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Phosphorescence Color Alteration by Changing Counter Anions on Tetrahedral Gold(I) Complexes; Intra- and Interligand π–π Interactions

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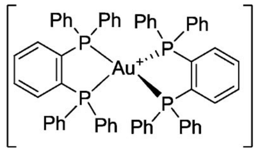
Tetrahedral gold(I) complexes containing the diphosphane ligand [dppb = 1,2-bis(diphenylphosphanyl)benzene], $[Au(dppb)_2]X$ {X = Cl (**1**), BF_4 (**2**) and PF_6 (**3**)}, were prepared and characterized by X-ray structural analysis. Complexes **1** and **2** have almost the same structure with two dppb ligands, which are symmetrically coordinated to the Au atom in the crystal. However, the two dppb ligands of **3** are asymmetrically bound to the gold(I) stom in the crystal. Both colorless complexes **1** and **2** exhibit intense blue phosphorescence with peak maxima at 481 nm ($\Phi_p = 0.86$) for **1** and 490 nm ($\Phi_p = 0.90$) for **2**, respectively. The pale yellow complex **3** shows weak yellow-orange phosphorescence with a peak maximum at 596 nm ($\Phi_p = 0.04$). A small conformational change in the crystal, which is caused by changing the counter anion, dramatically alters the optical properties of the tetrahedral gold(I) complexes in the solid state. The difference in the absorption and phosphorescence spectra between **1** and **3** has been interpreted on the basis of molecular arrangement including packing structures of the complexes and time-dependent density functional theory (TD-DFT) calculations.

Introduction

For emissive metal complexes in the solid state, their optical properties are largely governed by the molecular arrangements in the crystal.[1] Since the intermolecular and/or intramolecular interactions (e.g. hydrogen bonding, π–π and CH–π interactions) in the crystal significantly affect the molecular conformation of the complexes, the electronic states are changed by the nature of the crystal structure. In particular, the crystal structure and thus the molecular arrangement of cationic metal complexes can be largely affected by the size and the shape of their counter anions in solid state.[2]

In this paper, we describe the phosphorescence color alteration in the crystal on tetrahedral gold(I) complexes, $[Au(dppb)_2]X$ {dppb = 1,2-bis(diphenylphosphanyl)benzene}, by changing the counter anions [X = Cl (**1**), BF_4 (**2**) and PF_6 (**3**)]. Complexes **1** and **2** exhibit intense blue phosphorescence. Complex **3** gives weak yellow-orange phosphorescence. These observations are interpreted on the basis of molecular arrangements including packing structures and DFT calculations.



$X^- = Cl^-$ (**1**), BF_4^- (**2**), PF_6^- (**3**)

Several studies have been carried out for the photophysical properties of tetrahedral gold(I) complexes, $[Au(P^\wedge P)_2]^+$ with diphosphane ligands ($P^\wedge P$).[3] The key units in the tetrahedral $[Au(P^\wedge P)_2]^+$ for phosphorescence have been regarded as aromatic groups bonded to P atoms because the lowest energy absorption band must be an emissive state, $\sigma \rightarrow \pi^*$ (aromatic group).[3,4] The dppb ligand,[5] which has two types of aromatic groups attached to P atoms (one is the bridging *o*-phenylene group and the other is the phenyl group), is suitable for the synthesis of luminous tetrahedral gold(I) complexes.

Results and Discussion

To a thf solution of $Au(PPh_3)Cl$ was slowly added the dppb. After 20 min of standing still, colorless plate crystals were obtained almost quantitively. The reaction of **1** with an excess amount of NH_4BF_4 or KPF_6 in CH_2Cl_2 gave $[Au(dppb)_2]BF_4$ (**2**) or $[Au(dppb)_2]PF_6$ (**3**). The yellow cubic crystals of **3** were obtained by recrystallization from MeOH. The molecular structures of complexes **1**–**3** have been determined by X-ray diffraction analysis. The ORTEP

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drawing of **1** is shown in Figure 1, the two dppb ligands are symmetrically bound to the Au atom because of the space group, *P*2/*n*. The Au atom is in a highly distorted tetrahedral coordination geometry with a dihedral angle of 84.08(2)° between the planes defined by P(1)AuP(2) and P(1a)AuP(2a). Because of the short distance [3.770(1) Å] between the centers of gravity (cg) of two phenyl groups, we consider that there exists an intraligand π–π interaction between one nonbridging phenyl group on P(1) and that on P(2) in **1**. The structure of complex **2** bears a strong resemblance to that of **1** (space group *P*2/*n*; ORTEP drawing of **2** is shown in Figure S1, see Supporting Information). The two dppb ligands of **3** are coordinated asymmetrically to the Au atom to give a tetrahedral geometry more distorted than **1** [the dihedral angle is 77.06(2)° between the two planes, P(1)AuP(2) and P(3)AuP(4)] as shown in Figure 2. Although no intraligand π–π interaction of phenyl groups can be expected, we assume that one nonbridging phenyl group on P(2) and that on P(3) in **3** have an interligand π–π interaction [the cg distance is 3.873(1) Å].

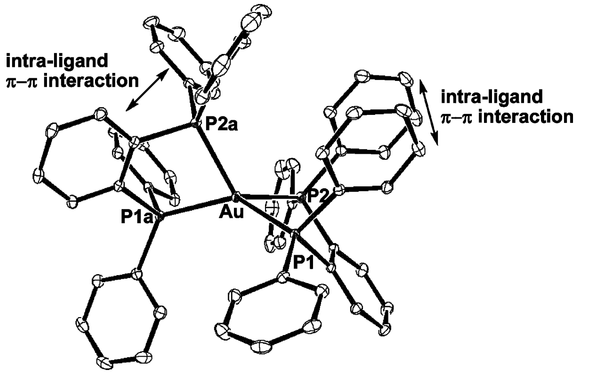

Figure 1. Molecular structure of the cation in **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and counter anion Cl^- are omitted for clarity.

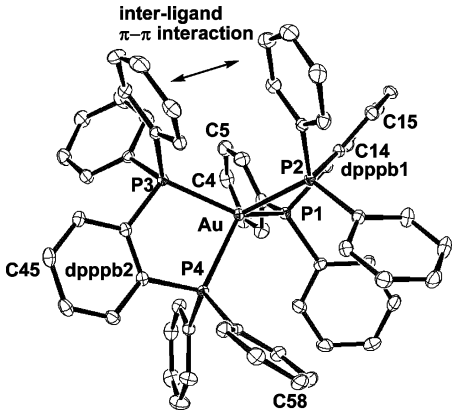

Figure 2. Molecular structure of the cation in **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and counter anion PF_6^- are omitted for clarity.

The PF_6 anion in **3** asymmetrically interacts with the two dppb ligands, which results in three CH–F interactions with dppb2 and five CH–F interactions with dppb1 (Figure S2 in the Supporting Information). Complex **3** has two intermolecular CH–π interactions:[6] one is C58–H58 (donor in dppb2)/C14 (acceptor in dppb1) and C15 (acceptor in dppb1), the other is C45–H45 (donor in dppb2)/C4 (acceptor in dppb1) and C5 (acceptor in dppb1) (Figure S3 in the Supporting Information). These interligand π–π interactions, CH–F and CH–π, make the two dppb ligands nonequivalent in the crystal of **3**.

Figure 3 shows the absorption of complexes **1**–**3** and the emission spectra of dppb and **1**–**3** at 293 K in the solid state. Table 1 summarizes the absorption and phosphorescence peaks, lifetimes, yields (**1**–**3**), and the transition energies (S1) calculated by DFT with the use of the X-ray analysis structure data (**1** and **3**). The colorless complexes **1** and **2** show broad bands with absorption maxima at 365 and 385 nm in the solid state, respectively. Complex **3** exhibits an absorption maximum at 420 nm. The redshift of the absorption maximum of **3** compared with that of **1** is well consistent with the calculated S1 values. Both complexes **1** and **2** emit bright blue light (λ_{max} = 481 nm for **1** and 490 nm for **2**), which resembles that of dppb (λ_{max} = 479 nm) in appearance, and complex **3** exhibits weak yellow-orange emission (λ_{max} = 596 nm) in the solid state (Figure 3). The structural analogues **1** and **2** exhibit the same optical properties (Figure 3 and Table 1). As listed in Table 1, the emission lifetimes are 3.6 μs for **1**, 4.0 μs for **2** and 0.35 μs for **3**, indicating that these emissions are phosphorescence. According to DFT calculations, the emitting states of complexes **1** and **3** are mainly CT states from a P atom to Ph groups on the dppb ligands. The MLCT character that contains a σ → π* contribution is not so strong, 15% for **1** and 14% for **3**.

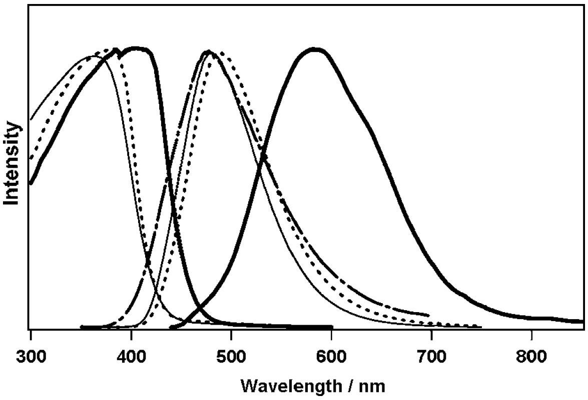

Figure 3. Absorption spectra of **1** (solid), **2** (dashed) and **3** (bold) in the solid state (left), and corrected emission spectra (right) of dppb (dashed-dotted), **1** (solid), **2** (dashed) and **3** (bold) in the solid state. Intensities of absorption and emission spectra in the solid state were adjusted arbitrarily for clarity. λ_{exc} = 350 nm for **1**–**3** and 300 nm for dppb.

A natural transition orbital (NTO) analysis[7] shows that these excitations can be described as single hole/electron pairs, which reproduce over 90% of the transition density. The hole (approximately HOMO) of **1** is essentially metal-based but also includes the Au–P bonds, and the electron (approximately LUMO) is largely confined to each symmetrically bridging *o*-phenylene group in the two dppb ligands

Table 1. Photophysical properties of **1**–**3**.

	λ_{max}[a] [nm]	S1[b] [nm]	λ_{max}[c] [nm]	τ_T [μs]	Φ_p[d]
1	365	363	481	3.6	0.86
2	385	–	490	4.0	0.90
3	420	393	596	0.35	0.04

[a] Absorption maxima. [b] Calculated transition energies. [c] Emission maxima. [d] Absolute photoluminescence (PL) quantum yield.

(Figure 4a). The hole of **3** is very similar in shape to that of **1**. However, the electron of **3** is mainly extended over dppb2, causing a redshift of the emission maximum (Figure 4b). This electron (approximately LUMO) location on dppb2 in complex **3** is well consistent with the CH–π (donor–acceptor) interactions as mentioned above because dppb2 has donor ability relative to dppb1.

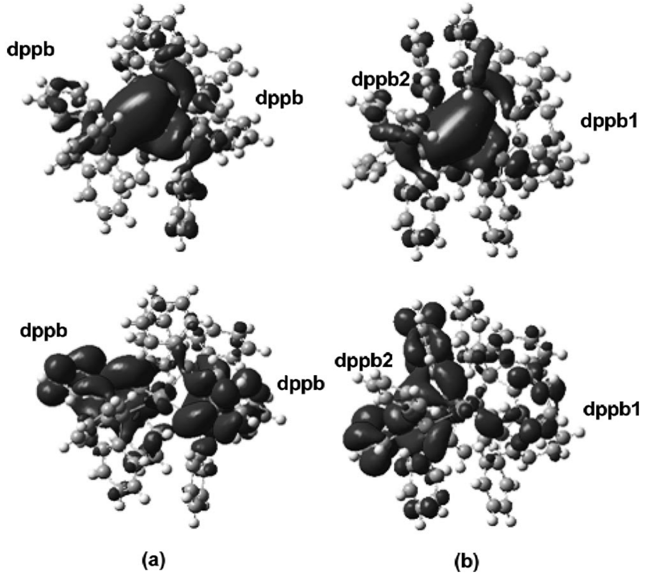

Figure 4. Natural transition orbital pairs for the lowest triplet state T1 of **1** (a) and **3** (b). The "hole" is on the top and the "electron" is on the bottom.

Complexes **1**–**3** show similar radiative rate constants, k_r, at 293 K. With the use of the triplet yield, Φ_{ST}, and the lifetime, τ_T [$= k_T^{-1} = 1/(k_r + k_{nr})$; k_{nr} = non-radiative rate constant], the phosphorescence yield, Φ_P, is expressed as Equation (1).

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

From that, the radiative rate constant, k_r, at T1 is formulated as Equation (2).

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

On the assumption that $\Phi_{ST} = 1.0$ for **1**–**3**, k_r is calculated to be 2.4×10^5 for **1**, 2.3×10^5 for **2** and 1.1×10^5 for **3**. This result agrees with their almost same oscillator strengths (0.000143 for **1** and 0.000156 for **3**) at 300 K from DFT calculations. However, the phosphorescence quantum yield ($\Phi_p = 0.04$) of **3** is very low in comparison to those of complexes **1** and **2** ($\Phi_p = 0.86$ for **1** and 0.90 for **2**), suggesting the conformational difference between complexes **1**, **2** and **3** has a large effect on their non-radiative rate constant, k_{nr} (3.9×10^4 for **1**, 2.5×10^4 for **2** and 2.7×10^6 for **3**).

Conclusions

We have reported a phosphorescence color alteration in the crystal of tetrahedral gold(I) complexes, [Au(dppb)$_2$]X, by changing counter anions [X = Cl (**1**), BF_4 (**2**) and PF_6 (**3**)]. The symmetrical coordination of two dppb ligands to the Au atom would seem to be necessary for the intense blue phosphorescence on tetrahedral gold(I) complexes because complexes **1** and **2** exhibit the same optical properties. We consider that the intraligand π–π interactions in complexes **1** and **2** support the symmetrical coordination geometry of the cationic molecule. A small conformational change of the two dppb ligands (symmetry reduction, caused by changing the counter anion) effects the localization of an electron (LUMO) on one dppb ligand and dramatically alters the optical properties of the gold(I) complexes in the crystal.

Experimental Section

General: All reactions were carried out under argon, unless otherwise indicated. $(CH_3)_2SAuCl$ and dppb were commercially available (Aldrich) and used without further purification. ^1H and ^{31}P NMR spectra (CD_2Cl_2) and were recorded with a JEOL EX-400 and a JEOL EX-500 instrument. Solid-state absorption and emission spectra were recorded with an upgraded version of JASCO MSV-350 and a RF-5300. The light-intensity distribution of a xenon lamp was corrected with the use of Rodamine B in ethyleneglycol, and the output of the photomultiplier was calibrated in the wavelength range 300–850 nm by using a secondary standard lamp. ES mass spectra were recorded with a ThermoQuest Finnigan LCQ Duo mass spectrometer. Laser photolysis studies were carried out with the use of an Nd:YAG laser (Sure Light 400 from Hoya Continuum Ltd.) equipped with second, third, and forth harmonic generators. Excitation light for lifetime measurements of the phosphorescence was third harmonics (355 nm): the duration and the energy of the laser pulse were 5 ns and 30 mJ/pulse, respectively. The monitoring system for the decay of phosphorescence has already been reported elsewhere.[8] Solid-state phosphorescence quantum yields were determined with an absolute PL quantum yield measurement system, C-9920-02 (Hamamatsu). Single crystals of **1**–**3** in quartze petri dishes were used for all optical measurements in the solid state.

Materials: Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Au(PPh$_3$)Cl was prepared according to a literature procedure.[9]

Synthesis of [Au(dppb)$_2$]Cl (1): To a thf solution (3 mL) of Au(PPh$_3$)Cl (0.15 g, 0.03 mmol) was slowly added dppb (0.268, 0.06 mmol). After 20 min of standing still, colorless plate single crystals were obtained almost quantitively (0.29 g, 89%). ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 7.542–7.451 (m, 8 H, *o*-phenylene), 7.342–7.306 (m, 8 H, phenyl), 7.108–7.025 (m, 32 H, phenyl) ppm. $^{31}P\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 293 K): δ = 21.80 (s) ppm. ES MS: *m*/*z* = 1089.9 [M – Cl]. $C_{60}H_{48}AuClP_4$ (1125.338): calcd. C 64.04, H 4.30; found C 63.86, H 4.39.

[Au(dppb)$_2$]BF$_4$ (2): To a CH_2Cl_2 solution (10 mL) of [Au(dppb)$_2$]Cl (**1**) (0.20 g, 0.18 mmol) was added an aq. NH_4PF_6 solution (1 N, 10 mL). After 2 h, the CH_2Cl_2 layer was evaporated to dryness. Recrystallization of the crude product from ethanol afforded analytically pure colorless crystals (0.16 g, 77%). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 7.542–7.451 (m, 8 H, *o*-phenylene), 7.342–7.306 (m, 8 H, phenyl), 7.108–7.025 (m, 32 H, phenyl) ppm. $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 293 K): δ = 21.80 (s) ppm. ES MS: *m*/*z* = 1089.9 [M – BF_4]. $C_{60}H_{48}AuBF_4P_4$ (1176.69): calcd. C 61.24, H 4.11; found C 61.34, H 3.96.

Synthesis of [Au(dppb)$_2$]PF$_6$ (3): This compound was prepared similarly to [Au(dppb)$_2$]BF_4 (**2**), except that an aq. KPF_6 solution (1 N, 10 mL) was used instead of an aq. NH_4BF_4 solution. Yield: 0.18 g (87%) of yellow crystals. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ = 7.537–7.4337 (m, 8 H, *o*-phenylene), 7.337–7.301 (m, 8 H, phenyl), 7.106–7.025 (m, 32 H, phenyl) ppm. $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 293 K): δ = 21.85 (s) ppm. ES MS: *m*/*z* = 1089.9 [M – PF_6]. $C_{60}H_{48}AuF_6P_5$ (1234.849): calcd. C 58.36, H 3.92; found C 58.13, H 4.19.

Crysyal-Structure Detamination: The crystallographic data and the results of the structure refinements are summarized in Table S2 (in the Supporting Informationarmation). In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections were made.[10] The structures were solved by direct methods (SIR2004).[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed at calculated positions. CCDC-702673 (for **1**), -733922 (for **2**) and -702674 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental details (ORTEP views of **2**, CH–π and CH–F interactions in **3** and TD-DFT calculations).

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