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Photoluminescent Gold(I) Complex with Biphenyl Acetylene Ligand Showing Stable Nematic Liquid-Crystalline Phase

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*A novel liquid-crystalline (LC) gold(I) complex (**Biph6**) having biphenyl acetylene ligand was designed and synthesized, and its LC behavior and photoluminescence properties were compared with those of a previously reported gold complex (**Ph6**) with phenyl acetylene ligand. **Biph6** exhibited an enantiotropic nematic phase in a temperature range wider than that of **Ph6**. **Ph6** and **Biph6** showed intense photoluminescence with different colors in the crystalline phase: blue and yellowish green luminescence, respectively. We demonstrated that the color of luminescence of the gold complexes could be changed by changing the structure of the molecules and molecular aggregates.*

Keywords Gold complex; liquid crystal; photoluminescence

Introduction

Complexes containing Au(I) atoms show strong luminescence due to intermolecular interaction between Au atoms (aurophilic interaction) [1]. Since luminescence results from the intermolecular interaction, gold complexes show much stronger luminescence in the solid state than in solution. Thus, they are expected to be potential materials for organic light-emitting diodes, chemical sensors, and so forth. Because the luminescence exhibited by the aggregates of Au(I) complexes is due to the aurophilic interactions, the luminescence properties, including intensity and color, depend on the structure of aggregates of these complexes [2,3]. For example, mechanical grinding of the crystals of the Au(I) complex (C₆F₅Au)₂ (μ -1,4-diisocyanobenzene) induced a change in the photoluminescence color because of a change in the crystal packing structure [3]. This suggests that it is important to control the aggregate structure of Au(I) complexes, for their utilization as luminescent materials with desired color and high efficiency [4].

To control the structure of aggregates, gold complexes showing liquid crystalline (LC) properties have been developed by several groups [5]. The LC materials have both fluidity and self-organizing nature, and they show responsivity to external fields such as

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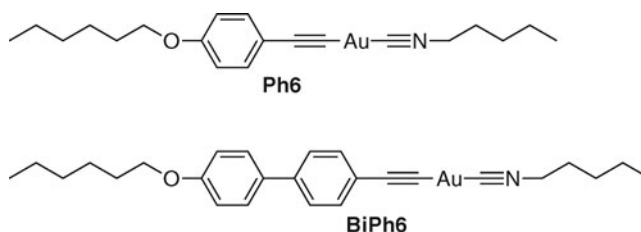


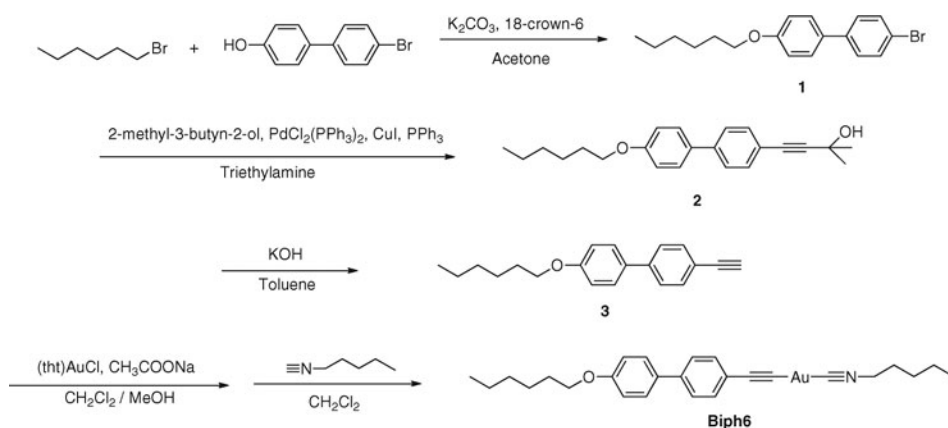
Figure 1. Molecular structures of gold complexes, **Ph6** and **BiPh6**, used in this study.

electric fields, magnetic fields, and light [6]. Therefore, the structures of aggregates of gold complexes may be controlled by means of their LC nature. In our previous study, gold(I) complexes having phenyl acetylene ligand exhibited an enantiotropic LC phase and showed strong photoluminescence in the condensed phases [7]. However, the temperature range over which the LC phase is maintained was very narrow (range of around 4 °C). For wider applications, gold complexes that exhibit the LC phase over a wider temperature range are needed. Generally, biphenyl derivatives tend to exhibit LC phases over a wide temperature range [8]. Therefore, in the present study, we designed and synthesized a new gold complex with biphenyl group (**BiPh6**) instead of the phenyl group (**Ph6**). In this paper, we report the LC behavior and photoluminescent properties of the gold complex with biphenyl acetylene ligand.

Experimental

Materials

The structure of the gold complexes used in the study is shown in Fig. 1. The complex **BiPh6** was first synthesized through a method similar to that used for preparing **Ph6** [7], as shown in Scheme 1. All solvents and reagents used in the preparation of the complex, were of reagent grade and commercially available. They were used without further purification, except as noted otherwise. ¹H NMR spectra were recorded on a JOEL ECS-400 (400 MHz) spectrometer. The chemical shifts were reported in parts per million (ppm), using the residual proton in the NMR solvent as an internal reference.



Scheme 1.

Table 1. Crystal data of complex **Biph6**

Empirical formula	C ₂₆ H ₃₂ AuNO
Formula weight	571.49
Temperature (K)	93.0(2)
Color, Habit	colorless, plate
Crystal size (mm)	0.15 × 0.15 × 0.05
Crystal system	monoclinic
$R[F^2 > 2\sigma(F^2)]$	0.0439
$wR(F^2)$	0.0976
Space group	$P2_1/n$
Z	8
a (Å)	9.6606(13)
b (Å)	14.538(2)
c (Å)	33.229(5)
α (degree)	—
β (degree)	93.054(2)
γ (degree)	—
V (Å ³)	4660.2(11)

To confirm the structure of **Biph6**, single-crystal X-ray structural analysis was performed. The obtained crystallographic data are summarized in Table 1. The data in Table 1 have been indexed and are included in the Cambridge Crystallographic Centre (CCDC) database with the reference number of CCDC 959978. The indexed database contains additional supplementary crystallographic data for this paper and may be accessed without charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html>. The CCDC may be contacted by mail at 12, Union Road, Cambridge CB2 1EZ, U.K., by fax at (44)1223–336–033, or by e-mail at deposit@ccdc.cam.ac.uk.

Synthesis of 1. 4-Bromo-4'-hydroxybiphenyl (300 mg, 1.2 mmol), potassium carbonate (330 mg, 2.4 mmol), and 1-bromohexane (198 mg, 1.2 mmol) were added to 5 mL of acetone, and the resulting mixture was refluxed for 24 h. The solid in the reaction mixture was filtered off, and the filtrate was evaporated. The residue was dissolved in ethyl acetate and then sequentially washed with water and brine. The organic layer was dried with anhydrous sodium sulfate, and then, the solvent was removed by evaporation. The residual crude product was dissolved in dichloromethane and then purified by reprecipitation from ethanol to obtain 114 mg (0.34 mmol) of **1** in 68% yield. ¹H NMR (400 MHz, CDCl₃, δ): 7.52 (dd, J = 6.7 and 2.1 Hz, 2H, 3,5-*H* in biphenyl), 7.47 (dd, J = 6.9 and 2.3 Hz, 2H, 3',5'-*H* in biphenyl), 7.41 (dd, J = 6.7 and 3.0 Hz, 2H, 2,6-*H* in biphenyl), 6.96 (dd, J = 6.9 and 2.3 Hz, 2H, 2',6'-*H* in biphenyl), 3.99 (t, J = 6.6 Hz, 2H, OCH₃), 1.80 (m, 2H, OCH₂CH₂), 1.51–1.30 (m, 6H, CH₂), 0.91 (t, J = 7.2 Hz, 3H, CH₃).

Synthesis of 2. **1** (114 mg, 0.34 mmol), 2-methyl-3-butyn-2-ol (0.14 mL, 1.4 mmol), bis(triphenylphosphine)palladium chloride (8.8 mg, 0.01 mmol), triphenylphosphine (1.6 mg, 0.007 mmol), and copper iodide (2.0 mg, 0.007 mmol) were dissolved in triethylamine (2.0 mL). The resultant solution was refluxed for 5 h under Ar. After the solid in the reaction mixture was removed by filtration, the filtrate was evaporated. The residue was dissolved in ethyl acetate, and then washed sequentially with water, saturated aqueous

ammonium chloride, and brine. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed by evaporation. The crude product obtained was purified by silica gel column chromatography (eluent: dichloromethane) to obtain 84 mg (0.25 mmol) of **2** in 74% yield. ^1H NMR (400 MHz, CDCl_3 , δ): 7.52–7.26 (m, 6H, 2,3,5,6,3',5'-H in biphenyl), 6.96 (dd, $J = 6.9$ and 2.3 Hz, 2H, 2',6'-H in biphenyl), 4.00 (t, $J = 6.6$ Hz, 2H, OCH_3), 2.01 (s, 1H, OH) 1.82–1.34 (m, 14H, CH_2 , $\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{OH}$), 0.91 (t, $J = 6.8$ Hz, 3H, $\text{O}(\text{CH}_2)_5\text{CH}_3$).

Synthesis of 3. **2** (84 mg, 0.25 mmol) and potassium hydroxide (44 mg, 0.75 mmol) were added to toluene (8.0 mL), and the mixture was refluxed for 5 h. After the solid in the reaction mixture was removed by filtration, the filtrate was evaporated. The obtained residue was dissolved in ethyl acetate and was then washed sequentially with water, saturated aqueous ammonium chloride, and brine. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed by evaporation. The crude product obtained was purified by silica gel column chromatography (eluent: dichloromethane/hexane (1/1)) to obtain 39 mg (0.14 mmol) of **3** in 56% yield. ^1H NMR (400 MHz, CDCl_3 , δ): 7.55–7.50 (m, 6H, 2,3,5,6,3',5'-H in biphenyl), 6.97 (dd, $J = 6.9$ and 2.3 Hz, 2H, 2',6'-H in biphenyl), 4.00 (t, $J = 6.4$ Hz, 2H, OCH_3), 3.11 (s, 1H, $\text{C}\equiv\text{CH}$), 1.78–1.35 (m, 14H, CH_2), 0.91 (t, $J = 6.8$ Hz, 3H, $\text{O}(\text{CH}_2)_5\text{CH}_3$).

Synthesis of Biph6. CH_3COONa (57 mg, 0.70 mmol) in a solution of dichloromethane/methanol (4.5/1.7 mL) was added to a solution of **3** (39 mg, 0.14 mmol) and (tht)AuCl (49 mg, 0.15 mmol) in dichloromethane/methanol (0.3/1.3 mL) under Ar. After the reaction mixture was stirred for 24 h, the precipitate was collected by filtration and then sequentially washed with methanol, water, methanol, and dichloromethane. The green solid obtained was suspended in dichloromethane (5 mL), and 1-pentylisocyanide (21 μL , 0.17 mmol) was added to the resultant suspension. By stirring the suspension for 3 h at room temperature, a purple homogeneous solution was obtained. The reaction mixture was filtered, and the solvent was evaporated. The solid obtained was recrystallized from the dichloromethane/heptane solution, and thus, 52 mg of **Biph6** (0.091 mol) was obtained as pale yellow needles in 73% yield. m.p. 146.7–147.5°C. ^1H NMR (400 MHz, CHCl_3 , δ): 7.50–7.45 (m, 6H, 2,3,5,6,3',5'-H in biphenyl), 6.94 (dd, $J = 6.9$ and 2.3 Hz, 2H, 2',6'-H in biphenyl), 3.98 (t, $J = 6.9$ Hz, 2H, OCH_2), 3.63 (t, $J = 6.9$ Hz, 2H, NCH_2), 1.83–1.76 (m, 4H, NCH_2CH_2 , OCH_2CH_2), 1.60–1.34 (m, 8H, CH_2), 0.97–0.89 (m, 6H, CH_3). MS-MALDI-TOF (m/z): 573 (4%, $\text{M} + 2$), 572 (25%, $\text{M} + 1$), 571 (100%, M^+). HRMS-ESI-TOF (m/z): $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{32}\text{AuNNaO}$, 594.2047; found, 594.2038.

Phase Transition Behavior

The LC behavior of the complex was observed by polarizing microscopy (POM) using an Olympus BX51 equipped with a hot stage (Instec, HCS302 hot-stage and mK1000 controller). Thermogravimetric-differential thermal analysis (TG-DTA) using a DTG-60AH unit (Shimadzu) at heating rate of 1.0°C/min was performed to check the thermal stability of the complexes. Thermodynamic properties of LCs were determined on a differential scanning calorimeter (DSC, SII X-DSC7000) at a heating and cooling rate of 5.0°C/min. At least three scans were performed to check reproducibility.

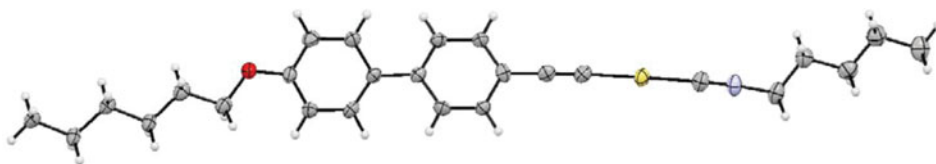


Figure 2. ORTEP view of the molecular structure of **Biph6** obtained by single-crystal X-ray structural analysis. Color legends: gray, C; white, H; red, O; purple, N; yellow, Au.

Photophysical Property

UV–visible absorption and steady-state photoluminescence spectra were recorded on a JASCO V-500 absorption spectrophotometer and on a Hitachi F-7500 fluorescence spectrophotometer, respectively.

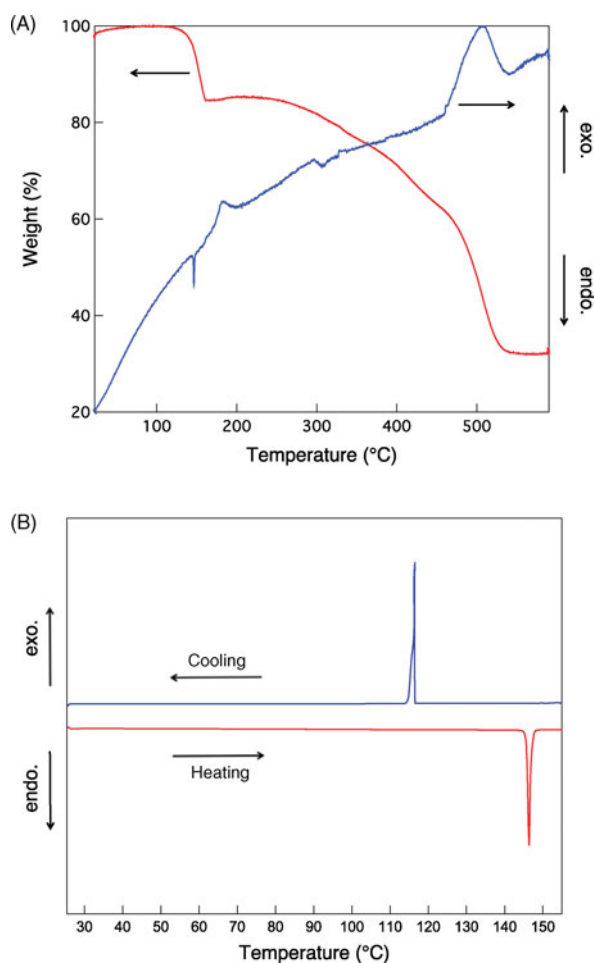


Figure 3. Thermodynamic behavior of **Biph6**: (A) TG (red) and DTA (blue) thermographs (heating rate = 1°C/min); (B) DSC thermogram (scan rate = 5°C/min).

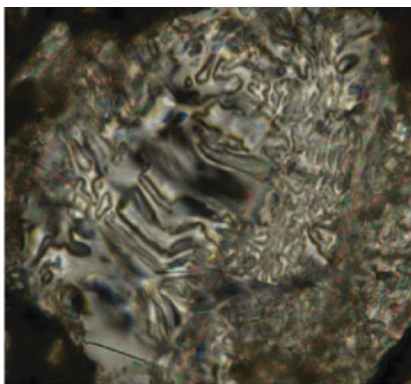


Figure 4. Polarizing optical micrograph of complex **BiPh6** observed in the heating process at 148°C.

Results and Discussion

Synthesis and Characterization of Complexes

The analytical data given in the Experimental section confirm that the desired compounds were obtained. The molecular structure obtained is shown in Fig. 2, and the key crystallographic data are summarized in Table 1. The compound was crystallized in the monoclinic space group $P2_1/n$, with eight formula units per unit cell. The Au atoms are linearly coordinated by the isocyanide and alkynyl ligands; thus, the core unit of the molecule exhibits a rod-like structure. Full characterization data for **Ph6** have been reported elsewhere [7]. Single-crystal X-ray analysis of **Ph6** suggested the existence of an aurophilic interaction between neighboring molecules, as the interatomic distance between Au atoms was 3.5 Å, which is much shorter than the sum of their van der Waals radii (3.8 Å) [9]. Thus, the complex may have formed a dimer in the **Ph6** crystal. On the other hand, the interatomic distance between Au atoms in neighboring molecules of the crystal **BiPh6** is 3.9 Å, excluding the existence of an interaction between Au atoms. Thus, in contrast to **Ph6**, the complex did not form a dimer in the **BiPh6** crystal.

The prepared complexes were stable in air at room temperature. Thermogravimetric analysis (TGA) was performed to assess their thermal stability (Fig. 3A for **Biph6**). We confirmed that **Biph6** was stable up to 165°C, and we defined the thermal decomposition temperature as the temperature corresponding to 5% weight loss. The thermal decomposition temperature of **Ph6** was 148°C. Above the decomposition temperature, **Ph6** and **Biph6** showed approximately 18% and 13% weight loss, respectively, which nearly correspond to the weight percentage of isocyanide ligands (20 wt% for **Ph6** and 17 wt% for **Biph6**). In addition, the thermal decomposition temperature is close to the boiling point of pentylisocyanide (137–138°C); thus, on heating to 140°C, the coordination bond between the Au atom and the isocyanide ligand may be cleaved, thereby liberating pentylisocyanide. Maximum weight loss was observed after the complex was heated to 400°C.

LC Behavior of the Au(I) Complex

The LC behavior of Au complexes was observed by POM, TGA, and differential scanning calorimetry. On the basis of their optical textures, the LC phase of both complexes was identified as nematic (N) by POM (Fig. 4). The phase-transition behaviors of the complexes

Table 2. Phase transition behavior of gold complexes **Ph6** and **Biph6**^a

Complex	Phase transition temperature ^b (°C)	
Ph6	Heating	Cr 89 N 93 I
	Cooling	Cr 70 N 94 I
Biph6	Heating	Cr 146 N 165 Dec.
	Cooling	Cr 117 N 165 Dec.

^aAbbreviations: Cr, crystalline; N, nematic; I, isotropic; Dec., decomposition. ^bData refer to DSC scan. Phase transition temperatures were determined as peak onset.

are summarized in Table 2. In the DSC thermogram of **Biph6** (Fig. 3B), the endothermic peak appearing at 146°C in the heating process could be assigned as the melting point. It was observed by POM that the N-to-isotropic phase transition of **Biph6** occurred at 165°C. However, thermal decomposition of the complex was also induced simultaneously with the phase transition, so the clearing temperature could not be determined exactly. Notably, **Biph6** showed a N phase in a temperature range of 19°C, which is considerably wider than that in the case of **Ph6** (4°C). As we previously reported, **Ph6** forms dimers in the N phase by intermolecular aurophilic interaction, and the dimer of the complex acts as a unit mesogen in the N phase [7]. However, the molecules in **Biph6** showed no intermolecular interaction in the crystal; thus, they might have existed as the monomeric form in the N phase as well as in the crystalline phase, and the monomer acted as the unit mesogen. Since the structures of the unit mesogen are quite different, the aspect ratio of the mesogen is different in both complexes: it should be much larger in **Biph6**. We believe that the difference in the aspect ratio of the unit mesogen results in a difference in the temperature range of the N phase.

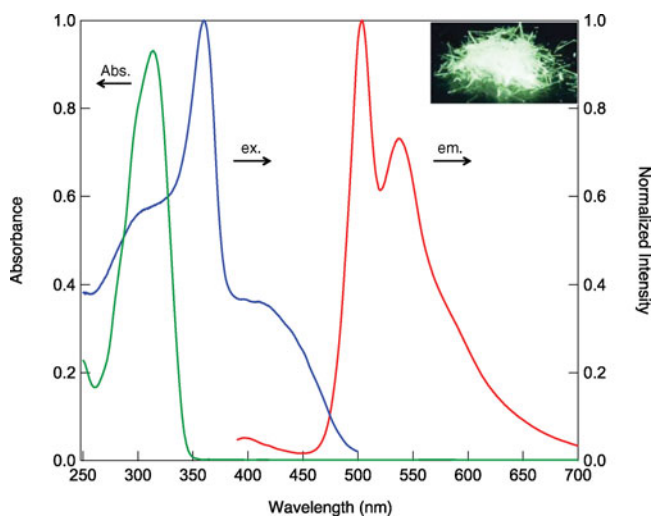


Figure 5. Normalized absorption and photoluminescence spectra of the complex **Biph6**. Green: absorption spectrum in dichloromethane solution (10^{-5} mol/L), blue: normalized excitation spectrum of the crystal ($\lambda_{\text{em}} = 504$ nm), and red: normalized photoluminescence spectrum of the crystal ($\lambda_{\text{ex}} = 360$ nm). Inset: photograph of luminescent crystals of **Biph6** taken under UV irradiation at 365 nm.

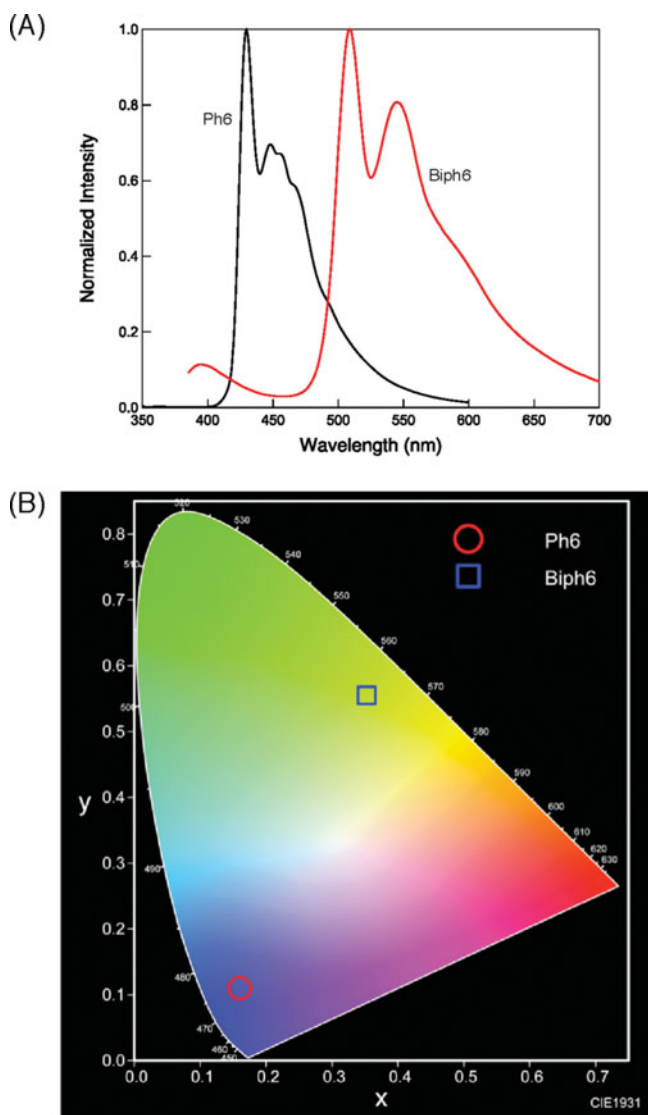


Figure 6. Comparison of luminescence properties between **Ph6** and **Biph6**. (A) Normalized photoluminescence spectra of both complexes in crystalline form: black, **Ph6** ($\lambda_{\text{ex}} = 340$ nm); red, **Biph6** ($\lambda_{\text{ex}} = 360$ nm). (B) CIE diagrams for photoluminescence of both complexes: \circ , **Ph6** ($\lambda_{\text{ex}} = 340$ nm); \square , **Biph6** ($\lambda_{\text{ex}} = 360$ nm).

Photophysical Property of the Au(I) Complex

Fig. 5 shows absorption spectra of **Biph6** in a dichloromethane solution (2.8×10^{-5} mol/L). An absorption band for the dilute solution appeared at 314 nm. Photoluminescence and excitation spectra of **Biph6** in the crystalline phase are also shown in Fig. 5. As shown in the inset of the figure, this complex showed relatively strong photoluminescence in the crystalline phase upon excitation at 360 nm. In the luminescence spectrum of the crystalline phase, the major and minor luminescence bands are at ~ 550 and ~ 400 nm, respectively.

However, the complex showed only the minor photoluminescence band at 400 nm in a dilute solution (10^{-5} mol/L). Therefore, the minor luminescence can be attributed to emission from the monomeric form of **Biph6**, and the major emission observed in the crystalline phase can be attributed to aggregation of the complexes. The results clearly indicate that the Au complexes synthesized in the study did not exhibit concentration quenching, but rather demonstrated aggregation induced emission (AIE). The same trends in photoluminescence were observed for **Ph6** in the crystalline phase (Fig. 4) [7].

Fig. 6 shows a comparison of photoluminescence properties between **Ph6** and **Biph6** in the crystalline phase at 25°C. As shown in Fig. 6A, the shapes of photoluminescence spectra of both complexes are very similar, but the emission maximum of **Biph6** is at approximately 100 nm above that of **Ph6**. Moreover, the photoluminescence colors were quite different for **Ph6** and **Biph6**: blue and yellowish green, respectively. We evaluated the photoluminescence color quantitatively using a Commission Internationale de l'Eclairage (CIE) chromaticity diagram (Fig. 6B). The CIE coordinates (x, y) were (0.16, 0.11) for **Ph6** and (0.35, 0.56) for **Biph6**. Since it is already known that the luminescent properties of gold complexes, such as color and intensity, depend on the structure of molecular aggregates, as well as the structure of the single molecules [2,3], the different properties of **Ph6** and **Biph6** indicate their different structures. The X-ray structural analysis indicated the difference in the crystal packing structure between them; **Ph6** was crystallized in the triclinic space group $P\bar{1}$, but **Biph6** was crystallized in the monoclinic space group $P2_1/n$, as mentioned above. Thus, we confirm that the color of photoluminescence of these LC gold complexes can be controlled by changing both structures of aggregates and of single molecules.

Conclusion

In this study, we developed a new LC gold complex having biphenyl acetylene ligand. It showed an enantiotropic N phase over a temperature range that is wider than that in the case of previously reported analog complex, which had a phenyl acetylene ligand. The gold complexes exhibited intense photoluminescence in the crystalline phase but no luminescence in dilute solutions. Therefore, we can safely conclude that these materials exhibit AIE and that the complexes are potential materials for use in practical light-emitting devices. We demonstrated that the color of luminescence from the gold complexes depended on both structures of molecules and molecular aggregates. To obtain a gold complex emitting light of the desired color, we thus need to design and control not only the molecular structure but also the structure of the molecular aggregates.

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