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## Luminescence color alteration induced by trapped solvent molecules in crystals of tetrahedral gold(I) complexes: Near-unity luminescence mixed with thermally activated delayed fluorescence and phosphorescence<sup>†</sup>

### Masahisa Osawa,<sup>\*a</sup> Hiroto Yamayoshi,<sup>a</sup> Mikio Hoshino,<sup>a</sup> Yuya Tanaka,<sup>b</sup> and Munetaka Akita<sup>b</sup>

#### Abstract

The tetrahedral gold(I)  $[Au(L_{tBu})_2]Cl$ 1Cl 1,2-bis[bis(4-tertcomplex [L<sub>tBu</sub> = butylphenyl)phosphino]benzene], having eight tert-butyl (tBu) groups, was synthesized and characterized. Emission color alteration caused by solvent molecules captured in the crystal lattice of 1Cl was investigated. The recrystallization of **1Cl** in mixed solvents of tetrahydrofuran, THF, and various alkanes afforded two single crystals: 1CI-THF (1BG), presenting intense blue-green luminescence with an emission peak wavelength,  $\lambda_{max}$ , = 507 nm and 1Cl•THF•0.5x*n*-hexane · H<sub>2</sub>O (1OR), exhibiting weak orange luminescence with  $\lambda_{\text{max}} = 625$  nm. The emission quantum yields,  $\Phi_{\text{PL}}$ , of the two complexes were 0.95 and 0.06, respectively. X-ray structural analysis revealed that all the solvent molecules captured in the crystal were located inside the spaces surrounded by the tBu groups of the  $1^+$  cation. Further, an n-hexane molecule in 10R was found to be sandwiched between two 1<sup>+</sup> cations via CH/ $\pi$  interactions. The structure of 1Cl in 10R could be distorted by the *n*-hexane molecule incorporated in the crystal, leading to the red-shift of the emission peak wavelength and the low quantum efficiency of 10R over that of 1BG. On the other hand,  $[Au(L)_2]Cl$  [L = 1,2-bis(diphenylphosphino)benzene], having no peripheral tBu groups, was unable to incorporate the solvent molecules in the crystal by recrystallization from the mixed solvents, and thus, the crystal solely yielded intense blue light emission. The results revealed that the tBu groups of the peripheral phenyl units are essential for the luminescence color alteration caused by the incorporation of organic solvent molecules into the crystal lattice. Finally, studies on the emission spectra and quantum yields in the temperature range 77-293 K revealed that luminescence from both 1BG and 1OR was composed of phosphorescence and thermally activated delayed fluorescence.

#### Introduction

Over the past decade, luminescence color alternation of metal complexes in the solid state induced by various external factors has been the subject of extensive studies.<sup>1,2</sup> In general, when excited, the molecule in fluid solutions freely undergoes thermal relaxation within its lifetime, giving rise to emission from the thermally relaxed excited state. However, because of the high rigidity of the surroundings, the excited molecule in the crystals is allowed to undergo thermal relaxation solely by minimum molecular motion. Thus, the structure changes between the ground and relaxed excited state in the crystals are regarded as being smaller than those in fluid solutions. Accordingly, the luminescence spectrum of the molecule in a crystalline solid is significantly dominated by the ground state structure.

In luminescence vapochromism, the incorporation of volatile organic compounds (VOCs) into crystals transforms the ground state structure of the luminescent complexes and thus, luminescence from the crystals is markedly changed by the incorporation of VOCs.<sup>3,4</sup> Similarly, the molecular structures of the luminescent complexes in crystals are modified by intra- and/or intermolecular weak interactions (e.g., hydrogen bond,  $\pi$ – $\pi$ , and CH/ $\pi$  interactions),<sup>5</sup> metal–metal bond formation,<sup>6,7</sup> and isomerization.<sup>8</sup> Because of the variety of emissions from these complexes, much effort is currently being made to understand the origin of the luminescence color alternation observed in metal complexes on the basis of their molecular structures.

In our previous studies,<sup>9,10</sup> we described luminescence color alteration by changing courter anions, X, of crystalline tetrahedral gold(I) complexes,  $[Au(L)_2]X$ , with the rigid diphosphine ligand [L = 1,2-bis(diphenylphosphino)benzene]. Scheme 1A presents the structure of  $[Au(L)_2]X$ . The changes in the luminescence color are induced by the presence of the counter anion, which affects the molecular structure of  $[Au(L)_2]^+$  in the crystalline state. Particularly, the volume of the anion intensely affects the molecular symmetry of the  $[Au(L)_2]^+$  ions in the crystals. Thus, the relatively small anions, e.g., Cl<sup>-</sup> (packing view in Scheme 1B), Br<sup>-</sup>, and I<sup>-</sup>, hardly affect the geometry of  $[Au(L)_2]^+$ . As a result, these complexes emit intense blue emission regardless of the halogen anion present. However, the large anions, namely PF<sub>6</sub><sup>-</sup> and B(C<sub>6</sub>H<sub>4</sub>F-4)<sub>4</sub><sup>-</sup>, induce the conformational change of the  $[Au(L)_2]^+$  species in the crystals to a less tetrahedral geometry, resulting in the large red-shift of the emission.<sup>9-11</sup>

According to the density functional theory (DFT) calculation, the HOMO and (HOMO-1) of an  $[Au(L)_2]^+$ cation with *perfect* tetrahedral symmetry are degenerated and thus, the energies of the two orbitals are identical. With an increase in distortion from this perfect tetrahedral symmetry, the energy difference,  $\Delta E_D$ , between the HOMO and (HOMO-1) of the Au(I) complexes increases and is accompanied by a decrease in the energy gap between the HOMO and LUMO.<sup>9</sup> These results imply that the increase in distortion from the tetrahedral structure is equivalent to the increase in  $\Delta E_D$ , leading to the red-shift in the emission from  $[Au(L)_2]^+$ . Therefore,  $\Delta E_D$  is regarded as an index for the evaluation of the distortion from tetrahedral Published on 07 May 2019. Downloaded by UNIV OF LOUISIANA AT LAFAYETTE on 5/9/2019 10:17:11 PM

symmetry. For example, for  $[Au(L)_2]^+$ , the  $\Delta E_D$  of the blue-light-emitting form is <0.1 eV, while that of the orange-light emitting form is >0.5 eV.9

As illustrated in Scheme 1C, the intraligand  $\pi$ - $\pi$  interactions between two phenyl groups of ligand L are essential to stabilize the symmetrical tetrahedral conformation of  $[Au(L)_2]^+$ , which emits in the blue region. Since this interaction reduces the distance between two P atoms in L, the bite angle (P-Au-P) becomes small  $[81.36(1)^{\circ}]$ . We thus considered that the small bite angle is the evidence of the intraligand  $\pi - \pi$  interactions between the two phenyl groups of L in  $[Au(L)_2]^+$ .

In this work, we have studied the luminescence color changes of Au(I) complexes caused by organic solvent molecules captured in the crystal lattice. To capture the solvent molecules, it is necessary for the complex to create space for the guest solvent molecule in the crystal lattice (Scheme 1B). Thus, the introduction of large substituents in L is assumed to create space for the organic molecules in the crystal lattice. In line with this assumption, 1,2-bis[bis(4-tert-butylphenyl)phosphino]benzene (L<sub>tBu</sub>)<sup>12</sup> was synthesized by the introduction of a tert-butyl (tBu) group at the para-position of each peripheral phenyl group in 1,2-bis(diphenylphosphino)benzene (Scheme 1D).<sup>13-15</sup> The intraligand  $\pi$ - $\pi$  interactions between the phenyl groups in L<sub>tBu</sub> become weaker than those in L. The tetrahedral Au(I) complex with the small anion Cl<sup>-</sup>, [Au(L<sub>tBu</sub>)<sub>2</sub>]Cl (1Cl), was readily synthesized, using L<sub>tBu</sub>, in good yield. The *t*Bu groups in 1Cl create sufficient space in the crystal lattice for the guest solvent molecule to occupy. Photophysical studies in the temperature range 293–77 K were carried out to elucidate the origin of the emission from crystalline 1Cl obtained by recrystallization from various organic solvents.



Scheme 1 (A) Molecular structure of  $[Au(L)_2]X [L = 1,2$ -bis(diphenylphosphino)benzene]. (B) Packing view (010) of  $[Au(L)_2]Cl$  in capped-stick style and an intermolecular space (red dotted circle). (C) Intense blue light-emitting form of  $[Au(L)_2]^+$  cation in capped-stick style; hydrogen atoms have been omitted for clarity. (D) Molecular structure of  $L_{tBu}$ .

#### **Results and Discussion**

#### Absorption Spectra in solution and related theoretical studies

Fig. 1 illustrates the absorption spectra of L,  $L_{tBu}$ ,  $[Au(L)_2]Cl$ , and **1Cl** in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) at 293 K. The absorption spectrum of  $L_{tBu}$ , having the peak wavelength at 379 nm, is very similar to that of L. The molar absorption coefficient ( $\varepsilon$ ) at 379 nm was determined as 15,000 M<sup>-1</sup>cm<sup>-1</sup> for L<sup>14</sup> and 17,000 M<sup>-1</sup>cm<sup>-1</sup> for  $L_{tBu}$ .

The [Au(L)<sub>2</sub>]Cl complex in CH<sub>2</sub>Cl<sub>2</sub> presented two absorption peaks at 280 and 295 nm with  $\varepsilon = 31,000 \text{ M}^{-1} \text{ cm}^{-1}$ , while **1Cl** displayed an absorption shoulder at 280 nm with  $\varepsilon = 40,000 \text{ M}^{-1} \text{ cm}^{-1}$ . Solutions containing [Au(L)<sub>2</sub>]Cl and **1Cl** were yellow due to absorption in the long wavelength region (>350 nm). According to the DFT calculation, the long wavelength absorption can be ascribed to the electronic transition,  $\sigma \rightarrow \pi^*$ , from the  $\sigma$  orbital composed of Au d-orbitals and phosphine p-orbitals to the  $\pi^*$  orbitals of the ligands.<sup>9,11</sup> Notably, although the crystals of both [Au(L)<sub>2</sub>]Cl and **1Cl** are colorless, the solutions are yellow. This color difference was elucidated on the basis of the DFT calculations.

Natural transition orbitals (NTO) analysis was carried out to assign the absorption bands. Figs. S1 and S2 display the optimized S<sub>0</sub> structures and index values ( $\Delta E_D$ ) for an evolution of tetrahedral symmetry of 1<sup>+</sup> and [Au(L)<sub>2</sub>]<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>, which were obtained from DFT calculations. The index values are a measure of the distortion from perfect tetrahedral symmetry. Both complexes at the S<sub>0</sub> state in CH<sub>2</sub>Cl<sub>2</sub> displayed a large index, 0.54 eV. Since this  $\Delta E_D$  was much larger than that calculated from the structure of [Au(L)<sub>2</sub>] in the crystals (<0.1 eV), we concluded that compared to those in solution, the complexes in the crystals were more likely to adopt structures close to tetrahedral symmetry.

Tables S1–S12 list the absorption maxima, oscillator strengths, NTO pairs, generation probability, and characters for selected transitions. We initially performed the calculations of  $[Au(L)_2]Cl$  using the atomic coordinates determined by X-ray structure analysis and then optimized the S<sub>0</sub> structure in CH<sub>2</sub>Cl<sub>2</sub>. The atomic coordinates of the crystals reveal that the structure was markedly affected by the intraligand  $\pi$ – $\pi$  interactions (Scheme 1C). However, the optimized structure seem to be free from intraligand interactions (Fig. S1). Accordingly, the results from the calculations obtained before optimization could be used to elucidate the properties of the molecules in the crystals, while those calculated after optimization could be used for the

molecules in the CH<sub>2</sub>Cl<sub>2</sub> solutions.

For  $[Au(L)_2]Cl$ , the  $S_1 \leftarrow S_0$  transition energy before optimization was determined as 3.55 eV (349 nm) (Table S17). After optimization of the structure, this value was reduced to 3.32 eV (374 nm). Clearly, the  $S_1 \leftarrow S_0$  transition shifted to a lower energy after optimization, in agreement with the observation that the colorless  $[Au(L)_2]Cl$  crystals become yellow when dissolved in  $CH_2Cl_2$ . This explanation could also be applied to **1Cl**.

The oscillator strengths of the  $S_n \leftarrow S_0$  ( $n \le 40$ ) transitions of  $[Au(L)_2]^+$  and  $1^+$  in  $CH_2Cl_2$  are presented in the inset of Fig. 1. The main transition for the lower-lying state ( $S_1 \leftarrow S_0$ ) of the  $1^+$  and  $[Au(L)_2]^+$  ions was established as  $\sigma \rightarrow \pi^*$  (the bridging phenylene unit): the  $S_1 \leftarrow S_0$  is governed by the HOMO-LUMO transition. Both complexes possess similar transitions in the UV-vis region; however, **1Cl** exhibits intense absorption at ~255 nm ( $S_{40} \leftarrow S_0$ ; inset of Fig. 1). The introduction of the strongly electron-donating group (*t*Bu) rises the energy level of the HOMO ( $\pi$ ) and thus, the  $\pi - \pi^*$  bands in the absorption spectrum of **1Cl** were expected to be red-shifted compared to those of  $[Au(L)_2]Cl$ . However, the absorption spectrum of **1Cl** was located at wavelengths shorter than that of  $[Au(L)_2]Cl$ . This suggested that the  $S_{40}$  transition ( $S_{40} \leftarrow S_0$ ), having a large oscillator strength assigned to  $\pi - \pi^*$  (transitions from a *p-t*Bu-phenylene ring to an *o*-phenylene ring) uplifts the absorption spectrum at ~250 nm, resulting in an apparent slight blue-shift in the maximum emission wavelength ( $\lambda_{max}$ ) of **1Cl** over that of  $[Au(L)_2]Cl$ .

As in the case of  $[Au(L)_2]X$ , **1Cl** did not present any detectable emission in the solutions because of the "pseudo-Jahn-Teller effect". <sup>11,14b</sup> The NTO analysis carried out for **1**<sup>+</sup> demonstrated that a structural change occurs from the tetrahedral to the flattened form at the T<sub>1</sub> optimized geometry. The dihedral angle between the two planes (P1–Au1–P2 and P3–Au1–P4) is as small as 38.02° and the  $\Delta E_D$  value is 1.90 eV for T<sub>1</sub> in CH<sub>2</sub>Cl<sub>2</sub>, indicating that the molecular structure of T<sub>1</sub> is more flattened than that of S<sub>0</sub> (Fig. S3). Because these two values (dihedral angle and  $\Delta E_D$ ) of **1**<sup>+</sup> are similar to those of  $[Au(L)_2]^+$ ,<sup>11</sup> we concluded that the bulky *t*Bu groups in **1**<sup>+</sup> were unable to prevent the structural changes, leading to the absence of emission in the solutions. As will be discussed later, crystalline  $[Au(L)_2]Cl$  and **1Cl** exhibited both phosphorescence and thermally activated delayed fluorescence (TADF). The T<sub>1</sub> state responsible for emission is composed of metal-centered (<sup>3</sup>MC) and ligand-to-metal charge-transfer (<sup>3</sup>LMCT: from the P atoms to the metal) states (Tables S13 and S14).



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**Fig. 1** Absorption spectra of L (red dots),  $L_{tBu}$  (blue dots),  $[Au(L)_2]Cl$  (red), and  $[Au(L_{tBu})_2]Cl$  1 (blue) in CH<sub>2</sub>Cl<sub>2</sub> at 293 K. Inset: oscillator strengths of the calculated  $S_n \leftarrow S_0$  (n  $\leq 40$ ) transitions at the optimized  $S_0$  geometry of  $[Au(L)_2]^+$  (red) and 1<sup>+</sup> (blue) in CH<sub>2</sub>Cl<sub>2</sub>.

#### Structures of the crystals obtained from a solvent mixture of THF and alkanes

The complex **1Cl** was recrystallized from the THF solution by the addition of poor solvents (alkanes). *n*-Pentane (1.7 mL) was slowly added to a yellow THF solution (1 mL) of **1Cl** (12 mg, 7.6 x 10<sup>-3</sup> mmol) in a test tube by a micro-syringe at 293 K and the tube was immediately closed with a lid. After 12 h, the solution turned from yellow to colorless, generating colorless crystals of **1Cl**•THF (**1BG**) (Fig. 2A). This **1BG** complex emitted intense blue-green light at 293 K with a  $\lambda_{max}$  of 507 nm and a quantum yield ( $\Phi_{PL}$ ) of 0.95.

The molecular structure of **1BG** determined by X-ray analysis is presented in Fig. 2B, while the crystallographic data and selected bond lengths and angles are summarized in Tables S15 and S16, respectively. The Au–P bond lengths (2.37–2.44 Å) of **1BG** were similar to those of tetrahedral [Au(L)<sub>2</sub>]Cl.<sup>9</sup> However, the two bisphosphine ligands in **1BG** asymmetrically coordinated to the Au center. Because of the relatively short distance [4.168(2) Å] between the centroids of the two 4-*t*Bu-phenylene groups (Fig. 2B), we assumed that one of the two bis-phosphine ligands displayed a weak intraligand  $\pi$ – $\pi$  interaction between the two 4-*t*Bu-phenylene groups.

The increase in  $\Delta E_D$ , the emission peak wavelengths from the Au(I) complexes shift to red and the emission yields decrease. <sup>9</sup> For example, the complex having the  $\Delta E_D$  of 0.1 eV presented intense blue emission, while that with an  $\Delta E_D$  of 0.5 eV displayed weak yellow-orange emission. The  $\Delta E_D$ , 0.37 eV, calculated for **1BG** in the present study is just in the range 0.1–0.5 eV, in accordance with the intense blue-green emission of crystalline **1BG** (Fig. 2C).

In the crystal lattice, one THF molecule is trapped by each 1Cl molecule. Fig. 2D displays the packing

view (010) of **1BG**; the THF molecules are located in the intermolecular space surrounded by the *t*-Bu groups of  $1^+$ .

Fig. 2 (A) Images of the yellow THF solution of 1Cl (left), colorless crystals of 1BG (center), and intense blue-green emission of 1BG;  $\lambda_{exc}$  =365 nm (right). (B) Crystal structure of 1BG in capped-stick style. Hydrogen atoms and the disordered atoms in the *t*Bu groups have been omitted. (C) Core structure of 1BG and (D) packing view (010) of 1BG and an intermolecular space in which the THF molecules exist (red dotted circle).

The recrystallization of **1Cl** from the THF solutions was examined using alkanes [*n*-hexane (C6), *n*-heptane (C7), *n*-octane (C8), *n*-nonane (C9), and *n*-decane (C10)] other than *n*-pentane (C5). Complex **1Cl** (72 mg, 4.6 x  $10^{-2}$  mmol) was dissolved in THF (6.0 mL, 74 mmol). After membrane filtration, 1 mL yellow THF solution was transferred to each of six test tubes. Each alkane (C5–C10, 1.3 mL, 6.4–11 mmol) was slowly added to the THF solution of **1Cl** in each test tube, at 293 K, and the tubes were then sealed with caps (Fig. 3A). After 12 h, colorless crystals of **1BG** were formed in the test tubes containing C5 and C7–C10 alkanes, while no crystal formation was observed for the yellow THF solution containing C6 (Figs. 3B and



3C). Thus, a further 0.5 mL *n*-hexane was added to the yellow solution of the C6 tube, resulting in the formation of yellow plate-like crystals of **1OR** after 24 h (Fig. 4A).

Complex **10R** displayed weak orange luminescence with a  $\lambda_{max}$  of 625 nm and  $\Phi_{PL}$  of 0.06. Fig. 4B illustrates the crystal structure of **10R**: one molecule of THF and a half molecule of *n*-hexane per one molecule of **1Cl** are captured in the yellow crystals. Crystallographic data and selected bond lengths and angles are summarized in Tables S15 and S16, respectively. Because of the  $P2_1/n$  space group, the *n*-hexane molecule is located at the inversion center. A weak interligand  $\pi - \pi$  interaction [centroid–centroid distance between two 4-*t*Bu-phenylene groups: 4.2332(3) Å] could be observed.

Fig. 4C presents a packing structure in which two  $1^+$  cations sandwich the *n*-hexane molecule at both ends via CH/ $\pi$  interactions and the THF molecule has an intermolecular CH/ $\pi$  interaction with one bridged phenylene unit of L<sub>tBu</sub>. The distances between the hydrogen atom of the CH unit and the  $\pi$  system, 2.81 Å (*n*-hexane– $1^+$ ) and 2.87 Å (THF– $1^+$ ), are in good agreement with those observed for other CH/ $\pi$  interactions.<sup>16</sup>

The large  $\Delta E_D$  of 0.73 eV and the dihedral angle of 69.29(4)° between two planes, P1–Au–P2 and P3–Au–P4, suggested that the 1<sup>+</sup> cation in the **1OR** crystals adopts a highly distorted tetrahedral geometry. This structural distortion destabilizes the HOMO energy and accelerates the non-radiative decay of the emissive excited state. The  $\Delta E_D$  of the **1OR** crystals was much larger than that of **1BG** and thus, (1) the former crystals were yellow, owing to the destabilization of the HOMO energy, even though the latter ones were colorless and (2) emission from the former crystals were redshifted and the emission quantum yield was lower than that of the latter crystals.

This implies that the trapped *n*-hexane molecule affects the structure of the  $1^+$  cation through CH/ $\pi$  interactions. However, DFT calculation results indicate that the *n*-hexane molecules have a minimum influence on the molecular orbitals of LUMO and HOMO which are responsible for emission from **10R** (Table S17). Dramatic changes in the emission from single crystals caused by the weak CH/ $\pi$  interaction have occasionally been reported in earlier papers.<sup>17</sup>

As previously mentioned, the THF solutions of **1Cl** only afforded a colorless **1BG** crystal when C5 and C7–C10 alkanes were added, while yellow crystals of **1OR** were obtained with *n*-hexane. In the **1OR** crystals, an *n*-hexane molecule is sandwiched between two  $I^+$  cations via CH/ $\pi$  interaction. We assumed that among the alkanes studied, *n*-hexane exhibited the best molecular length and volume to be incorporated in the crystals. The branched hexanes, 2-methylhexane and 3-methylhexane, were added to the THF solutions of **1Cl** as poor solvents. However, these branched hexanes were not captured in the crystals and only colorless crystals of **1BG** were obtained.

Similarly, recrystallization of [Au(L)<sub>2</sub>]Cl was carried out in THF with the use of these alkanes as poor

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solvents. However, this solely afforded intense blue light-emitting crystals with two symmetrical diphosphine ligands (Scheme 1C). No incorporation of THF and alkanes was observed, leading to the conclusion that the tBu groups of the peripheral phenyl units in **1Cl** are essential for emission color alterations by incorporation of organic solvents into the crystal lattice.



**Fig. 3** Recrystallization procedure with THF and alkanes (C5–C10): (A) image of the solutions just after alkane addition; (B) image of the solutions after 12 h; and (C) emission images from **1BG**;  $\lambda_{exc} = 365$  nm.



**Fig. 4** (A) Image of crystals of **1OR** (left) and luminescence image of **1OR** (right);  $\lambda_{exc} = 365$  nm. (B) Crystal structure and the core structure of **1OR** in capped-stick style. Hydrogen atoms, disordered atoms in the *t*Bu groups, and oxygen atoms in water have been omitted for clarity. (Ci) Packing view (100) of **1OR**. (Cii) Magnified view of the CH/ $\pi$  interactions (red lines) between *n*-hexane and **1**<sup>+</sup> (two THF molecules and two 4-tert-butylphenyl groups are omitted for clarity). (Ciii) Magnified view of the CH/ $\pi$  interactions (red lines) between THF and **1**<sup>+</sup>.

#### Structure of crystals obtained from a solvent mixture of CH<sub>2</sub>Cl<sub>2</sub> and alkanes

Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), instead of THF, was used as a good solvent. Complex **1Cl** (12 mg, 7.6 x  $10^{-3}$  mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL, 7.8 mmol). The alkane (C6–C10, 1.3 mL, 6.4–10 mmol) was slowly added to the 0.5 mL yellow CH<sub>2</sub>Cl<sub>2</sub> solution and the tubes were then sealed with a perforated cap at 293 K. Crystallization was successfully carried out by the evaporation of CH<sub>2</sub>Cl<sub>2</sub> at room temperature via a

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perforated cap. After 12 h, pale yellow crystals of 1Cl•1.5xCH<sub>2</sub>Cl<sub>2</sub>•2.5xH<sub>2</sub>O (1YL) were formed, independent of the alkane used (Fig. 5A). This complex emitted yellow light at 293 K with a  $\lambda_{max}$  of 580 nm and  $\Phi_{PL}$  of 0.23. The crystallographic data and selected bond lengths and angles are summarized in Tables S15 and S16, respectively. Fig. 5B displays the crystal structure of 1YL: one very weak intraligand  $\pi$ - $\pi$ interaction [centroid–centroid distance = 4.669(4)] and one very weak interligand  $\pi$ - $\pi$  interaction [centroidcentroid distance = 4.437(4)] were observed. The dihedral angle [78.83(8)°] and  $\Delta E_D$  (0.42 eV) of 1YL in Fig. 5C were very similar to those (78.52° and 0.54 eV, respectively) of the optimized S<sub>0</sub> structure of 1<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> (Fig. S2). These values ranged between those of 1BG and 1OR. Thus, the above-mentioned emission properties were well consistent with the structural features of 1YL. As in the cases of 1BG and 1OR, CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>O, and Cl<sup>-</sup> were located in the intermolecular space (Fig. 5D), which might be important to stabilize the structure of 1YL.



Fig. 5 (A) Image of the 1YL crystals (left) and luminescence image of 1YL (right);  $\lambda_{exc} = 365$  nm. (B) Crystal structure of 1YL in capped-stick style. Hydrogen atoms, oxygen atoms in the water molecules, and disordered atoms in the *t*Bu groups have been omitted for clarity. (C) Core structure of 1YL and (D) Packing view (100) of 1YL and intermolecular space (red dotted circle).

#### Photophysical properties of Au(I) complexes in crystal form

The emission and excitation spectra of the crystals of **1BG**, **1YL**, and **1OR** at 293 K are presented in Fig. 6 and the photophysical data of  $[Au(L)_2]Cl$ , **1BG**, **1YL**, and **1OR** at 293 and 77 K are summarized in Table 1. All these gold complexes exhibit very broad and unstructured emission spectra. Emission energies of the three complexes are in the order of **1BG** > **1YL** > **1OR** as listed in Table 1. Taking account of the fact that the dihedral angles are in the order of **1BG**(83.88°) > **1YL**(78.83°) > **1OR**(69.29°), the emission energy is considered to be closely related to the degree of the distortion from the perfect tetrahedral symmetry. Since the  $\Delta E_D$  values, a measure of the distortion, are in the order of **1BG** < **1YL** < **1OR**, the emission peak wavelengths shift to red with an increase in the degree of the distortion. Emission from  $[Au(L)_2]Cl$ , **1BG**, and **1OR** decays according to first order kinetics in the temperature range 77–293 K. However, the decay of the emission lifetimes of **1YL** obtained at 77 and 293 K are listed in Table 1. All the studied the complexes have relatively short lifetimes (0.48–3.4 µs) at 293 K. The lifetimes of the emission at 77 K are one order of magnitude longer than those at 293 K. These observations suggest that room temperature emission can be ascribed to TADF.<sup>18</sup> Because of the small singlet (S<sub>1</sub>)-triplet (T<sub>1</sub>) energy gap, TADF occurs from S<sub>1</sub>, which is thermally populated from T<sub>1</sub> via the reverse-intersystem crossing process.



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Fig. 6 Corrected emission and excitation spectra of 1BG, 1YL, and 1OR crystals;  $\lambda_{exc} = 355$  nm,  $\lambda_{em} = 507$  nm for 1BG, 580 nm for 1YL, and 625 nm for 1OR.

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		293 K		$\Delta E(S_1-T_1)$			
	$\lambda_{max}$ / nm(eV) <sup>a</sup>	τ(=1/k) / μs <sup>b</sup>	$\Phi^c$	$\lambda_{max}/nm(eV)^a$	$\tau(=1/k)/\mu S^b$	${\it \Phi}^{c}$	- / cm⁻¹(eV)
[Au(L)₂]Cl	485(2.556)	3.4	0.95	485(2.556)	18	0.95	720(0.089) <sup>d</sup>
1BG	507(2.445)	3.3	0.95	510(2.431)	48	0.95	380(0.047) <sup>d</sup>
1YL	580(2.138)	1.3 [0.53(31), 1.62(69)] <sup>e</sup>	0.23	585(2.119)	24 [4.3(27), 31(73)] <sup>e</sup>	0.90	-
10R	625(1.984)	0.48	0.06	650(1.907)	10	0.28	320(0.040) <sup>d</sup>

Table 1 Photophysical properties of the [Au(L)<sub>2</sub>]Cl, 1BG, 1OR, and 1YL crystals

<sup>*a*</sup> Emission maxima;  $\lambda_{exc} = 355 \text{ nm.}^{b}$  Emission decay time;  $\lambda_{exc} = 355 \text{ nm.}^{c}$  Absolute PL quantum yield (error ± 8%);  $\lambda_{exc} = 355 \text{ nm.}^{d}$ <sup>*d*</sup> Energy gap between the S<sub>1</sub> and T<sub>1</sub> levels obtained by temperature dependence of the decay time. <sup>*e*</sup> Two-component. The percentage given inside parentheses represents the composition ratio of the lifetime.

We next measured the decay rate constants, k, of emission as a function of temperature, T, in the temperature range 77–293 K to determine the S-T energy gap [ $\Delta E(S_1-T_1)$ ] for [Au(L)<sub>2</sub>]Cl, **1BG**, and **1OR**. The temperature-dependent changes of the corrected emission spectra and the lifetimes are presented in Figs. S4–S6.

The decay rate constant,  $k (=1/\tau_{av})$ , is defined by eq. (1):<sup>19</sup>

$$k = \frac{3k_{\rm T} + k_{\rm S} \exp(-\Delta E({\rm S}_{\rm I} - {\rm T}_{\rm I})/k_{\rm B}T)}{3 + \exp(-\Delta E({\rm S}_{\rm I} - {\rm T}_{\rm I})/k_{\rm B}T)}$$
(eq. 1)

where  $k_{\rm B}$  represents the Boltzmann constant and  $k_{\rm S}(=1/\tau_{\rm S})$  and  $k_{\rm T}(=1/\tau_{\rm T})$  denote the rate constants for the decay of the singlet and the triplet state, respectively. Curve fitting analyses of the plots of *k* versus *T* obtained for [Au(L)<sub>2</sub>]Cl, **1BG**, and **1OR** were carried out to determine the values of  $k_{\rm T}$ ,  $k_{\rm S}$  and  $\Delta E(\rm S_1-T_1)$  using eq. 1 and the least-square method. The  $\Delta E(\rm S_1-T_1)$  values of [Au(L)<sub>2</sub>]Cl, **1BG**, and **1OR** were determined as 720, 380, and 320 cm<sup>-1</sup>, respectively. The rate constants,  $k_{\rm T}$ , for these complexes were in the range 2 x 10<sup>4</sup> – 1.00 x 10<sup>5</sup> s<sup>-1</sup>, while the  $k_{\rm S}$  values were in the range 6 x 10<sup>6</sup>–2.4 x 10<sup>7</sup> s<sup>-1</sup>. These results suggest that [Au(L)<sub>2</sub>]Cl, **1BG**, and **1OR** afford emissions from both the triplet and the thermally activated singlet states. The  $\Delta E(\rm S_1-T_1)$  values of these complexes are listed in Table 1, while their *k*s and  $k_{\rm T}$  values are listed later in the manuscript in Table 2.

Since the emission decay from **1YL** was not expressed as a single exponential function of time, no detailed analysis was carried out in the temperature range 77–293 K. However, emission from **1YL** was assumed to

be a mixture of phosphorescence and TADF since the emission peak wavelengths and lifetimes measured at 77 and 293 K are in agreement with those of **1BG** and **1OR**.

As mentioned above, the emissions of  $[Au(L)_2]Cl$ , 1BG, and 1OR originate from the excited triplet, T<sub>1</sub>, and thermally activated singlet, S<sub>1</sub>, states. The radiative rate constants at T<sub>1</sub> and S<sub>1</sub> are determined as follows: From eq. 1, the radiative rate constant, k(r) for emission is:

$$k(\mathbf{r}) = \frac{3k_{\rm T}(\mathbf{r}) + k_{\rm S}(\mathbf{r}) \exp(-\Delta E(\mathbf{S}_1 - \mathbf{T}_1)/k_{\rm B}T)}{3 + \exp(-\Delta E(\mathbf{S}_1 - \mathbf{T}_1)/k_{\rm B}T)}$$
(eq. 2)

where  $k_{\rm T}({\rm r})$  and  $k_{\rm S}({\rm r})$  are the radiative rate constants of T<sub>1</sub> and S<sub>1</sub>, respectively. From eqs. 1 and 2, the quantum yield ( $\mathcal{P}$ ) is formulated as:

$$\Phi = \frac{k(\mathbf{r})}{k} = \frac{3k_{\mathrm{T}}(\mathbf{r}) + k_{\mathrm{S}}(\mathbf{r}) \exp(-\Delta E(\mathbf{S}_{1} - \mathbf{T}_{1})/k_{\mathrm{B}}T)}{3k_{\mathrm{T}} + k_{\mathrm{S}} \exp(-\Delta E(\mathbf{S}_{1} - \mathbf{T}_{1})/k_{\mathrm{B}}T)}$$
(eq. 3)

The values of  $k_{\rm S}(r)$  and  $k_{\rm T}(r)$  are calculated from,  $k_{\rm S}$ ,  $k_{\rm T}$ ,  $\Delta E(\rm S_1-T_1)$ , and the emission quantum yields,  $\Phi$ , at 77 and 293 K. For [Au(L)<sub>2</sub>]Cl, the values  $k_{\rm T}$  (= 1/ $\tau_{\rm T}$ ) = 5.56 x 10<sup>4</sup>,  $\Phi_{293}$  = 0.95, and  $\Phi_{77}$  = 0.95 and those determined from the curve fitting  $\Delta E(\rm S_1-T_1)$  = 720 cm<sup>-1</sup>,  $k_{\rm S}$  (= 1/ $\tau_{\rm S}$ ) = 2.42 x 10<sup>7</sup>, led to eqs. 4 and 5:

$$\Phi_{293} = 0.95 = \frac{3k_{\rm T}({\rm r}) + k_{\rm S}({\rm r}) \ge 2.97 \ {\rm X}10^{-2}}{8.85 \ {\rm X}10^5}$$
(eq. 4)

$$\Phi_{77} = 0.95 = \frac{3k_{\rm T}({\rm r}) + k_{\rm S}({\rm r}) \ge 1.54 \ge 10^{-8}}{1.67 \ge 10^{5}}$$
(eq. 5)

The radiative rate constants can be obtained with values of  $k_{\rm S}(r) = 2.30 \text{ x } 10^7$  and  $k_{\rm T}(r) = 5.28 \text{ x } 10^4$  by applying eqs. 4 and 5.

The quantum yields of the TADF and phosphorescence,  $\Phi(TADF)$  and  $\Phi(Phos)$ , respectively, can be obtained from eqs. 6 and 7:

$$\Phi(\text{TADF}) = \frac{k_{\text{S}}(r) \exp(-\Delta E(S_1 - T_1)/k_{\text{B}}T)}{3k_{\text{T}} + k_{\text{S}} \exp(-\Delta E(S_1 - T_1)/k_{\text{B}}T)} \quad (\text{eq. 6})$$

$$\Phi(\text{Phos}) = \frac{3k_{\text{T}}(r)}{3k_{\text{T}} + k_{\text{S}} \exp(-\Delta E(S_1 - T_1)/k_{\text{B}}T)} \quad (\text{eq. 7})$$

Thus, the composition of  $\Phi_{293}(TADF)$  and  $\Phi_{293}(Phos)$  for  $[Au(L)_2]Cl$  were calculated as 0.81 and 0.19,

respectively, and that of  $\Phi_{77}(TADF)$  and  $\Phi_{77}(Phos)$  as 0.0 and 1.0, respectively. These results suggest that the [Au(L)<sub>2</sub>]Cl emission is TADF containing 20% phosphorescence at 293 K and pure phosphorescence at 77 K. The rate constants and TADF-to-phosphorescence ratios for [Au(L)<sub>2</sub>]Cl, **1BG**, and **1OR** are presented in Table 2. [Au(L)<sub>2</sub>]Cl, **1BG**, and **1OR** have similar  $k_T(r)$  values (Table 2). Since  $k_T(r)$  is governed by the spin orbit interaction, all these complexes are assumed to have a magnitude similar to that of spin-orbit coupling (SOC).

							Ф(TADF)	⊅(TADF) : ⊅(Phos)			
	$k_{\rm S}$ (= 1/ $\tau_{\rm S}$ ) / S <sup>-1</sup>	$k_{\rm T}$ (= 1/ $\tau_{\rm T}$ ) / s <sup>-1</sup>	<i>k</i> <sub>S</sub> (r) / s <sup>-1</sup>	<i>k</i> s(nr) <sup><i>a</i></sup> / s <sup>-1</sup>	<i>k</i> <sub>T</sub> (r) / s⁻¹	<i>k</i> <sub>T</sub> (nr) <sup><i>b</i></sup> / s <sup>-1</sup>	293 K	77 K			
[Au(L) <sub>2</sub> ]Cl	2.42 X107	5.56 X 104	2.30 X 10 <sup>7</sup>	1.20 X 10 <sup>6</sup>	5.28 X 10⁴	2.80 X 10 <sup>3</sup>	81 : 19	0 : 100			
1BG	5.88 X 10 <sup>6</sup>	1.89 X 104	5.59 X 10 <sup>6</sup>	2.90 X 10⁵	1.79 X 10⁴	1.00 X 10 <sup>3</sup>	94 : 6	8 : 92			
10R	2.27 X 10 <sup>7</sup>	1.00 X 10⁵	9.80 X 10⁵	2.17 X 10 <sup>7</sup>	3.25 X 10⁴	6.75 X 10⁴	32 : 68	2 : 98			
${}^{a}$ $k_{\rm S}({\sf nr}) = k_{\rm S} - k_{\rm S}({\sf r}), {}^{b}$ $k_{\rm T}({\sf nr}) = k_{\rm T} - k_{\rm T}({\sf r})$											

**Table 2** Rate constants and TADF-to-phosphorescence ratios for  $[Au(L)_2]Cl$ , **1BG**, and **1OR**.

The excited singlet and triplet states of these complexes reached thermal equilibrium in the studied temperature. Thus, the emission quantum yield TADF-to-phosphorescence ratio,  $\mathcal{P}(TADF)/\mathcal{P}(Phos)$ , becomes large with an increase in the thermal population of the excited singlet state. It is therefore reasonable to assume that **1BG**, with a small  $\Delta E(S_1-T_1)$  value, displays larger  $\mathcal{P}(TADF)/\mathcal{P}(Phos)$  ratios than those of [Au(L)<sub>2</sub>]Cl. However, **1OR**, with the smallest  $\Delta E(S_1-T_1)$  among the studied complexes, presented the smallest  $\mathcal{P}(TADF)/\mathcal{P}(Phos)$  ratios. This was attributed to the significantly larger  $k_S(nr)$  value of **1OR** over those of [Au(L)<sub>2</sub>]Cl and **1BG** due to the distorted structure in the crystal. Further, the smallest  $k_S(r)$  value of

 $[Au(L)_2]Cl$ , **1BG**, and **1OR** exhibit luminescence mixed with TADF and phosphorescence at 293 K, presumably due to the enhancement of the SOC by the heavy atom effect of the Au atom. In particular,  $[Au(L)_2]Cl$  and **1BG** exhibit near-unity blue or blue-green luminescence at both 293 and 77 K. There are several reports on Cu(I) and Ag(I) complexes displaying efficient room-temperature emission mixed with TADF and short-lived phosphorescence according to the effective SOC.<sup>20</sup>

1OR is responsible for the low emission quantum yield of 0.06 at 293 K.

#### Summary

The Au(I) complex,  $[Au(L_{tBu})_2]Cl \ 1Cl \ [L_{tBu} = 1,2-bis[bis(4-tert-butylphenyl)phosphino]benzene], having$ eight external*t*Bu groups, was synthesized and characterized. Recrystallization of 1Cl in organic solventsrevealed that the solvent molecules were captured inside the intermolecular space surrounded by*t*Bu groupsof 1Cl molecules in the crystal lattice. The THF solution of 1Cl was yellow, suggesting that the stablestructure in the ground state was markedly distorted from the tetrahedral symmetry in the fluid solutions. Thecomplex, 1BG, was considered to release molecular distortion by capturing THF in crystals and therefore, $the 1BG crystals were colorless and emitted intense blue-green emission with <math>\lambda_{max} = 507$  nm and  $\Phi_{PL} = 0.95$ . On the other hand, because of the substantial distortion from tetrahedral symmetry, 1OR crystals comprising THF, *n*-hexane, and water molecules were yellow and exhibited weak orange emission with  $\lambda_{max} = 625$  nm and  $\Phi_{PL} = 0.06$ . These results suggest that the molecular structure of 1Cl in crystals can be altered by capturing the solvent molecule into an intermolecular space surrounded by *t*Bu groups. Furthermore, thermogravimetric analyses displayed in Fig. S11 reveal that the solvent molecules are stably trapped in the space at room temperature with supramolecular interactions.

Luminescence studies carried out in the temperature range 77–293 K demonstrated that  $[Au(L)_2]Cl$ , **1BG**, and **1OR** emit TADF and phosphorescence at 293 K with phosphorescence ratios of ~20, 6, and 70%, respectively.

#### Experimental

#### Materials

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1,2-Bis(dichlorophosphino)benzene was purchased from FUJIFILM Wako Pure Chemical Co, while 4-tertbutylmagnesium bromide and chloro(dimethylsulfide)Au(I) were purchased from Sigma-Aldrich Co. LLC. All the recrystallization organic solvents (THF, CH<sub>2</sub>Cl<sub>2</sub>, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, 2-methylhexane, and 3-methylhexane) were purchased from FUJIFILM Wako Pure Chemical Co. and used as received without further purification.

1,2-bis[bis(4-tert-butylphenyl)phosphino]benzene ( $L_{tBu}$ )

A THF solution of 4-*tert*-butylphenyl magnesium bromide (0.5 M, 100 mL) was added dropwise to a THF solution (20 mL) of 1,2-bis(dichlorophosphino)benzene (2.0 g, 7.14 mol) at 0 °C. The reaction mixture was stirred under reflux for 2 h and subsequently cooled to room temperature. A solution of saturated aqueous NH<sub>4</sub>Cl (100 mL) was next added to the reaction mixture. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 60 mL) and the combined organic extracts were dried over MgSO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed in vacuo to produce a pale yellow solid. The residue was purified by chromatography on silica gel (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, 3:1) to afford  $L_{tBu}$ , 3.51 g (74%) as white powder. <sup>1</sup>H NMR

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(400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K)  $\delta$  7.32 (m, 8H, *p*-*t*Bu-phenylene), 7.25 (m, 2H, *o*-phenylene), 7.12 (m, 8H, *p*-*t*Bu-phenylene), 7.08 (m, 2H, *o*-phenylene), 1.31 (s, 36 H, *t*Bu); <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -15.34 (s). Anal. Calcd. for C<sub>46</sub>H<sub>56</sub>P<sub>2</sub>: C, 82.35; H, 8.41; Found: C, 82.15; H, 8.29.

 $[Au(L_{tBu})_2]Cl(1Cl)$ 

A CH<sub>2</sub>Cl<sub>2</sub> solution (10 mL) of Me<sub>2</sub>SAuCl (44 mg, 0.15 mmol) was added to a solution of L<sub>tBu</sub> (200 mg, 0.30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The mixture was stirred for 3 h at room temperature. The yellow reaction mixture was filtrated and the solvent was removed in vacuo to produce a yellow amorphous solid. The residue was purified by recrystallization from diethyl ether under ultrasonic waves to produce colorless microcrystals. Yield 221 mg, 94%. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.51 (m, 2H, *o*-phenylene), 7.40 (m, 2H, *o*-phenylene), 7.14 (m, 8H, *p*-tBu-phenylene), 7.01 (m, 8H, *p*-tBu-phenylene), 1.29 (s, 36 H, tBu); <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  18.14 (s). Anal. Calcd. for C<sub>92</sub>H<sub>112</sub>AuClP<sub>4</sub>: C, 70.19; H, 7.17; Found: C, 70.33; H, 7.39.

#### 1BG (1CI•THF)

Colorless micro crystals of **1Cl** (50 mg,  $3.2X10^{-2}$  mmol) were dissolved in THF (2.0 mL). After membrane filtration, 1.5 mL of *n*-pentane was slowly added to the yellow THF solution of **1Cl** in test tube at 293 K, and the tubes were then sealed with caps. After 24 h, colorless crystals of **1BG** (37 mg,  $2.3X10^{-2}$  mmol) were formed in the test tubes. Isolated yield is 71% as single crystals. Anal. Calcd. for C<sub>96</sub>H<sub>120</sub>AuClOP<sub>4</sub>: C, 70.04; H, 7.35; Found: C, 70.15; H, 7.26.

#### 1OR (1Cl•THF•0.5x*n*-hexane•H<sub>2</sub>O)

Colorless micro crystals of **1Cl** (50 mg,  $3.2X10^{-2}$  mmol) were dispersed in *n*-hexane (5.0 mL). Then, 2 mL of THF was slowly added to the *n*-hexane solution in test tube at 50 °C. After standing for 48 h at 293 K, yellow crystals of **1OR** (24 mg, 1.4 X10<sup>-2</sup> mmol) were formed in the test tubes. Isolated yield is 44% as single crystals. Anal. Calcd. for C<sub>99</sub>H<sub>129</sub>AuClO<sub>2</sub>P<sub>4</sub>: C, 69.64; H, 7.62; Found: C, 69.47; H, 7.52.

#### $1YL \left(1Cl\bullet 1.5xCH_2Cl_2\bullet 2.5xH_2O\right)$

Colorless micro crystals of **1Cl** (50 mg,  $3.2X10^{-2}$  mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2.0mL). After membrane filtration, 2.0 mL of *n*-hexane was added to the yellow CH<sub>2</sub>Cl<sub>2</sub> solution at 293 K. After standing for 48 h, pale yellow crystals of **1YL** (22mg,  $1.3 \times 10^{-2}$ ) were obtained. Small yellow amorphous portion is observed. Isolated yield is 41% as single crystals. Anal. Calcd. for C<sub>187</sub>H<sub>240</sub>Au<sub>2</sub>Cl<sub>8</sub>O<sub>5</sub>P<sub>8</sub>: C, 64.30; H, 6.93; Found: C, 64.72; H, .7.10.

#### Sample preparations for photophysical measurements

Single crystals of **1BG**, **1OR** and **1YL** were used for photphysical measurements. These single crystals are stable at 293 K based on thermogravimetric analyses (Fig. S11).

**General Information** Details are given in the ESI<sup>+</sup>.

#### **Conflicts of interests**

There are no conflicts of interest to declare.

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#### Notes and References

<sup>a</sup> Department of Applied Chemistry, Nippon Institute of Technology, Gakuendai 4-1, Miyashiro-Machi, Saitama, 345-8501, Japan

<sup>b</sup> Laboratory for Chemistry and Life Science Institute of Innovative Research, Tokyo Institute of Technology R1-27, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

<sup>†</sup> Electronic Supplementary Information (ESI) available: general information, crystallographic data, NMR spectra, theoretical calculations, and crystallographic data of **1BG**, **10R**, and **1YL**; CCDC 1902631–1902633. For ESI and crystallographic data in CIF or other electronic formats see DOI: 10.1039/X000000x

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#### For Table of Contents

Luminescence color alteration induced by trapped solvent molecules in crystals of tetrahedral gold(I) complexes: Near-unity luminescence mixed with thermally activated delayed fluorescence and phosphorescence<sup>†</sup>

Masahisa Osawa, Hiroto Yamayoshi, Mikio Hoshino, Yuya Tanaka, and Munetaka Akita



#### SYNOPSIS

Emission color alteration caused by captured solvent molecules in the crystal lattice of tetrahedral gold(I) complexes.