Photocrystallographic analysis of [AuCl(PPh₃)₂] for elucidation of the crystal packing effect on the photophysical properties[†]

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A metal–ligand bond shortening of [AuCl(PPh₃)₂] by photoexcitation was analyzed by the photocrystallographic method in the unsolvated crystal. The gradual structural change of photoexcited and ground-state molecules with cooling explains the temperature dependence of the emission spectrum and the excited-state lifetime. Actually, on cooling, the ground-state molecular structure approached the excited-state structure. As a result, the HOMO–LUMO gap of [AuCl(PPh₃)₂] became narrower and a red shift of the absorption and emission bands were observed. Below 180 K, inhibition of the bond shortening was observed due to the intermolecular interactions, which was confirmed by the temperature dependence of the photoexcited phase cell volume, the integrated emission intensity, and the excited-state lifetime measurement.

Introduction

Photocrystallography, which is a study using multiple techniques based on crystallography and photochemistry, has been applied for the study of solid-state photoreaction, photoinduced spin-transition and photo-switching metal-insulator phase transition.¹⁻³ In particular, structural analysis of the photoexcited molecule has received much attention, because the structure leads to information about photophysical and photochemical properties. Especially for molecular devices and functional materials, such information is important to control their characteristic features. But since the lifetime of photoexcited molecules is very short (typically, a few nanoseconds or microseconds), the special set-up for the stroboscopic pump-probe diffraction experiment using short X-ray pulses synchronized with a pulsed laser is required.^{4,5} By this kind of technique, Coppens et al. revealed photoexcited molecular structures of several complexes.⁵ For example, the diplatinum complex, $[Pt_2(pop)_4]^4$ (pop = diphosphonate, $(H_2P_2O_5)^{2-}$), and the dirhodium complex, $[Rh_2(dimen)_4]^{2+}$ (dimen = 1,8-diisocyano-*p*-menthane), showed contraction of the M. M distance by photoexcitation.^{6,7} In addition, they also reported that relative orientation of ligands changed from perpendicular to planar by photoexcitation in $[Cu(dmp)(dppe)]^+$ (dmp = 2,10-dimethylphenanthroline; dppe = 1,2-bis(diphenylphosphino)ethane).8

On the other hand, the photoexcited molecular structure can be analyzed by X-ray diffraction from a continuously photoirradiated crystal in which an equilibrium state between the ground and photoexcited state was generated ("photo-stable crystal").

Using this "photo-stable diffraction method", the Pt ··· Pt contraction by photoexcitation in [Pt₂(pop)₂(popH)₂]²⁻ was also reported by Yasuda et al. (using a laboratory system) and Ozawa et al. (using synchrotron radiation).^{9,10} Because the Pt · · · Pt contractions are almost the same among these three reports (-0.28 Å (Coppens et al.), -0.23 Å (Ozawa et al.), and -0.27 Å (Yasuda et al., under the assumption that the population of photoexcited molecules is 1.4%), the photo-stable diffraction method should be an effective alternative to the stroboscopic pump-probe method. However, it should be noted that the observed photoexcited structures can differ from each other because the photo-stable crystal is not generated by the stroboscopic method. This difference is reflected in the observation of a crystal lattice change induced by photoexcitation. Yasuda et al. reported a shift in the powder diffraction pattern corresponding to the contraction of the crystal lattice by continuous photoirradiation.9 Additionally, the photo-stable diffraction method does not require the pulsed X-ray and laser equipment; it is more convenient for the laboratory system. We reported the structural change of $[VO(acac)_2]$ by photoexcitation using a laboratory system, which is an elongation of the V=O and V-O bonds.11

The three-coordinate monovalent gold complex $[AuCl(PPh_3)_2]$ (Scheme 1) has a long excited-state lifetime ($\tau = 3.7 \mu$ s, at an ambient temperature) and shows bright green phosphorescence on UV irradiation.¹² Because of these photophysical properties, $[AuCl(PPh_3)_2]$ is expected to be a phosphorescent material.¹³ To know the emission mechanism in detail, many studies on the photoexcited states have been carried out using various techniques, such as spectral measurement and theoretical calculations.¹⁴ As for the photoexcited molecular structure, it was suggested that large structural change by photoexcitation is related to its



Scheme 1

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phosphorescence. From MO analysis and spectral measurements, Gray et al. suggested that the considerable contraction of the AuL₃ unit is induced by photoexcitation.¹⁵ On the other hand, from theoretical calculation, Omary et al. reported that the excited structure deforms toward a T-shape with elongation of the metalligand bonds.¹⁶ In our previous study using the photo-stable X-ray diffraction method, the photoexcited molecular structure of [AuCl(PPh₃)₂] in the solvated crystal, [AuCl(PPh₃)₂]·CHCl₃, showed shortening of metal-ligand bonds.17 However, the amount was not so large (ca. 0.005 Å shortening). Additionally, the photoexcited molecular structure differed from the theoretically calculated structure. These results suggest that the crystal packing (e.g. steric hindrance, intermolecular interactions) would affect the structural change by photoexcitation as external pertubations.¹⁷ In this paper, correlation between the crystal packing and structural change by photoexcitation are examined by the photo-stable X-ray diffraction method. To examine the effect of the crystal packing by the gradual change of its condition, a temperature change was applied to change the crystal packing. To avoid a solvent molecule working as an additional factor toward the structural change by cooling or photoirradiation, solvate-free [AuCl(PPh₃)₂] crystals was prepared.¹⁸ Furthermore, the relationship between photophysical properties (such as absorption, emission and lifetime) and crystal structure is discussed based on the results of X-ray structural analysis.

Results and discussion

Crystal structure

The molecular and crystal structure of $[AuCl(PPh_3)_2]$ are shown in Fig. 1 and 2, respectively. The crystal system is triclinic (space group $P\overline{1}$, Z = 2), and one $[AuCl(PPh_3)_2]$ molecule exists in an asymmetric unit (Z' = 1). There are weak interand intramolecular C–H···Cl interactions, shown by red broken lines in Fig. 2. Two $[AuCl(PPh_3)_2]$ molecules are weakly bound as a dimer by two intermolecular C(114)–H(114)···Cl(1) interactions (C(114)···Cl(1) = 3.5354(15) Å, C(114)–H(114)– Cl(1) = 139.3(19)°, at 118 K and the light-off stage). While in the solvate crystal, $[AuCl(PPh_3)_2]$ ·CHCl₃,¹⁷ one $[AuCl(PPh_3)_2]$ molecule binds to the CHCl₃ molecule by the intermolecular C–H···Cl interaction.



Fig. 1 ORTEP diagram of $[AuCl(PPh_3)_2]$ at 118 K (light-off), showing atoms with 50% thermal ellipsoids.



Fig. 2 Crystal structure of $[AuCl(PPh_3)_2]$ viewed along the *c* axis.

Generation of the photo-stable crystalline phase and structural change by photoexcitation

All crystallographic data and differences of cell volume between the light-off and light-on stages are shown in Tables 1 and 2, respectively. By continuous photoirradiation of the crystal, the cell volume decreased at every temperature. Since the volume increased with temperature rise at the light-off stage, such lattice contractions by photoirradiation indicate the generation of excited-state molecules in the crystal and the formation of the photo-stable crystalline phase. Additionally, because the lattice deformation by photoirradiation and heating has the opposite tendency, and the lattice contraction is easily recognized in this study, the temperature rise by continuous photoirradiation was so small that having little effect on the examining structural change by photoexcitation. The Wilson-type plot of $(2\sin\theta/\lambda)^2 vs. -\ln(I_{on}/I_{off})$ also indicates that the temperature rise by photoirradiation is negligible on the structural change by photoexcitation (see Fig. S1 in the ESI†).¹⁹

The maximum lattice volume change by photoexcitation was observed at 177 K. Thus, selected bond lengths, bond angles and differences of these between the light-on and light-off stages at this temperature are shown in Table 3 (Table S1 in the ESI[†] for the full geometric parameters). In this table, two Au-P bonds and the Au-Cl bond were significantly shortened by photoirradiation. The change of the Au(1)–P(1), Au(1)–P(2) and Au(1)–Cl(1) were -0.0065(5) Å, -0.0076(5) Å and -0.0052(5) Å, respectively. The P(1)-C(131) and P(2)-C(211) bonds and the P(1)-Au(1)-Cl(1) angle were also slightly changed. But these were within experimental error at other temperatures (shown in Table 4). Other changes in bonds, angles and torsion angles (Table S2 in the ESI[†]) were also within experimental error. In our previous report, similar shortening of the metal-ligand bond by photoexcitation (-0.0057(4) Å in the Au-Cl bond, -0.0056(4) Å and -0.0054(4) Å in two Au–P bonds) was observed in [AuCl(PPh₃)₂]·CHCl₃.¹⁷ Thus, the structural change by photoexcitation, shortening of metal-ligand bonds, was clearly reproduced again in the present

 Table 1
 Crystallographic data

	177 K		156 K		137 K		118 K		215 K	
	Light-off	Light-on	Light-off	Light-on	Light-off	Light-on	Light-off	Light-on	Light-off	Light-on
a/Å	10.8650(2)	10.8219(3)	10.8666(2)	10.8463(2)	10.8546(2)	10.8497(2)	10.8426(2)	10.8346(2)	10.8846(2)	10.8751(2)
$b/ m \AA$	11.8353(1)	11.8053(2)	11.8354(1)	11.8202(2)	11.8287(1)	11.8235(2)	11.8248(1)	11.8202(1)	11.8478(1)	11.8388(2
$c/ m \AA$	14.2085(2)	14.1589(3)	14.1974(2)	14.1697(3)	14.1760(2)	14.1665(2)	14.1569(2)	14.1569(2)	14.2488(2)	14.2303(3)
$lpha/^{\circ}$	113.3174(10)	113.2433(14)	113.1999(9)	113.1231(12)	113.0546(10)	113.0306(11)	112.9509(10)	112.9509(10)	113.6079(10)	113.5728(1
$\beta/^{\circ}$	95.3078(8)	95.5275(12)	95.3789(8)	95.5306(10)	95.5288(8)	95.5779(9)	95.6325(8)	95.6325(8)	95.0211(8)	95.1053(1
ν/°	109.5394(9)	109.5034(13)	109.5993(8)	109.5776(11)	109.6372(9)	109.6278(10)	109.6808(9)	109.6808(9)	109.4016(9)	109.3924(1
$V/Å^3$	1526.96(4)	1511.40(6)	1526.30(4)	1518.65(5)	1521.82(4)	1519.50(4)	1517.64(4)	1515.93(4)	1535.78(4)	1530.97(5)
μ/mm^{-1}	5.034	5.085	5.036	5.061	5.051	5.058	5.065	5.070	5.005	5.020
$2\theta_{\rm max}/^{\circ}$	64.66	65.16	64.62	64.86	64.62	64.68	64.66	64.70	64.64	64.78
Refls collected/	44680/10782	42794/10819	45112/10803	44220/10785	46909/10772	45386/10769	43895/10750	43837/10750	48846/10875	46132/1087
anhma B	0.021	0.000	0.021	0.021	0.021	000	0.077	0.077	0.000	000
R , $[I > 2\sigma(I)]$	0.0145	0.0160	0.0140	0.0146	0.0135	0.0139	0.0136	0.0136	0.0159	0.0162
wR_2	0.0360	0.0479	0.0367	0.0411	0.0361	0.0375	0.0399	0.0373	0.0400	0.0412
GOF	1.103	1.209	1.171	1.147	1.123	1.112	1.127	1.110	1.114	1.136

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Table 2 Cell volume change $(Å^3)$

	Light-off stage	Light-on stage	$\Delta_{\mathrm{on-off}}{}^a$
215 K	1535.78(4)	1530.97(5)	-4.81(5)
177 K	1526.96(4)	1511.40(6)	-15.56(6)
156 K	1526.30(4)	1518.65(5)	-7.65(5)
137 K	1521.82(4)	1519.50(4)	-2.32(4)
118 K	1517.64(4)	1515.93(4)	-1.71(4)

^{*a*} Difference between the light-on and light-off stages (esds are the larger of the two in the calculation).

Table 3 Selected bond lengths (Å) and angles (°) at 177 K

	Light-off stage	Light-on stage	$\Delta_{\mathrm{on-off}}{}^a$
Au(1) - P(1)	2.3244(3)	2.3179(5)	-0.0065(5)
Au(1) - P(2)	2.3127(3)	2.3051(5)	-0.0076(5)
Au(1)-Cl(1)	2,5432(3)	2.5380(5)	-0.0052(5)
P(1)-C(111)	1.8137(13)	1.8098(18)	-0.0039(18)
P(1) - C(121)	1.8206(14)	1.8156(19)	-0.0050(19)
P(1) - C(131)	1.8145(13)	1.8048(18)	-0.0097(18)
P(2) - C(211)	1.8211(14)	1.813(2)	-0.008(2)
P(2) - C(221)	1.8143(14)	1.809(2)	-0.005(2)
P(2) - C(231)	1.8201(14)	1.816(2)	-0.004(2)
P(1) - Au(1) - P(2)	136.695(12)	136.642(16)	-0.053(16)
P(1) - Au(1) - Cl(1)	108.733(12)	108.802(16)	+0.069(16)
P(2) - Au(1) - Cl(1)	114.206(12)	114.189(17)	-0.017(17)
Au(1) - P(1) - C(111)	119.55(4)	119.52(6)	-0.03(6)
Au(1) - P(1) - C(121)	113.09(5)	113.27(7)	+0.18(7)
Au(1) - P(1) - C(131)	108.41(4)	108.29(6)	-0.12(6)
Au(1) - P(2) - C(211)	109.36(5)	109.45(7)	+0.09(7)
Au(1) - P(2) - C(221)	119.58(5)	119.49(6)	-0.09(6)
Au(1)–P(2)–C(231)	111.20(5)	111.09(7)	-0.11(7)

^{*a*} Difference between the light-on and light-off stages (esds are the larger of the two in the calculation).

unsolvated crystal, indicating the metal-ligand bond shortening by photoexcitation is essential character of [AuCl(PPh₃)₂].

Effect of gradual change of the crystal packing by cooling on the molecules and the emission property

The maximum lattice contraction appeared at 177 K and the amount of contraction gradually decreased with cooling below 177 K. This temperature dependence indicates that the crystal packing change by cooling affects the photoexcited structure below 177 K.[‡] Therefore, the molecular structure change at the ground state by cooling is examined first. The bond lengths of Au(1)–P(1), Au(1)–P(2) and Au(1)–Cl(1) at the light-off stage are given in Table 5. By cooling from 215 to 118 K, the contraction of two Au–P bonds was observed. Additionally, distances of two intramolecular C–H···Cl interactions were clearly shortened by cooling. From these observations, it is revealed that shortening of metal–ligand bonds was induced not only by photoexcitation but also by cooling. That is, the ground-state molecule gradually approached a structure similar to the excited molecule by cooling

 $[\]ddagger$ Degradation of the crystal also could be thought of as the reason of this phenomenon. But if the crystal was damaged, the amount of structural change at 215 K would be the same or smaller than the one immediately before (at 118 K). Because the amount of structural change at 215 K was larger than at 118 K (and even at 137 K), the decreasing amount of structural change was not caused by damage of the crystal.

Table 4 Differences of selected bond lengths (Å) and an angle (°) between the light-on and light-off stages^a

	215 K	177 K	156 K	137 K	118 K
Au(1)–P(1)	-0.0023(4)	-0.0065(5)	-0.0043(4)	-0.0008(4)	-0.0009(4)
Au(1) - P(2)	-0.0023(4)	-0.0076(5)	-0.0045(4)	-0.0022(4)	-0.0011(4)
Au(1)-Cl(1)	-0.0013(4)	-0.0052(5)	-0.0018(4)	-0.0004(4)	-0.0008(3)
P(1) - C(131)	-0.0023(15)	-0.0097(18)	-0.0039(15)	-0.0018(14)	-0.0009(14)
P(1) - C(211)	-0.0025(17)	-0.008(2)	-0.0035(16)	-0.0006(15)	-0.0015(14)
P(1) - Au(1) - Cl(1)	$+0.042(15)^{-1}$	+0.069(16)	+0.052(14)	+0.039(12)	-0.011(12)

" Esds are the larger of the two in the calculation.

Table 5 Metal-ligand bond lengths [Å] and C · · · Cl distances [Å] at the light-off stage

[AuCl(PPh ₃) ₂]	215 K	177 K	156 K	137 K	118 K
Au(1)–P(1)	2.3265(4)	2.3244(3)	2.3254(4)	2.3238(3)	2.3230(4)
Au(1) - P(2)	2.3138(4)	2.3127(3)	2.3134(4)	2.3122(3)	2.3121(3)
Au(1)-Cl(1)	2.5428(4)	2.5432(3)	2.5438(4)	2.5443(3)	2.5439(3)
$C(116) \cdots Cl(1)$	3.5391(18)	3.5321(14)	3.5312(16)	3.5281(14)	3.5277(14)
$C(226) \cdots Cl(1)$	3.6343(18)	3.6295(15)	3.6314(17)	3.6278(15)	3.6255(15)
$C(114)\cdots Cl(1)^a$	3.5739(17)	3.5564(15)	3.5491(17)	3.5428(15)	3.5354(15)
"Intermolecular distance	9				

below 177 K, and therefore the amount of structural change by photoexcitation would gradually become smaller by cooling. This would be the reason for the temperature dependent lattice deformation by photoexcitation.

Next, the relationship between the structural change and emission properties is discussed. The shortening of bonds by cooling enhances overlapping and repulsion of orbitals in a bonding atom. That is, bonding orbitals would become more stable and antibonding orbitals would become more unstable. Also, the result of metal–ligand bond shortening by photoexcitation clearly indicates that the HOMO has an antibonding character and the LUMO has a bonding character. So it would be suggested that the energy gap between HOMO and LUMO becomes smaller on contraction of the molecule with cooling. The corresponding potential energy curve change is shown in Fig. 3. This change of the potential curves was also suggested from the temperature dependence of UV-vis absorption and emission spectra. UV-vis absorption spectra at 294.2 and 78.7 K are shown in Fig. 4. On



Contraction of the molecular structure

Fig. 3 Change of the potential energy curves by molecular contraction with cooling (black line to red line).



Fig. 4 UV-vis absorption spectra of $[AuCl(PPh_3)_2]$ at 294.2 and 78.7 K. Both intensities of absorbance were normalized.

cooling from 294.2 to 78.7 K, the red shift of the absorption band maximum from 261 to 272 nm was observed. Furthermore, the emission band was also red-shifted from 502.2 to 523.0 nm by cooling from 295 to 75 K (Fig. 5, details are summarized in the Table S3 of the ESI \dagger). In solution studies, spectral shifts with temperature are generally caused by structural rearrangements,



Fig. 5 Temperature dependence of the emission spectrum of $[AuCl(PPh_3)_2]$.

which introduce a large change of the dipole moment of ground and excited molecules.²⁰ But in the crystal, such large rearrangement is not allowed by the crystal packing force. So the observed spectral shifts should be due to structural change by cooling, which is the contraction of two Au-P bonds. Since these red shifts of spectra corresponded to the suggested spectral change from the potential energy carves (Fig. 3), it is clearly shown that the crystal packing change also affects the energy gap between HOMO and LUMO. That is to say, change of emission from $[AuCl(PPh_3)_2]$ is accompanied with change of the crystal packing. Additionally, similar temperature dependences of emission shift in mononuclear Pt(II) complex crystals were also reported.^{21,22} These reports also conclude that the red-shift of emission by cooling relates to the change of molecular arrangement in the crystal; the HOMO-LUMO gap becomes smaller by a shortening of intermolecular Pt ··· Pt distances with cooling. So, in these Pt(II) complexes, the crystal packing changes by cooling also strongly relate to their emission properties as observed in $[AuCl(PPh_3)_2]$. However the photo-stable X-ray diffraction method employed in the present work would reveal the structural and emission relationship more directly.

Effect of the crystal structure change by cooling of the photoexcited structure

Temperature dependence of the cell volume is given in Fig. 6. In this plot, based on the difference of temperature dependency, the range of 215 to 118 K was divided into three regions. In the region A (215–177 K), the cell volumes at the light-off and light-on stages decreased, and the volume change by photoexcitation increased by cooling. In the region B (177–137 K), the cell volume was decreased at the light-off stage and, in contrast, it was increased at the light-on stage by cooling. In the region C (137–118 K), the cell volumes at both the light-off and light-on stages were decreased, but unlike in the region A, the volume change by photoexcitation was also decreased by cooling.



Fig. 6 Temperature dependence of the cell volume at the light-off and light-on stages; the temperature range is divided into three regions (A, B and C).

Among these three regions, only region B showed a gradual increase of the cell volume at the light-on stage with cooling. Since photo-induced crystal lattice contraction relates to metal– ligand bond shortening by photoexcitation, this increase of the cell volume at the light-on stage on cooling would indicate a kind of inhibition factor against bond shortening, which should have an attracting character toward the molecule by photoexcitation, is working in this region. Only intermolecular interactions can act as the inhibition factor in this crystal. For example, the intermolecular C(114) \cdots Cl(1) distance became gradually short with cooling (Table 5). It means that intermolecular C-H \cdots Cl interactions becomes strong and works as an inhibition factor against the shortening of bonds by photoexcitation. That is, structural change by photoexcitation was inhibited by intermolecular interactions in this region.

Then, the intermolecular interactions are discussed by comparison with temperature dependences of the emission lifetime and the integrated emission intensity in this region (Fig. 7 and 8, respectively). Both the lifetime and the integrated intensity increased rapidly in the region A and almost reached a constant value in region B. This behavior means that thermal deactivation of molecular motion was fully eliminated by cooling in the region B. From the crystal packing point of view, molecules are weakly bound by intermolecular interactions due to rather larger thermal motion in the region A. On the other hand, the molecules are strongly bound by the intermolecular interactions in region B (lower temperature range). Thus in region B, the interaction works well as an inhibition factor toward the structural change by photoexcitation. The cell volume increase at light-on stage by cooling is also explained by this increase of intermolecular interaction and the inhibition of the molecular contraction.



Fig. 7 Temperature dependence of the lifetime measured at $\lambda = 510$ nm.



Fig. 8 Temperature dependence of the integrated emission intensity.

During the cooling process from region B to C, the lifetime and the integrated intensity almost stayed constant. This means inhibition by intermolecular interactions is still working in the region C. But the cell volume at the light-on stage became gradually smaller and the volume difference between the light-off and light-on stages also became smaller with cooling. It could be explained as the contraction by cooling and the inhibition by intermolecular interactions almost reaching an equilibrium condition.

Consequently, it is revealed that intermolecular interactions affect the structural change by photoexcitation, which is observed by photocrystallographic analysis, as well as the emission spectrum and the lifetime, which are observed by spectroscopic measurements.

Conclusion

In this study, structural change of [AuCl(PPh₃)₂] by photoexcitation, *i.e.* shortening of metal-ligand bonds, was revealed using the photo-stable X-ray diffraction method at low temperatures. In our previous study, similar shortening was also observed in the solvated crystal, [AuCl(PPh₃)₂]·CHCl₃, so this study confirmed the structural change in [AuCl(PPh₃)₂] by photoexcitation and the effectiveness of the photo-stable X-ray diffraction method. By comparing the structural change by photoexcitation with the UVvis absorption and emission spectral data, it was revealed that contraction of the ground-state molecular structure with cooling affects the energy gap between HOMO and LUMO. This result also indicates that emission from the crystal is highly sensitive to change of the crystal packing. The change also strengthens the intermolecular interactions, as a result structural change of [AuCl(PPh₃)₂] by photoexcitation was inhibited by these interactions and the amount of structural change by photoexcitation was decreased below 177 K. That is, the crystal packing also clearly affects photophysical properties in the crystalline or solid state. This means that the photoexcited structure and emission color of $[AuCl(PPh_3)_2]$ can be controlled by designing the crystal structure with crystal engineering techniques (such as the supramolecular synthon, making the inclusion crystal or polymorphic crystal). This kind of technique could be tried to utilize [AuCl(PPh₃)₂] as a novel EL material.

Experimental

Preparation of the single crystal of [AuCl(PPh₃)₂]

The two-coordinated complex, [AuCl(PPh₃)], was synthesized by using the reported method.²³ [AuCl(PPh₃)] and an equimolar amount of triphenylphosphine were dissolved in warm acetonitrile. The colorless single crystal of [AuCl(PPh₃)₂] was obtained by evaporating the solution slowly.

Measurement of UV-vis absorption spectra and selection of an excitation light source

Well-ground powder of $[AuCl(PPh_3)_2]$ was combined with mineral oil and sandwiched between KBr disks. The sample was attached on the cold finger of a cryostat (Oxford OptistatCF-V). The cryostat was set in the sample compartment of a JASCO V-560 spectrometer, and UV-vis absorption spectra were collected at 294.2 and 78.7 K. To estimate effects of contact between the sample and KBr disks, a diffuse reflectance spectrum was also collected by using the same spectrometer at an ambient temperature.§ The absorbance converted by the Kubelka-Munk equation (shown in Fig. 9) was about the same as the spectra corrected with using KBr disks, so there were no effects to the sample by KBr. The absorption band of [AuCl(PPh₃)₂] was observed in the UV region, which was assigned to the transition of $6p_{z}$ (bonding) \leftarrow $5d_{xy}$, $5d_{x^2-y^2}$ (antibonding).^{12,15} An ultrahigh pressure mercury lamp with an optical glass filter (TOSHIBA UV-D33S) was selected as an excitation light source. The wavelength of this light roughly corresponded to the threshold of the absorption band, so the light would be able to penetrate deeply in the crystal.²⁴ By applying this photoirradiation method to the photo-stable diffraction method, photoexcited molecules could be steadily generated in the crystal at the detectable level by X-ray structural analysis (about 5% from comparison with the molecular structure led by theoretical calculation or EXAFS).9,11,17 The wavelength distribution of the light is also shown in Fig. 9. By irradiating with this UV light to the single crystal of $[AuCl(PPh_3)_2]$, green emission was observed, Fig. 10.



Fig. 9 Absorbance of $[AuCl(PPh_3)_2]$ and the wavelength distribution of the excitation light source.



Fig. 10 Photographs of the single crystal of [AuCl(PPh₃)₂]: (a) light-off, (b) light-on.

Measurement of emission spectra and the emission lifetime

The crystalline sample was attached to a cold finger of a cryostat with a closed-cycle helium compressor. Measurements of an emission spectrum and an excited-state lifetime were performed at every 20 K between 295 and 75 K. The emission spectrum at every temperature was collected using a HITACHI F-4500

 $A powder mixture of [AuCl(PPh_3)_2] (7 mg) and BaSO_4 (350 mg) was packed into a sample holder. An integrating sphere accessory was equipped for collecting data.$

spectrophotofluorometer. Lifetime measurements were performed with using the 355 nm third harmonic of an Nd-YAG laser.

Photo-stable X-ray diffraction experiments and crystal structure analysis

A single crystal of $[AuCl(PPh_3)_2]$ with the dimensions of 0.20 × 0.20×0.20 mm was used for the X-ray diffraction experiment. Intensity data were collected at four temperatures (177, 156, 137, and 118 K, in this order) in the dark (light-off) and under photoirradiation (light-on) on a Rigaku R-AXIS Rapid installed at a rotating anode source (Mo K α radiation, $\lambda = 0.71073$ Å) and equipped with a Rigaku nitrogen-gas stream temperature control system. After the data collection at 118 K, the temperature was raised to 215 K and intensity data at the light-off and light-on stages were collected in the same way. A set of data frames (in the 0° to 160° range, ω scan) were collected at four φ orientations (0, 90, 180 and 270°), and the χ arm was fixed in 45°. The integration and Lorentz-polarization and absorption correction were performed by using a program HKL-2000.25 Each structure was solved by direct methods (SIR2002)²⁶ and refined by the full-matrix least-square method (SHELXL-97).27 All the nonhydrogen atoms were refined with anisotropic temperature factors. All the hydrogen atoms were found in the difference Fourier map and refined isotropically using the relation for $U_{iso} = 1.2U_{co}$ of the connected carbon atom. Since structures at the ground and photoexcited states almost overlapped in the light-on stage, the photoexcited structure could not be refined as a disordered model. So the obtained structure was an average of the groundstate and photo-excited structure. Thus the structural change by photoexcitation was calculated between the averaged structure (light-on stage) and ground-state structure (light-off stage). CCDC reference numbers 708777-708786. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b820066a

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