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Synthesis and Characterization of Phenanthrylphosphine Gold Complex: Observation of Au-Induced Blue-Green Phosphorescence at Room Temperature

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A new 9-diphenylphosphinophenanthrene ligand (9DPP, **1**), its oxide (9DPPO, **2**), and its gold complex [(AuCl(9DPP)] (**3**) were synthesized. The Au(I) complex **3** was found to exhibit intense blue-green, room-temperature phosphorescence ($\Phi_p = 0.06$ and $\tau_T = 22.7\ \mu$s) originating in the locally excited triplet of the phenanthrene moiety (^{3}LE) in degassed 2-methyltetrahydrofuran solution. On the assumption that $\Phi_{ST} = 1.0$ for **3**, the radiative rate constant (k_r) in the triplet state is calculated to be 2.6×10^3 s^{-1}. This value is 4 orders of magnitude larger than the radiative rate constant of the triplet phenanthrene (0.26 s^{-1}). Thus, the coordinated Au(I) atom is concluded to have a markedly large heavy-atom effect on k_r of the phenanthrene chromophore in **3**.

In recent years, phosphorescent heavy metal complexes have attracted considerable interest[1] partly because of their importance as efficient luminescent dopants in organic light-emitting diodes (OLEDs).[2] These complexes exhibit strong room-temperature phosphorescence, mostly originating in terms of the ^{3}MLCT (metal to ligand charge-transfer) excited state, which is located in energy below the locally excited triplet state of the organic ligand, ^{3}LE.

A limited number of examples which emit visual phosphorescence from ^{3}LE at room-temperature include metal complexes[3a] with a heavy metal such as Pd, Pt, or Rh, in which the metal acts as a heavy atom perturber. In general, phosphorescence of polyaromatics including free porphyrins is usually not observed at room temperature because of the fact that the nonradiative rate constant, k_{nr} ($=10^2-10^3$ s^{-1}), of the aromatics is much larger than the radiative rate constant, k_r ($=10^{-1}-10^{-2}$ s^{-1}), of the T$_1$ state.[4] With the use of the triplet yield, Φ_{ST}, and the lifetime, τ_T ($=k_T^{-1} = 1/(k_r + k_{nr})$), the phosphorescence yield Φ_P, is expressed as

$$\Phi_P = \Phi_{ST} k_r \tau_T \tag{1}$$

Equation 1 implies that a large k_r value is favorable for the observation of visual room-temperature phosphorescence. The increase in k_r in the T$_1$ state of the aromatics can be attained by either external[5] and/or internal[3,4] heavy atom effects. Although enhanced spin−orbit coupling by heavy atom effects affords an increase in not only k_r and Φ_{ST}, but also k_{nr}, the increase in k_r and Φ_{ST} is essentially important for observation of room-temperature phosphorescence from the aromatics. This paper reports on room-temperature phosphorescence from an aromatic ligand observed with gold(I) complex, in which the heavy atom, Au(I), is coordinated to a phosphorus atom in a newly synthesized diphenylphosphino-phenanthrene[6] ligand.

The syntheses of the ligand and the related compounds are as follows. Lithiation of 9-bromophenanthrene with

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(1) For selected examples, see: (a) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647. (b) Yam, V. W. W.; Li, C. K.; Chan, C. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2857. (c) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2001**, *40*, 1704. (d) Yam, V. W. W.; Chan, C.-L.; Li, C.-K.; Wong, K. M.-C. *Coord. Chem. Rev.* **2001**, *216*−*217*, 173. (e) Lee, Y.-A.; McGarrah, J. E.; Lachicotte, R. J.; Eisenberg, R. *J. Am. Chem. Soc.* **2002**, *124*, 10662.

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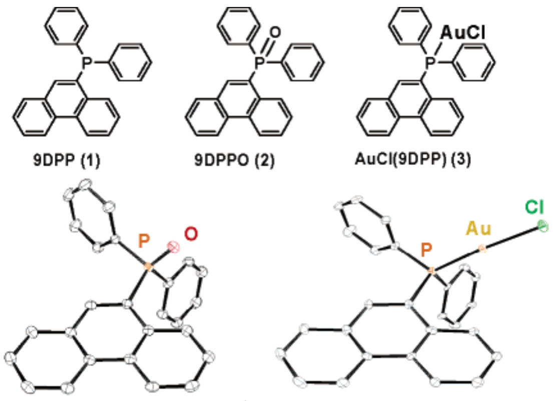

Figure 1. The structures of **1**, **2**, and **3**.

n-BuLi in THF took place smoothly and was followed by addition of an equimolar amount of PClPh$_2$. After chromatographic purification, the desired ligand (9DPP, **1**) was obtained as a white powder. Compound **1** is fairly stable in CHCl$_3$ and does not react with oxygen in the dark. However, upon illumination with UV light, **1** is readily converted to its oxide (9DPPO, **2**). An authentic sample of **2** was prepared by oxidation of **1** with hydrogen peroxide.[6a]

The Au complex (**3**) was prepared by the reaction of AuCl(Me$_2$S)[7] with a stoichiometric amount of **1** in dichloromethane to give a white powder in high yield. Analytically pure compounds (**1**−**3**) have been characterized by ^{1}H NMR, ^{31}P NMR, and MS spectroscopy.

The structures of **2** and **3** determined by X-ray crystallography are shown in Figure 1.[8] The two structures including the geometry near the P atom are very similar. The bond lengths of Au−P and Au−Cl are 2.236(1) and 2.302(1) Å, respectively. These values are identical with those of the structural analogue, [AuCl(PR$_3$)] (R = Ph,[9a] Me,[9b] ^{i}Pr[9b]).

Absorption spectra of **1**−**3** in CH$_2$Cl$_2$ are shown in Figure 2. In comparison with the absorption spectrum of phenanthrene (PT), the phosphorus substitution in **1**−**3** commonly induces a red shift of the absorption bands of the phenanthrene chromophore. Because of the absence of lone pair electrons at the phosphorus atom, the absorption spectra of **2** and **3** are very similar. The molecular absorption coefficients (ϵ's) for the first absorption bands of **2** and **3** (320−360 nm) are ca. 2 times that of PT.

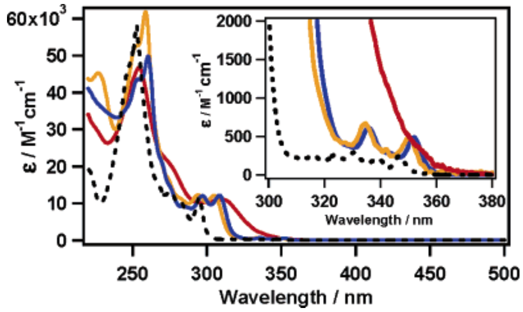

Figure 2. Absorption spectra of phenanthrene (- - -), **1** (red), **2** (yellow), and **3** (blue) in CH$_2$Cl$_2$.

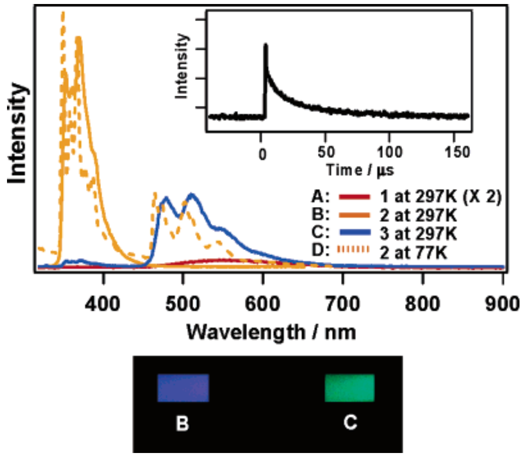

Figure 3. Emission spectra A−D in degassed 2-MeTHF (λ_{exc} = 300 nm). The inset shows the decay profile of emission observed for **3** after 266 nm laser pulse at 297 K. The initial spike observed immediately after the pulse is due to fluorescence. The picture displays luminescence of degassed 2-MeTHF solutions of B and C at 297 K.

Figure 3 shows emission spectra of **1**−**3** observed in degassed 2-methyltetrahydrofuran (2-MeTHF) (**1**−**3**, at 297 K; **2**, at 77 K). Fluorescence of **1** at 297 K shows a weak and broad band centered at ca. 550 nm, and the Stokes' shift is as large as ca. 14000 cm^{-1} (A in Figure 3). This featureless fluorescence is tentatively assigned to the ICT (intramolecular charge-transfer) fluorescence from the diphenylphosphino group to the PT moiety on the basis of the marked red-shift in polar solvents.[10,11] In sharp contrast to **1**, **2** and **3** do not display the ICT fluorescence.

The fluorescence spectrum of **2** observed at 298 K (B in Figure 3) is almost identical with that of PT suggesting that a strong emission band in the region of 360−410 nm is attributed to fluorescence from the locally excited singlet state of the PT moiety in **2**, ^{1}LE. The fluorescence quantum

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(6) Several diphenylphosphino substituted polyaromatic fluorescent materials have been reported, see: (a) Akasaka, K.; Suzuki, T.; Ohrui, H.; Meguro, H. *Anal. Lett.* **1987**, 731. (b) Heuer, L.; Schmultzler, R. *J. Fluorine Chem.* **1988**, *39*, 197. (c) Padmaperuma, A. B.; Schmett, G.; Forgarty, D.; Washton N.; Nanayakkara, S.; Sapochak, L.; Ashworth, K.; Madrigal, L.; Reeves, B.; Spangler, C. W. *Mater. Res. Soc. Symp. Proc.* **2000**, *621*(Electron-Emissive materials, Vacuum Microelectronics and Flat-Panel Displays), Q3.9.1−Q3.9.6. (d) Yip, J. H. K.; Probhavathy, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2159. (e) Fei, Z.; Kocher, N.; Mohrschladt, C. J.; Ihmels, H.; Stalke, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 783.

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(8) X-ray data were collected at 100.2 K on a Rigaku RAXIS-CS Imaging Plate diffractometer with Mo Kα radiation. Structure solutions were obtained by standard Patterson and difference Fourier methods and refined on F^2. 9DPPO: a = 9.0031(6) Å, b = 10.5751(8) Å, c = 11.1424(7) Å, α = 80.126(2)°, β = 73.148(2)°, γ = 75.032(2)°, V = 975.5(1) Å^3, triclinic $P\bar{1}$, Z = 2, $\theta_{min/max}$ = 1.90/30.3°, 5180 unique observed reflections were used to refine 253 atomic parameters and gave a final R factor of 0.0674. AuCl(9DPP): a = 8.9688(5) Å, b = 10.9280(5) Å, c = 11.7414(7) Å, α = 91.210(3)°, β = 109.454(2)°, γ = 97.417(3)°, V = 1073.5(1) Å^3, triclinic $P\bar{1}$, Z = 2, $\theta_{min/max}$ = 1.80/30.3°, 5781 unique observed reflections were used to refine 262 atomic parameters and gave a final R factor of 0.0423.

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yield of **2** ($\Phi_F = 0.17^{12}$ in 2-MeTHF) at 297 K is higher than that of PT ($\Phi_F = 0.06^{12}$ in 2-MeTHF). At 77 K, the phosphorescence spectrum with peaks at 470, 502, and 540 nm is observed for **2** (D in Figure 3), and the phosphorescence lifetime is determined to be ca. 5 s. The phosphorescence spectrum is very similar to that of PT, indicating that phosphorescence originates in the locally excited triplet of the PT moiety in **2**, ^{3}LE.

The Au complex (**3**) in degassed 2-MeTHF demonstrates blue-green emission at ca. 500 nm at 297 K (C in Figure 3). This emission is attributed to room-temperature phosphorescence from phenanthrene chromophore (^{3}LE) of **3** on the basis of the following observations: (1) the lifetime of the emission is as long as 22.7 μs, and (2) the emission spectrum with the vibronic structure (intervals are ca. (1.3−1.4) × 10^3 cm^{-1}) agrees well with that of the phosphorescence spectrum of PT at 77 K. It is noteworthy that fluorescence from the phenanthrene chromophore in **3** is very weak.

As mentioned above, room-temperature phosphorescence of the Au(I) complex (**3**) in 2-MeTHF occurs from the phenenthrene chromophore. Presumably, the MLCT state of the Au complex (**3**) is located higher in terms of energy than the ^{3}LE state. It is suggested that the strong spin−orbit coupling caused by the Au atom ($Z = 79$)[13] in **3** leads to (1) an efficient intersystem crossing from the singlet to the triplet excited state, and (2) the large k_r value of the phenanthrene chromophore at T_1 due to partial removal of the spin-forbidden nature of the T_1-S_0 radiative transition.

From eq 1, the radiative rate constant, k_r, at T_1 is formulated as

$$k_r = \Phi_P/(\tau_T\Phi_{ST}) \qquad (2)$$

The Au(I) complex (**3**) affords $\Phi_p = 0.06^{12}$ and $\tau_T = 22.7$ μs at 298 K. On the assumption that $\Phi_{ST} = 1.0$ for **3**, k_r is calculated to be 2.6×10^3 s^{-1}. This value is 4 orders of magnitude larger than the radiative rate constant of the triplet phenanthrene (0.26 s^{-1}).[14a] Thus, the coordinated Au(I) atom is found to give a markedly large heavy atom effect on k_r of the phenanthrene chromophore in **3**, and the use of Au(I) atom is more effective in increasing k_r than halogen substituents which are expected to have a significant heavy atom effect (k_r values of 9-bromo- and 9-iodophenanthrene are 92.6 and 578 s^{-1}, respectively).[14b]

The present results are summarized as follows: (1) molecule **1** gives ICT fluorescence, (2) molecule **2** exhibits fluorescence much stronger than PT, and (3) molecule **3** emits blue-green room-temperature phosphorescence due to the effects of Au(I) atom.

The detailed photophysical studies of these compounds as well as the synthesis of related heavy atom metal complexes are in progress.

Supporting Information Available: Synthetic procedures, characterization data, X-ray crystallographic data (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The fluorescence quantum yields were determined by standard methods with anthracene in EtOH ($\Phi_F = 0.27$ for **2**) and quinine sulfate in 1 N H_2SO_4 ($\Phi_F = 0.546$ for **3**) as references: Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1055.

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