Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for Photochemistry and photophysics of the tetrahedral silver(I) complex with diphosphine ligands: $[Ag(dppb)_2]PF_6$ (dppb = 1, 2-bis[diphenylphosphino]benzene)

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Experimental Detail

General Information

All reactions were carried out under an atmosphere of Ar, unless otherwise indicated. All solvents used for spectroscopic measurement, 2-methyltetrahydrofuran, 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.

Steady-state absorption and emission spectra were recorded by a Shimadzu UV-3100 and a RF-5300. The Xenon lamp has been corrected by Rodamine B spectrum and the wavelength-dependent characteristics of photomultiplier have been calibrated by a secondary standard lamp in the 300-850nm. For the emission studies, dissolved dioxygen was removed by repeated freeze-pump-thaw cycles. The relative fluorescence quantum yields were determined by standard methods with $[Ru(bpy)_3]\cdot 2PF_6$ in acetonitrile (Φ = 0.062) and quinine sulfate in 1N H_2SO_4 (Φ = 0.546) as references.

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.[1]

The EPR spectrum of a radical cation specie was recorded on a JEOL-RSV2000 spectrometer at 293 K.

1. M. Hoshino, H. Sonoki, Y. Miyazaki, Y. Iimura, K. Yamamoto, *Inorg. Chem.* 2000**, 39**, 4850-4857.

The luminescence quantum yield of 1 at 77 K.

Measurements at 77 K were performed using a specially constructed low-temperature quartz dewar. The corrected spectra were employed for the determination of the luminescence quantum yield. From the wavenumber-integrated area of the corrected spectra, we obtained the quantum yield for the Ag complex with reference to 9,10-Diphenylanthracene (at 77 K, Φ_{fl} = 1.00).[1] For the calculation, the excitation wavelength was chosen such that the standard reference and sample absorptions were equal (λ_{exc} = 254 nm, O.D. = 0.06). The quantum yield Φ was calculated by eqn. (1), where Abs_s and Abs_r are, respectively, the absorption values of samples and reference, and n_s and n_r are their refractive indices. Since Abs_s and Abs_r are equal and the refractive indices are assumed to be similar, eq (1) can be modified to (2).

$$\Phi_s = \Phi_r (Abs_r/Abs_s) (n_s/n_r)^2 (area_s/area_r) \qquad (1)$$

$$\Phi_s = \Phi_r (area_s/area_r) \qquad (2)$$

1. (a) G. Heinrich, S. Schoof and H. Gusten, *J. Photochem.*, 1974, **3**, 315-320; (b) J. R. Huber, M. A. Mahaney and W. W. Mantulin, *J. Photochem.,*1973, **2**, 67-70.

Synthetic Procedures

$[Ag(dppb)_2]PF_6$ (**1**)

$AgClPF_6$ (28.3mg, 0.112mmol) and 1,2-bis[diphenylphosphino]benzene (dppb) (100mg, 0.224mmol) were stirred for 12 hour in CH_2Cl_2. After evaporation of CH_2Cl_2, The recrystallization of the crude product from MeOH afforded analytical pure $[Ag(dppb)_2]PF_6$ (**1**) as colorless crystals (117mg, 91%).

^{1}H NMR (400MHz, CD_2Cl_2, 293K): δ 7.529 (m, 8H), 7.328 (m, 8H), 7.113-7.098 (m, 32H); $^{31}P\{^1H\}$ NMR (160MHz, 293K): δ 2.763(dd, $^1J(^{31}P\text{-}^{107}Ag)$ = 231Hz, $^1J(^{31}P\text{-}^{109}Ag)$ = 264Hz) in CD_2Cl_2, δ 1.271(dd, $^1J(^{31}P\text{-}^{107}Ag)$ = 230Hz, $^1J(^{31}P\text{-}^{109}Ag)$ = 265Hz) in d_8-THF, ES MS (m/z): 999.2 [$M - PF_6^-$], calcd for $C_{60}H_{48}AgP_4$: 999.18, Anal. Calcd for $C_{60}H_{48}AgF_6P_5$: C, 62.90; H, 4.22. Found C, 62.76; H, 4.39.

X-ray single crystal structure determination of $[Ag(dppb)_2]PF_6$

Crystal Data $C_{60}H_{48}AgF_6P_5$, M = 1145.77, monoclinic, space group $C2/c$, a = 27.151(3) Å, b = 25.983(3) Å, c = 18.573(2) Å, β = 124.920(2) deg, V = 10743(2) Å^3, T = 130(1) K, Z = 8, 15648 unique observed reflections (R_{int} = 0.056) were used to refine 651 atomic parameters and gave a final $R_1[F > 2\sigma(F)]$ = 0.0541, wR_2 (all data) = 0.1194.

Selected bond lengths (Å) and angles (°) of **[Ag(dppb)$_2$]PF$_6$** (molecule 1 & 2)

molecule 1

Ag(1)-P(1)	2.4621(7)	P(1)-Ag(1)-P(2)	79.99(2)
Ag(1)-P(2)	2.5063(6)	P(1)-Ag(1)-P(1)a	133.32(2)
		P(2)-Ag(1)-P(2)a	125.97(2)

a = 2-x,y,3/2-z

molecule 2

Ag(2)-P(3)	2.5461(6)	P(3)-Ag(2)-P(4)	79.25(2)
Ag(2)-P(4)	2.4635(6)	P(3)-Ag(2)-P(3)b	117.03(2)
		P(2)-Ag(2)-P(2)b	131.77(2)

b = 1-x,y,1/2-z

Fig. S1 Absorption spectra of dppb and **1** in 2-MeTHF

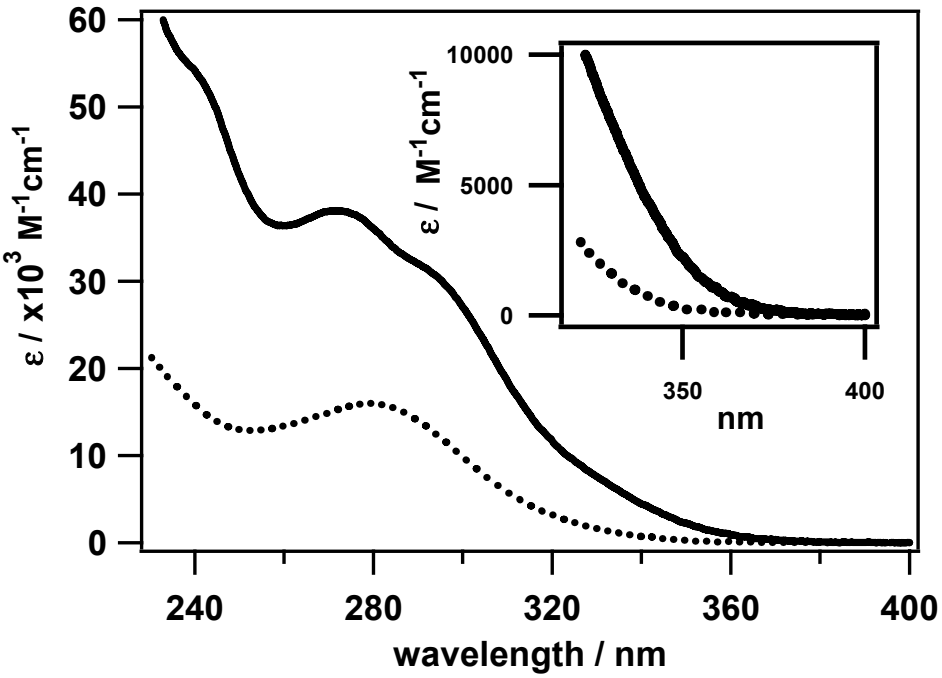

Fig. S2 Excitation (emission: 660 nm) and absorption spectra of **1**