.41 (s) in CD_2Cl_2, δ 45.13(s) and 35.99 (s) in d_8-THF; Anal. Calcd for $C_{46}H_{37}Au_2Cl_1O_4P_2$: C,48.25; H, 3.26; P, 5.41. Found C, 48.61; H, 3.48; P, 5.32.

Crystal structure determinations

The crystallographic data and the results of the structure refinements are summarized in Table 1. In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections were made.[10] The structures were solved by the direct method (SIR2004).[11] All non-hydrogen atoms were refined with anisotoropic thermal parameters. Hydrogen atoms were fixed at calculated positions.

Table 1 Crystallographic data for **1** and **2**

	1	2
Formula	$C_{28}H_{22}AuP$	$C_{46}H_{37}Au_2ClO_4P_2$
Formula weight	586.42	1145.1
Cryst syst	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	16.523(2)	14.5352(14)
b/Å	10.0926(15)	13.7991(13)
c/Å	14.4157(18)	20.974(2)
β/deg	114.104(4)	103.2925(15)
V/Å^3	2194.4(5)	4094.2(7)
Z	4	4
d_{calcd}/g cm^{-3}	1.775	1.858
T/K	213	90.0
Radiation	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
μ/cm^{-1}	6.813	7.370
Diffractometer	Rigaku RAXIS IV	Rigaku AFC-8
Max 2θ/deg	55	60
Reflns collcd	16914	82832
Indep reflns	4973 (Rint = 0.043)	11963 (Rint = 0.057)
No. of param refined	272	497
$R1$, $wR2$ ($I > 2\sigma I$)	0.0281, 0.0721	0.0543, 0.1360
S	1.095	1.144

Results and discussion

Synthesis and crystallographic results

The structures of **1** and **2** determined by X-ray crystallography are shown in Fig. 1. Crystal and data collection parameters are given in Table 1, and representative structural parameters are summarized in Table 2. The Au atom in the molecule **1** adopts almost linear coordination geometry due to d^{10} electron configuration, the corresponding bond angle is 177.90(10)°. The bond distances of Au–P and Au–C are typical values for aryl

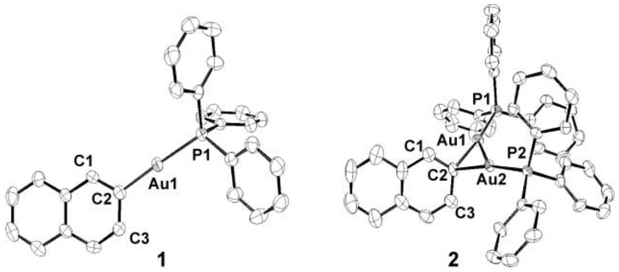


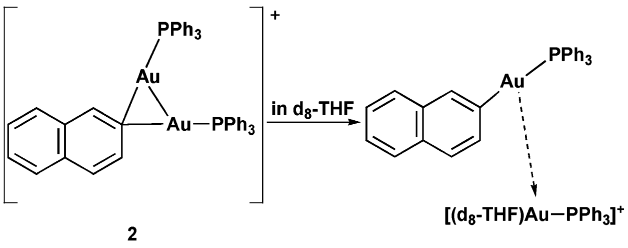
Fig. 1 The X-ray structures of **1** and **2**; (elliposoids at 50%, H atoms and counter anion, ClO_4^- in **2** are excluded for clarity).

Table 2 Selected bond distances (Å) and angles (deg) for **1** and **2**

	1	2
Bond distances (Å)		
Au1–P1	2.2975(8)	2.271(2)
Au1–C2	2.040(3)	2.126(5)
Au2–P2	—	2.272(2)
Au2–C2	—	2.140(5)
Au1–Au2	—	2.7731(4)
Bond angles (deg)		
C2–Au1–P1	177.90(10)	168.8(2)
C2–Au1–P2	—	169.4(2)
Au1–C2–Au2	—	81.1(2)
C1–C2–C3	115.8(3)	118.0(5)

phosphine gold(I) complexes,[3b,5c],[12] the corresponding distances are 2.2975(8) and 2.040(3) Å for Au–P and Au–C, respectively, in **1**. The naphthyl ring of the present compounds displays a slightly distorted angle of 115.8(3)° at the C2 carbon. Such distortions are a common feature of aryl phosphine gold(I) complexes (Fig. 1 and Table 2).[3b,5c,12] The long Au$\cdots$Au distance in the crystal lattices of **1** suggests that the intermolecular Au$\cdots$Au interaction is negligibly small. In the molecule **2**, the Au1–Au2 distance (2.7731(4) Å) is shorter than that in metallic gold (2.88 Å) because of gold-gold bonding. In addition, the distorted P–Au–C*ipso* angles from the linear configuration also support the existence of the Au–Au bond, the angles are 168.8(2)° and 169.4(2)° for P1–Au1–C2 and P2–Au2–C2, respectively. Two Au atoms are bonded to C2 almost equivalently and the plane of the C2–Au1–Au2 triangle is approximately perpendicular to that of naphthyl unit, the angle is 83.2(3)°. The bond style in the triangle C2–Au1–Au2 is considered to be a three-centre two-electron (3c-2e) bond on the basis of the following aspects: (i) the angle, 81.1(2)°, at the bridging carbon (Au1–C2–Au2) is acute,[13] (ii) the Au1–C2 and Au2–C2 bonds (2.126(5) and 2.140(5) Å) are longer than the normal 2c–2e bonds (2.04–2.08 Å) between Au and aryl groups.[5c,12] This binuclear structure in **2** resembles the known structurally characterized complexes with two gold atoms bridged by an aryl group.[14] The formations of such triangle fragments have been often found in the multimetallic supramolecular systems.[15]

The structure of **2** in solutions is, however, complicated. ^{31}P NMR spectrum of **2** in CD_2Cl_2 taken at 297 K exhibits only one signal (δ 36.41 ppm with H_3PO_4 as external standard), indicating that **2** adopts the symmetrical C*ipso*-Au1-Au2 triangle structure. On the other hand, in d_8-THF solution, two signals of the same intensity due to the two non-equivalent phosphorous atoms (δ 45.13 ppm and δ 35.99 ppm) are observed. The former signal is near to that of **1** (δ 43.8 ppm) and the latter is close to that of cationic Au-phosphine complex,[16] [AuPPh$_3$]$^+$ (δ 33.8 ppm) in d_8-THF. The structure of **2** in d_8-THF might be written as Scheme 2.



Scheme 2

The proposed structure in Scheme 2 can be regarded as a intermediate in the another synthetic route of the type **2** complex; [AuPPh$_3$]ClO$_4$ + NaphAuPPh$_3$ (**1**) → μ-Naph(AuPPh$_3$)$_2$ClO$_4$ (**2**).[6c] THF molecules might contribute to stabilize the cationic structure, [AuPPh$_3$]$^+$ by coordination.

Photophysical properties of 1 and 2 in solid state

The UV/Vis and emission data of **1** and **2** in solid state are summarized in Fig. 2 and Table 3. The structured absorption band (280–310 nm) of **1** is originated from the naphthalene moiety as shown in Fig. 2. The absorption band of **2** (300–350 nm) is slightly red-shifted compared to that of **1**. No MLCT band and [$d_{\sigma*} \rightarrow p_{\sigma}$] transition band[17] based on polynuclear d^{10}–d^{10} system can been seen in the wavelength region 240–400 nm. Upon excitation at 266 nm, **1** and **2**, in both solution and solid state at room temperature, afford emission spectra very similar to the phosphorescence spectrum of naphthalene (Fig. 2 and Table 3). Though the complex **1** shows weak green emission, the complex **2** displays more intense yellow green structured phosphorescence.‡ The quantum yield of **2** (0.19) is twice larger than that of **1** (0.08) (Table 3). These observations clearly suggest that the triangle structure, C*ipso*-Au1-Au2 is a strong heavy atom perturber for realizing room-temperature phosphorescence in solid state.

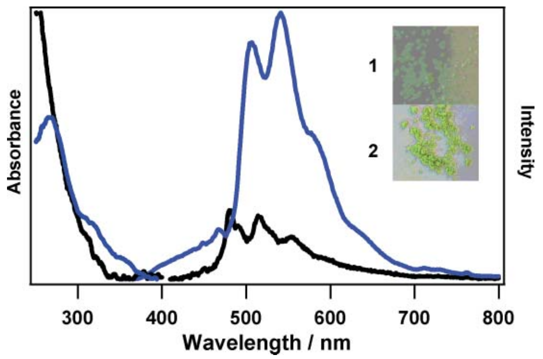


Fig. 2 Electronic absorption and emission spectra of **1** (full) and **2** (blue) in solid state at 298 K ($\lambda_{ex} = 266$ nm). Intensities of emission spectra were adjusted arbitrarily for clarity. The inset pictures are shown for the emissions of **1** and **2** in microcrystalline solid at ambient temperature under UV lamp ($\lambda_{ex} = 254$ nm).

Photophysical properties of 1 and 2 in solutions

The absorption spectra of 2-bromonaphthalene, **1**, and **2** in 2-MeTHF are shown in Fig. 2. 2-Bromonaphthalene displays the structured band at 260–300 nm. Complexes **1** and **2** show almost same spectra of which the first absorption band at ca. 280–310 nm are slightly red-shifted in comparison to that of 2-bromonaphthalene. The moderately strong absorption of **2** at 300–350 nm in the solid-state (blue in Fig. 2) disappears in the 2-MeTHF solution.

As shown in Fig. 3, the Au(I) complex (**1**) shows intense green emission at 479, 514, 555 nm in degassed 2-MeTHF at 298 K. This emission is assigned to room-temperature phosphorescence from naphthalene chromophore (^{3}LE) of **1** on the basis of the following observations: (1) the lifetime of the emission is as long as 124 μs (Table 3), (2) the emission is substantially quenched in the presence of oxygen, and (3) the emission spectrum with the vibronic structure agrees well with that of phosphorescence spectrum of 2-bromonaphthalene at 77 K (Fig. 3). It is noteworthy that fluorescence from the naphthalene moiety is very weak for **1** and **2**.

These observations suggest that the strong spin–orbit interaction caused by the Au atom ($Z = 79$) in **1** leads to (1) an efficient intersystem crossing from the singlet to the triplet excited state and (2) the large k_r value of the naphthyl chromophore at T_1 by

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‡ When the microcrystalline sample of **2** is pounded in a mortar, it exhibits intense structureless yellow phosphorescence. This observation indicates the polymorphs of **2**.[17b]

Table 3 Photophysical data for **1** and **2**

Complex	Medium (T/K)	λ_{abs}/nm ($\varepsilon \times 10^{-3}$/M^{-1}cm^{-1})	λ_{ph}/nm^{a} (τ_0/µs)	Φ_p
[2-naphthylAu(PPh$_3$)] **1**	Microcrystalline solid (297)	—^{e}	480 (27, 1.9)^{b,c}	0.08
	2MeTHF (297)	242(55), 290(sh), 300(sh)	479 (124)	0.20
	2MeTHF (77)	—	476	—
	CH_2Cl_2 (297)	242(58), 290(sh), 300(sh)	481 (92)^{d}	0.27^{d}
[µ-2-naphthyl(AuPPh$_3$)$_2$]ClO$_4$ **2**	Microcrystalline solid (297)	266, 312(sh), 353(sh)	507 (38, 2.8)^{b}	0.19
	2MeTHF (297)	243(56), 268(sh), 275(sh), 287(sh), 300(sh)	479 (56)	0.10
	2MeTHF (77)	—	476	—
	CH_2Cl_2 (297)	261(50), 300(sh), 312(10), 350(sh)	507 (12)^{d}	>0.03

[a] λ(0,0). [b] Two-component. [c] Weak. [d] Decomposed during measurement. [e] Very broad.

partial removal of the spin-forbidden nature of the T_1-S_0 radiative transition.

The radiative rate constant, k_r, at T_1 is formulated as eqn (1)

$$k_r = \Phi_P/(\tau_T\Phi_{ST}) \qquad (1)$$

The Au(I) complex (**1**) affords, $\Phi_p = 0.20$ and $\tau_T = 124$ µs in 2-MeTHF at 298 K. Since the fluorescence yield of **1** is very small ($\Phi_f < 10^{-3}$), we assumed $\Phi_{ST} = 1.0$ for **1**. With the use of eqn (1) and $\Phi_{ST} = 1.0$ for **1**, k_r is calculated to be 1.61×10^3 s^{-1}. This value is *ca.* 2 order of magnitude larger than the radiative rate constant of the triplet 2-bromonaphthalene (56.8 s^{-1}: $\lambda_{ex} = 307$ nm).[18] Thus, the coordinated Au(I) atom is concluded to give a markedly large heavy-atom effects on k_r of the naphthalene chromophore in **1**.

The absorption and phosphorescence spectra of the binuclear gold complex (**2**) closely resembles those of **1** (Fig. 3 and Table 3), suggesting **2** takes a mononuclear structure in 2-MeTHF solution at room temperature (Scheme 2). This observation is well consistent with ^{31}P NMR results in d$_8$-THF. The experimental phosphorescence quantum yield (0.10) of **2** (completely divided into **1** and [Au(PPh$_3$)]$^+$) in 2-MeTHF is close to the calculated value (0.12) based on Φ_p of **1** in 2-MeTHF and ε values of **1** and **2** at 266 nm (Table 3).

Fig. 4 shows emission spectra of **1** and **2** in degassed 2-MeTHF at 77 K. The vibrational structures of the phosphorescence spectrum of **1** (full) are more sharp than those at 298 K. The phosphorescence spectrum of **2** (blue) at 77 K is found to be composed of two spectra: one is the spectrum of **1** at 77 K and another, an additional spectrum. The additional spectrum is obtained by subtracting the phosphorescence spectrum of **1** from that of **2** at 77 K. Here the spectra of **1** and **2** at 77 K are normalized at 476 nm before subtraction. The difference spectrum (dashed red), thus obtained, is very similar to the phosphorescence spectrum of **2** in solid state at 297 K (blue in Fig. 2), indicating both binuclear and mononuclear structures of **2** exists in 2-MeTHF at 77 K (Scheme 3).

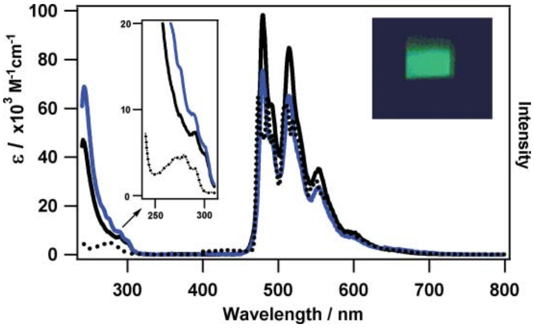


Fig. 3 Electronic absorption spectra of 2-bromonaphthalene (dashed), **1** (full) and **2** (blue) in 2-MeTHF at 298 K. Emission spectra of **1** (full) and **2** (blue) in degassed 2-MeTHF at 298 K ($\lambda_{ex} = 266$ nm). The luminescence spectrum of 2-bromonaphthalene in 2-MeTHF at 77 K ($\lambda_{ex} = 266$ nm). Intensities of emission spectra were adjusted arbitrarily for clarity. The inset picture displays phosphorescence of degassed 2-MeTHF solution of **1** at 298 K.

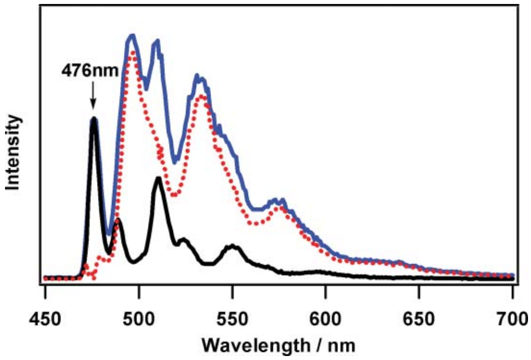
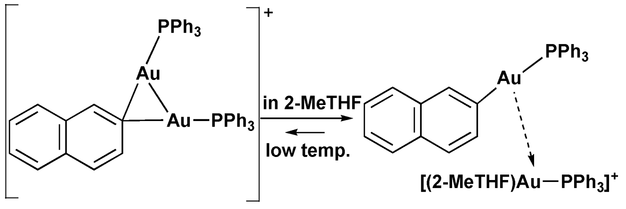


Fig. 4 Emission spectra of **1** (full) and **2** (blue) in 2-MeTHF at 77 K (λ_{ex} = 266 nm) and the difference spectrum (dashed red) between **1** and **2** under the condition that two spectra were normalized at 476 nm. Intensities of emission spectra were adjusted arbitrarily for clarity.



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Scheme 3

In CH_2Cl_2 solutions, the absorption spectra of the Au complexes, **1** and **2**, are very different each other (Fig. 5). In comparison with **1**, the absorption band at 300–350 nm of **2** is markedly red-shifted. The features of each absorption spectra in CH_2Cl_2 bear a strong resemblance to those in the solid state.

The Au complex (**1**) shows intense green emission in degassed CH_2Cl_2 at 298 K as seen in 2-MeTHF solution. The phosphorescence quantum yield of **1** in CH_2Cl_2 is larger than that in

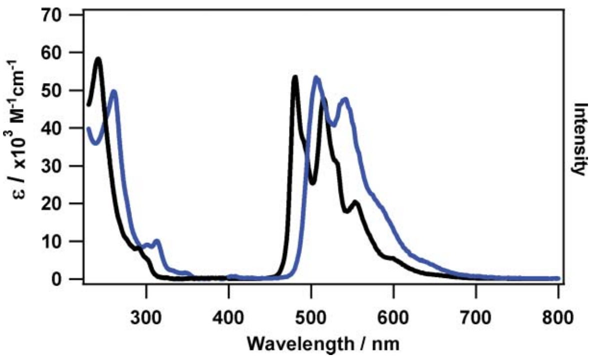

Fig. 5 Electronic absorption and emission spectra of **1** (full) and **2** (blue) in degassed CH_2Cl_2 at 298 K ($\lambda_{ex} = 266$ nm). Intensities of emission spectra were adjusted arbitrarily for clarity.

2-MeTHF (Table 3). The binuclear gold complex (**2**) shows yellow green emission at 507, 541 nm, slightly red-shifted compared with **1** (Fig. 5). This red shift is probably caused by the substituent effect of the second gold(I) phosphine unit. The green emission of **1** and yellow green emission of **2** can be assigned to the phosphorescence from the naphthalene moiety. Both complexes **1** and **2** are unstable in CH_2Cl_2 solution. They gradually decomposed during the life time measurement of phosphorescence.§

Conclusion

The two type complexes [2-naphthylAu(PPh_3)] and [μ-2-naphthyl($AuPPh_3$)$_2$]ClO_4 (**1**, **2**) have been synthesized and characterized by X-ray crystallography. Two complexes show intraligand phosphorescence from the naphthyl unit (^{3}LE) at room-temperature in both solutions and solid state. In the solid state, the dinuclear complex **2** exhibits more intense phosphorescence than the mononuclear complex **1**, suggesting the triangle structure, C*ipso*–Au1–Au2 can be regarded as an effective heavy atom perturber for realizing room-temperature phosphorescence. In 2-MeTHF solution, the mononuclear complex (**1**) shows intense green room temperature phosphorescence ($\Phi_p = 0.20$ and $\tau_T = 124$ μs) from the locally excited triplet of the naphthalene moiety (^{3}LE). Since the complex **2** exists as an equilibrium mixture of dinuclear and mononuclear structures in 2-MeTHF at 77 K, it exhibits the mixed phosphorescence spectrum from the two structures.

Acknowledgements

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Notes and references

1 (*a*) For selected reviews, see: R. C. Evans, P. Douglas and C. J. Winscom, *Coord. Chem. Rev.*, 2006, **250**, 2093–2126; (*b*) M. A. Baldo, M. E. Thompson and S. R. Forrest, *Pure Appl. Chem.*, 1999, **71**, 2095–2106; (*c*) I. Sanchez-Barragan, J. M. Costa-Fernandez, A. Sanz-Medel, M. Valledor and J. C. Campo, *Trends Anal. Chem.*, 2006, **25**, 958–967; (*d*) J. Kuijt, F. Ariese, Udo, A. Th. Brinkman and C. Gooijer, *Anal. Chim. Acta*, 2003, **488**, 135–171.

2 (*a*) For selected reviews, see: K. N. Solovyov and E. A. Borisevich, *Physics-Uspekhi*, 2005, **48**, 231–253; (*b*) M. A. Omary, A. A. Mohamed, M. A. Rawashdeh-Omary, Manal and J. P. Fackler, *Coord. Chem. Rev.*, 2005, **249**, 1372–1381.

3 (*a*) B.-C. Tzeng, D. Li, S.-M. Peng and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 2365–2371; (*b*) X. Hong, K.-K. Cheung, C.-X. Guo and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1994, 1867–1871; (*c*) C.-M. Che, H.-Y. Chao, V. M. Miskowski, Y. Li and K.-K. Cheung, *J. Am. Chem. Soc.*, 2001, **123**, 4985–4991; (*d*) H.-Y. Chao, W. Lu, Y. Li, M. C. W. Chan, C.-M. Che, K.-K. Cheung and N. Zhu, *J. Am. Chem. Soc.*, 2002, **124**, 14696–14706; (*e*) M. A. Omary, M. A. Rawashdeh-Omary, H. V. K. Diyabalanage and H. V. Rasika Dias, *Inorg. Chem.*, 2003, **42**, 8612–8614; (*f*) D. V. Partyka, M. Zeller, A. D. Hunter and T. G. Gray, *Angew. Chem., Int. Ed.*, 2006, **45**, 8188–8191.

4 (*a*) S. Hamai, *J. Am. Chem. Soc.*, 1989, **111**, 3954–3957; (*b*) M. R. Haneline, M. Tsunoda and F. P. Gabbai, *J. Am. Chem. Soc.*, 2002, **124**, 3737–3742; (*c*) M. A. Omary, R. M. Kassab, M. R. Haneline, O. Elbjeirami and F. P. Gabbai, *Inorg. Chem.*, 2003, **42**, 2176–2178; (*d*) C. N. Burress, M. I. Bodine, O. Elbjeirami, J. H. Reibenspies, M. A. Omary and F. P. Gabbai, *Inorg. Chem.*, 2007, **46**, 1388–1395.

5 (*a*) M. Osawa, M. Hoshino, M. Akita and T. Wada, *Inorg. Chem.*, 2005, **44**, 1157–1159; (*b*) M. Osawa, M. Hoshino, T. Wada, Y. Araki and O. Ito, *Chem. Phys. Lett.*, 2006, **427**, 338–342; (*c*) M. Osawa, M. Hoshino and D. Hashizume, *Chem. Phys. Lett.*, 2007, **436**, 89–93.

6 (*a*) Complexes **1** and **2** are known: A. N. Nesmeyanov, E. G. Perevalova, O. G. Afanasova, M. V. Tolstaya and K. I. Granberg, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1978, **5**, 1118–1122; (*b*) R. Uson, A. Laguna and P. Brun, *J. Organomet. Chem.*, 1979, **182**, 449–454; (*c*) R. Uson, A. Laguna and P. Brun, *J. Organomet. Chem.*, 1980, **197**, 369–373.

7 (*a*) W. M. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229–235; (*b*) D. F. Eaton, *Pure Appl. Chem.*, 1988, **60**, 1107–1114.

8 M. Hoshino, H. Sonoki, Y. Miyazaki, Y. Iimura and K. Yamamoto, *Inorg. Chem.*, 2000, **39**, 4850–4857.

9 N. Mézailles, L. Ricard and F. Gagosz, *Org. Lett.*, 2005, **19**, 4133–4136.

10 T. Higashi, *Program for absorption correction*, Rigaku Corp.Tokyo, Japan, 1995.

11 M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *SIR2004*, 2005.

12 K. A. Porter, A. Schier and H. Schmidbaur, in *Perspectives in Organometallic Chemistry, Special Publication No. 287*, ed. B. R. Steele and C. G. Screttas, The Royal Society of Chemistry, Cambridge, 2003, pp. 74–85.

13 (*a*) R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, 1967, **89**, 3121–3126; (*b*) J. F. Malone and V. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1970, 2646–2648.

14 (*a*) S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1983, 1304–1306; (*b*) R. Uson, A. Laguna, E. J. Fernandez, A. Mendia and P. G. Jones, *J. Organomet. Chem.*, 1988, **350**, 129–138.

15 (*a*) E. Cerrada, M. Contel, A. D. Valencia, M. Laguna, T. Gelbrich and M. B. Hursthouse, *Angew. Chem., Int. Ed.*, 2000, **39**, 2353–2356; (*b*) E. J. Fernandez, A. langna, J. M. Lopez-de-Luzuriaga, M. Montiel, M. E. Olmos, J. Perez and R. C. Puelles, *Organometalics*, 2006, **25**, 4307–4315.

16 N. C. Payne, R. Ravindranath, G. Schoettel, J. J. Vittal and R. J. Puddephatt, *Inorg. Chem.*, 1991, **30**, 4048–4053.

17 (*a*) For selected reviews, see: V. W.-W. Yam and K. K.-W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323–334; (*b*) A. L. Balch, in *Structure & Bonding vol. 123*, ed. V. W.-W. Yam, Springer, Berlin - Heidelberg, 2007, pp. 1–40.

18 J. C. Miller, J. S. Meek and S. J. Strickler, *J. Am. Chem. Soc.*, 1977, **99**, 8175–8179.

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§ Complex **1** decomposes to naphthalene and Au(PPh_3)Cl *via* the homolytic cleavage of the Au–C bond under irradiation in CH_2Cl_2.[5c] Since this photo reaction occurs even under the aerobic condition, we consider that the excited singlet state is responsible for this dissociation reaction. The quantum yield of this dissociation reaction is 0.03. Though the complex **2** decomposes with purple deposits in CH_2Cl_2 in short period, the decomposition is more slowly in 2-MeTHF. With decomposition, phosphorescence intensity decreases and fluorescence intensity of naphthalens (at 310–400 nm) increases.